

MicroDICE short exchange visit – Final Report

Purpose of visit

The proposed purpose of the exchange visit, as outlined in the original proposal, was to utilize the expertise of multiple research groups (University of Gothenburg (GU) – Molecular Kinetics, Grain Boundaries, Paul Scherrer Institute (PSI) – Surface Chemistry, Trace Gases, WSL Institute for Snow and Avalanche Research SLF (SLF) – Snow Microstructure) to contribute to the understanding of exchange and emission processes from atmosphere-snowpack interactions. Specifically, we proposed detailed experimental studies of volatile organic compounds (VOCs) in simulated snowpack. The experiments were to focus on two important but relatively unconstrained issues regarding the physicochemistry of ice and snow surfaces. First, the effect of molecular size on chemical uptake behavior was to be investigated. The second goal was to examine the interplay between ice microstructure, in particular grain boundaries and other areas of increased mobility as the melting temperature T_m is approached, and chemical processes. However, initial tests with organics proved that achieving these goals simultaneously would be difficult in the six-week time frame. Thus, hydrogen peroxide (H_2O_2) was identified as a more effective probe molecule and a new type of ice reactor was developed. Proof of concept experiments were completed for H_2O_2 uptake using the new ice reactor and plans were put in place for continued work and collaboration. The end result of the exchange visit was a productive collaboration that produced a new and tested experimental method with the potential to be used in high-impact experiments. Details of the exchange visit work and plans for future collaboration are detailed below.

Description of work

The experimental system designed to investigate air – trace gas interactions in this exchange work consists of a gas-dosing unit, a reactor where the trace gas interacts with the ice or snow sample, and a detection unit to monitor the gas-phase concentration of the trace gas with time upon contact with the ice sample. A calibrated permeation source introduces the chemical species of interest into the flow which is then directed through the sample container and into an analyzer. Bypass and exhaust loops insure that the background gas and source can be measured independently of the ice and snow samples. The final design is illustrated in Figure 1. Initial experiments were conducted to assess the viability of flow tube and snow diffusion reactor chamber experiments using formic acid, trifluoroacetic acid, and formaldehyde as the chemical species of interest. In order to perform experiments on ice and snow samples an important balance must be struck between the sensitivity of detection and therefore the amount of volatile initially introduced, and the sample's ability to interact with the volatile in a manner which produces a clearly measurable signal. In the case of the aforementioned compounds a Chemical Ionization Mass Spectrometer (CIMS) was used for detection. Unfortunately, in each case the VOC concentrations were found to be below the detection limit, possibly due to limited ionization ability. This discovery forced a reconsideration of the goals of the six-week project and as a result it was decided that H_2O_2 , another chemical species of environmental interest should be investigated. Hydrogen peroxide interactions with ice have previously been studied with some interest [1, 2], but the effect of microstructure remains largely unconstrained.

The choice to work with H_2O_2 was also motivated by results of an ongoing research project

