

## MicroDICE short term visit

Sönke Maus (University Bergen, Norway) visiting the Swiss Light Source (Villigen, Switzerland)

Experiment: *Synchrotron-based X-ray microfocus-spectroscopy of sea ice*

Time period: 13.02.-17.02.2012

### 1) Purpose of visit

The purpose of the visit by the author (*Sönke Maus*) at the Swiss Light Source (SLS) synchrotron of the Paul-Scherrer-Institute (PSI) in Villigen, Switzerland, was to prepare and perform X-ray microspectroscopic imaging of sea ice samples at the PHOENIX-beamline of the SLS. The goal of the experiment was to

- use X-ray fluorescence micro-focus spectroscopy ( $\mu$ -XRF) to localise and quantify fractionation of different seawater ions
- demonstrate the intrinsic crystallisation of sea salts by micro-focused synchrotron-based X-ray absorption spectroscopy ( $\mu$ -XAS)
- determine the abundance and stability of calcium carbonates *Calcite* and *Ikaite* during warming

The results will be important for understanding solid salt precipitation thermodynamics, and transport of chemical species within sea ice, critical in several environmental topics (e.g., tropospheric ozone depletion).

### 2) Work carried out

The present experiment was a feasibility study performed within commissioning time at the new PHOENIX beamline, operative since 2011, in cooperation with PHOENIX beamline scientist Thomas Huthwelker. Originally the visit had been planned during december 2012, yet had to be delayed due to shutdown of the ring at the Swiss Light Source and rearrangement of user time. The visit then lasted from 13.02.2012 (arrival) to 17.02.2012 (departure). Imaging of sea ice samples and first image postprocessing was performed from 14.01. to 16.02.2012.

### 3) Main results of experiment

In the present experiment samples were prepared in the following way. Sea ice cores with known pore structure and salinity were cut to a size of approximately 1 cm height and 2 cm diameter and then frozen by freshwater into a flat disc-like aluminium measuring cell of the same inner diameter and 0.5 cm height. The cell was tightened with a micrometer thick capton foil, sufficiently thin to let radiation penetrate and sufficiently thick to withstand the pressure difference when the sample was mounted in a vacuum chamber. The temperature control consisted of a cold plate cooled by liquid nitrogen (heat removal) and an adjustable current flux (heat added).

Because the PHOENIX beamline is operative since 2011, and still under development, a CCD camera is not available yet. The experiments were thus restricted to micro-fluorescence elemental mapping and to X-ray Absorption Near Edge Structure (XANES) spectra. Upon comparison with reference spectra, XANES allows the determination of the phase in which

the sea salts are present. The procedure was to 1. perform a low resolution scan of the major seawater elements and 2. evaluate the temperature variability of XANES spectra at particular spots for each element, in a temperature regime of interest.

We first performed the procedure for two sea salts for which the eutectic temperatures are reasonably known, NaCl (precipitates near  $-23\text{ }^{\circ}\text{C}$ ) and KCl (precipitates near  $-34\text{ }^{\circ}\text{C}$ ). XANES spectra were then obtained while raising and lowering the temperatures across the critical eutectic points. During this procedure we identified two problems: (i) a sample must be absolutely air-tightened; otherwise the sublimation from the sample surface may cool it and create surface temperatures different from the target temperature of the bulk sample. Second (ii) in case of too rapid cooling/warming ( $>0.1\text{K}/\text{min}$ ) XANES spectra appeared noisy and unstable, indicating ongoing phase transitions. We typically found that stable spectra were obtained when samples were equilibrated for 15 minutes.

Figure 1 shows XANES spectra for Calcium for different temperatures. The spectra remained stable over the whole temperature range. At present we have no reference spectra to decide if these spectra reflect *Calcite* or *Ikaite*, which will be determined in future studies.

