

# **14th International Conference on the Physics and Chemistry of Ice (PCI-2018 in Zürich)**



## **Report of Contributions**

Contribution ID: 17

Type: **Poster**

## Grand Canonical Monte Carlo Simulations of the Ammonia clathrate hydrate

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Overcoming the important deficiencies of the clathrate equilibrium data at low temperatures by using theoretical approaches such as the van der Waals & Platteeuw method seems truly tempting. However, this thermodynamic route is usually based on descriptions with simplified intermolecular potentials calibrated using equilibrium data obtained at high temperatures. As a consequence, the theoretical model's ability to

predict the composition of clathrates in the outer Solar System could be easily questioned. In the current work, we show that Monte Carlo simulations performed on the Grand Canonical ensemble (GCMC) can be efficiently used to determine theoretically the amount of gas species trapped in the clathrate hydrates at low temperature in various situations as encountered in the Solar System.

In this study, the NH<sub>3</sub> molecule has been considered which is thought to contribute to the outgassing of methane clathrate hydrates into the atmosphere of Titan and Enceladus due to its role as a water-ice antifreeze and methane clathrate thermodynamic inhibitor. However, recent experimental results have indicated that NH<sub>3</sub> clathrate of structure I could be stable at the very low temperatures

typical of these Moon's atmospheres (i.e., below 150 K). GCMC simulations have thus been performed to determine the amount of NH<sub>3</sub> trapped in clathrate as a function of the partial pressure at different temperatures. The obtained results show that the strong tendency of hydrogen bond formation between NH<sub>3</sub> and water molecules leads to the destabilization of the clathrate cages. As a consequence, stabilizing the ammonia clathrate in molecular simulations appears very challenging, indicating that this clathrate could be stable only under very specific conditions.

This application illustrates the efficiency of the GCMC method for studying gas trapping in clathrates at low temperatures of interest for planetary sciences.

### Significance statement

Grand Canonical Monte Carlo simulations of the ammonia clathrate are performed for the first time. Results show that this clathrate could be stable in specific conditions relevant to planetary sciences.

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**Session Classification:** Poster & Lunch

Contribution ID: 18

Type: **Poster**

## Adsorption of halogenated methane derivatives at the ice surface under tropospheric conditions, as seen from Grand Canonical Monte Carlo simulations

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The adsorption of all the fluorinated and chlorinated methane derivatives at the surface of Ih ice is studied by grand canonical Monte Carlo simulations at 200 K.

The adsorption isotherms are simulated and their shape is discussed in terms of the interplay of adhesive and cohesive interactions. It is found that in cases when the adhesive interaction is clearly the stronger one, multilayer adsorption occurs; when the cohesive interaction is the dominant one, no considerable

adsorption is observed, while in cases when the two interactions are of roughly the same strength, the formation of a saturated monolayer occurs. The isotherms exhibit the Langmuir shape, at least up to the

pressures where multilayer adsorption starts to occur, given that the cohesion acting between the adsorbate molecules is only moderately strong. Too strong cohesion, on the other hand, leads to the deviation of the

isotherm from the Langmuir shape. While the strength of cohesion depends on the properties of the adsorbate molecules, that of adhesion is determined by hydrogen bond formation between the adsorbed molecules and

the ice surface. Our results also reveal that the surface orientation of all these adsorbed molecules is such that at least one of their halogen atoms is exposed to the vapour phase, which makes it easily accessible for reactions with gas phase species, and also easily releasable in photodissociation processes.

### Significance statement

First full characterization of the adsorption process of halogenated methane derivatives on ice, by means of Monte Carlo simulations in the Grand Canonical Ensemble.

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**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 19

Type: PICO talk

## Room-temperature Salt Solutions L-VI-VII Icing by Compression

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

We show that transiting NaX/H<sub>2</sub>O solutions of 0.016 molar concentration (X = F, Cl, Br, I) [1, 2] and NaI/H<sub>2</sub>O of different concentrations into an ice VI phase and then into an ice VII at 298 K proceeding in different ways. The solute-type-resolved critical pressures PC1 and PC2 increases simultaneously in the Hofmeister series order: X = I > Br > Cl > F > 0; comparatively, concentration-resolved PC1 increases faster than the PC2 that remains almost constant at higher NaI/H<sub>2</sub>O concentration. The PC1 moves along the Liquid-VI phase boundary and merges to PC2 at the Liquid-VI-VII phase junction of 350 K and 3.05 GPa. Observations confirmed that the solute solvation creates electric fields that lengthen and soften the O:H nonbonds and meanwhile shorten and stiffen the H-O bonds [3, 4], being the same to molecular undercoordination [5-7]. Compression, however, does it oppositely [8]. Therefore, compression recovers the electrification-deformed O:H-O bond first and then proceeds to the phase transitions. The concentration-raised anion-anion interaction weakens the electric field within the hydration shell, which discriminates the effect of NaI/H<sub>2</sub>O concentration from solute types at an identical concentration.

1. Sun, C.Q. and Y. Sun, The Attribute of Water: Single Notion, Multiple Myths. Springer Ser. Chem. Phys. Vol. 113. 2016, Heidelberg: Springer-Verlag. 494 pp.
2. Zeng, Q., et al., Compression icing of room-temperature NaX solutions (X= F, Cl, Br, I). Physical Chemistry Chemical Physics, 2016. 18(20): p. 14046-14054.
3. Zhou, Y., et al., Water molecular structure-order in the NaX hydration shells (X= F, Cl, Br, I). Journal of Molecular Liquids, 2016. 221: p. 788-797.
4. Gong, Y., et al., Raman spectroscopy of alkali halide hydration: hydrogen bond relaxation and polarization. Journal of Raman Spectroscopy, 2016. 47(11): p. 1351-1359.
5. Sun, C.Q., et al., Density, Elasticity, and Stability Anomalies of Water Molecules with Fewer than Four Neighbors. Journal of Physical Chemistry Letters, 2013. 4: p. 2565-2570.
6. Zhang, X., et al., A common supersolid skin covering both water and ice. Physical Chemistry Chemical Physics, 2014. 16(42): p. 22987-22994.
7. Zhang, X., et al., Nanobubble Skin Supersolidity. Langmuir, 2016. 32(43): p. 11321-11327.
8. Sun, C.Q., X. Zhang, and W.T. Zheng, Hidden force opposing ice compression. Chem Sci, 2012. 3: p. 1455-1460.

### Significance statement

Salting and compressing have opposite effect on the H-O bond energy that determines the critical pressures for room-temperature liquid-VI-VII phase transition of solutions.

**Primary author:** Prof. SUN, Changqing (NTU, Singapore)

**Presenter:** Prof. SUN, Changqing (NTU, Singapore)

**Session Classification:** Poster & Lunch

Contribution ID: 21

Type: **Talk**

## Why is Ice Less-dense and Slippery?

*Monday, January 8, 2018 1:20 PM (20 minutes)*

As the source and central part of all lives, water is most abundant yet least known. This presentation shares the recent progress [1-6]: (i) correlation of the length scale, structure order, and mass density of molecular packing in water ice; (ii) potential paths for O:H-O bond at relaxation; and anomalies of water ice under (iii) compression; (iv) molecular under-coordination; and (v) thermal excitation. Hydrogen bond (O:H-O) possesses memory and extreme deformation recoverability, which resolves mysteries of: (i) density of ice [7]; (ii) slipperiness of ice [8]; (iii) Mpemba paradox - hot water freezes faster [9]; (iv) Regelation [10] - ice melts under compression and freezes again when the pressure is relieved. Understanding may extend to fields such as water - bio-molecular interaction, water purification, energy management, etc.

1. Sun, C.Q. and Y. Sun, *The Attribute of Water: Single Notion, Multiple Myths*. Springer Ser. Chem. Phys. Vol. 113. 2016, Heidelberg: Springer-Verlag. 494 pp.
2. Huang, Y.L., et al., Hydrogen-bond relaxation dynamics: Resolving mysteries of water ice. *Coordination Chemistry Reviews*, 2015. 285: p. 109-165.
3. Zhang, X., et al., Water's phase diagram: from the notion of thermodynamics to hydrogen-bond cooperativity. *Progress in Solid State Chemistry*, 2015. 43: p. 71-81.
4. Sun, C.Q., X. Zhang, and W.T. Zheng, Hidden force opposing ice compression. *Chem Sci*, 2012. 3: p. 1455-1460.
5. Sun, C.Q., et al., Density and phonon-stiffness anomalies of water and ice in the full temperature range. *Journal of Physical Chemistry Letters*, 2013. 4: p. 3238-3244.
6. Sun, C.Q., et al., Density, Elasticity, and Stability Anomalies of Water Molecules with Fewer than Four Neighbors. *Journal of Physical Chemistry Letters*, 2013. 4: p. 2565-2570.
7. Sun, Q., Raman spectroscopic study of the effects of dissolved NaCl on water structure. *Vibrational Spectroscopy*, 2012. 62: p. 110-114.
8. Zhang, X., et al., From ice superlubricity to quantum friction: Electronic repulsivity and phononic elasticity. *Friction*, 2015. 3(4): p. 294-319.
9. Zhang, X., et al., Hydrogen-bond memory and water-skin supersolidity resolving the Mpemba paradox. *Physical Chemistry Chemical Physics*, 2014. 16(42): p. 22995-23002.
10. Zhang, X., et al., Ice Regelation: Hydrogen-bond extraordinary recoverability and water quasisolid-phase-boundary dispersivity. *Scientific Reports*, 2015. 5: p. 13655.

### Significance statement

presents quantitative and consistent resolution to the properties of ice friction and ice density from the perspective of hydrogen bond relaxation and electron polarization.

**Primary author:** Prof. ZHANG, Xi (Shenzhen University)

**Co-authors:** Prof. SUN, Changqing (NTU, Singapore); Prof. HUANG, Yongli (Xiangtan University)

**Presenter:** Prof. SUN, Changqing (NTU, Singapore)

**Track Classification:** Phases of Ice

Contribution ID: 23

Type: **Talk**

## Snowflake growth in supersaturated atmosphere using a three-dimensional phase-field model

*Monday, January 8, 2018 2:50 PM (20 minutes)*

Simulating ice crystal growth is a major issue for meteorology and aircraft safety [1]. Notwithstanding, very few models currently succeed in reproducing the diversity of snowflake forms in three dimensions, and the link between model parameters and thermodynamic quantities is far from being established. Here, we present a 3D modified phase field model that describes the subtlety of the ice-vapor phase transition leading to snow crystal growth, through anisotropic water molecules attachment and condensation, surface diffusion, and strongly anisotropic surface tension [2]. We demonstrate that this model is capable of reproducing properly the morphology and growth kinetics of snowflakes in supersaturated atmosphere. Aside from that, we show that the growth dynamics of snow crystals simulated thereby, satisfies the selection theory, consistently with previous experimental observations [3]. Finally, we present a morphology diagram in experimentally accessible units, that links the manifold of simulated snowflake shapes to atmospheric parameters.

[1] BRUNEL, M., DEMANGE, G., FROMAGER, M., et al. Instrumentation for ice crystal characterization in laboratory using interferometric out-of-focus imaging. *Review of Scientific Instruments*, 2017, vol. 88, p. 083108.

[2] DEMANGE, G., ZAPOLSKY, H., PATTE, R., et al. A phase field model for snow crystal growth in three dimensions. *NPJ Computational Materials*, 2017, vol. 3, p. 1.

[3] DEMANGE, G., ZAPOLSKY, H., PATTE, R., et al. Growth kinetics and morphology of snowflakes in supersaturated atmosphere using a three-dimensional phase-field model. *Physical Review E*, 2017, vol. 96, p. 022803.

### Significance statement

1/ New numerical model:

-3D phase field model for highly anisotropic crystal growth with sixfold symmetry.

-Synergistic effect of kinetic and surface tension effects

2/ Encouraging results

-Selection theory for snowflake growth

-Quantitative link with experiments

**Primary author:** Dr DEMANGE, gilles (GPM, University of Rouen)

**Co-authors:** Prof. ZAPOLSKY, Helena (University of Rouen); Prof. BRUNEL, Marc (University of Rouen); Dr PATTE, Renaud (University of Rouen)

**Presenter:** Dr DEMANGE, gilles (GPM, University of Rouen)

**Track Classification:** Ice Crystal Growth

Contribution ID: 24

Type: Talk

## Laboratory Experiments on Heterogeneous Nucleation and Growth Rates of pure H<sub>2</sub>O ice and hydrates of HCl and HNO<sub>3</sub> in the range 165-195 K.

*Monday, January 8, 2018 5:30 PM (20 minutes)*

A multidagnostic Stirred Flow Reactor has been used to investigate heterogeneous nucleation of pure H<sub>2</sub>O ice from water vapor depositing on a silicon substrate mounted in a cryostat at controlled temperatures. The gas phase has been monitored using residual gas mass spectrometry, the cryogenic deposit was investigated using FTIR spectroscopy in transmission in the range 650 to 4000 cm<sup>-1</sup> across typically 0.5 to 2 micrometer thick ice films. Subsequent to ice deposition controlled amounts of HCl and HNO<sub>3</sub> were deposited on top of the previously deposited thin ice film all the while monitoring both FTIR absorption as well as the partial pressures of H<sub>2</sub>O and HCl or HNO<sub>3</sub> using m/e 18, 36 and 46 amu, respectively. Ice deposition on the Si substrate of the cryostat required a supersaturation ratio  $r$  (with respect to pure ice) varying from 2.22 to 16.45 with decreasing temperature at a typical growth rate of 2 monolayers (ML) s<sup>-1</sup>. The data lie on a straight line when plotted as  $\ln(1/r)$  vs.  $1/T$  with an activation energy of  $20.2 \pm 2.6$  kJ mol<sup>-1</sup> (Arrhenius plot). The underlying idea of the rate model for ice nucleation is that  $1/r$  is proportional to the encounter probability (or rate) of individual H<sub>2</sub>O molecules adsorbed on the thin (hydroxylated) SiO<sub>2</sub> (quartz) surface of the Si window. Low temperature leads to a high surface coverage of adsorbed H<sub>2</sub>O and to a large encounter probability to form a viable ice embryo at the SiO<sub>2</sub> interface. However, the surface self-diffusion of adsorbed H<sub>2</sub>O is an activated process whose rate slows down with decreasing temperature. The measured activation energy of 20.2 kJ mol<sup>-1</sup> corresponds to the bond energy of a single Hydrogen bond between a H<sub>2</sub>O molecule adsorbed onto a surface OH-group of SiO<sub>2</sub>. In contrast, when depositing HCl from the gas phase onto the thin H<sub>2</sub>O ice film we observe barrierless, that is spontaneous nucleation of HCl hexahydrate (HCl•6H<sub>2</sub>O or HH) at  $T < 173$  K monitored by FTIR absorption in situ. With increasing HCl deposition the growth rate of HH, typically 2 ML s<sup>-1</sup>, slows down owing to the decrease of the surface diffusion rate of adsorbed HCl across the existing HH film and comes to a halt after approximately 500 ML of deposited HCl. When depositing HNO<sub>3</sub> on pure thin ice films we essentially observe barrierless spontaneous formation of alpha-NAT (HNO<sub>3</sub>•3H<sub>2</sub>O) or NAD (HNO<sub>3</sub>•2H<sub>2</sub>O) at typical growth rates of 0.6 ML s<sup>-1</sup> akin to the HCl/ice system. In some cases a very small supersaturation is required to initiate crystal growth. The key message from this work is that spontaneous, that is barrierless, nucleation enables the formation of HCl and HNO<sub>3</sub> hydrates (type II Polar Stratospheric Clouds or PSC's) in the presence of stratospheric ice (type I PSC's).

### Significance statement

This work's key message is that spontaneous nucleation enables the formation of HCl and HNO<sub>3</sub> hydrates in the presence of stratospheric ice. The efficiency of this process is at variance with the reported difficulty to nucleate HCl and HNO<sub>3</sub> hydrates in the laboratory starting with the gas-phase components.

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**Co-author:** Dr IANNARELLI, Riccardo (EPFL)

**Presenters:** Dr ROSSI, Michel J. (Paul Scherrer Institute (PSI)); Dr IANNARELLI, Riccardo (EPFL)

**Track Classification:** Nucleation

Contribution ID: 25

Type: **Poster**

## Mass Accommodation and Rates of Evaporation of H<sub>2</sub>O, HNO<sub>3</sub> and HCl on HNO<sub>3</sub> hydrates (alpha-NAT, beta-NAT, NAD) in the range 175-200 K

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Experiments have been performed using a multidagnostic stirred-flow reactor (SFR) in which the gas- as well as the condensed phase have been simultaneously investigated under stratospheric temperatures in the range 175-200 K. Wall interactions of the title compounds have been taken into account using Langmuir adsorption isotherms in order to close the mass balance between deposited and desorbed (recovered) compounds. Thin solid films of 1 micrometer typical thickness have been used as a proxy for atmospheric ice particles and have been deposited on a Si window of the cryostat with the optical element being the only cold point in the deposition chamber. FTIR absorption spectroscopy in transmission in the range 650 to 4000 cm<sup>-1</sup> as well as partial and total pressure measurement using residual gas MS and sensitive pressure gauges have been employed in order to monitor growth and evaporation processes as a function of temperature using both pulsed and continuous gas admission and monitoring under SFR conditions. Thin solid H<sub>2</sub>O ice films were used as the starting point throughout, with the initial spontaneous formation of alpha-NAT followed by the gradual transformation of alpha- to beta-NAT at T > 185 K. NAD was spontaneously formed at somewhat larger partial pressures of HNO<sub>3</sub> deposited on pure H<sub>2</sub>O ice. In contrast to published reports the formation of alpha-NAT proceeded without prior formation of an amorphous HNO<sub>3</sub>/H<sub>2</sub>O layer and always resulted in beta-NAT. For alpha- and beta-NAT the temperature dependent accommodation coefficient  $\alpha(\text{H}_2\text{O})$  and  $\alpha(\text{HNO}_3)$ , the evaporation flux  $J_{\text{ev}}(\text{H}_2\text{O})$  and  $J_{\text{ev}}(\text{HNO}_3)$  and the resulting saturation vapor pressure  $P_{\text{eq}}(\text{H}_2\text{O})$  and  $P_{\text{eq}}(\text{HNO}_3)$  were measured and compared to binary phase diagrams of HNO<sub>3</sub>/H<sub>2</sub>O in order to afford thermochemical check of the kinetic parameters. The resulting kinetic and thermodynamic parameters of activation energies for evaporation ( $E_{\text{ev}}$ ) and standard heats of evaporation  $\Delta H_{\text{ev}}^0$  of H<sub>2</sub>O and HNO<sub>3</sub> for alpha- and beta-NAT, respectively, led to an estimate for the relative standard enthalpy difference between alpha- and beta-NAT of  $-6.0 \pm 20$  kJ/mol in favor of beta-NAT, as expected, despite a significantly larger value of  $E_{\text{ev}}$  for HNO<sub>3</sub> in alpha-NAT. This in turn implies a substantial activation energy for HNO<sub>3</sub> accommodation in alpha- compared to beta-NAT where  $E_{\text{acc}}(\text{HNO}_3)$  is essentially zero. The kinetic ( $\alpha(\text{HCl})$ ,  $J_{\text{ev}}(\text{HCl})$ ) and thermodynamic ( $P_{\text{eq}}(\text{HCl})$ ) parameters of HCl-doped alpha- and beta-NAT have been determined under the assumption that HCl adsorption did not significantly affect  $\alpha(\text{H}_2\text{O})$  and  $\alpha(\text{HNO}_3)$  as well as the evaporation flux  $J_{\text{ev}}(\text{H}_2\text{O})$ .  $J_{\text{ev}}(\text{HCl})$  and  $P_{\text{eq}}(\text{HCl})$  on both alpha- and beta-NAT are larger than the corresponding values for HNO<sub>3</sub> across the investigated temperature range but significantly smaller than the values for pure H<sub>2</sub>O ice at T < 200 K.