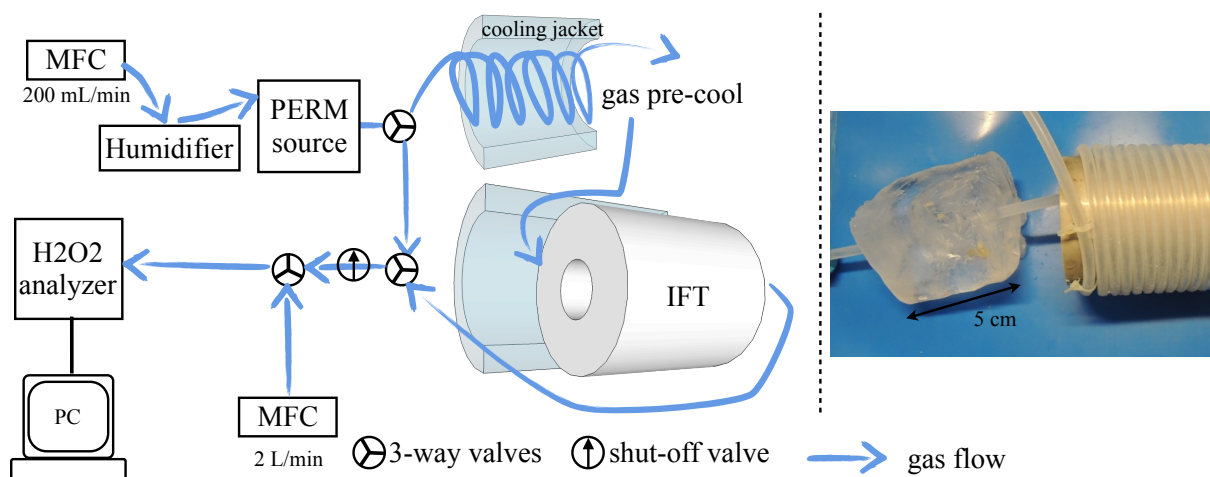


Figure 1: A schematic of the flow system (left) and *ice flow tube* (IFT, right) used for experimental measurements. Dry nitrogen is input into the system using mass flow controllers (MFC). The air that will circulate through the ice sample is humidified to the appropriate saturation vapor pressure over ice and dosed with H₂O₂ from a permeation source. The dosed gas can be flowed directly to the analyzer or through the IFT.

at PSI, where the interaction of H₂O₂ with thin ice films is studied. These experiments have revealed a slow H₂O₂ loss process to the ice. Diffusion into grain boundaries may be one cause of this long-term behavior. However, the grain boundaries of the thin ice films cannot be analyzed or controlled, which has inhibited drawing concrete conclusions regarding the role of the microstructure. In contrast, similar experiments with VOCs do not indicate such a diffusive loss – another reason why experiments with H₂O₂ were deemed more promising for this exchange project. The H₂O₂ is injected, by a permeation source, into a humidified flow of 0.2 L/min of nitrogen that is pre-cooled before being flowed through the ice sample (Figure 1). Dry nitrogen (2 L/min) is added to the flow before an Aero Laser H₂O₂ gas analyzer is used to measure the peroxide concentration with data output and stored at three second increments. Measurements are collected for the pure dry nitrogen system to determine background H₂O₂ levels and uptake experiments are performed by switching from measurements of the H₂O₂ source to flow through an *ice tube*.

An important new result of this six week collaboration is the development of *ice flow tubes* (IFTs) with different levels of polycrystallinity. A working principle has been demonstrated, but the IFT development is ongoing and more thoroughly described in the next section.

Description of results

The unique resources and expertise of this collaboration have allowed us to develop IFTs, which enable direct probing of the chemical behavior of ice, allow for the selection and quantification of the ice microstructure, and eliminate all superfluous material surfaces. The absence of surfaces other than ice in the sample holder is essential when working with H₂O₂. Previous experiments at PSI clearly showed that the interaction of H₂O₂ with glass, teflon, and/or metal surfaces can exceed that of ice, making experiments in the presence of those surfaces impossible. Very nearly single crystal ice tubes can be made from high quality bubble free ice. Figure 2 shows a thin section taken from just such an IFT. Surrounding the drilled flow hole