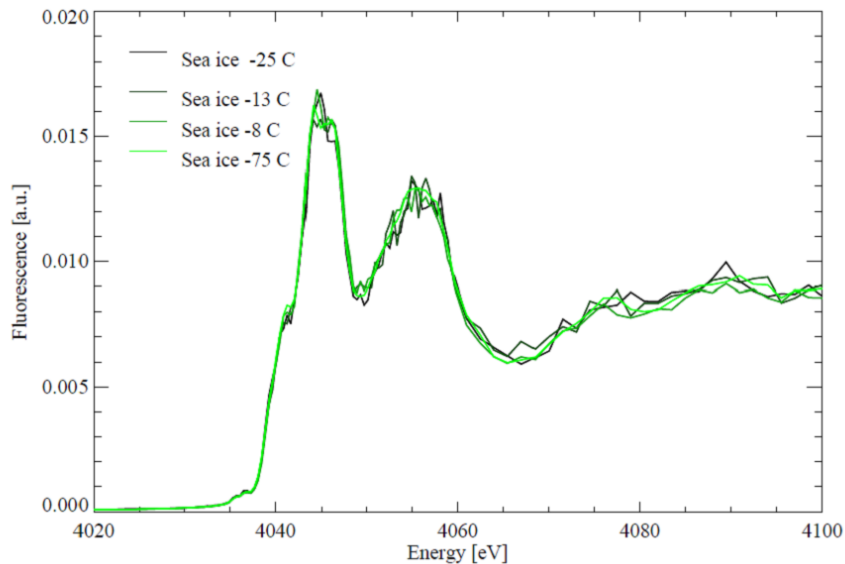


Figure 1: X-ray Absorption Near Edge Structure (XANES) spectra for calcium, obtained at PHOENIX at different temperatures.

#### 4) Future collaboration

The soft X-ray PHOENIX beamline is one of the few beamlines in the world that allows for determination of XANES spectra of all major seawater elements. In our pilot experiment we have successfully shown that the method yields stable results for sea ice, and may be applied to determine the eutectic precipitation temperatures of major sea salts. In terms of our experimental setup minor improvements are needed for the temperature control, for which we will construct an air-tight growth cell. As noted, at present we have no reference spectra to determine if the XANES spectra in Figure 1 reflect *Calcite* or *Ikaite*, and we will determine this in future studies. The method then qualifies to image sea ice in terms of calcite and ikaite formation that has been recently discussed for both Antarctic and Arctic sea ice (Dieckmann et al., 2008, 2010), with implications for its chemistry and environmental issues, i.e. the enhancement of bromine explosion and catalysis for destruction of stratospheric ozone (Sander et al., 2006; Morin et al., 2008; Marion et al., 2009).

To perform the mentioned work in future collaboration the author has submitted the proposal *Eutectic precipitation of cryohydrates in freezing seawater* to apply for beamtime at the PHOENIX beamline. The proposed experiment will allow a refinement of the sea ice phase relationship via direct determination of the eutectic temperatures of sea salts, that presently are only approximately known by means of indirect observations (Ringer, 1906; Nelson and Thompson, 1954; Gitterman, 1937). To perform and prepare this experiment the author plans a longer (1 month) guest visit at the PHOENIX beamline.

### 5) Projected publications

A publication of the results is projected after a longer follow-up experiment and visit at the SLS.

## References

- Dieckmann, G. S., Nehrke, G., Papadimitriou, S., Göttlicher, J., Steininger, R., Kennedy, H., Wolf-Gladrow, D., Thomas, D. N., 2008. Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophys. Res. Lett.* 35, L08501.
- Dieckmann, G. S., Nehrke, G., Uhlig, C., Göttlicher, J., Gerland, S., Granskog, M., Thomas, D., 2010. Brief communication: Ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) discovered in arctic sea ice. *The Cryosphere* 4, 227–230.
- Gitterman, K. E., 1937. Thermal analysis of seawater (termichesky analiz morskoy vody). *Trudy Solyanoy Laboratorii Akad. nauk SSSR* 15 (1), 5–23.
- Marion, G., Millero, F. J., Feistel, R., 2009. Precipitation of solid phase calcium carbonates and their effect on application of seawater S-T-P models. *Ocean Sci.* 5, 285–291.
- Morin, S., Marion, G. M., von Glasow, R., Voisin, D., Bouchez, J., Savarino, J., 2008. Precipitation of salts in freezing seawater and ozone depletion: a status report. *Atmos. Chem. Phys.* 8, 7317–7324.
- Nelson, K. H., Thompson, T. G., 1954. Deposition of salts from seawater by frigid concentration. *J. Mar. Res.* 13 (2), 166–182.
- Ringer, W. E., 1906. De veranderingen in samenstelling van zeewater bij het bevroren. *Chemisch Weekblad* 3 (15), 223–249.
- Sander, R., Burrows, J., Kaleschke, L., 2006. Carbonate precipitation in brine - a potential trigger for tropospheric ozone depletion events. *Atmos. Chem. Phys.* 6, 4653–4658.