### Significance statement

Thermochemical closure has been achieved in the measurements of mass accommodation coefficients and absolute rates of evaporation of H<sub>2</sub>O, HCl and HNO<sub>3</sub> interacting with ice solids of atmospheric importance. These results provide accurate surface residence times of trace gases on ices and evaporative lifetimes of atmospheric ices.

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**Presenter:** Dr ROSSI, Michel J. (Paul Scherrer Institute (PSI))

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 26

Type: **Poster**

## Dielectric Response in Ice Ih: Signals Perpendicular to an Electric Field of 1 Hz to 1 MHz Applied to Cubes of Ice

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

In ice, the dielectric response signals of a Debye relaxation process have been measured parallel to the applied electric field. Here, we report response signals detected perpendicular to the applied field for ice samples. An alternating electric field (applied voltage  $V_0$ : 5 Vp-p) of 1 Hz to 1 MHz was applied to a cube ( $1 \times 1 \times 1$  cm) of single-crystal ice Ih between one pair of planes along the c-axis of the sample. We observed the dielectric response signal (detected voltage  $V_s$ ) between a pair of planes perpendicular to the applied electric field. The measurements were obtained with a frequency response analyzer from  $-3$  to  $-56$  °C. The frequency dependence of the response signal ( $V_s/V_0$ ) showed a peak in the kilohertz frequency range. The peak strength at  $-21$  °C was 1.2% of the applied voltage. The peak strength decreased with decreasing temperature, and the peak faded below  $-50$  °C. Peak frequency  $f_0$  (1065 Hz at  $-21$  °C) also shifted to the low-frequency side with decreasing temperature. The frequency dependence of the response signal was described with a simple equation related to the current oscillating in an inductor-resistor-capacitor (LRC) series circuit. The temperature dependence of the characteristic time,  $1/(2\pi f_0)$ , showed that the activation energy was 0.30 eV in the range of  $-10$  to  $-50$  °C. This result means that the proton mechanism of the response signal (0.30 eV) is different to that of the Debye dielectric dispersion (0.58 eV) in ice. The peak phenomenon related to the response signal suggests that there was some kind of proton oscillating current (e.g. the migration of point defects) on the ice crystal lattice in only the high-temperature region above  $-50$  °C.

### Significance statement

We will report new experimental results in ice Ih, as response signals detected perpendicular to the applied field for ice cube samples. The signal showed a peak in the kilohertz frequency range. Simple discussion for the peak phenomenon is given.

**Primary author:** Prof. TAKEI, Iwao (Hokuriku University)

**Presenter:** Prof. TAKEI, Iwao (Hokuriku University)

**Session Classification:** Poster & Lunch

Contribution ID: 27

Type: **Poster**

## The phase diagram of ice

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Many regions of the phase diagram of ice remain unclear. Through measurements of the near static dielectric constant a) the ice Ih/XI phase boundary line is confirmed to occur at 73 K along with the existence of the ice Ih/II/XI triple point residing at 0.07 GPa and 73 K [Phys. Chem. Chem. Phys. 2015, 17, 12458]; b) a critical point is identified to reside near 33-50 MPa and below 210 K believed to be the first direct measurement of the 2nd critical point of water [J. Phys. Chem. C 2015, 119, 20168]; c) the ice II/V/VI triple point is verified to occur at 0.62 GPa and 208 K; d) the ice IV/VI boundary line is extended to 1.2 GPa; and e) macroscopic quantum phenomenon in the form of correlated proton tunneling is identified to occur below 20 K [J. Phys. Chem. Lett. 6, 2822].

### Significance statement

A resolved phase diagram of H<sub>2</sub>O will help better understand a) the molecular dynamics of protons in ice; b) ice nucleation processes in outer space conditions, and; c) the interior composition of many icy planets.

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**Presenter:** Dr YEN, Fei (Southern University of Science and Technology)

**Session Classification:** Poster & Lunch

Contribution ID: 28

Type: **Poster**

## The Effects of H<sub>2</sub>SO<sub>4</sub> on the Mechanical Behavior and Microstructural Evolution of Polycrystalline Ice

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

It is well established that the Earth's large continental ice sheets contain a variety of naturally occurring impurities, both soluble and insoluble. Understanding how these impurities affect the rheology, intrinsic thermodynamic properties, and fate of these ice sheets is much less understood. To investigate the effects that trace amounts of H<sub>2</sub>SO<sub>4</sub> have on the flow and ductility of polycrystalline ice, a series of mechanical tests were conducted at -6°C, -10°C, -12.5°C, and -20°C using laboratory-prepared specimens of polycrystalline ice doped with 1-15 ppm of H<sub>2</sub>SO<sub>4</sub>. Parallel tests were performed on identical, but undoped specimens of polycrystalline ice. Mechanical testing included constant-load tensile creep tests at an initial stress of 0.75 MPa and compression tests at constant displacement rates with initial strain rates ranging from  $1 \times 10^{-6} \text{ s}^{-1}$  to  $1 \times 10^{-4} \text{ s}^{-1}$ . It was found that H<sub>2</sub>SO<sub>4</sub>-doped specimens of ice exhibited faster creep rates in tension and significantly lower peak stresses in compression, when compared to the undoped ice. Post-mortem microstructural analyses were performed using cross-polarized light thin section imaging, X-ray computed microtomography, Raman spectroscopy, and electron backscatter diffraction. These analyses showed that H<sub>2</sub>SO<sub>4</sub>-doped specimens had a larger grain size at strains  $\leq 15\%$ , and an earlier onset of micro-cracking at lower strain rates than the undoped ice. Strain-induced boundary migration was the predominant mechanism of recrystallization in both doped and undoped specimens. Further, a liquid-like phase containing H<sub>2</sub>SO<sub>4</sub> was found to be present at the grain boundaries of the H<sub>2</sub>SO<sub>4</sub> doped ice at temperatures close to the melting point.

### Significance statement

Following the mechanical testing in tension and compression of laboratory prepared specimens of polycrystalline ice doped with sulfuric acid, differences in the microstructural evolution between the doped and undoped ice were attributed to the presence of a liquid phase at grain boundaries and triple junctions due to impurity segregation.

**Primary author:** Prof. HAMMONDS, Kevin (Montana State University)

**Co-author:** Dr BAKER, Ian (Dartmouth College)

**Presenter:** Dr BAKER, Ian (Dartmouth College)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 29

Type: **Poster**

## **Ice freezing and gas hydrate formation in water-in-oil emulsions**

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Experimental investigations carried out in this work allowed us to elucidate a number of new aspects in the ice freezing and gas hydrate formation processes in water-in-hydrocarbon emulsions. Various types of oils, including one with different biodegradation levels, and n-decane were used as disperse media. As it has been shown there are several hydrate and ice formation ways in the emulsions. (1) Primary nucleation of a solid phase on any of water droplet leads to a rapid secondary nucleation in a region of the emulsion adjacent to the droplet. The thermal effect is characterized by a rapid rise in temperature at the leading edge and a slow decrease at the trailing edge. Since a significant thermal effect can be observed by thermal methods, it makes possible to use them to study primary nucleation. (2) Primary nucleation of a solid phase on any of water droplet leads to a rapid secondary nucleation in a small number of neighboring droplets. Then the secondary nucleation decays. In this case, there is one or more small exothermal effects on the thermal curve. (3) Primary nucleation on any of the water droplet leads to an occurrence of rapid secondary nucleation only in a certain fraction of cases (if nucleation has occurred in a droplet agglomerate for instance). In this case, the thermal effect can be indistinguishable from the case (1). However, the statistics of the thermal effects appearance reflects not only the dynamics of the primary nucleation, but also the structural features of this emulsion. (4) Primary nucleation of the solid phase on any of the water droplet leads to a slow secondary nucleation in some region of the emulsion adjacent to this drop. This type of nucleation process relates to hindered germination of the crystallites through the medium. Release of heat in this process seems to will increase due to the involvement of free water droplets into it until some moment. In this case, an extended exothermal effect will appear on the thermal curve, the shape of which may be close to a symmetric. (5) Primary nucleation of the solid phase on any water droplet never leads to the secondary nucleation process. In this case, latent crystallization of the solid phase occurs during the emulsion cooling. A noticeable exothermal effect is manifested only about a point of homogeneous ice nucleation. It should be noted that the presence of secondary nucleation can have a significant effect on the agglomeration of hydrate and ice particles in oil suspensions. The germination of a crystal from one water particle to another indeed creates a mechanical connection between them. Thus, the particles involved in the secondary nucleation process will be agglomerated to a great extent. It was also shown that the appearance of biodegradation products in oil leads to an easier process of secondary nucleation of gas hydrates and ice in the emulsion and slightly increases the probability of hydrate nucleation.

Acknowledgments (This work was supported by Russian Science Foundation grant No 17-17-01085)

### **Significance statement**

The results of this work extend comprehension of the mechanisms of ice freezing and gas hydrates formation in water-in-oil emulsions.

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**Presenter:** STOPOREV, Andrey (Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk State University)

**Session Classification:** Poster & Lunch



Contribution ID: 30

Type: **Poster**

## Unexpected formation of sII methane hydrate in some water-in-oil emulsions

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The structures of methane hydrate obtained from emulsions of water in some crude oils have been studied. It was shown that in some of these emulsions, a hydrate of the cubic structure II (sII) instead of the expected the cubic structure I (sI) hydrate was formed when a methane-saturated sample was rapidly cooled to temperatures below -35 °C. All experiments were carried out at a cooling rate of about 14 °C/min and a methane pressure of about 12 MPa. The sII hydrate formation in the emulsions occurred at temperatures lower than pour point of the oils. As far as we know, such an opportunity has not been previously considered in the literature. A more detailed study showed that in one of these emulsions the sII hydrate formed is metastable because sI hydrate forms in this emulsion during a long synthesis. In another case, the formation of sII hydrate can be related to both the kinetic factor (the formation of a metastable hydrate) and the presence of C3-C4 hydrocarbons in the corresponding oil in a sufficient amount. sI methane hydrate only in small amounts was formed in this oil. We assume that the reason for a metastable phase appearance in a methane – water-in-oil emulsion system is the delayed nucleation of the sI hydrate at the water – oil phase boundary. Due to this fact, the emulsions saturated with methane can be supercooled to temperatures at which the nucleation of sII hydrate is preferred.

Acknowledgments (This work was supported by Russian Science Foundation grant No 17-17-01085)

### Significance statement

To the best of our knowledge, this is the first time that in some methane – water-in-oil emulsion systems sII hydrates instead of sI methane hydrate can be formed. Results of this work extend comprehension of mechanisms of gas hydrate nucleation in water-in-oil emulsions at nanoscale stage.

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**Presenter:** STOPOREV, Andrey (Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk State University)

**Session Classification:** Poster & Lunch

Contribution ID: 31

Type: **Talk**

## Water Mobility in the Interfacial Quasi-Liquid Layer of Ice/Clay Nanocomposites

*Thursday, January 11, 2018 9:35 AM (20 minutes)*

At ice/solid interfaces, a quasi-liquid premelting layer (qll) is formed at temperatures below the melting point of bulk water. This qll affects the properties of ice/clay nanocomposites found in ground ice and permafrost. One of the decisive parameters is the water mobility within the qll. Using quasi elastic neutron scattering, the translational diffusion constant of the qll was studied for model systems prepared from clay minerals with large surface to volume ratios. Measurements on a series of charged (vermiculite), hydrophilic (kaolin), and hydrophobic (talc) ice/clay nanocomposites unravel the influence of the solid surfaces. For all composites, the translational diffusion constants within the qll are strongly reduced compared to super cooled bulk water. Depending on their surface properties, significant differences were found for the studied clay minerals. This indicates that beside of confinement effect, intermolecular interactions between the water molecules and the solid surfaces play an important role for the water mobility in the qll.

### Significance statement

Material properties of permafrost strongly depend on the molecular scale structure and dynamics of the qll at ice/solid interfaces. Here, we report a QENS study on ice/clay nanocomposites that serve as model systems for permafrost. The results have implications to understand contaminant migration in frozen soils.

**Primary author:** Prof. MEZGER, Markus (Max Planck Institute for Polymer Research)

**Co-authors:** Dr LI, Hailong (MPI Polymer Research); Mr WEISS, Henning (MPI Polymer Research); Mr MARS, Julian (MPI Polymer Research); Dr LOHSTROH, Wiebke (Heinz Maier-Leibnitz Zentrum)

**Presenter:** Prof. MEZGER, Markus (Max Planck Institute for Polymer Research)

**Track Classification:** The surface and interface of ice

Contribution ID: 32

Type: **Poster**

## Interfacial premelting of ice in nanocomposite materials

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Material properties of ground ice and permafrost strongly depend on the molecular scale structure and dynamics of the quasi-liquid premelting layer (qll) formed at ice/solid interfaces. Already in 1859, Faraday proposed the existence of a qll at ice surfaces. However, despite the extensive amount of research devoted to the understanding of interfacial ice melting, the structure of the qll adjacent to solids is still under debate. Layered sheet silicates with high interface to volume ratios such as vermiculite or kaolin are ideal model systems to study the interfacial melting of ice in geologically relevant materials. We employed high-energy x-ray diffraction (HEXRD) to measure the temperature dependence of the crystalline ice fraction in these ice/clay composites. Well below the melting point of bulk water, the formation of a qll was observed. The thickness of this qll is gradually increasing with temperature. Pronounced differences in the growth law are observed between the charged vermiculite and uncharged kaolin minerals. For higher temperatures, the qll thickness is compared with theoretical predictions from continuum models. The data is best described by a logarithmic growth law, originating from short range interactions.

### Significance statement

Using well defined and characterized ice/clay nano composite samples, this work bridges the gap between studies on single crystalline ice/solid model interfaces and naturally occurring soils and permafrost.

**Primary author:** Dr LI, Hailong (Max Planck Institute for Polymer Research)

**Co-authors:** Dr DIPPEL, Ann-Christin (PETRAIII, DESY); Mr WEISS, Henning (Max Planck Institute for Polymer Research); Mr MARS, Julian (Max Planck Institute for Polymer Research); Prof. MEZGER, Markus (Max Planck Institute for Polymer Research); Mr GUTOWSKI, Olof (PETRAIII, DESY); Dr HONKIMÄKI, Veijo (ESRF-The European Synchrotron)

**Presenter:** Dr LI, Hailong (Max Planck Institute for Polymer Research)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 33

Type: **Talk**

## Bilayer-by-Bilayer Surface Melting of Crystalline Ice

*Wednesday, January 10, 2018 5:50 PM (20 minutes)*

Over 150 years ago, Faraday proposed the existence of a liquid-like layer at ice surfaces below the bulk melting temperature. This layer is important for surface chemistry and glacier sliding close to sub-freezing conditions. Since Faraday's discovery, the properties of this water-like layer have been intensely debated, entailing considerable controversy. The experimentally reported onset temperature for quasi liquid layer (QLL) formation varies between 200 K and 271 K. Moreover, most experimental work shows that with increasing temperature, the QLL thickness gradually and continuously increases from the onset temperature up to the bulk melting point, with reported thicknesses varying from 2 nm to over 45 nm at 271 K. In contrast, early simulations showed that the QLL is formed in a more quantized, bilayer-by-bilayer manner.

To elucidate the precise temperature variation of the QLL, and its nature, we investigate the surface melting of ice Ih by combining non-contact, surface-specific vibrational sum frequency generation (SFG) spectroscopy and spectra calculated from molecular dynamics simulations. In our SFG experiment an 800 nm and a 3  $\mu\text{m}$  laser pulse are combined at the interface and the sum-frequency light is detected. Being a second-order nonlinear process, SFG is forbidden in centrosymmetric materials such as the proton disordered ice studied here. At the interface this symmetry is broken, thus allowing us to specifically probe the vibrational response of the interfacial region. The signal is strongly enhanced when the infrared laser pulse is resonant with a molecular vibration. Here we use the O-H stretch vibration of the interfacial water molecules to report on the (molten or non-molten) state of the interface.

Using SFG, we probe the outermost water layers of distinct single crystalline ice faces at different temperatures. Macroscopic single-crystalline ice samples are grown from a melt using the seed extraction method. Afterwards the samples are oriented and cut to obtain a specific face. For the basal face, a stepwise, sudden shift in the SFG spectrum to higher frequency occurs around 257 K, which means that the hydrogen-bonded structure of the outermost water layers weakens at this temperature. The spectral calculations from the molecular dynamics simulations reproduce the experimental findings. Moreover, both the experimental and the calculated spectra show only a very weak change in the dangling OH bond. From the combined experimental and simulated surface-specific vibrational spectroscopy, we conclude that the thickness of the quasi liquid layer changes in a non-continuous, stepwise fashion around 257 K. Below this temperature, the first bilayer is already molten; the second bilayer melts at this transition temperature.

### Significance statement

For reactions taking place on ice surfaces the molecular level structure is very important, i.e. an ice- or liquid-like surface. Our results show a weakening of the hydrogen bond structure around 257 K, which we assign to a phase transition from one-to-two molten bilayers.

**Primary author:** BACKUS, Ellen (Max Planck Institute for Polymer Research)

**Co-authors:** SANCHEZ, Alejandra (Max Planck Institute for Polymer Research); BONN, Mischa (Max Planck Institute for Polymer Research)

**Presenter:** BACKUS, Ellen (Max Planck Institute for Polymer Research)

**Track Classification:** The surface and interface of ice

Contribution ID: 34

Type: **Poster**

## Vibrational Relaxation of water at the Ice – Air Interface

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The surface of ice is relevant for various important phenomena including glacier sliding, and (photo-) chemical conversion of molecules on that surface.

For chemical reactions occurring on the ice surface, the dynamics of the surface water molecules and energy flow pathways play an important role: following a chemical reaction, the rate of excess energy dissipation determines the probability of a back-reaction occurring. Here we elucidate the relaxation dynamics of water molecules at the surface of single crystalline hexagonal ice after exciting the O-H stretch vibration. We compare our results with the relaxation dynamics of the liquid water-air interface.

To study the vibrational dynamics we apply time-resolved sum frequency generation spectroscopy (SFG). With this method we can specifically study the outermost molecular water layer at the ice-air interface and follow the relaxation dynamics of those interfacial water molecules following vibrational excitation. Time-resolved SFG is a laser-based spectroscopic technique that involves vibrationally exciting a fraction of surface molecules with a femtosecond infrared excitation pulse, and probing the dynamics of the interfacial molecules with the sum frequency generation process using a visible and an infrared pulse resonant with the O-H stretch vibrations. This detection scheme ensures that only the interfacial water molecules contribute to the signal, and the use of ~50 fs laser pulses ensures high time resolution in the experiments.

Our results show that the relaxation dynamics of the O-H stretch mode after excitation at 3100  $\text{cm}^{-1}$  at the basal plane of ice is around 70 fs. This is three times faster than for the water-air interface. A potential reason for the faster relaxation could be the stronger hydrogen bonding of water molecules on the ice surface, compared to water. We discuss the implications of this fast energy dissipation in terms of more effectively catalyzing reactions on ice than on water.

### Significance statement

We determine the vibrational energy relaxation of water molecules at the ice–air interface and compare it to the water-air interface. Vibrational energy relaxation rates reflect the local H-bonding network of water molecules. Our results shed light on interfacial energy dissipation, relevant for atmospheric catalytic reactions.

