SCIENTIFIC REPORT

for project entitled:

Cryo-SEM survey of dihedral angle/equilibrium microstructures in various quenched binary ice+melt systems

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Purpose

The purpose of this exchange visit was to characterize the equilibrium microstructure of ice+sulfuric acid in laboratory-prepared specimens using a cryogenic scanning electron microscope (CSEM). In particular, we sought to measure the dihedral angle θ between solid ice and quenched H_2O-H_2SO_4 solution. To do so, we used an SEM that has been specially equipped with a cryogenic stage and prepping chamber. The work builds on previous measurements of the ice+brine system made by the host and her coworkers [*Blackford et al.*, 2007], but instead examining here, for the first time, the ice+sulfuric acid system. This system was chosen because sulfuric acid has been identified in Antarctic ice cores [*Mulvaney et al.*, 1988] and has been suggested as a potential second phase on icy satellites [*Carlson et al.*, 2002]. Because of the deep eutectic that sulfuric acid displays with ice (T_E = -62°C), the acid in such settings would likely be found in liquid form at the grain boundaries and triple junctions of ice grains. The goal of our research was to determine the dihedral angle θ, which influences the interconnectedness of the acid solution phase (θ<60° means that melt can travel through an interconnected network; θ>60° means that melt is trapped). The broader impact of the project is that with this information we can make predictions about the transport and mechanical behavior of an ice layer containing even small amounts of sulfuric acid as an impurity. Such behaviors can then be used, for instance, to assure the integrity of ice core records or model the dynamics of ice layers.

Description of work carried out

The first part of the project involved planning and obtaining all the necessary safety and logistical equipment to create the samples. Concentrated sulfuric acid was mixed with water in a fume hood and then sprayed into a reservoir of liquid nitrogen. The solidified particles were ground with a mortar and pestle, carefully collected, and placed in small aluminum capsules that were specially made for use with this system (the sulfuric acid will corrode most other materials). Although we employed the method previously used by the host, many adaptations had to be made during the process to account for the acidity of samples.

Once samples were fabricated, the individual capsules (15 in total) were placed in freezers at various temperatures and allowed to "cook". By this I mean that the samples rested at a constant temperature above the eutectic temperature for a given duration so that the equilibrium solid+melt microstructure could form. Samples were then quenched in liquid nitrogen to capture this microstructure. We systematically varied the duration time from four days to two weeks in order to confirm that equilibrium had been reached.

While the samples "cooked", the host and I traveled to Grenoble to attend the Micro-DIce conference and discuss the project with colleagues in the ice community.

Upon returning to Edinburgh, we initiated the survey of the microstructure using the CSEM located in the Biology department of the University of Edinburgh. The host kindly paid for the cost of SEM-usage and technician time to run such tests.

Results obtained

Since the dihedral angle represents a three-dimensional feature that we are measuring with a two-dimensional method, the difference between the plane of view and the junction itself can influence the measurements. It has been found, however, that with a statistically significant sampling, the "true" angle can be obtained with some confidence. The general consensus is that over 100 angles should be obtained for a reliable measurement. In such a short exchange visit (with only two days of SEM time scheduled), we feared that such a requirement would be prohibitive. However, the scientist running the SEM, Dr. Christopher Jeffree, was extremely skilled and expertly managed to take images supplying several hundred measureable angles.

I am still measuring the angles from these images. I will employ two methods: one is to measure by hand using printouts and a protractor; the second is to use a digital image analyzer in which two lines are drawn with the mouse and the computer calculates the angle between the two. I plan to report the results from both methods and also to send a blind selection of images to the host so that she can independently measure a smaller sample set by her own means. Since initial observations indicate the presence of some (but not many) long features of quenched melt connecting triple junctions, I predict that the median angle will be between 20° and 60° (i.e., low enough to be interconnected, but not so low as to have fully wetted grain boundaries).

Future collaboration

I found the visit extremely fruitful for many reasons. In addition to the directly applicable publication listed below, the host and I have made plans to write another article based on our shared knowledge of the solid-solid microstructure of salt+ice and some previous unpublished micrographs that she has.

She has also provided me with invaluable advice for the ice-ice friction experiments that I will commence when I return to New York. In that regard, we hope to collaborate on future experimental friction proposals. Since she has considerable experience in the tribology field and I am only just beginning, her input will be very helpful.

Additionally, we have discussed future collaboration with another lab in Europe, in which partially molten ice+sulfuric acid samples can be tested for their bulk mechanical properties (viscosity and possibly elastic modulus). In this way we will directly test the predictions made by this current project. For this collaboration, I hope to apply for another MicroDice exchange visit for the 2012 calendar year.

Projected publication

Results from the visit will be published in a refereed journal article, currently in preparation, entitled:
Cryo-SEM study of dihedral angle in the ice-I/sulfuric acid partially molten system, by Christine McCarthy, Jane R. Blackford, and Christopher E. Jeffree. ESF and MicroDICE will be acknowledged in the publication.

References cited

Blackford, J.R., C.E. Jeffree, D.F.J. Noake, and B.A. Marmo (2007) Microstructural evolution in sintered ice particles containing NaCl observed by low-temperature scanning electron microscope, *Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications* 221: 151.

Carlson, R.W., M.S. Anderson, R.E. Johnson, M.B. Schulman, and A.H. Yavrouian (2002) Acid Production on Europa: The Radiolysis of Sulfur in Water Ice*, Icarus* 157, 456-463, doi:10.1006/icar.2002.6858.

Mulvaney, R. E.W. Wolff, and K. Oates (1988) Sulphuric acid at grain boundaries in Antarctic ice, *Nature* Vol. 331:21.