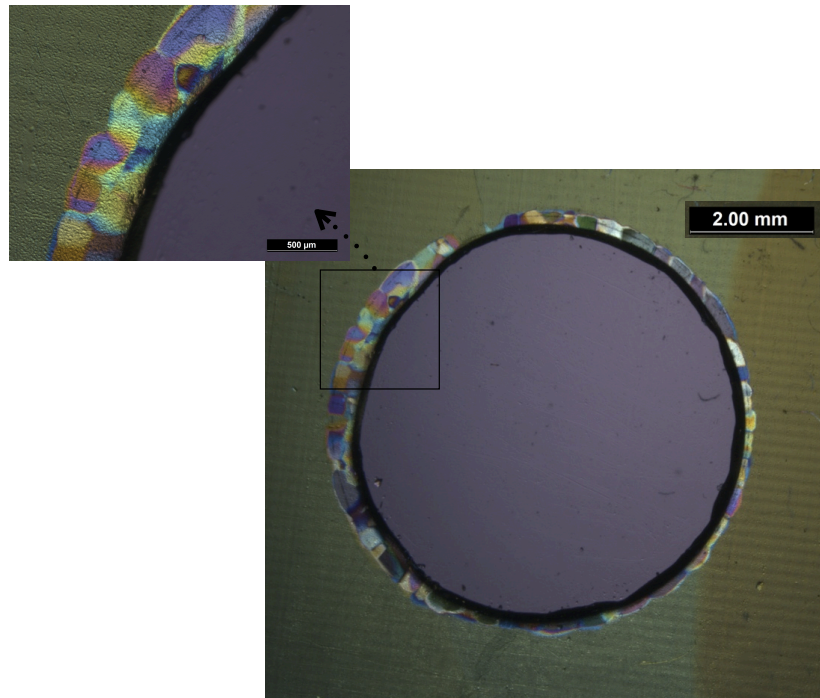


Figure 2: An ice thin section viewed using cross-polarized light. The 6 mm central hole for the gas flow has been drilled to allow the gas flow tubing to be pressure fit directly into the ends of the hole. An annulus of recrystallized ice that is formed during drilling is observed immediately around the hole (zoom – inset).

a thin annulus of recrystallized ice results from damage due to the pressure of the drilling. A washing procedure is being refined to insure that this region is removed prior to single crystal experiments. However, the surprising extent of the recrystallization zone may enable multiple microstructure experiments using identical ice samples.

Polycrystalline ice can also be used for constructing IFTs (Figure 3). Thus, three different categories of ice can be tested, (1) single (or nearly single) crystals, (2) single crystal ice with polycrystallinity directly around the gas flow hole, and (3) bulk polycrystalline ice. This allows for differentiation between pure surface adsorption, adsorption at grain boundary interfaces with the surface, and adsorption into the extended grain boundary network of a bulk polycrystal.

Several experiments were conducted on various IFTs as a proof of the concept and showed results that encourage a multitude of systematic experiments to examine ice behavior over a range of temperature. Figure 4 shows an uptake recovery curve measured for a 4.9 cm single crystal IFT. The observed incomplete recovery has been seen in similar systems, including analogous coated wall flow tube experiments. Currently, the potential reasons for this partial recovery are under investigation and it is hoped that H_2O_2 sinks will be distinguished using the aforementioned method.

Future Work and Collaboration

A joint PSI/SLF post-doc is employed to continue to work on the IFT technology and measurements until March 2013. In addition there is an on-going discussion between the partners

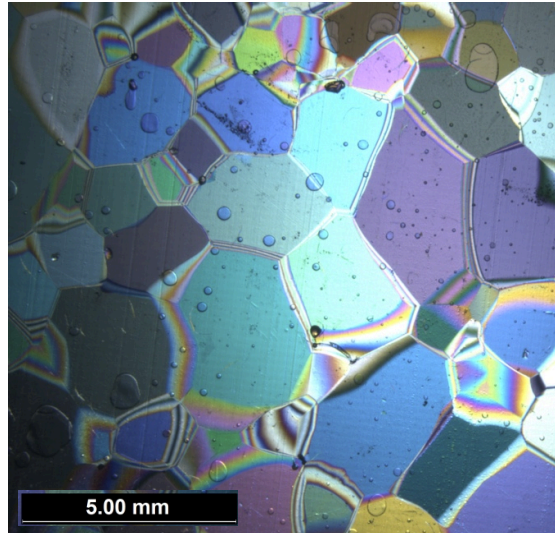


Figure 3: An example ice thin section taken from a polycrystalline sample grown to be used as an IFT.