**Primary author:** Ms SUDERA, Prerna (PhD student)

**Co-authors:** Dr SÁNCHEZ, Alejandra (Max Planck Institute for Polymer Research); BACKUS, Ellen (Max Planck Institute for Polymer Research); Dr CYRAN, Jenee (Max Planck Institute for Polymer Research); Prof. BONN, Mischa (Max Planck Institute for Polymer Research)

**Presenter:** Ms SUDERA, Prerna (PhD student)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 35

Type: **Poster**

## Polycyclic Aromatic Hydrocarbons on Ice

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Ice has significant effects on the climate and biogeochemical systems and plays a role in reactions known to contribute to ozone depletion and atmospheric pollution. Long range transport of hazardous pollutants, such as polycyclic aromatic hydrocarbons (PAHs), on ice contributes to the disruption of these biogeochemical systems. PAHs and their derivatives from photolysis are known to be carcinogenic to humans and hazardous to plants and animals. Despite the global impact, the adsorption of PAHs and their derivatives on ice surfaces and the mechanism for photolysis have yet to be determined. To observe the absorption of PAHs on ice surfaces, a surface-selective technique with molecular specificity is essential. Moreover, to study the photolysis of PAHs on ice surfaces in real time ultrafast time resolved measurements are required. Time resolved sum frequency generation spectroscopy (SFG) is a surface selective technique that probes reactions on sub-picosecond timescales by monitoring vibrations of molecules especially at an interface. Therefore, measuring PAHs on ice surfaces with SFG spectroscopy would provide a molecular scale understanding of the adsorption of PAHs on ice surfaces and the photolysis mechanism. As a first step in unraveling the mechanism, we probe the adsorption of naphthalene and anthracene on the surface of well-defined single crystalline ice, using molecular vibrations intrinsic to both the PAHs and ice. Determining the adsorption of PAHs on ice surfaces and the role of ice in their subsequent photochemical fate can resolve which molecules have a higher propensity for the ice surface and how their photo reactivity is affected. Such insights will aid in understanding both long range transport and surface reactivity of contaminants. In this way, better models to predict the disruption of biogeochemical cycles can be developed.

### Significance statement

Ice acts like a sink for organic pollutants and can serve as catalyst and reaction site. Specifically, upon adsorption on ice, PAHs undergo significant red shifts in their absorption spectra, overlapping with the solar output. We aim to elucidate adsorption and photochemical reactions of PAHs on ice surfaces.

**Primary author:** Dr CYRAN, Jenee (Max Planck Institute for Polymer Research)

**Co-authors:** BACKUS, Ellen (Max Planck Institute for Polymer Research); Prof. BONN, Mischa (Max Planck Institute for Polymer Research); Ms SUDERA, Prerna (PhD student)

**Presenter:** Dr CYRAN, Jenee (Max Planck Institute for Polymer Research)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 36

Type: **Poster**

## A new parametrization and minimal model for glacier calving

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The iceberg calving process influences the geometry of a tidewater glacier, and is in turn controlled by the terminus geometry through the stress field which controls damage and fracture of the ice. A simple parametrization of the stress field at the glacier terminus is obtained from the results of a Finite Element model with varying water depths. Using this stress field in an isotropic damage evolution equation yields calving rates in dependence of calving front thickness and water depth. These parametrized calving rates compare favorably with observations, and extend well established parametrizations. The proposed calving parametrization is easy to implement in numerical ice sheet models. Using these parametrized calving rates in a minimal calving model allows us to analyze the intricate feedbacks of the calving process, reproduce observed tidewater glacier dynamics, and to analyze the stability of glacier termini.

### Significance statement

This work presents a new, physics-based and experimentally validated parametrization for glacier calving. Parameters of a damage evolution law applicable to glacier ice can therefore be inferred.

**Primary author:** Dr LUETHI, Martin (University of Zurich, Geography)

**Co-authors:** Dr VIELI, Andreas (University of Zurich); Mr MERCENIER, Remy (University of Zurich)

**Presenter:** Dr LUETHI, Martin (University of Zurich, Geography)

**Session Classification:** Poster & Lunch



Contribution ID: 38

Type: **Talk**

## Enhanced heterogeneous ice nucleation by special surface geometry

*Tuesday, January 9, 2018 2:05 PM (20 minutes)*

Surface roughness has been long known to affect nucleation, but its role in ice formation remains controversial and poorly understood. Experiments showed ice nucleation is significantly promoted by surface irregularities on hematite, mica, and potassium-rich feldspar, but is relatively insensitive to the roughness of superhydrophobic surfaces.

By employing large-scale, accelerated molecular simulations, here we show that heterogeneous ice nucleation is strongly affected by surface geometry<sup>1</sup>. An atomically sharp, concave wedge is found to significantly enhance ice nucleation rate by many orders of magnitude over flat surface. However, in contrast to classical nucleation theory, the enhancement is found to occur only under special surface geometries. These include the 70- and 110-degree wedges that match the two intersecting {111} planes of cubic ice lattice simultaneously, thus significantly enhancing the formation of cubic ice. Remarkably, significant enhancement of ice nucleation also occurs when lattice match does not exist, as in a 45-degree wedge. In this geometry, the 45-degree wedge is found to facilitate the formation of special topological defects of ice that subsequently catalyze the growth of regular ice. Therefore, our study not only highlights the active role of defects in nucleation, but also suggests the traditional concept of lattice match between a nucleation center and crystalline lattice should be extended to include a broader match with metastable, non-crystalline structural motifs.

1. Bi, Y., Cao, B. & Li, T. Enhanced heterogeneous ice nucleation by special surface geometry. *Nat Commun* 8, 15372 (2017).

### Significance statement

Traditional wisdom believes a good ice nucleator must be capable of inducing water ordering coherent to ice lattice. We presented the first computational evidence that challenges this understanding by showing ice nucleation can be equally or even more effectively promoted by special surface geometry through inducing a non-crystalline ordering.

**Primary author:** Prof. LI, Tianshu (George Washington University)

**Co-authors:** Mr CAO, Boxiao (George Washington University); Mr BI, Yuanfei (George Washington University)

**Presenter:** Prof. LI, Tianshu (George Washington University)

**Track Classification:** Nucleation

Contribution ID: 40

Type: PICO talk

## Formation of quasi-liquid layers on polycrystalline ice

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Surface melting of ice occurs below  $0^{\circ}\text{C}$ , and then ice surfaces are covered with quasi-liquid layers (QLLs). Our previous studies revealed that QLLs are formed kinetically on ice single crystals only in the temperature range higher than  $-2^{\circ}\text{C}$  [1, 2]. However, other studies reported the appearances of QLLs even below  $-10^{\circ}\text{C}$  [3]. To clarify the cause for this big discrepancy, in this study we focused on polycrystalline ice that includes a large amount of lattice defects and grain boundaries, and aimed to find the difference in the emergence of QLLs on poly- and single crystalline ice.

A thin film of polycrystalline ice with the size smaller than  $0.5 \times 0.5 \text{ mm}^2$  was prepared on a glass plate. Then the glass plate with the ice thin film was placed in an observation chamber, in which temperature of the ice thin film (T) and water vapor pressure (P) can be controlled separately. First, QLLs were formed on the polycrystalline ice thin film under a P-T range (P: supersaturated and  $T > -2^{\circ}\text{C}$ ), in which QLLs are formed spontaneously on an ice single crystal. Second, T was decreased to a certain T ( $< -2^{\circ}\text{C}$ ), and then at this constant T, P was decreased gradually. Throughout these processes, the surface of the polycrystalline ice thin film was observed by two kinds of optical microscopy: bright-field optical microscopy and Michelson-type interferometry. These two kinds of microscopy were combined with laser confocal microscopy.

When QLLs were formed on the polycrystalline ice thin film at  $T > -2^{\circ}\text{C}$ , we could observe the QLLs, by bright-field microscopy, as objects with a dark contrast, which corresponded to the contrast formed by the interference between light beams reflected at an air-QLL interface and a QLL-ice interface. The QLLs with the dark contrast showed significant fluidity, clearly demonstrating that they were not solid but liquid.

After T was decreased to a certain T ( $< -2^{\circ}\text{C}$ ), we observed the QLLs by Michelson interferometry. On the QLLs, we could observe interference fringes formed by the interference between light beams reflected at the air-QLL interface and a reference mirror. From the moving direction of these interference fringes, we found that after the decrease in T, QLLs were growing. Then at the constant T, we gradually decreased P. When P became smaller than a certain critical value, the interference fringes were moved in the opposite direction, indicating that the QLLs started to shrink. The critical P shows the pressure above which the QLLs could grow stably.

We performed similar experiments under various temperatures. Then we found that on polycrystalline ice, QLLs can exist stably at least in the temperature range of  $-15$  to  $0^{\circ}\text{C}$ , which is significantly lower than that on single crystalline one.

### References

- 1) H. Asakawa, et al., PNAS, 113, 1749-1753 (2016).
- 2) K. Murata, et al., PNAS, 113, E6741-E6748 (2016).
- 3) M. Elbaum, et al., J. Cryst. Growth, 129, 491-505 (1993).

### Significance statement

We directly visualized the growth and shrinkage of quasi-liquid layers (QLLs) on polycrystalline ice by bright-field optical microscopy and Michelson-type interferometry. Then we experimentally proved that QLLs can appear on polycrystalline ice at a much lower temperature range than that on single crystalline one.

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**Presenter:** Mr CHEN, Jialu (Institute of Low Temperature Science, Hokkaido University)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 41

Type: PICO talk

# Temperature dependence of the growth kinetics of elementary spiral steps on ice basal faces grown from water vapor

Wednesday, January 10, 2018 6:10 PM (3h 5m)

Ice is one of the most abundant materials on the earth. Hence, crystal growth of ice governs a wide variety of phenomena in nature. For example, most rains fallen outside tropical regions are formed by the melting of ice crystals (snowflakes) that were grown in the sky and then descended to the ground [1]. Therefore, to understand the growth kinetics of ice crystals is extremely important. Recently, we improved laser confocal microscopy combined with differential interference microscopy (LCM-DIM) [2] further, and then succeeded in visualizing individual elementary steps (0.37 nm in thickness) on ice crystal surfaces growing in supersaturated water vapor by LCM-DIM [3]. Hence, in this study, we tried to reveal the temperature dependence of the growth kinetics of elementary steps on ice basal faces.

We measured velocity  $V_{\text{step}}$  of isolated elementary spiral steps and distance  $L_{\text{eq}}$  between adjacent equivalent spiral steps on ice basal faces by LCM-DIM. We determined the step kinetic coefficient  $\beta$  from  $V_{\text{step}}$  measured under various supersaturations. We performed similar experiments under various temperatures  $T$ , and determined the temperature dependence of  $\beta$  of ice basal faces, for the first time, in the temperature range of  $-26.0$  to  $-2.7^\circ\text{C}$ . When  $-6.2 \leq T \leq -2.7^\circ\text{C}$ , the value of  $\beta$  decreased significantly with decreasing  $T$ . In contrast, when  $-15.0 \leq T \leq -6.2^\circ\text{C}$ , the value of  $\beta$  increased with decreasing  $T$ , and had the maximum at  $T \approx -15^\circ\text{C}$ . When  $-26.0 \leq T \leq -15.0^\circ\text{C}$ , the value of  $\beta$  decreased monotonically with decreasing  $T$ . Such complicated temperature dependence of  $\beta$  strongly implies the existence of unknown phenomena in the temperature range examined.

To obtain a clue to the complicated behavior of  $\beta$ , we also measured dependence of  $L_{\text{eq}}$  on surface supersaturation  $\Delta\mu^{\text{surf}}$ . When  $-9.2 \leq T \leq -3.2^\circ\text{C}$ , plots of  $L_{\text{eq}}$  vs.  $1/\Delta\mu^{\text{surf}}$  satisfactorily follow the spiral growth model. However, when  $-26.0 \leq T \leq -13.0^\circ\text{C}$ , the  $L_{\text{eq}}$  vs.  $1/\Delta\mu^{\text{surf}}$  plots do not follow any model: this temperature range agrees with the temperature range in which  $\beta$  decreased monotonically with decreasing  $T$ .

## References

- 1) Pruppacher, H. R.; J.D.Klett, Microphysics of clouds and precipitation. ed.; Springer: 1996; Vol. 18.
- 2) Sazaki, G.; Matsui, T.; Tsukamoto, K.; Usami, N.; Ujihara, T.; Fujiwara, K.; Nakajima, K., In situ observation of elementary growth steps on the surface of protein crystals by laser confocal microscopy. *Journal of Crystal Growth* 2004, 262, (1-4), 536-542.
- 3) Sazaki, G.; Zepeda, S.; Nakatsubo, S.; Yokoyama, E.; Furukawa, Y., Elementary steps at the surface of ice crystals visualized by advanced optical microscopy. *Proceedings of the National Academy of Sciences of the United States of America* 2010, 107, (46), 19702-19707.

## Significance statement

We measured the growth kinetics of “elementary steps” on ice basal faces under various temperatures. Then we found that the temperature dependence of the growth kinetics shows a significantly complicated behavior, demonstrating that there still exist unknown phenomena in the growth of elementary steps on ice basal faces.

**Primary author:** Mr INOMATA, Masahiro (Institute of Low Temperature Science, Hokkaido University)

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**Presenter:** Mr INOMATA, Masahiro (Institute of Low Temperature Science, Hokkaido University)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 42

Type: **Poster**

## Experimental and model based investigation of the links between snow bidirectional reflectance and snow microstructure

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Snow optical properties are unique among Earth surfaces and crucial for a wide range of applications. The bi-directional reflectance factor, hereafter BRDF, of snow is sensitive to snow microstructure. However the complex interplays between different parameters of snow microstructure, namely size and shape parameters, on reflectance are challenging to disentangle both theoretically and experimentally. An accurate understanding and modelling of snow BRDF is required to correctly process satellite data. BRDF measurements might also provide means to characterize the snow morphology. This study presents one of the very few datasets that combines bi-directional reflectance measurements over 500-2500 nm and X-ray tomography of the snow microstructure for three different snow samples and two snow types. The dataset is used to evaluate the approach from Malinka, 2014 that relates snow optical properties to the chord length distribution in the snow microstructure. For low and medium absorption, the model simulated BRDF accurately reproduces the measurements but tends to slightly overestimate the anisotropy of the reflectance. The simulated reflectance is strongly affected by the uncertainties in the imaginary part of the ice refractive index for several wavelength ranges. The model indicates that the deviation of the ice chord length distribution from the exponential one, that can be understood as related to snow types, does not impact the reflectance for such absorptions. The study also indicates that crystal habits might play a significant role for the reflectance under high absorption and oblique viewing and incidence. However, quantitative relationship between crystal habits and reflectance alongside with potential optical methodologies to classify snow morphology, would require an extended dataset over more snow types. It might be achieved by means of ray tracing models on tomography images of the snow microstructure.

### Significance statement

This study presents a unique dataset that combines micro-tomographic images of snow microstructure with measurements of bi-directional reflectance in the solar spectrum.

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**Co-authors:** Dr MALINKA, Aleksey (Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus); FLIN, Frederic (Meteo-France CNRS / CNRM UMR 3589 / CEN); Dr BRISSAUD, Olivier (Univ. Grenoble Alpes - CNRS, IPAG, Grenoble, France); Dr HAGEMULLER, Pascal (Meteo-France - CNRS, CNRM UMR 3589, Centre d'Etudes de la Neige, Grenoble, France); Mr LAPALUS, Philippe (Meteo-France - CNRS, CNRM UMR 3589, Centre d'Etudes de la Neige, Grenoble, France)

**Presenters:** FLIN, Frederic (Meteo-France CNRS / CNRM UMR 3589 / CEN); Dr DUMONT, Marie (Meteo-France - CNRS / CNRM / CEN)

**Session Classification:** Poster & Lunch

Contribution ID: 43

Type: **Poster**

## Icicle ripples: toward a model with impurities

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Icicles observed in nature and the laboratory often exhibit ribs or ripples with a wavelength close to 1cm around their circumference. Previous experiments on laboratory-grown icicles have shown that the existence of these ripples depends on the presence of (very small) concentrations of impurities in the feed water. However, all existing theoretical models of the icicle ripple instability have ignored the purity of the water.

We present a model of solid icicle growth incorporating the effects of impurities on the freezing point. This model is based on previous work that assumed a thin-film flow over solid ice. We introduce realistic, physically derived boundary conditions for both heat transfer and impurity concentration. A linear stability analysis of this model was performed numerically to high orders of ripple wavenumber.

We show that this more physically complete model of solid icicle growth cannot account for the 1cm wavelength of the ripple instability, because the effects of impurities are inherently too weakly coupled to the freezing dynamics. This suggests that a more complex model must be used, possibly one involving so-called “spongy” ice. Models of the freezing and growth of spongy ice are more strongly affected by impurities in the water. We propose experiments to look for the presence of spongy ice in laboratory-grown icicles in order to test this hypothesis.

### Significance statement

Icicles are an ideal test-case for understanding the morphology of “wet” ice growth. We present theory and experiments on the icicle rippling instability and show that ripples cannot be explained by a straightforward extension of previous models. This is significant for mitigating the engineering hazards of wet ice formation.

**Primary author:** Mr LADAN, John (University of Toronto)

**Co-author:** Prof. MORRIS, Stephen W (University of Toronto)

**Presenter:** Mr LADAN, John (University of Toronto)

**Session Classification:** Poster & Lunch

Contribution ID: 44

Type: **Poster**

## Electrocrystallisation of water/ice nano-droplets

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Elucidating water-to-ice freezing, especially in “No Man’s Land” ( $150\text{ K} < T < 235\text{ K}$ ) is fundamentally important (e.g., predicting upper-troposphere cirrus-cloud formation) – and elusive. An oft-neglected aspect of tropospheric ice-crystallite formation lies in inevitably-present electric fields’ role. Exploring nucleation in No Man’s Land is technically demanding, owing to rapid nucleation rates, to mention nothing of difficulties of applying relevant electric fields thereto. Here, we tackle these intriguing open questions, via non-equilibrium molecular-dynamics simulation of sub-microsecond formation of ice Ic nano-crystallites from aggressively-quenched supercooled water nano-droplets in the gas phase, in external static electric fields. We explore droplets’ nano-confined geometries and the entropic-ordering agent of external electric fields as a means of realising cubic-ice formation. We also discuss stability of ice and water nano-droplets in a variety of electric fields.

### Significance statement

Realising cubic ice is very challenging experimentally, as is probing of No Man’s Land. Here, we show a reproducible way of obtaining cubic ice, as well as probing the intriguing vagaries of field-mediated entropic ordering.

**Primary author:** Prof. ENGLISH, Niall (UCD)

**Presenter:** Prof. ENGLISH, Niall (UCD)

**Session Classification:** Poster & Lunch



Contribution ID: 45

Type: **Talk**

## Born-Oppenheimer molecular-dynamics study of ice polymorphs

*Monday, January 8, 2018 10:50 AM (20 minutes)*

We report ab-initio molecular dynamics, using state-of-the-art non-local dispersion, to study, inter alia, the structural, hydrogen-bonding, vibrational and Raman properties of ices Ih, VII and XVII at appropriate temperature and pressure ranges for their stability. In many senses, probing of ice Ih serves as a validation tool for the functional, with reasonable agreement with experiment.

In the case of ice VII, we are motivated to elucidate any possible hints of intramolecular strain that may serve as precursor events for proton hopping to unfold. We determine such equilibrium properties to be in reasonable agreement with experiment, although we do not detect any water-dissociation and proton-hopping events per se, owing to still-large water-dissociation free-energy barriers. The observed anomalous self-diffusivity of ice VII in the region of 10 GPa at ~400 K has been suggested to arise from a change in proton-hopping mechanism involving a transition from ionic-defect-driven diffusivity to that dominated by diffusion of rotational defects.

In the case of ice XVII, we probe the stability of the cage structure, and dissect the vibrational properties, obtaining reasonable agreement with recently-reported experiments.

### Significance statement

Empirical forcefields often give unsatisfactory agreement for various equilibrium properties of ice polymorphs, especially vibrational ones. Here, using state-of-the-art functionals with non-local dispersion, we overcome these problems, to a good degree.

**Primary author:** Prof. ENGLISH, Niall (University College Dublin, Chemical Engineering)

**Presenter:** Prof. ENGLISH, Niall (University College Dublin, Chemical Engineering)

**Track Classification:** Phases of Ice

Contribution ID: 46

Type: **keynote**

## Optical properties of ice and snow

*Friday, January 12, 2018 8:35 AM (45 minutes)*

Radiative properties of ice, and of ice-containing media such as snow and clouds, are determined by ice's refractive index and absorption coefficient ("optical constants"). The dominant absorption mechanisms are electronic in the ultraviolet and visible, molecular vibration in the near-infrared, (hindered) rotation in the thermal IR, and lattice translations in the far-IR.

The molecular vibrations of water vapor are seen also in liquid water and ice; they are shifted somewhat in frequency by formation of the hydrogen bond. Cubic and hexagonal ice have nearly identical absorption spectra. The spectrum of liquid water is close to that of ice from the UV to the near-IR, but they diverge in the thermal-IR and become very different in the far-IR, microwave, and radiowave regions.

The absorption coefficient of ice depends slightly on temperature ( $\sim 1\%/K$ ) in all weakly-absorbing regions from the UV to the microwave. The temperature dependence increases rapidly with wavelength beyond 1 cm.

The absorption coefficient varies by ten orders of magnitude from the near-UV (300 nm wavelength) to the near-IR (3 micrometers). The blue and near-UV absorption is so weak, with photon mean-free-path  $\sim 1000$  m in pure ice, that it is essentially zero for many purposes, but its exact value does matter for computation of photochemical fluxes in snow and of ice thickness on the tropical ocean of "Snowball Earth".

Proceeding across the visible spectrum from blue to red, the absorption length decreases from  $\sim 1000$  m to 2 m, explaining the blue color of crevasses and icebergs. But snow is white. The reflection of sunlight by snow is the result of successive refraction through small snow grains ( $\sim 100$  micrometers); the short total path length through ice experienced by a solar photon means that nearly all UV and visible photons survive to re-emerge from the snowpack. Indeed, the snow surface of Antarctica has been used as a calibration target for visible channels on satellites.

Because the absorption of visible and UV radiation by ice is so weak, the absorption of sunlight at these wavelengths in natural snow is dominated by trace amounts of absorptive impurities such as black carbon (soot) and mineral dust.

Although neither clouds nor snow absorb significantly at visible wavelengths, clouds can be detected over snow in reflected sunlight by satellite remote-sensing because they alter the angular reflectance pattern.

Half the solar energy is in the near-IR, where ice is sufficiently absorptive that the near-IR flux-reflectance (albedo) becomes sensitive to the area-to-mass ratio (specific surface area, SSA). As snow ages the SSA decreases, darkening the snow.

Beyond the solar spectrum, at thermal infrared wavelengths, ice is moderately absorptive, so snow is nearly a blackbody, with emissivity  $\sim 99\%$ . But continuing on to longer wavelengths we come to the second region of weak absorption, the microwave and radiowave region (centimeters to meters), so that radiowaves can penetrate several kilometers of ice-sheet depth for sounding of ice thickness.

### Significance statement

Optical constants of ice are needed for understanding radiative properties of ice and ice-containing media such as snow, sea ice, and clouds, with applications to energy budgets, satellite-remote

sensing, and radio-echo sounding of glaciers and ice sheets.

**Primary author:** Prof. WARREN, Stephen (University of Washington)

**Presenter:** Prof. WARREN, Stephen (University of Washington)

Contribution ID: 48

Type: **Poster**

## Enhancement of dipolar dynamics and hydrogen ordering: Dielectric studies of doping effects

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The crystalline ices can be divided into two groups, the hydrogen disordered and the hydrogen ordered ices. Phase transitions between ordered/disordered pairs that share the same oxygen lattice require the rearrangement of hydrogen bonds. These reorientational processes can only take place if point defects are present that locally violate the Bernal-Fowler ice rules, and the concentration of such defects can be increased by the addition of dopants. A large variety of dopants has been examined so far and in principle acid, base, and salt dopants can be used. Their effectiveness in enhancing the charge dynamics and enabling the formation of ordered phases is still in the focus of intensive research [1].

Dielectric spectroscopy is a method well suited to examine the potential enhancement of dipolar dynamics. In the present contribution we study the high-pressure ice phases ice V, VI, and XII. In these phases the number of intrinsic point defects is too low to induce a hydrogen ordering to the less entropic partners XIII, XV, and XIV, respectively. However, the addition of dopants increases the dynamics of the dipolar relaxation and can promote the transition to their hydrogen ordered partners. We compare a variety of dopants (HCl, HBr, HF, KOH, NH<sub>3</sub>) and present an overview regarding the efficiency of these dopants in ice V, VI, and XII and in the resulting cubic and hexagonal ices that form upon heating [2,3].

We find HCl to be the dopant that enhances the dipolar dynamics the most and in agreement with previous work [4,5] we also observe order-disorder-transitions in the HCl doped ices V, VI, and XII. KOH, the dopant that is known to be the most effective in hexagonal ice, is one of the least effective in these high-pressure ices.

Furthermore, we investigate the enhancement of dynamics in ice XII as a function of the HCl-dopant concentration with the objective to determine the minimum amount of HCl needed to induce hydrogen ordering and to check whether there is a maximum of enhancement that cannot be exceeded even if large amounts of the dopant are added.

Support of this project by the Deutsche Forschungsgemeinschaft (DFG) under grant No BO1301/12-1 is gratefully acknowledged.

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### Significance statement

The dipolar dynamics in ice can be enhanced by adding dopants. In many ice phases dopants are needed to induce the phase transition from a hydrogen disordered to a hydrogen ordered phase.

We study the dopant efficiency in several high-pressure ice phases and in cubic and hexagonal ice.

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**Presenter:** Ms PLAGA, Lucie (TU Dortmund)

**Session Classification:** Poster & Lunch

Contribution ID: 49

Type: PICO talk

## Fundamental Similarity of Water and Ice Dielectric Responses

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Presently, the wideband dielectric spectra of water and ice are accumulated to be accessible for comparative analysis [1, 2]. The spectra reveal striking similarities such as a unified temperature dependence of the dielectric constants [3], related forms of dielectric relaxations (shifted by 6 decades on frequency) [4, 10], close matching of infrared resonances [6], abnormally high dc-conductivities [3, 5].

There is no model to describe the quoted features consistently. Moreover, there is no perspective on resolving the problem because water and ice are mainly studied separately by independent scientific schools. The structure dynamics of water is assumed to be motion of structural polar regions consisting of the long-lived H<sub>2</sub>O molecules, while the defects migration mechanisms is considered for ice.

There are two related facts which are commonly ignored but seem important: i) the high proton mobility in both water and ice measured electrically is not supported by diffusion measurements [7, 8], ii) any H<sub>2</sub>O molecule in ice diffuses with  $D \sim 2 \cdot 10^{-15} \text{ m}^2/\text{s}$  at  $-10 \text{ }^\circ\text{C}$  [6] for a thousand of intermolecular distances during the time of X-ray diffraction measurements; this is in poor agreement with an occurrence of sharp X-ray reflections.

In our study, we analyze critically the outlined issues and construct the model of molecular structure that provides a common background to water and ice dielectric responses [9-11]. The model implies a high concentration of the inherent counter charges in the form of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions in both water and ice. The observed dielectric responses are due to bipolar diffusion of the ions and their interconversion with the neutral H<sub>2</sub>O molecules via the proton exchange.

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### Significance statement

Despite the importance, the water and ice dielectric properties are poorly understood. Here we build conceptually new model where simple periodic localizations and mutual transformations of H<sub>2</sub>O molecules and H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions are completely responsible for both water and ice wideband dielectric response between kilohertz and terahertz.

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**Presenter:** Dr ARTEMOV, Vasily (Prokhorov General physics institute of Russian academy of sciences)

**Session Classification:** Poster & Lunch

Contribution ID: 50

Type: **Talk**

## Calorimetric studies on doped high-density amorphous ices

*Tuesday, January 9, 2018 9:15 AM (20 minutes)*

Studies on doped crystalline ice phases have been done over the past decades. Dopants have allowed unlocking the kinetically hindered, but thermodynamically favored transitions to hydrogen ordered ices, allowing the discovery of ices XI[1], XIII[2], XIV[2] and XV[3]. The role of these dopants is to enhance the microscopic dynamics up to 100.000[4], as revealed by the dielectric studies. This enhancement is the key to induce hydrogen-ordering transitions at  $T < 150\text{K}$ . Given the claim of a high similarity between amorphous ices and crystalline ices (e.g., high-density amorphous ice and ice VI[5] or ice VII[6]), it is of interest to study which impact these dopants might have on hydrogen-ordering in amorphous ice. In the present contribution we discuss the influence of dopants on equilibrated high-density amorphous ice (e-HDA) by differential scanning calorimetry and compare the phenomenology (i.e., appearance of latent heat associated with hydrogen ordering, impact on glass transition step) with those cases usually reported for crystalline ices. None of the large variety of studied dopants has an influence like that seen earlier on crystalline ice, thereby refuting the claim of crystalline-like nature of e-HDA.

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### Significance statement

The influence of dopants on amorphous ice was not studied in the past. Given the claim of high similarity between amorphous ices and crystalline ices, we present a detailed calorimetric study of how these dopants might influence amorphous systems. Concluding that no enhancement of hydrogen-ordered transitions can be observed.

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**Track Classification:** Amorphous Ice



Contribution ID: 51

Type: **Talk**

# Ice particle detection in clouds using a high-speed Particle Phase Discriminator

*Friday, January 12, 2018 11:40 AM (20 minutes)*

Mixed-phase clouds (MPCs), composed of both liquid droplets and ice crystals, play a crucial role in the global radiation budget. Yet, a reliable detection of liquid and ice cloud fraction remains difficult. This in turn hinders a complete understanding of the complex microphysical processes that occur within these clouds, and ultimately renders estimation of the radiative properties of MPCs difficult. Current devices are either only capable of counting the number of particles of different sizes without discriminating phase or cannot resolve to small enough scales (Baumgardner et al, 2011). However, detection of ice particle fraction down to particle sizes at the micrometer scale is critical. Here, we present a new instrument, the high-speed Particle Phase Discriminator (PPD-HS), significantly reducing shortcomings of earlier devices.

PPD-HS sizes particles by passing a continuous laser beam (similarly to commercial Optical Particle Counters) and discriminates their phase by analyzing scattering patterns of forward scattered light. Compared to PPD-2K presented by Vochezer et al. (2016), our new instrument reduces the information collected per particle, used for phase discrimination, and thus allows for an increased detection rate of cloud particles.

Phase discrimination is achieved by evaluating the spatial symmetry of the scattering pattern, allowing for classification of spherical cloud droplets and aspherical ice crystals. Here we present an in-depth analysis of instrumental performance.

The phase discrimination potential of PPD-HS is determined through a suite of laboratory experiments, using particles with well-controlled properties. These include spherical and aspherical particles covering a size range from approximately 1 to 15  $\mu\text{m}$ . Our results show that PPD-HS detects particles larger than approximately 1  $\mu\text{m}$  in diameter and reliably discriminates ice crystals from other cloud particles for particle size  $> 3 \mu\text{m}$ , providing the capabilities to detect freshly nucleated ice in MPCs.

In a second round of experiments, we coupled PPD-HS to the Horizontal Ice Nucleation Chamber (HINC), a Continuous Flow Diffusion Chamber (CFDC). HINC allows us to mimic formation of real cloud hydrometeors and assess the performance of PPD-HS to determine the hydrometeor phase under atmospherically relevant MPC conditions. Results from such experiments will be presented to assess the performance of PPD-HS in discriminating accurately the liquid and ice fractions formed in HINC. These will help us to evaluate whether PPD-HS could improve our ability to identify ice and water cloud fractions in the real atmosphere.

## Significance statement

A new device, the high-speed Particle Phase Discriminator (PPD-HS), is presented that allows to discriminate liquid droplets from ice crystals under mixed-phase cloud conditions. We evaluate the performance of PPD-HS using a suite of well controlled laboratory experiments with well characterized particles.

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**Presenter:** Mr WIEDER, Jörg (Institute for Atmospheric and Climate Science, ETH Zurich, Zurich, 8092, Switzerland)

**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 53

Type: **Talk**

## Ice crystal formation on soot particles

*Monday, January 8, 2018 4:50 PM (20 minutes)*

Soot particles are primary particles produced by incomplete combustion of both biomass and/or fossil fuels and thus constitute a major anthropogenic pollutant. They are generally complex internal mixtures of black carbon (BC) and organic matter (OM) (Bond et al., 2013; Petzold et al., 2013). While these properties strongly depend on the emission sources, they can be altered during atmospheric cycling, including interactions of the primary particles with other atmospheric matter and/or gases. Physically, soot particles usually form fractal-like aggregates composed of the primary carbonaceous spherules. Such aggregates include a variety of cavities and pores that are formed between primary carbonaceous spherules or as a result of random packing of the fractal chains.

Overall, estimates of the net radiative forcing associated with BC are still associated with large uncertainties, even though being one of the most important climate forcing agents (Bond et al., 2013).

While BC generally absorbs solar radiation, thus contributing to a warming effect on global climate it can also act as a heterogeneous ice nucleating particle (INP) and impact cloud-radiation interactions, potentially cooling the climate (Lohmann, 2002). Prediction of the ice nucleation behavior of soot particles requires consideration of both, the chemical and physical properties of the particles.

Here, we present a systematic laboratory-based investigation of the ice formation behavior of a set of soot particles. Different commercial soot samples are used, along with a soot produced by a propane diffusion burner, using a Combustion Aerosol Standard Generator (miniCAST, JING AG). miniCAST burners are frequently used as proxy for atmospheric soot particles. Ice nucleation ability of these soot types is tested on size-selected particles covering the size range between 100 and 400 nm and a temperature range from 253 K to 218 K, using the Horizontal Ice Nucleation Chamber (HINC, Lacher et al. 2017), a Continuous Flow Diffusion Chamber (CFDC).

We complement our ice nucleation experiments with auxiliary measurements including BET-surface determination and thermogravimetric analysis, in order to characterize the physio-chemical properties of the tested aerosol particles. In addition, analysis of Transmission Electron Microscope (TEM) images allows for a detailed characterization of the morphology associated with our soot samples. This supports investigating the influence of any cavities on our ice nucleation results, considering a Pore Condensation Freezing (PCF) mechanism for ice nucleation onto soot particles. During PCF liquid water is taken up within pores below water saturation due to the inverse Kelvin effect, which can subsequently freeze heterogeneously in presence of an active site (for  $T > 235$  K) or homogeneously (for  $T < 235$  K) causing ice to nucleate on the soot aggregate.

Results show different activation behavior of the soot over the temperature range investigated. While the commercial soot samples show freezing well below water saturation in the cirrus regime, CAST-brown soot needs conditions above water saturation to show any activation. For the mixed-phase cloud conditions all soot types show droplet activation for high supersaturations w.r.t water.

### Significance statement

We present a systematic laboratory study on the ice nucleation behaviour of different soot particles

along with detailed measurements on the particle physico-chemical properties. This allows us to shed light on the ice nucleation mechanism of soot, which is poorly understood so far.

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**Presenter:** Mr MAHRT, Fabian (Institute for Atmospheric and Climate Science, ETH Zurich, Zurich, 8092, Switzerland)

**Track Classification:** Ice Crystal Growth

Contribution ID: 54

Type: **Talk**

## In situ observation of ice-water interfaces by advanced optical microscopy

*Thursday, January 11, 2018 8:35 AM (20 minutes)*

Ice crystallization from supercooled water, more generally, crystallization from its own supercooled melt (the so-called melt growth), is one of the fundamental phase transitions seen everywhere in nature. Despite its ubiquity, the microscopic view of the melt growth is still far from completely understood, contrary to the crystal growth from vapor and solutions. It is well-known that the kinetics of the interface is responsible for the ordering process of crystallization, especially after initial nucleation, because of its strong first order nature. However, it still remains elusive how the liquid and the solid (crystal) phase, of which densities are no more different than several percent, are microscopically distinguished each other at their interface. The main difficulty comes from the significantly high crystal growth rate in melt, hampering direct and precise observations of the interface. Moreover, effects of the latent heat diffusion often obscure the molecular uptake mechanism at the growth front, revealing the microscopic information on the interface.

Here we focus on two kinds of ice-water interfaces, ice/quasi-liquid layer (ice/QLL) and ice/bulk water interfaces. We performed in situ observations of these two interfaces by an advanced optical microscopy, whose resolution in the height direction reaches the order of an angstrom. We succeeded in making direct visualization of elementary steps at ice/QLL interfaces and bunching steps at ice/bulk water interfaces. These two exhibit characteristic behaviors different from each other although both systems are the same crystal-melt interface.

### Significance statement

We performed in situ observations of two kinds of ice-water interfaces by an advanced optical microscopy (laser confocal microscopy combined with differential interference contrast microscopy). We made direct visualization of elementary steps and random bunching steps at their interfaces, which have not been experimentally accessible so far.

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**Presenter:** Dr MURATA, Ken-ichiro (Institute of Low Temperature Science, Hokkaido University)

**Track Classification:** The surface and interface of ice

Contribution ID: 55

Type: **Poster**

## Effect of Electric Field on Optical Phonon Modes of Solid CO

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

We examined the effect of applied electric field on collective phonon modes of a CO solid crystal. A strong electric field ( $\sim 10^8$  V/m) was applied across a thin CO film grown on a metal substrate at 7 K by using the ice film capacitor method. Reflection absorption infrared spectroscopy (RAIRS) was used for monitoring the optical phonon modes of a CO film, where a longitudinal optical (LO) mode appeared at  $2143\text{ cm}^{-1}$  and a transverse optical (TO) mode appeared at  $2139\text{ cm}^{-1}$ . The peak position of LO mode was blue-shifted by the external field and that of TO mode was red-shifted. This field-induced LO-TO splitting may occur as a result of a vibrational Stark shift of the phonon modes which have specific directions of progression in CO crystal domains. To explore the origin of the LO-TO splitting, we studied the effect of electric field on diluted  $^{13}\text{CO}$  molecules in a  $^{12}\text{CO}$  film, where the  $^{13}\text{C-O}$  vibration is isolated from the intermolecular coupling of  $^{12}\text{CO}$  vibrations in the lattice. When the external field was applied, the decoupled  $^{13}\text{C-O}$  stretching appeared as a single peak and showed a vibrational Stark broadening because  $^{13}\text{CO}$  molecules have an isotropic orientation in the lattice. These observations indicate that the field effect on collective phonon motions of CO molecules in the crystal causes the LO-TO splitting.

### Significance statement

The effect of applied electric field on collective phonon modes of a CO solid crystal was examined by using the ice film capacitor method. The field-induced LO-TO splitting was observed as a result of a vibrational Stark shift of the phonon modes.