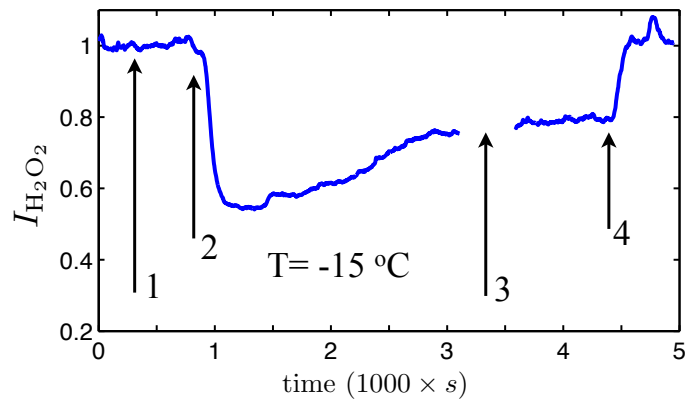


Figure 4: A plot of normalized H₂O₂ concentration $I_{H_2O_2}$ versus time showing the dosing and recovery of the IFT. Arrows are added to illustrate important times, 1 – H₂O₂ directly from permeation source, 2 – H₂O₂ redirected through IFT, 3 – redacted data due to corruption from a flow verification measurement, 4 – IFT bypassed once again. The jump at position 4 is a result of the incomplete recovery.

to identify students to participate in a measurement campaign using the IFT system during the first half of 2013. The potential for useful measurements coming from the method is limited only by the availability of human resources. Clearly, the method is flexible and open to the use of other chemical dopants and detection methods. Unfortunately, the short time frame of the exchange visit did not allow for a full assemblage of experiments to be run. Thus, all partners have an interest in continuing the fruitful collaboration.

Projected publications

Currently, an abstract submission related to the IFT method is being considered for the April 2013 EGU meeting. A peer-reviewed publication will require further experiments at multiple ice temperatures. Ice tubes are expected to be constructed and used for measurements before March 2013, when it is anticipated there will be sufficient data for one, and possibly two publications. In the long term the flexibility of the method could lead to a nearly inexhaustible number of climate relevant, interesting measurements.

Other Comments

As a final comment I will simply suggest that perhaps for visitors to Switzerland an extra allowance be considered for such exchange visits. This is simply due to the observation that currently Switzerland has a very high cost of living compared to other European countries.

To this report I append a spreadsheet summary of my travel and living expenses.

References

- [1] M H Conklin, A Sigg, A Neftel, and R C Bales. Atmosphere-snow transfer function for H₂O₂: Microphysical considerations. *Journal of Geophysical Research*, 98(10):18367–18376, October 1993.
- [2] N. Pouvesle, M. Kippenberger, G. Schuster, and J. N. Crowley. The interaction of H₂O₂ with ice surfaces between 203 and 233 k. *Phys. Chem. Chem. Phys.*, 12:15544–15550, 2010. doi: 10.1039/C0CP01656J. URL <http://dx.doi.org/10.1039/C0CP01656J>.

Micro-DICE costs -- reported in currency paid and rounded to nearest whole number.

Travel + Commuting:

From	To	SEK	CHF	USD	Euro	Explanation
Gothenburg	Zurich Airport		2250		258.92	Trip to/from Switzerland
Zurich Airport	Zurich Apt.			9	7.44	Trip to/from Switzerland
Zurich Apt	Zurich Airport			3	2.48	
Zurich Apt	PSI		281		232.23	Daily commuting (Oct. 14 - Nov. 13)
Zurich Apt	PSI		82		67.60	Daily commuting (Nov. 14 - Nov. 16)
Zurich Apt	PSI		89		73.55	Daily commuting (Nov. 19 - Nov. 22)
Zurich HB	Davos			52	42.98	Oct. 31 trip to Davos, SLF WSL laboratories for planning meeting

Subtotal Travel: 685.20

Housing:

Apartment in Zurich			3735		3086.78	Apartment for 6 weeks
cleaning fee			120		99.17	

Subtotal Apt: 3185.95

Total Expenses 3871.15