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**Presenter:** Mr KANG, Hani (Seoul National University)

**Session Classification:** Poster & Lunch

Contribution ID: 56

Type: **Poster**

## Ion diffusion on amorphous ice surface

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

In interstellar molecular clouds, various molecules (for instance, H<sub>2</sub>O, NH<sub>3</sub>, CO, CO<sub>2</sub>, and so on) are formed from elements such as H, C, O, and N [1]. Most of H<sub>2</sub>O exists as a thin shell of amorphous ice around dust grain. The molecules undergo chemical evolutions to organic molecules through various processes on the surface of amorphous ice [2]. Thus, the surface structure of amorphous ice is an important factor to understand the molecular evolution of organic molecules in molecular clouds [3]. To investigate the effects of adsorption of ion on the surface structure of amorphous ice, the molecular dynamics (MD) calculations of amorphous ice with ions (H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup>) were performed.

The MD calculations were performed using an atom-atom potential model, KAWAMURA potential model [4]. The amorphous ice was prepared by quenching of a liquid phase consisting of 2760 water molecules from 280 to 235 K with 2.5 K/fs in cooling rate. After annealing at 235 K, the system was cooled to 10 K with 2.5 K/fs. To equilibrate the fundamental cell, the MD code was run for 40 ps at 10 K. Then, an ion (H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, or NO<sub>3</sub><sup>-</sup>) was put in a position, such the center of ion was at a distance of 0.5 nm from the outermost hydrogen atom in surface. Then, the temperature was changed to a temperature in the range of 15–130 K to analyze the ion diffusion. An infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The pressure was kept at 0.1 MPa. The layer with 0.5 nm in thickness from the outmost atom was analyzed as the surface layer.

From an observation of the trajectory of ion on the surface, the diffusion mechanism was analyzed. The result shows that the adsorbed H<sup>+</sup> diffuses on the surface with formation and dissociation of H<sub>3</sub>O<sup>+</sup>. Using the frequencies of the formation and dissociation of H<sub>3</sub>O<sup>+</sup>, the activation energy of diffusion of H<sup>+</sup> was estimated. On the other hand, no diffusion hop was observed for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the simulation period of 80 ps. The adsorbed NH<sub>4</sub><sup>+</sup> (or NO<sub>3</sub><sup>-</sup>) forms four (or three) hydrogen bonds with water of the surface layer. Therefore, the activation energies for the ions are extremely higher than that for H<sup>+</sup>. The atomic displacement parameters (ADP) of oxygen and hydrogen of water molecules in surface layer increase during the adsorption of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. This suggests that, the rotational motion of water is one of the driving forces of hops for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. The effects of ion adsorption might have important implications for surface reaction in interstellar molecular clouds.

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- [4] N. Kumagai, K. Kawamura, T. Yokokawa, 1994, *Mol. Simul.* 12, 177.

### Significance statement

To investigate the effects of ion adsorption on surface structure of amorphous ice, the molecular dynamics calculations of amorphous ice with ions (H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup>) were performed. From the results, the processes and mechanisms of adsorption and diffusion are discussed.

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**Co-authors:** Mr AOKI, Masaya (Department of Applied Chemistry, Meiji University, Japan); Prof. IKEDA-FUKAZAWA, Tomoko (Department of Applied Chemistry, Meiji University, Japan)

**Presenter:** Mr HARA, Norifumi (Department of Applied Chemistry, Meiji University, Japan)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)



Contribution ID: 57

Type: **Poster**

## Interaction of Low Energy (0-20 eV) Electrons with Sulfur Dioxide on Ice Surfaces

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

We studied the interaction of low energy (0-20 eV) electrons with sulfur dioxide (SO<sub>2</sub>) on a crystalline ice film surface. An ice film was prepared by H<sub>2</sub>O vapor deposition on a Pt(111) substrate at 150 K for thickness of >100 BL inside a vacuum chamber and was annealed at 165 K to produce a crystalline ice film with a flat (0001) surface. SO<sub>2</sub> gas was adsorbed on the crystalline ice film through a tube doser. The surface adsorbates were analyzed using the methods of Cs<sup>+</sup> reactive ion scattering (RIS) and low energy sputtering (LES), which revealed molecular SO<sub>2</sub> adsorption at ~95 K and the occurrence of the hydrolysis of SO<sub>2</sub> at >100 K.<sup>1</sup> We irradiated low energy electrons, produced from an electron flood gun, onto the ice film surface with adsorbed SO<sub>2</sub> at 95 K. While the low energy electrons transmit through an ice film, they were trapped quite efficiently by the SO<sub>2</sub> adsorbates on the surface. The amount of SO<sub>2</sub>-trapped electrons was estimated by measuring the film voltage with a Kelvin probe at various incident energies of the electrons. RIS and LES measurements of the surface show that the electron-trapping by SO<sub>2</sub> produces various negative ion species, such as OH<sup>-</sup>, SO<sub>2</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup>, and HSO<sub>3</sub><sup>-</sup>.

(1) Bang, J.; Shoaib, M. A.; Choi, C. H.; Kang, H. Efficient Thermal Reactions of Sulfur Dioxide on Ice Surfaces at Low Temperature: A Combined Experimental and Theoretical Study. *ACS Earth and Space Chem.* 2017

### Significance statement

SO<sub>2</sub> adsorbates on crystalline ice film can trap low energy (0-20 eV) electrons, and it produces various negative ion species such as OH<sup>-</sup>, SO<sub>2</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup>, and HSO<sub>3</sub><sup>-</sup> at 95 K.

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**Co-author:** Prof. KANG, Heon (Department of Chemistry, Seoul National University)

**Presenter:** Mr BANG, Jaehyeock (Department of Chemistry, Seoul National University)

**Session Classification:** Poster & Lunch

Contribution ID: 58

Type: **Poster**

## Ice particle classification using a deep learning algorithm

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

For a better understanding of cloud processes, accurate observations of ice crystal number concentrations and size spectra are important. We measure the cloud microphysics with the holographic imager HOLIMO. Holography is the only measurement technique, which allows the recording of the concentration, the size, the shape, as well as the spatial distribution of cloud particles. The classification into water droplets and ice particles is based on the particle shape (spherical or non-spherical) and is done using supervised machine learning. Since ice particles are quite variable in size and shape and rare compared to water droplets, a conventional classification tool, like a tree, is incapable of identifying ice particles sufficiently well. In order to improve the automated classification of cloud particles, we are developing a deep learning algorithm. The algorithm hopefully recognizes important features, which are overlooked by a human user. Above that, it can work with nonlinear functions and is thus able to find complex correlations between input parameters and the cloud particle classes, for example, if the interference pattern may state something about the particle phase or shape.

### Significance statement

Imaged-based probes have the advantage that no assumptions are necessary on the shape of recorded particles. Yet the classification remains time-consuming and error-prone, due to the variable shape of ice crystals. Recent progress in deep learning techniques provides confidence in improving the automated classification of ice particles.

**Primary author:** Ms LAUBER, Annika (ETH Zürich, IAC)

**Co-authors:** Dr BECK, Alexander (ETH Zürich, IAC); Dr HENNEBERGER, Jan (ETH Zürich, IAC); Prof. LOHMANN, Ulrike (ETH Zürich, IAC)

**Presenter:** Ms LAUBER, Annika (ETH Zürich, IAC)

**Session Classification:** Poster & Lunch

Contribution ID: 59

Type: **Talk**

## What we can learn about dislocations in ice from EBSD analyses

*Wednesday, January 10, 2018 10:45 AM (20 minutes)*

For some years now, Electron Backscattering Diffraction (EBSD) analysis has been applied to characterise, with high spatial and angular resolution the texture and microstructure of natural ice samples [Obbard et al. *J. Glaciol.* 2006], or artificially deformed samples [e.g. Piazzolo et al. *J. Microscopy* 2008, Weikusat et al. *J. Microscopy* 2011]. Contrary to classical optical measurements performed on ice (Rigsby stage, Automatic Ice Texture Analyzer...), EBSD provides the full crystallographic orientation at every analysis point with a spatial resolution down to 0.5 micron.

When the resolution and the indexation ratio are large enough, full crystallographic orientations can be used to evaluate the lattice misorientations [Weikusat et al. 2011, Chauve et al. 2017 *Phil. Trans. Roy. Soc. A*], and therefore access information about Geometrically Necessary Dislocations (GNDs) that remain within the sample after deformation.

Piazzolo et al. [2008] first used the “boundary trace analysis” to derive the type of dislocations consistent with EBSD data forming a given subgrain boundary. From that, GNDs in laboratory deformed samples appeared to be mostly basal, with an edge characteristic when forming the very common tilt or kink bands, or with a screw or mixed characteristics when forming more continuous substructures. More recently, Piazzolo et al. [*Acta Mater.* 2015] and Chauve et al. [EPSL 2017] applied the Weighted Burgers Vector technique [Wheeler et al. *J. Microscopy* 2009] to well-indexed, high resolution EBSD maps, providing a more precise characterization of GNDs. The WBV technique derives a 2D equivalent of the Nye tensor from EBSD data collected from the sample surface. Although it does not provide the full misorientation tensor (the Nye tensor), this tool is well adapted to the limitation of the 2D orientation data extracted from EBSD measurements and enables to discriminate between the Burgers vectors of sampled GNDs.

Thanks to detailed WBV analyses performed on laboratory deformed ice samples (in compression and torsion), we were able, for the first time, to show that a non-negligible amount of GNDs have a Burgers vector component along the c-axis [Chauve et al. EPSL 2017]. This type of dislocations was rarely evidenced before, and has been assumed to play a minor role in the ductile deformation of ice [Hondoh 2000, Hokkaido Univ. Press]. Although GNDs do not directly relate to the dislocations responsible for local plastic gliding, the observed contribution of up to 30% of non-basal c-component GNDs points to a non-negligible role of such dislocations in ice viscoplastic flow, offering a more complex picture of the key plasticity processes responsible for ice deformation.

This presentation will detail the experimental observations and the WBV tool used to evidence the c-component dislocations in the laboratory deformed samples. We will then discuss the importance of such observations for defining constitutive mechanical laws for ice deformation modelling up to the ice sheet scale.

### Significance statement

For the first time, the potential significance of non-basal c-dislocations is evidenced in polycrystalline ice, thanks to an original EBSD data analysis.

**Primary author:** Mrs MONTAGNAT, Maurine (IGE - CNRS - UGA)

**Co-authors:** Dr TOMMASI, Andrea (Géosciences Montpellier - Univ. Montpellier - CNRS); Dr JOURNAUX, Baptiste (NASA Astrobiology Institute - USRA - Univ. Washington - USA); Dr MAIN-PRICE, David (Géosciences Montpellier - Univ. Montpellier - CNRS); Dr BAROU, Fabrice (Géosciences Montpellier - Univ. Montpellier - CNRS); Prof. WHEELER, John (Univ. Liverpool, UK); Prof. PIAZOLO, Sandra (Univ. Leeds, UK); Dr CHAUVE, Thomas (UGA - CNRS - IGE)

**Presenter:** Mrs MONTAGNAT, Maurine (IGE - CNRS - UGA)

**Track Classification:** Mechanics & Microstructure

Contribution ID: 61

Type: **keynote**

## Exploring new phenomena in ice, salty ice, and ice clathrates under extreme conditions

*Monday, January 8, 2018 10:05 AM (45 minutes)*

Compressed water is overspread on Earth at depth and in the extra-terrestrial space, both interstellar and on outer planets and moons (ice bodies) [1]. Under the conditions experienced in these celestial bodies water displays an incredibly rich phase diagram, including seventeen known crystalline phases and three amorphous states, and predicted exotic properties like plasticity [2], ionization [3], and superionicity [4].

In this talk I will review some of our recent experimental results on pure ice, salty (LiCl, LiBr, NaCl) ices, and ice (H<sub>2</sub>, CH<sub>4</sub>) clathrates under extreme conditions including: new dynamical effects in ice VII [5], salty ice crystallization under high pressure [6,7], hydrogen bond symmetrisation in salt-doped ices at Mbar pressures [8,9], methane ultra fast diffusion and locking in methane hydrates [10,11].

[1] De Pater, I., and Lissauer, J.J. Planetary Sciences, Cambridge University Press (2004).

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### Significance statement

The behaviour of high pressure ice phases, either pure or ion and gas filled is of paramount importance for the description of the interior of ice bodies in our universe and gives deeper insights on both quantum effects and hydrophobic/hydrophilic interactions in ice.

**Primary author:** Mrs BOVE, Livia Eleonora (CNRS & Université P&M Curie, EPFL)

**Co-authors:** Mr FALENTY, Andrzej (Goettingen University); Mr KOZA, Marek M. (ILL); Mr KLOTZ, Stefan (CNRS & Université P&M Curie); Mr RANIERI, Umberto Luca (ILL & EPFL); Prof. KUHS, Werner F (University of Göttingen); Mrs POLIDORI, annalisa (EPFL)

**Presenter:** Mrs BOVE, Livia Eleonora (CNRS & Université P&M Curie, EPFL)

Contribution ID: 62

Type: PICO talk

## Pattern Formation in Ice Under Selective Infrared Radiation

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Spontaneous self-organization of a system can lead to pattern formation. Many examples for that are found in nature, such as dividing cells in the developing embryo, dendritic growth of crystals, and the formation of brine channels in sea ice. Here we present a new pattern formation in ice under selective infrared (IR) radiation. Unlike Tyndall flowers, which are dendritic melting of super heated ice under IR radiation, we demonstrate a completely different pattern of thin ice crystals in the shape of holes and micro-channels. The difference in the IR absorption of ice and water enabled us to heat ice more than water in an ice/water system. We illuminated 10 - 80  $\mu\text{m}$  thick ice crystals in solution using up to 2 W IR radiation (1540 nm). The system developed spatial pattern, and under some conditions, also growth and melt oscillations. Applying the ice-selective radiation resulted in pattern that started with holes of  $7\pm 1 \mu\text{m}$  diameter that, with time, became smaller and closed. Equal-sized holes were opened again in various areas of the ice crystal and eventually developed into micro-channels. We were able to inhibit the pattern formation by using carbon black particles, which elevated the water absorption while maintaining the ice absorption. In addition, under water-selective radiation up to 4 W (980 nm), the ice crystals assumed a pattern of stripes while growing.

Heat transfer and phase field simulations showed that larger ice crystals absorb more energy than the smaller ones, and implied that there is a typical width of the micro-channels, similar to the experimental value. We interpreted our results as a unique pattern formation that stems from a negative feedback of growth and melt.

We showed that selective radiation influences ice morphology. Therefore, it holds the potential to interfere and affect ice growth, and thus, improve cryopreservation protocols.

Supported by the European-Research-Council (ERC), the National-Science-Foundation (NSF), and the Israel-Science-Foundation (ISF).

### Significance statement

We present a new physical phenomenon involving pattern formation of ice under selective infrared radiation, in which thin ice crystals assumed a spatial pattern of holes and micro-channels.

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**Presenter:** Mrs PREIS, Shlomit (Institute of Biochemistry, Food Science and Nutrition, Robert H.

Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, Israel.)

**Session Classification:** Poster & Lunch

Contribution ID: 63

Type: **Talk**

## Hypothetical Ultralow-density Ice Polymorphs

*Monday, January 8, 2018 4:30 PM (20 minutes)*

Among 17 known ice polymorphs, only two are less dense than normal ice, and they are made very recently by a tricky procedure, vacuum pumping the small guest molecules from clathrate hydrate. The discovery of low-density ice polymorphs opens the door to the survey on ices under negative pressures. Negative pressure is very hard to be accessed experimentally, and theoretical predictions are indispensable. How many stable phases are possible for ices under negative pressures? Are two ices really the most stable phases at some thermodynamic conditions? How low can the density of ice be? Exhaustive evaluation of sparse ice structures and theoretical considerations provide unexpected answers to these questions.

### Significance statement

This is the first exhaustive survey on the low-density ice polymorphs. We found a couple of more stable zeolitic ices ever, and also a family of many possible low-density structures named “aeroices”.

**Primary author:** Mr MATSUI, Takahiro (Graduate School of Natural Science and Technology, Okayama University)

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**Presenter:** Dr MATSUMOTO, Masakazu (Research Institute for Interdisciplinary Science, Okayama University)

**Track Classification:** Ice Crystal Growth



Contribution ID: 64

Type: Talk

## New hydrates in the Ne-, He- and D<sub>2</sub>-water system via a high-pressure route

Monday, January 8, 2018 11:10 AM (20 minutes)

Formation of gas hydrates from ice is generally a slow process due to the intrinsically sluggish solid-state mass transfer (Salamatin et al. 2015). Small size Ne, H<sub>2</sub> and He are an exception to this rule by being able to penetrate into the lattice of the ordinary ice Ih with ease. Upon further compression ice Ih presaturated with He-gas was found to transform rapidly into gas-filled ice II. Interestingly, H<sub>2</sub> and Ne were found also to form a cubic sII clathrate hydrate at intermediate pressures. In planetary science, such ices filled with Ne, H<sub>2</sub> and He are seen as potent materials selectively trapping and fractionating these primordial gases. Moreover, in the context of fundamental clathrate research Ne- and H<sub>2</sub>-hydrates have played the unorthodox role as starting point for the formation of ice XVI, the empty clathrate structure sII (Falenty et al. 2014).

Here we report on the gas loading into ice Ih spheres. The pressure in the system was increased stepwise to 320MPa for D<sub>2</sub> and 400MPa for He and Ne. All guest types were found to rapidly penetrate into ice yet with marked differences. Pressurization of ice with deuterium lead to a rapid formation of sII D<sub>2</sub>-hydrate initiated already at 110 MPa. The sII structure remained stable at least up to 320MPa. Ice loaded with Ne remained stable up to 210MPa, i.e. to approximately the stability boundary between pure Ih and unfilled ice II. After crossing this threshold, the sample adopted the sII Ne-hydrate structure and remains stable at least up to 350MPa. Further compression up to ~400MPa resulted in a new Ne-hydrate, topologically similar to the H<sub>2</sub>-filled chiral C0-structure and the recently discovered C0 structure of CO<sub>2</sub> (Amos et al. 2017). Upon decompression to 350MPa C0 structure reverted back to sII Ne-hydrate. Upon recovery at liq. N<sub>2</sub> temperature to ambient pressure, cage occupancies in Ne- and D<sub>2</sub>-hydrates rapidly readjust by decreasing the number of guests in all cages. A similar pattern can be seen upon guest-removal under vacuum where larger cages empty much faster than the smaller ones; curiously D<sub>2</sub> molecules at comparable conditions seems to leave the sII structure slower than the larger Ne atoms. Smaller cavities seem to be much more difficult to empty and may require the presence of water vacancies for the cage-to-cage hopping.

The He-water system has proven to be the most peculiar one as the compression up to 300MPa did not yield any structural change. He-loaded ice Ih remained stable in the whole investigated pressure range. Still, for the first time we succeeded to form unequivocally sII He-clathrate by filling ice XVI at 120K with 150MPa of He gas; both, the crystal structure and the He-uptake and release, was studied as a function of pressure.

Amos et al.(2017) J.Phys.Chem.Lett. 8, 4295-4299

Falenty, Hansen & Kuhs (2014) Nature 516, 231-233

Salamatin, Falenty, Hansen & Kuhs (2015) Energy & Fuels 29, 5681-5691

### Significance statement

We represent two new high pressure phases in small gas - water systems: A Ne-hydrate with a chiral water structure and the long-searched Helium form of sII clathrate hydrate. These new structural forms are manifestations of the importance of van der Waals interactions between water and small gas molecules.

**Primary author:** Prof. KUHS, Werner F (University of Göttingen)

**Co-authors:** Dr FALENTY, Andrzej (GZG Abt. Kristallographie Uni Göttingen); Dr WALLACHER, Dirk (Helmholtz-Zentrum für Materialien & Energie Berlin); Dr HANSEN, Thomas C (Institut Laue-Langevin Grenoble)

**Presenter:** Dr FALENTY, Andrzej (GZG Abt. Kristallographie Uni Göttingen)

**Track Classification:** Amorphous Ice

Contribution ID: 65

Type: **Talk**

## Investigation of Antifreeze Proteins on the Surface of Ice using Vibrational Sum-Frequency Generation Spectroscopy

*Thursday, January 11, 2018 3:40 PM (20 minutes)*

Antifreeze proteins (AFPs) and Antifreeze Glycoproteins (AFGPs) collectively abbreviated as AF(G)Ps are a unique class of proteins that modify ice crystal growth and thereby ensure the survival of organism in freezing and subfreezing habitats. The molecular working mechanism behind AF(G)Ps freezing inhibition is not well understood, because, as yet, there are no experimental techniques that allow obtaining molecular details on how antifreeze proteins function directly at the surface of ice. Here we use surface specific heterodyne-detected vibrational sum-frequency generation spectroscopy (HD-VSFG) to study the properties of antifreeze proteins directly at the ice surface and at the molecular level.

### Significance statement

Antifreeze proteins (AFPs) enable the survival of various organisms in freezing or subfreezing habitats by preventing the macroscopic growth of ice crystals. Understanding how AFPs recognize and bind ice crystals is the most important step to unravel their working mechanism.

**Primary author:** Dr MEISTER, Konrad (AMOLF)

**Co-authors:** Prof. DEVRIES, Art (University of Illinois); Ms MOLL, Carolyn (AMOLF); Prof. RAMLOV, Hans (Roskilde University); Prof. BAKKER, Huib J. (AMOLF)

**Presenter:** Dr MEISTER, Konrad (AMOLF)

**Track Classification:** Ice Binding Proteins

Contribution ID: 66

Type: Talk

## Experimental evidence for a second hydrogen ordered phase of ice VI

Monday, January 8, 2018 1:40 PM (20 minutes)

In the last decade five new ice phases were experimentally prepared. Two of them(1, 2) are empty clathrate hydrates and three of them(3, 4) represent hydrogen ordered counterparts of previously known disordered ice phases. In our experiments, we investigated hydrogen ordering in ice VI samples upon cooling at pressures up to 1.8 GPa. Using calorimetry, dielectric relaxation spectroscopy, Raman spectroscopy, and powder X-ray diffraction we provide evidence for the existence of a second hydrogen ordered phase related to ice VI, that we call ice  $\beta$ -XV. This phase is more ordered than ice XV by 14% and directly transforms to ice XV above 103K and to ice VI above 129K. That is, upon heating an order- $\rightarrow$ order- $\rightarrow$ disorder transition is experienced. The new phase is thus thermodynamically more stable than ice XV requiring a new stability region in the phase diagram of water. Raman spectroscopy indicates ice XV and ice  $\beta$ -XV to be different in terms of symmetry and space group. The activation energies, measured by dielectric spectroscopy, are 45 kJ mol<sup>-1</sup> in ice  $\beta$ -XV compared to 18 kJ mol<sup>-1</sup> in ice XV. Powder X-ray data show the oxygen network to be the one of ice VI. The ordering of hydrogen atoms induces a significant peak shift to lower d-spacings at  $d=0.265$  nm in ice  $\beta$ -XV, whereas for ice XV shifts to higher d-spacings are found. The reproduction of these effects with fully deuterated samples would be desirable to refine the crystal structure of ice  $\beta$ -XV. Unfortunately, a pronounced isotope effect precludes such experiments and leads us to the temporary name ice  $\beta$ -XV. We suggest to change this name to ice XVIII as soon as the crystal structure is known. Our experiments represent a unique realization of a second electric ordering in an ice phase, including the identification of two triple points between three hydrogen ordered phases.

1. del Rosso L, et al. (2016) Refined Structure of Metastable Ice XVII from Neutron Diffraction Measurements. *J. Phys. Chem. C* 120(47):26955-26959.
2. Falenty A, Hansen TC, & Kuhs WF (2014) Formation and properties of ice XVI obtained by emptying a type sII clathrate hydrate. *Nature* 516(7530):231-+.
3. Salzmann CG, Radaelli PG, Hallbrucker A, Mayer E, & Finney JL (2006) The preparation and structures of hydrogen ordered phases of ice. *Science* 311(5768):1758-1761.
4. Salzmann CG, Radaelli PG, Mayer E, & Finney JL (2009) Ice XV: A New Thermodynamically Stable Phase of Ice. *Phys. Rev. Lett.* 103(10):105701.

### Significance statement

We found experimental evidence for an unknown hydrogen ordered proxy of ice VI, which has been scrutinized by differential scanning calorimetry, dielectric relaxation spectroscopy, Raman spectroscopy and X-ray diffraction. Therefore, ice VI is the first polymorph of ice with two experimentally realized types of hydrogen ordering.

**Primary author:** Mr GASSER, Tobias M. (University of Innsbruck)

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(DESY); Prof. BÖHMER, Roland (TU Dortmund); Prof. LOERTING, Thomas (University of Innsbruck)

**Presenter:** Mr GASSER, Tobias M. (University of Innsbruck)

**Track Classification:** Phases of Ice

Contribution ID: 67

Type: **Talk**

## Study of crystallite size distributions in ices and gas hydrates using a novel X-ray diffraction procedure

*Tuesday, January 9, 2018 9:55 AM (20 minutes)*

Crystallite size distributions (CSDs) provide important insights into the formation processes of materials, in particular the balance between nucleation and growth rates. Both equilibrium and non-equilibrium physical properties of the resulting polycrystalline gas hydrate assemblages will depend on the CSDs, in particular their mechanical properties as well as their interactions with any surrounding fluid phase or other transport properties alike. We have developed over the last years a fast X-ray diffraction based procedure to determine CSDs with unprecedented precision and have applied this method to the study of ices and gas hydrates (Chaouachi et al. 2017) amongst other examples from material science. Various gas hydrates (GH) were analyzed during formation and coarsening in a sedimentary matrix. The GH crystallites have a size of a few  $\mu\text{m}$  when formed (confirmed also by synchrotron X-ray tomography), followed by a coarsening process which mainly takes place at the surface of GH aggregates. Important conclusions can be drawn from the time-dependent analysis of CSDs: (1) Coarsening by normal grain growth proceeds several orders of magnitude slower than in normal ice Ih at similar temperatures; this points to very slow grain boundary migration rates seemingly related to the complexity of topological reconstruction of the crystalline network across a disordered grain boundary. (2) The persisting small crystallites together with their known high resistance against deformation by dislocation motion must lead to grain size sensitive creep, most likely governed by grain boundary sliding. (3) The CSDs of GHs formed in the laboratory appear to have distinctly smaller sizes compared to natural GHs. In consequence, laboratory-based studies of GH can only be safely related to the natural situation once the mutual CSDs are characterized. Starting from crystallites of a few  $\mu\text{m}$  in size, obtained under common laboratory conditions from liquid water and gas, it would take hundreds to thousands of years to reach crystal sizes encountered in some NGHs, at least when assuming a normal grain growth mechanism. Anomalous grain growth may intervene and increase crystal sizes, in particular under overburden load and local stresses. Such an anomalous grain growth was indeed observed in natural air hydrates found in Greenland deep ice cores. Finally, we like to mention that our FXR-CSD method is particularly powerful for small crystallites ( $\mu\text{m}$  to tens of  $\mu\text{m}$  in size) and will allow quantitative studies of in-situ processes occurring during snow coarsening or dynamic recrystallization in ice.

M. Chaouachi, S.H. Neher, A. Falenty & W.F. Kuhs (2017) *Crystal Growth & Design* 17, 2458-2472

### Significance statement

A new diffraction-based method adapted for in-situ study of crystal growth and coarsening phenomena in a large variety of materials including ices and gas hydrates is presented. Normal grain growth processes of gas hydrates are found to be orders-of-magnitude slower than similar processes in ice Ih.

**Primary author:** Prof. KUHS, Werner F (University of Göttingen)

**Co-authors:** Dr FALENTY, Andrzej (GZG Abt. Kristallographie Uni Göttingen); Dr CHAOUACHI, Marwen (GZG Abt. Kristallographie Uni Göttingen); Mr NEHER, Sigmund H (GZG Abt. Kristallographie Uni Göttingen)

**Presenter:** Prof. KUHS, Werner F (University of Göttingen)

**Track Classification:** Phases of Ice

Contribution ID: 69

Type: **Poster**

## SEM observation on hydrate formation from TBAB aqueous solution and memory effect

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Clathrate hydrate of tetra-n-butylammonium bromide (TBAB) is expected as a cold storage material for air conditioning, but supercooling is a problem for practical use. The supercooling, widely known, is the state of maintaining the liquid phase even if it is cooled below freezing point, but the detailed mechanism is not clarified. For the purpose of visualization of the supercooling phenomenon, both the structures of TBAB clathrate hydrate and TBAB aqueous solution were observed. In general, although SEM is widely used in the observation of microstructure, it had not been possible to observe such as a solution or a gel directly since the inside of the SEM is under a high vacuum. Therefore, SEM observation was performed by a freeze-fracture replica method. Freeze-fracture replica method is utilized not only in medicine and biology fields but also in various fields since it is possible to obtain both of the information of a solution itself and the state of particles having a microstructure simultaneously. Specifically, cut-surface of the quenched sample was prepared and thin film is fabricated on the cut-surface. And by soaking it in an appropriate solvent, the thin film and the sample were separated to recover a replica film reflecting the morphology of quenched cut-surface. Finally, the replica film was observed by SEM.

From the observation results of TBAB clathrate hydrate, whose decomposition temperature is 285 K, the crystalline state has a closely packed structure with clusters of 10 ~ 20 nm or more in diameter. As the decomposition proceeds, the cluster size shrinks overall, in part, on the contrary, expands larger than a diameter of 60 nm. Finally, there is no grain boundary and structural features disappear. As a result, remaining clusters are negligible. In the formation process, the presence of a cluster is sparse at 293 K which is 8 K higher than the equilibrium decomposition temperature. At 270 K, with the passage of time, loose network appears and in a part, the clusters also generate. When it comes to hydrate at 263 K, clusters with a diameter of about 20 nm are spread to the whole in the dense state.

In the decomposition and formation processes, since reversible behavior has been observed, the generation and disappearance of the clusters were found to be explained as a significant step for the phase change of TBAB clathrate hydrate. Specifically, in the decomposition process, while the cluster disappeared within 20 seconds when heated at a temperature 2 K higher than the decomposition temperature, in the formation process at 270 K which is 15 K lower than the decomposition temperature, even after 15 minutes or more, generation of clusters is limited to a small part. That is, supercooling degree and induction time are necessary for the generation of the cluster from a homogeneous solution structure without clusters. In other words, it was found that the supercooling phenomenon depends on how long it takes to generate the large number of clusters at temperatures below equilibrium decomposition temperature.

### Significance statement

In the decomposition and formation processes of TBAB clathrate hydrate, since reversible behavior has been observed, the generation and disappearance of the clusters were found to be explained as a significant step for the phase change of TBAB clathrate hydrate.



**Primary author:** Mr MACHIDA, Hironobu (Panasonic Corporation)

**Co-authors:** Prof. HIRASAWA, Izumi (Waseda University); Prof. SUGAHARA, Takeshi (Osaka University)

**Presenter:** Mr MACHIDA, Hironobu (Panasonic Corporation)

**Session Classification:** Poster & Lunch

Contribution ID: 71

Type: **keynote**

## CHARACTERIZATION OF SNOW, FIRN AND ICE

*Wednesday, January 10, 2018 10:00 AM (45 minutes)*

In this presentation we give an overview of techniques used to characterize the microstructures of snow, firn (multi-year snow) and ice found in both cold regions and in polar ice sheets. These techniques include: transmission electron microscopy, synchrotron-based X-ray topography, cold-stage scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, electron channeling patterns, and electron backscatter patterns; cold stage confocal scanning optical microscopy coupled with Raman spectroscopy; and micro X-ray computed tomography. The capabilities and information obtainable along with the limitations and challenges of each technique will be discussed. Examples of each technique will be presented and future prospects discussed.

### **Significance statement**

Understanding the microstructure of snow, firn and ice and how they evolve is key to understanding both their mechanical properties and physical properties.

**Primary author:** Dr BAKER, Ian (Dartmouth College)

**Presenter:** Dr BAKER, Ian (Dartmouth College)

Contribution ID: 72

Type: **Talk**

## Ice Formation on Organic Crystals: Molecular Simulations Tell their Stories

*Tuesday, January 9, 2018 2:25 PM (20 minutes)*

The formation of ice is one of the most ubiquitous examples of crystal nucleation and growth, affecting our everyday life as well as technologies such as cryotherapy [1] or fossil fuel extraction [2]. However, pure water freezes only when cooled about 30 K below its melting point [3]. Thus, ice on earth forms mostly heterogeneously, facilitated by substrates which lower the free energy cost needed to nucleate a sufficiently large (or critical) ice nucleus. Experiments can assess whether a specific material is good or bad at promoting ice formation. For instance, both inorganic and biological particles have been found capable of boosting the ice nucleation rate at few degrees only below the freezing point of water [4], with great impact on the formation of clouds in the atmosphere. In particular, recent evidence suggests that some materials such as pyroelectric systems or polar crystals have the potential to induce local electric fields within the water network [5,6], with a spectacular enhancement of the kinetics of crystal nucleation and growth. However, the microscopic details of ice formation on this class of most promising ice nucleating agents remain largely unknown.

Here, we have investigated by means of atomistic simulations the formation of ice on two organic crystals: cholesterol (CHL) and metaldehyde (MDHE) - a polar crystal [7]. The low Miller index surfaces of these crystals are characterized by the presence of hydroxyl (-OH, MDHE) and etheric (R-O-R', MDHE) groups. The presence of these functional groups influences the structure and the dynamics of the water network in proximity of the water-crystal interface, consolidating the hydrogen bond network in different, albeit similarly effective, ways. This evidence directly translates into a huge boost of the ice nucleation rate, which we quantify by means of enhanced sampling (forward flux sampling [8]) simulations that also allow us to unravel the molecular-level details of the nucleation mechanism on both CHL and MDHE.

These results offer a comprehensive, microscopic picture of ice formation enhanced by organic crystals, paving the way to long-awaited molecular simulations of ice formation in biological matter. While the vast majority of the literature has been focusing on hydroxylated surfaces, we demonstrate the importance of functional groups such as the etheric R-O-R' groups in the context of heterogeneous ice nucleation.

[1] R. Y. Tam, C. N. Rowley et al., *J. Am. Chem. Soc.* 131, 15745 (2009). [2] C. A. Koh, *Chem. Soc. Rev.* 31, 157 (2002). [3] J. A. Sellberg, C. Huang et al., *Nature* 510, 381 (2014).

[4] B. J. Murray, D. O' Sullivan et al., *Chem. Soc. Rev.* 41, 6519 (2012).

[5] D. Ehre, E. Lavert et al., *Science* 327, 672 (2010).

[6] A. Belitzky, E. Mishuk et al., *J. Phys. Chem. Lett.* 7, 43 (2016).

[7] N. Fukuta, *Nature* 199, 475 (1963).

[8] R. J. Allen, C. Valeriani et al., *Journal of Physics: Condensed Matter* 21, 463102 (2009).

### Significance statement

We report the first (to our knowledge) atomistic simulations of ice formation on organic crystals. We provide microscopic insight into the mechanism and the kinetics of ice nucleation in the presence of organic compounds characterized by different functional groups - a first step toward the simulations of ice in biological matter.

**Primary author:** Dr SOSSO, Gabriele Cesare (University of Warwick)

**Co-authors:** Dr KISELEV, Alexei (Institute of Meteorology and Climate Research , Karlsruhe Institute of Technology); Prof. MICHAELIDES, Angelos (Thomas Young Centre, London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom); Prof. MURRAY, Benjamin (Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom); Dr HOLDEN, Mark (Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom); Dr PEDEVILLA, Philipp (Thomas Young Centre, London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom); Dr WHALE, Thomas (Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom)

**Presenter:** Dr SOSSO, Gabriele Cesare (University of Warwick)

**Track Classification:** Nucleation

Contribution ID: 73

Type: **Talk**

## **Elevated mercury and major ion concentrations in snowmelt runoff from a small Arctic Alaska watershed**

*Thursday, January 11, 2018 12:10 PM (20 minutes)*

Mercury is deposited to polar snow and ice surfaces during springtime atmospheric mercury depletion events (AMDEs). AMDEs require sunlight, frozen surfaces, and a reactive bromine source such as sea ice or halogen-rich snow. During these events gaseous elemental mercury (Hg<sub>0</sub>; GEM) is oxidized to reactive gaseous mercury (Hg<sub>II</sub>; RGM) which can associate with particles to form particulate Hg (PHg). Hg concentrations above 1,000 ng/L have been measured in polar snow and ice, following AMDEs, far greater than that found in lower latitude snow. RGM can be photochemically reduced back to GEM and emitted to the atmosphere or retained by the snowpack and released in spring when snow melts. The majority of polar surface runoff, including AMDE-sourced Hg, occurs during this spring freshet, but the fate of the Hg in the snow is complex, with the Hg depositing in lakes, exporting to the ocean, sorbing to vegetation or soil, or accumulating in soil by microbes.

In this study we tracked the fate of snowpack Hg in meltwater percolating through snowpack and snowmelt runoff near Utqiagvik (formerly Barrow), Alaska. We worked in a small (2.5 ha) watershed near the Arctic Ocean coast where active AMDE chemistry and elevated Hg in snow and ice have been reported. In late winter prior to snowmelt (April) and during snowmelt runoff (May and June) in 2008 and 2009 we made over 10,000 snow depth measurements and 36 snow water equivalent (SWE) measurements in the watershed to calculate the end of winter SWE and Hg load. Gaseous elemental Hg in air and local meteorology were also measured. Snowpack, meltwater, and stream channel water were collected and analyzed for total Hg and major ion concentrations and stable oxygen and hydrogen isotopes. We calculated total snowpack and runoff water Hg fluxes.

Results show a snowmelt “ionic pulse” of Hg and major ions during both melt seasons with the total dissolved Hg in meltwater in 2008 at 14.3 mg/ha and 8.1 mg/ha in 2009. These values are 5 to 7 times higher than reported from other Arctic watersheds. Record low summer 2007 precipitation may have led to 50% higher major ion and Hg concentrations during the 2008 melt compared to 2009. We calculated that 78% of snowpack Hg was exported with snowmelt runoff in 2008 and 41% in 2009. From these results we estimate roughly 25% of snowmelt Hg is attributable to AMDEs. We argue a projected warmer future Arctic with more ice sea ice leads, will provide greater halogen sources for AMDEs in the future, and this may increase Hg deposition, reduce Hg re-emission due to higher snow pack halogen concentrations and, ultimately, increase snowpack and meltwater Hg concentrations.

### **Significance statement**

A springtime pulse of mercury and major ions in a high Arctic watershed; links between mercury runoff and watershed snow and melt water hydrology; potential impacts on these processes by a projected warmer future Arctic

**Primary author:** Dr DOUGLAS, Thomas (Cold Regions Research and Engineering Laboratory)

**Co-authors:** Dr STEFFEN, Alexandra (Environment and Climate Change Canada Toronto); HIEM-STRÄ, Christopher (U.S. Army Cold Regions Research & Engineering Laboratory Alaska); Dr POLASHENSKI, Christopher (U.S. Army Cold Regions Research & Engineering Laboratory Alaska); Dr BLUM, Joel (Department of Earth & Environmental Sciences, University of Michigan); Dr STURM, Matthew (Geophysical Institute University of Alaska Fairbanks); Mr PREVOST, Romain (Rue Poissonaire 64100 Bayonne France); Dr FILHOL, Simon (University of Oslo Department of Geosciences Norway); Dr STUEFER, Svetlana (College of Engineering and Mines, University of Alaska Fairbanks)

**Presenter:** Dr DOUGLAS, Thomas (Cold Regions Research and Engineering Laboratory)

**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 74

Type: **Poster**

## Enhanced redox chemical transformation in ice and its environmental implications

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Ice is one of the simplest crystalline materials on earth and plays various important roles on earth environmental system. Although enormous progress has been made in understanding on physics and chemistry of ice, we have still a large number of mysterious features on ice. In most cases, chemical reactions take place slowly when temperature drops according to Arrhenius Equation. However, several processes are very accelerated by freezing compared to aqueous solution. Furthermore, the reaction mechanism during chemical transformation in ice is different from that in aqueous water. For example, Takenaka et. al., found that the NO<sub>2</sub><sup>-</sup> oxidation in the presence of oxygen to NO<sub>3</sub><sup>-</sup> was 100,000 times enhanced by freezing. The unexpected accelerated chemical reactions in ice have significant impacts on earth environment. In spite of the ice's important roles on various Earth's system, the investigation on chemical reaction in ice is insignificant. The redox transformation and speciation affect bioavailability, mobility, environmental fate, and toxicity of metals or inorganic elements. In this talk, I want to introduce our experimental results about accelerated redox reaction in ice such as enhanced dissolution of metal oxide particles, fast detoxification of harmful heavy metals and organic pollutants, and the enhanced chemical transformation of halogen species.

### Significance statement

In spite of the ice's important roles on various Earth's system, the investigation on chemical reaction in ice is insignificant. Several reactions are very accelerated by freezing and have significant environmental implications.

**Primary author:** Dr KIM, KITAE (Korea Polar Research institute(KOPRI))

**Presenter:** Dr KIM, KITAE (Korea Polar Research institute(KOPRI))

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 75

Type: **Talk**

## Confinement effects in premelting dynamics

*Thursday, January 11, 2018 9:15 AM (20 minutes)*

We examine the effects of confinement on the dynamics of premelted films driven by thermomolecular pressure gradients. Our approach is to modify a well-studied setting in which the thermomolecular pressure gradient is driven by a temperature gradient parallel to an interfacially premelted elastic wall. The modification treats the increase in viscosity associated with the thinning of films, studied in a wide variety of materials, using a power law and we examine the consequent evolution of the confining elastic wall. We treat (1) a range of interactions that are known to underlie interfacial premelting and (2) a constant temperature gradient wherein the thermomolecular pressure gradient is a constant. The difference between the cases with and without the proximity effect arises in the volume flux of premelted liquid. The proximity effect increases the viscosity as the film thickness decreases thereby requiring the thermomolecular pressure driven flux to be accommodated at higher temperatures where the premelted film thickness is the largest. Implications for experiment and observations of frost heave are discussed.

### Significance statement

The persistence of premelted liquid flow at low temperatures is a key aspect of frost heave as well as biological viability.

**Primary author:** Prof. WETTCLAUFER, John (Yale University)

**Co-author:** Dr PRAMANIK, Satyajit (Nordic Institute for Theoretical Physics)

**Presenter:** Prof. WETTCLAUFER, John (Yale University)

**Track Classification:** The surface and interface of ice



Contribution ID: 76

Type: Talk

## Modeling Elementary Heterogeneous Atmospheric and Interstellar (Photo)chemical Processes on Ice and their Dynamics using Amorphous Solid Water

Thursday, January 11, 2018 11:30 AM (20 minutes)

A thermodynamically reversible path was suggested to exist linking the low density forms of amorphous ice (LDA) and deeply supercooled liquid water (LDL), through the so-called no man's land and finally onto normal liquid water.<sup>(1)</sup> Furthermore, at temperatures below its calorimetric glass transition temperature ( $T_g \sim 136\text{K}$ ), transport kinetics are exceedingly slow in amorphous solid water (ASW). Therefore, it might provide a convenient model system to study elementary heterogeneous atmospheric and interstellar chemistry processes that occur on the quasi-liquid layer (QLL) that forms at the air-ice interface in the atmosphere at  $T < T_m$ . We will discuss how studying interfacial dynamics at cryogenic temperatures enables the decoupling of processes occurring onto the surface of ASW from those that take place within the bulk by strongly inhibiting the diffusive uptake kinetics. Using this strategy, we will show that ionic dissociation of simple acids [i.e., HF,<sup>(2)</sup> HCl,<sup>(3)</sup> HNO<sub>3</sub><sup>(4)</sup>] remain facile down to temperatures as low as 20K at the surface of ASW. We will also demonstrate that heterogeneous nitrates photolysis can be enhanced up to 3-fold at the ASW surface hinting at a significant contribution from heterogeneous (photo)chemistry to the photochemical NO<sub>x</sub> fluxes that emanate from the sunlit snowpack to polar boundary layer.<sup>5</sup>

(1) O. Mishima and H.E. Stanley, *Nature* 396, 329–335 (1998).

(2) P. Ayotte, M. Hébert, and P. Marchand, *J. Chem. Phys.* 123 184501 (2005); R. Iftimie, V. Thomas, S. Plessis, P. Marchand, and P. Ayotte, *J. Am. Chem. Soc.* 130, 5901-5907 (2008); P. Ayotte, S. Plessis and P. Marchand, *Phys. Chem. Chem. Phys.* 10, 4785-4792 (2008); P. Ayotte, Z. Rafiei, F. Porzio, and P. Marchand, *J. Chem. Phys.* 131, 124517 (2009); G. Marcotte and P. Ayotte, *J. Chem. Phys.* 134, 114522 (2011).

(3) P. Ayotte, P. Marchand, J. L. Daschbach, R. S. Smith, and B. D. Kay, *J. Phys. Chem. A* 115, 6002-6014 (2011).

(4) P. Marchand, G. Marcotte, and P. Ayotte, *J. Phys. Chem. A* 116, 12112-12122 (2012); G. Marcotte, P. Ayotte, A. Bendounan, F. Sirotti, C. Laffon and P. Parent, *J. Phys. Chem. Lett.* 4, 2643-2648 (2013).

(5) Guillaume Marcotte, Patrick Marchand, Stéphanie Pronovost, Patrick Ayotte, Carine Laffon and Philippe Parent, *J. Phys. Chem. A* 119, 1996-2005 (2015).

### Significance statement

Modeling of ice surface Chemistry using advanced spectroscopic tools and ASW allows slow interfacial dynamic processes to be studied with surface science approaches.

**Primary author:** Prof. AYOTTE, Patrick (Université de Sherbrooke)

**Presenter:** Prof. AYOTTE, Patrick (Université de Sherbrooke)

**Track Classification:** Chemistry

Contribution ID: 77

Type: **Poster**

## Humic-like products formation via the reaction of phenol with nitrite in ice phase

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Understanding the chemical nature of humic substances is very important but the origin of humic substances in nature is not well known. Therefore, elucidating the mechanisms leading to the generation of humic substances in nature is of great interests. It is believed that humic substances are produced from the transformation of natural organic matters, like lignin, by biological pathways. Recently, it has been reported that monomer molecules like quinones and sugars could be polymerized with amino compounds to form humic-like substances. This humification process is considered as a possible mechanism of humic substances production in the environment. In this work, we report the first observation on the formation of humic-like substances from the reaction between phenol and nitrite under a frozen state. In aqueous solution, nitrite slowly reacts with phenol, producing phenolic compounds like nitrophenol. Under frozen state, however, phenol reacted rapidly with nitrite and produced diverse organic compounds, like hydroquinone, dimerized phenolic substances, and much bigger molecules such as humic-like substances. The humic-like substances produced in ice are likely caused by the formation of phenolic radical and nitrosonium ion. This work may provide some insights into unknown pathways for the origin of humic substances especially in frozen environments.

### Significance statement

Chemical reaction in ice, Geochemistry, Organic chemistry, Reaction acceleration by freezing

**Primary authors:** Mr MIN, Dae Wi (POSTECH); Prof. CHOI, Wonyong (POSTECH)

**Presenter:** Mr MIN, Dae Wi (POSTECH)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 78

Type: **Talk**

## Hydrochloric acid droplets on ice crystal surfaces embedded in ice by vapor growth

*Monday, January 8, 2018 5:10 PM (20 minutes)*

Ice crystal surfaces are covered with quasi-liquid layers (QLLs) and it leads great influence on the global environment whether ice surfaces are dry or wet. For example, since QLLs enhance various chemical reactions in ice clouds, the formation of QLLs by atmospheric gases has been studied intensively. In particular, chemical reactions on ice surfaces in the presence of hydrogen chloride (HCl) gas play important roles in ozone-depleting reactions [1].

However, such studies were performed using spectroscopy techniques, which did not have enough spatial and temporal resolution. After that previous method would not reveal the dynamic behavior of individual QLLs because we revealed by advanced optical microscopy that the QLLs are not static complete wetting but dynamic partial wetting on ice surfaces [2]. Therefore, we show direct visualization of QLLs on ice basal faces in the presence of 0.1% HCl gas by advanced optical microscopy.

We found that the HCl gas induced the appearances of liquid layers with a droplet shape in the temperature range of  $-15.0 \sim -1.5$  degC, where no QLL appears in the absence of HCl gas [3]. However, note that since the lowest temperature of our experimental setup is  $-15.0$  degC, the lowest temperature for the appearance of the droplet QLLs is still unknown. We concluded that the droplets were not bulk pure water but HCl solution because we observed various features of the HCl-induced droplets as described below, which were not observed in the absence of HCl gas.

Under undersaturated condition, the HCl droplets were irregularly moving and broke into smaller ones [3]. Because the HCl droplets could be assumed to be equilibrium with ice crystals, the HCl concentration is adjusted by melting and freezing of ice crystal so that its melting point equals to the ice temperature. Therefore, these phenomena are closely related to the evaporation of the HCl droplets and subsequent melting of ice crystals caused by the increase in the HCl concentration.

Under supersaturated condition, the HCl droplets were quickly embedded into ice crystals because growth of ice crystals preferential started from the droplets surface and spread in the horizontal direction. After that, when we gradually decreased the water vapor pressure to undersaturated condition, the embedded droplets reappeared on ice crystal surfaces by the evaporation of ice. The HCl droplets were equilibrium with ice crystals around the droplets because reappearance droplets were same size as embedded droplets. Therefore, when the temperature of ice crystals were  $-10$  degC, the HCl concentration of the embedded droplets were estimated at 7 wt.% by the melting point of HCl solution.

The new incorporation mechanism of HCl gas into ice crystals suggested the possibility that natural ice crystals also include soluble atmospheric gases. For example, this mechanism might explain a large amount of chloride ions stored in the polar stratospheric clouds that cause ozone depletion.

[1] McNeill et al. (2006) PNAS 103, 9422.

[2] Sazaki et al. (2012) PNAS 109, 1052.

[3] Nagashima et al. (2016) Cryst. Growth Des. 16, 2225.

### Significance statement

We succeeded in direct visualization of HCl-induced droplets on ice basal faces in the temperature range of  $-15.0 \sim -1.5$  degC by advanced optical microscopy. Because the HCl droplets were embedded in ice crystals by vapor growth, natural ice crystals might incorporate soluble atmospheric gases by this mechanism.

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**Co-authors:** Prof. SAZAKI, Gen (Institute of Low Temperature Science, Hokkaido University); Dr MURATA, Ken-ichiro (Institute of Low Temperature Science, Hokkaido University); Dr HAMA, Tetsuya (Institute of Low Temperature Science, Hokkaido University, Japan); Prof. FURUKAWA, Yoshinori (Institute of Low Temperature Science, Hokkaido University)

**Presenter:** Dr NAGASHIMA, Ken (Institute of Low Temperature Science, Hokkaido University, Japan)

**Track Classification:** Ice Crystal Growth

Contribution ID: 79

Type: **Talk**

## Photolysis rate differences of impurities in various frozen matrices, including nature-identical snow crystals

*Thursday, January 11, 2018 11:10 AM (20 minutes)*

Chemical compounds can be incorporated into snow crystals during formation, for example by co-deposition with water vapor, or after the crystal is formed, such as by vapor deposition onto the surface of the crystal. As fallen snow crystals consolidate in a snowpack, entrained compounds can remain at the ice-air interface of the snowpack (i.e., in the quasi-liquid layer (QLL) of the disordered interface), or be trapped in liquid-like regions (LLRs) at grain boundaries in the ice matrix. More than just a reservoir for these materials, snow can be an important location for a variety of chemical reactions, such as transformations of pollutants.

Some recent work has suggested that some photochemical reactions proceed faster in surface QLLs than in either internal LLRs or in aqueous solution. This phenomenon has not been well studied. If photolysis at the air-ice is faster, it might have significant implications for our understanding of chemical fate in snow-covered regions.

Laboratory studies have attempted to reproduce the physical reaction environment of snow by a variety of methods, including freezing aqueous solutions in molds, spraying aqueous solutions into liquid nitrogen to form ice grains, or grinding solute-containing ices into small pieces. However, natural snow crystals are quite complex, and while current snow surrogate preparation methods have yielded important insights, they do not accurately mimic the structure and physical properties of newly-fallen natural snow crystals.

Here, we describe our work to study photolysis in various frozen matrices, including nature-identical snow samples. We built a snow-making machine, modeled on earlier efforts from other laboratories, which is based on the principle of nucleating supersaturated water vapor to form snow crystals. We incorporate chemicals into/onto the snow crystals either during the formation process or by treating the snow afterwards. Then, we illuminate this snow (or other samples) using the output from an arc lamp, filtered to approximate polar sunlight.

We have measured photolysis rates for several compounds in both frozen and aqueous matrices. Our results have found similar photolysis rates in aqueous and frozen solutions for all tested compounds, suggesting chemical reactions in internal LLRs proceed similarly as in aqueous solution. However, reaction rates for some chemicals deposited to snow or ice surfaces are up to 20 times faster than in aqueous solution, while other compounds show no enhancement. We will discuss which compounds and freezing conditions lead to an enhancement.

### Significance statement

We have identified some compounds that photolyze faster on snow or ice surfaces than in either aqueous solution or frozen within the ice matrix. Enhanced photolysis rates at the air-ice interface suggest certain chemicals may degrade or transform faster than previously believed.

**Primary author:** Dr HULLAR, Ted (University of California at Davis)

**Co-authors:** Dr ANASTASIO, Cort (University of California at Davis); Ms MAGADIA, Danielle

(University of California at Davis); Mr OLIVER, Palmer (University of California at Davis)

**Presenter:** Dr HULLAR, Ted (University of California at Davis)

**Track Classification:** Chemistry

Contribution ID: **80**Type: **Poster**

## Proton Tunneling in High Pressure Ices

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Recently, Bove et al. (Phys. Rev. Lett. 103 165901) have found a supporting evidence for the existence of concerted proton tunneling along hydrogen bonds of six-membered rings in ice Ih using neutron incoherent quasi-elastic scattering measurement. Since the height of the potential barrier can be controlled by the distance between the nearest oxygen atoms or by the external pressure, study of pressure effect on tunneling is interesting and important to understand hydrogen bonds under high pressure. In this study, the pressure effect, its physical consequences, and experimental measurement are discussed.

### Significance statement

In ice phases with random hydrogen bonds, water molecules are dancing the dance of concerted quantum tunneling, hand in hand, in a circle of six members. We study theoretically how the rhythm of the dance changes with pressure and suggest how to observe the dance experimentally.

**Primary author:** Dr IITAKA, Toshiaki (RIKEN)

**Presenter:** Dr IITAKA, Toshiaki (RIKEN)

**Session Classification:** Poster & Lunch

Contribution ID: 81

Type: Talk

## Increased ice nucleation efficiency of mineral dusts in dilute ammonium sulfate solutions

*Tuesday, January 9, 2018 11:35 AM (20 minutes)*

Mineral dust has lifetimes of several days in the atmosphere and can be transported over long distances. During transport, mineral dust particles may acquire a coating when they come in contact with reactive gases and semivolatile species or when they undergo cloud processing (e.g. Tang et al., 2016). Coatings can influence the ice nucleation (IN) efficiency of mineral dust in different ways. Water-soluble coatings reduce the critical supersaturation required for cloud droplet activation. Coatings may chemically change the mineral surfaces. Moreover, coatings open up a pathway for immersion freezing below water saturation in concentrated solutions. In many cases, the freezing temperature of mineral dust in solutions can be predicted by the water-activity based IN theory (Zobrist et al., 2008).

Here we show examples where this approach to predict freezing temperatures in solutions failed because of specific interactions between the solutes and the ice-nucleating surface. Our focus was on microcline, a K-feldspar known to be highly IN active (e.g. Atkinson et al., 2013). We performed immersion freezing experiments of emulsified droplets with a differential scanning calorimeter. At low concentrations of  $\text{NH}_4^+$ -containing salts, namely  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{NH}_4\text{Cl}$ , the ice freezing temperature was increased by up to almost 5 K above the value in pure water, whereas at high concentrations the ice freezing temperature was decreased below the predictions from the water activity-based IN theory for all investigated solutes ( $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{KCl}$ ). An increase in IN efficiency was also present in the case of dilute  $\text{NH}_3$  solutions. An increase of the IN efficiency in very dilute  $\text{NH}_3$  and  $\text{NH}_4^+$ -containing solutions followed by a decrease with increasing concentration was also observed for sanidine (a K-feldspar) and andesine (a Na/Ca-feldspar), as well as for mica and kaolinite. This indicates the presence of specific chemical interactions between solutes and the feldspar surface which are not captured by the water activity-based IN theory. We hypothesize that the hydrogen bonding of  $\text{NH}_3$  molecules with surface -OH groups could be the reason for the enhanced freezing temperatures in dilute ammonia and ammonium containing solutions as they could form an ice-like overlayer providing hydrogen bonding groups for ice to nucleate on top of it. This enhanced IN efficiency might be of relevance for freezing in condensation mode when ammonium sulfate coatings on mineral dust particles dilute during cloud droplet activation.

Atkinson, J. D., Murray, B. J., Woodhouse, M. T., Whale, T. F., Baustian, K. J., Carslaw, K. S., Dobbie, S., O'Sullivan, D., and Malkin, T. L, *Nature*, 498, 355–358, 2013.

Tang, M., Cziczo, D. J., and Grassian, V. H, *Chem. Rev.*, 116, 4205–4259, 2016.

Zobrist, B., Marcolli, C., Peter, T., and Koop, T, *J. Phys. Chem. A*, 112, 3965–3975, 2008.

### Significance statement

Mineral dust particles may acquire coatings during long-range transport in the atmosphere. We show here that in the case of ammonium sulfate coatings different types of mineral dusts may have an increased ice nucleation efficiency in condensation mode when the coating dilutes during cloud droplet activation.

**Primary author:** Mr KUMAR, Anand (ETH Zurich, Institute for Atmospheric and Climate Science)



**Co-authors:** Dr MARCOLLI, Claudia (ETH Zurich, Institute for Atmospheric and Climate Science); Prof. PETER, Thomas (ETH Zurich, Institute for Atmospheric and Climate Science)

**Presenter:** Dr MARCOLLI, Claudia (ETH Zurich, Institute for Atmospheric and Climate Science)

**Track Classification:** Nucleation

Contribution ID: 82

Type: **Talk**

## Acid-Promoted Crystallization of Amorphous Solid Water

*Tuesday, January 9, 2018 9:35 AM (20 minutes)*

Amorphous solid water (ASW) has attracted much attention in the ice research community because of its unique properties as a metastable solid form of water and possible existence in interstellar clouds. ASW is kinetically metastable and undergoes a phase transition to crystalline ice (CI) upon heating; these phenomena have been studied in depth in recent years. [1-3] In this presentation, we discuss the effect of excess protons (hydroniums) on the crystallization of ASW. We prepared an ASW film sample by water vapor deposition on a Pt(111) single crystal surface in an ultra-high vacuum environment. Excess protons were generated by the ionization of adsorbed hydrogen chloride (HCl) gas on the ASW surface. The crystallization of an ASW film was monitored by temperature-programmed desorption and reflection-absorption infrared spectroscopy measurements. In contrast to a normal behavior that solute species retard the crystallization of ASW due to an entropic effect, the excess protons released from HCl molecules facilitated the crystallization of ASW. This phenomenon was observed when HCl was supplied not only at the surface of an ASW film but also in the interior region. In both cases, the crystallization was initiated at the location where the acid was provided to the sample. The presence of excess protons lowered the apparent activation energy of the crystallization of ASW. A possible promotion mechanism for the crystallization of ASW is discussed in relation to the properties of excess protons in ASW.

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[2] Backus, E. H.; Grecea, M. L.; Kley, A. W.; Bonn, M. Surface crystallization of amorphous solid water. *Phys. Rev. Lett.* (2004) 92, 236101.

[3] Yuan, C; Smith, R. S.; Kay B. D. Surface and bulk crystallization of amorphous solid water films: Confirmation of “top-down” crystallization. *Surf. Sci.* (2016) 652, 350-354.

### Significance statement

A solute species usually suppresses the crystallization of aqueous solution due to an entropic effect. However, a contrasting effect was observed for hydrogen chloride in ASW, which promotes the crystallization of ASW. This unique phenomenon brings attention to the ASW crystallization mechanism in relation to the behavior of excess protons.

**Primary author:** Mr LEE, Du Hyeong (Seoul National University)

**Co-authors:** Prof. KANG, Heon (Seoul National University); Mr BANG, Jaehyeock (Department of Chemistry, Seoul National University); Dr SHIN, Sunghwan (Seoul National University); Dr KIM, Youngsoo (Seoul National University); Mr PARK, Youngwook (Seoul National University)

**Presenter:** Mr LEE, Du Hyeong (Seoul National University)

**Track Classification:** Amorphous Ice

Contribution ID: 83

Type: **keynote**

# Ice Binding Proteins and Their Interaction With Ice Crystals

*Thursday, January 11, 2018 1:55 PM (45 minutes)*

We investigate the interactions of ice-binding proteins, IBPs, with ice surfaces. In particular, we investigate the dynamic nature of the protein&ice interaction using fluorescence microscopy techniques combined with temperature-controlled microfluidic devices. The results show that binding of IBP to ice is irreversible and that the freezing temperature depression is sensitive to the time allowed for the proteins to accumulate on ice surfaces. This time sensitivity changes dramatically between different types of IBPs. Our results relate the dynamics and level of activity of various types of IBPs to their ability to bind to specific ice orientations, in particular to the basal plane of the ice. These results contribute to the understanding of the mechanisms by which IBPs act that will be critical for the successful use of IBP in cryobiological applications.

## References:

Ice-Binding Proteins and Their Function, M. Bar-Dolev, I. Braslavsky, and P.L. Davies, *Ann. Rev. Biochem.* 2016

Cryoprotective effect of an ice-binding protein derived from Antarctic bacteria M. Mangiagalli, et al. *FEBS* 2016

Putting life on ice: bacteria that bind to frozen water, M. Bar-Dolev et al. *R. Soc. Interface* 2016  
Microfluidic Cold-Finger Device for the Investigation of Ice-Binding Proteins, L. Haleva et al. *Biophysics J.* 2016

When are antifreeze proteins in solution essential for ice growth inhibition? R. Drori et al. *Langmuir*, 2015

Experimental Correlation between Thermal Hysteresis Activity and the Distance between Antifreeze Proteins on an Ice Surface, R. Drori, P.L. Davies and I. Braslavsky, *RSC Adv.*, 2015

Ice-Binding Proteins that Accumulate on Different Ice Crystal Planes Produces Distinct Thermal Hysteresis Dynamics, Drori, R., et al., *R. Soc. Interface* 2014.

LabVIEW-operated Novel Nanoliter Osmometer for Ice Binding Protein Investigations, I. Braslavsky, and R Drori,

*Journal of Visualized Experiments* 2013.

Microfluidic experiments reveal that antifreeze proteins bound to ice crystals suffice to prevent their growth,

Y Celik et al. *PNAS* 2013.

New Insights into Ice Growth and Melting Modifications by Antifreeze Proteins, M. Bar-Dolev et al. *R. Soc. Interface* 2012

Superheating of ice crystals in antifreeze protein solutions, Y Celik et al. *PNAS* 2010.

Supported by the European-Research-Council (ERC), the National-Science-Foundation (NSF), and the Israel-Science-Foundation (ISF).

## Significance statement

Our results show that binding of IBPs to ice is irreversible and that the freezing temperature depression is sensitive to the time. These results contribute to the understanding of the mechanisms by which IBPs act that will be critical for the successful use of IBP in cryobiological applications.

**Primary author:** Prof. BRASLAVSKY, Ido (The Hebrew University of Jerusalem)

**Presenter:** Prof. BRASLAVSKY, Ido (The Hebrew University of Jerusalem)

Contribution ID: 84

Type: **keynote**

## Anisotropic impurity effect for ice crystal growth in supercooled water

*Monday, January 8, 2018 2:05 PM (45 minutes)*

Antifreeze protein (AFP) and antifreeze glycoprotein (AFGP) molecules adsorb on ice-water interfaces and control the ice crystal growth. However, there still remain many missing pieces of the puzzle for the growth control mechanism. The basic observations from the viewpoint of crystal growth, for example, in-situ observations of morphologies, precise measurements of growth rates, understandings of the adsorption states of these molecules on ice-water interface, are important to clarify the mechanism of crystal growth control. We carried out various experiments on free growth of ice crystals in supercooled water both on the ground and under the microgravity condition without any influence of convection, which is realized in the International Space Station. Based on these experiments, we discuss about the anisotropic effect of AFGP molecules as an impurity for ice crystal growth [1].

In situ observation of ice crystal growth in a supercooled water including AFGP molecules labeled by the fluorescent molecules indicated that growth of the prismatic (and/or pyramidal) faces was inhibited by the adsorption of AFGP molecules. Growth inhibition for these faces is explained by the pinning effect of adsorbed AFGP molecules, which is the well-known impurity effect for the crystal growth. In contrast, long-term continuous measurements of growth rates performed in ISS clarified that the growth of basal face is promoted by the effect of AFGP molecules. Namely, the adsorbed AFGP molecules may work as the inhibitor for prismatic and pyramidal faces but as the promoter for basal faces. These results indicate the anisotropic impurity effect depending on the crystallographic orientation of interfaces. On the contrary, we found that the growth rates of basal faces were periodically changed as a function of growth time. The growth enhancement and oscillation observed on the ice basal faces are the previously unknown impurity effects for crystal growth of not only the ice crystal but also the other crystals. A preliminary explanation for this anisotropy will be given on the basis of the preferential adsorption of AFGP molecules on the prismatic and/or pyramidal faces [2,3].

Our findings will lead to a better understanding of a novel process for ice growth kinetics, and shed light on the role that crystal growth kinetics has in the onset of the mysterious antifreeze effect in living organisms, namely, how this protein can prevent freezing of living organisms under sub-zero temperature condition.

### References:

- [1] Y. Furukawa et al.: Scientific Reports, 7:43157, (2017), doi:10.1038/srep43157.
- [2] S. Zepeda, E. Yokoyama, Y. Uda, C. Katagiri and Y. Furukawa, Cryst. Growth Des. 8, 3666-3672, (2008), doi:10.1021/cg800269w.
- [3] Y. Uda, et al.: J. Phys. Chem. B, 111, 14355-14361(2007), doi:10.1021/jp075429s.

### Significance statement

We present about the anisotropic effects of antifreeze glycoprotein molecules adsorbed on the ice/water interface for its growth, based on the results of ground and space experiments.

**Primary author:** Prof. FURUKAWA, Yoshinori (Institute of Low Temperature Science, Hokkaido University)

**Co-authors:** Prof. YOKOYAMA, Etsuro (Gakushuin Univ.); Prof. SAZAKI, Gen (Institute of Low

Temperature Science, Hokkaido University); Dr NAGASHIMA, Ken (Institute of Low Temperature Science, Hokkaido University, Japan); Dr MURATA, Ken-ichiro (Institute of Low Temperature Science, Hokkaido University); Dr ZEPEDA, Salvador (Institute of Low Temperature Science, Hokkaido Univ.); Mr NAKATSUBO, Shun-ichi (Institute of Low Temperature Science, Hokkaido Univ.)

**Presenter:** Prof. FURUKAWA, Yoshinori (Institute of Low Temperature Science, Hokkaido University)

Contribution ID: 85

Type: **Poster**

## Structure and dynamics of amorphous ice including gas molecules

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Various gaseous species such as H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>3</sub>OH, H<sub>2</sub>CO, and NH<sub>3</sub> are condensed onto dust grains in interstellar molecular clouds. The H<sub>2</sub>O ice, which is formed by vapor deposition onto the dust grains under low temperature and pressure conditions, is amorphous ice. The amorphous ice includes various gas molecules, and the molecules undergo chemical evolutions to organic molecules through various processes [1]. Thus, the structure and properties of amorphous ice including gas molecules are important factors to understand the molecular evolution of organic molecules [2]. To investigate the effects of included gas molecules on the structure and properties of amorphous ice, the molecular dynamics (MD) calculations of amorphous ice including CO<sub>2</sub> and CO were performed.

We used an interatomic potential model (KAWAMURA potential model) for the MD simulations [3]. The results showed that CO<sub>2</sub> molecules form a cluster when n = 10, whereas CO exists as an individual molecule.

The result showed that the CO<sub>2</sub> molecules form a cluster when n = 10, whereas CO exists as an individual molecule.

### References

- [1] A. Kouchi, T. Yamamoto, T. Kuroda, J. M. Greenberg, 1994, *Astron. Astrophys.* 290, 1009.
- [2]. Y. Kumagai, T. Ikeda-Fukazawa, 2017, *Chem. Phys. Lett.* 678, 153.
- [3] N. Kumagai, K. Kawamura, T. Yokokawa, 1994, *Mol. Simul.* 12, 177.

### Significance statement

Molecular dynamics simulations of amorphous ice including CO<sub>2</sub> and CO were performed. The results showed that CO<sub>2</sub> and CO has effects to change the density of surrounding ice matrix. From these results, we discuss the effects of gas inclusions on structure of amorphous ice.

**Primary author:** Mr NAOSHIMA, Yasuhito (Department of Applied Chemistry, Meiji University, Japan)

**Co-author:** Prof. IKEDA-FUKAZAWA, Tomoko (Department of Applied Chemistry, Meiji University, Japan)

**Presenter:** Mr NAOSHIMA, Yasuhito (Department of Applied Chemistry, Meiji University, Japan)

**Session Classification:** Poster & Lunch

Contribution ID: 86

Type: **Talk**

## Freezing by protein cages

*Thursday, January 11, 2018 3:20 PM (20 minutes)*

Assembled proteins, esp. cages and viruses, are essential ingredients of life [Calo 2016a]. Some assemblies appear to tolerate the contact to ice, or even the growth of ice. While the interaction of single proteins or simple biopolymers with ice is increasingly investigated [Hiranuma 2015], assemblies are new territory [Wilson 2015]. We pose two questions:

1. Molecular geometry: Is there evidence for the proposal of flat and large surfaces as efficient ice binders or nucleators? This idea [Davies 2014] is intriguing because it puts a purely physical mechanism above the usually assumed biochemical processes, although arguments such as hydrophobicity are also linked to the surface chemistry.
2. Cloud glaciation by biological ice nuclei: Can viruses induce freezing of water? This question is a natural extension from standard ice nucleating particles (mineral dust), over organic matter to “living” objects, which are indeed present in large numbers in sea water [Wilson 2015].

Since the surfaces even of small viruses are less curved and larger than the surface of a single protein, both questions are related. We are answering them by testing the freezing of supercooled water by selected proteins and protein assemblies. Our methods are microscopy, AFM [Calo 2016b], (nano)FTIR [Amenabar 2013] and environmental SEM [Alonso 2013a]; our proteins were the cages ferritin and apoferritin (each with 24 proteins), casein (aggregating to hundreds of nm), and a standard plant virus, Tobacco Mosaic Virus (TMV), which features a helical sheath of 2130 proteins [Alonso 2013b, Calo 2016b]. This virus is hydrophilic, and can be transported in clouds [Castello 1995].

We found a preference for ice growth induced by aggregated (assembled) proteins. Apoferritin and ferritin are especially effective. These assemblies are virus-like cages, constructed from 24 proteins, with a natural tendency to form aggregates (e.g. oligomers). Based on our studies on virus hydration [Alonso2013a], we now demonstrate that ice can grow on viruses without destruction. High-resolution AFM shows surface reconstructions of irregular lateral spacings (ca. 10 nm) that are caused by water adsorption, which is the precursor for ice formation.

Literature:

[Alonso 2013a] J.M. Alonso, F. Tatti, A. Chuvilin, K. Mam, T. Ondarçuhu, A.M. Bittner, *Langmuir* 29 (2013) 14580-14587

[Alonso 2013b] J.M. Alonso, M.L. Gorzny, A.M. Bittner, *Trends Biotechnol.* 31 (2013) 530-538

[Amenabar 2013] I. Amenabar, S. Poly, W. Nuansing, E.H. Hubrich, A. Govyadinov, F. Huth, R. Krutokhvostov, L. Zhang, M. Knez, J. Heberle, A.M. Bittner, R. Hillenbrand, *Nature Commun.* 4 (2013) 2890

[Calo 2016a] A. Calò, S. Eiben, M. Okuda, A.M. Bittner, *Jap. J. Appl. Phys.* 55 (2016) 03DA01

[Calo 2016b] A. Calò, A. Eleta-Lopez, P. Stoliar, D. de Sancho, S. Santos, A. Verdaguer, A.M. Bittner, *Sci. Rep.* 6 (2016) 21899

[Castello 1995] J.D. Castello et al., *Phytopathology* 85 (1995) 409

[Davies 2014] P.L. Davies, *Trends in Biochem. Sci.* 39 (2014) 548

[Hiranuma 2015] N. Hiranuma et al., *Nature Geoscience* 8 (2015) 273

[Wilson 2015] T.W. Wilson et al., *Nature* 525 (2015) 234



**Significance statement**

Protein assemblies, such as protein cages and viruses, can induce ice growth. We provide a nanoscale view on this phenomenon. We propose that surface hydration is the first stage of ice nucleation.

**Primary author:** Prof. BITTNER, Alexander (CIC nanogune)

**Co-authors:** Dr ELETA-LOPEZ, Aitziber (CIC nanogune); Dr MARCOLLI, Claudia (ETHZ ENV); Dr CASCAJO, Maria (CIC nanogune); Mr DAVID, Robert (ETHZ ENV); Ms LOCARNO, Silvia (CIC nanogune); Dr KANJI, Zamin (ETHZ ENV)

**Presenter:** Prof. BITTNER, Alexander (CIC nanogune)

**Track Classification:** Ice Binding Proteins

Contribution ID: 87

Type: **Talk**

## A statistical fracture model for Antarctic ice shelf regions

*Friday, January 12, 2018 11:20 AM (20 minutes)*

Creating an effective model of the calving process in Antarctica is a challenging task in ice sheet modelling.

The recent calving of Larsen B and Larsen C ice shelves has raised a number of questions as to the nature of the key factors that triggered these calving events and whether they are caused by natural ice sheet dynamics or climate change. To address this, a reliable calving model is required and previous studies and models have not been able to be utilised across the Antarctic continent. In fact, a comprehensive calving model needs to include components such as information about surface and basal crevasses (location and depth), advection of the crevasses downstream, the intersection of the surface and basal crevasses as well as estimation of the critical depth of a crevasse when calving occurs.

The purpose of this research is to use observational data to construct a fracture model that can be applied to any selected ice shelf/glacier in Antarctica. The main aspects explored are the determination of the location of both surface and basal fractures as well as propagation of surface crevasses when meltwater is added.

First, the basis of this project was to create a statistical model that can improve the predictability of the location of surface fractures. We used a logistic regression algorithm and a set of predictors taken from observations of glaciers/ice shelves. The modelled probability function varies from zero to one and in this way is similar to the previously proposed damage function. It can predict fractures for grounded ice as well as for floating ice shelves.

Second, we used Linear Elastic Fracture Mechanics as a basis for modelling the depth of fractures. Then, based on the misfit between observed and modelled fracture depth we were able to perform an inversion for melt rate and, thus, obtain a depth of crevasses in better agreement with observations.

Lastly, we explored the correlation between surface troughs and basal crevasses using altimetry data for over 45 glacier regions. Our findings confirm the previously suggested theory that these two processes are highly correlated. We use this results together with statistical algorithms to predict the location of basal crevasses.

We found that statistical methods can provide valuable information for predicting zones of fractures. Our model shows a good agreement with the data about fractures taken from satellite imagery for any selected ice shelf in Antarctica. Furthermore, we found that different conditions of fracturing require different water levels inside crevasses in order to keep them open. Our inversion allows for predicting the depth of crevasses in a better agreement with the observed depth of crevasses obtained from radar data sets. The combination of these methods provides a good basis for future calving parameterisation.

### Significance statement

This research provides a background for modeling of calving process in Antarctica by combining statistical and physics-based methods. More precise prediction of the location and depth of surface and basal crevasses can help to estimate where on an ice shelf calving is more likely to take place.

**Primary author:** Ms EMETC, Veronika (Research School of Earth Sciences, Australian National University)

**Co-authors:** Prof. MORLIGHEM, Mathieu (Department of Earth System Science, University of California, Irvine, USA); Dr TREGONING, Paul (Research School of Earth Sciences, Australian National University)

**Presenter:** Ms EMETC, Veronika (Research School of Earth Sciences, Australian National University)

**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 89

Type: **Poster**

## Investigation of Ethanol at the Ice Surface using Sum-Frequency Generation Spectroscopy

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The properties of small organic molecules at the ice/air interface are crucial for the understanding of fundamental processes in fields spanning from molecular physics to chemistry in the stratosphere. Here we use surface-specific heterodyne-detected vibrational sum-frequency generation spectroscopy (HD-VSFG) to investigate the molecular properties of ethanol at the air-water and the ice-water interfaces. We can determine the absolute orientation of ethanol molecules at the ice-water interface, and by comparing the results at both interfaces we obtain detailed information on the distribution and arrangement of the alcohol and water molecules.

### Significance statement

Investigation of the behaviour and properties of small organic molecules at ice/air and water/air interface to gain insights in fundamental processes which are important in a variety of research fields (e.g. molecular physics or chemistry in the stratosphere).

**Primary author:** Mr KIRSCHNER, Johannes (AMOLF)

**Co-authors:** Ms MOLL, Carolyn (Amolf); Prof. BAKKER, Huib (Amolf); Dr MEISTER, Konrad (AMOLF)

**Presenter:** Mr KIRSCHNER, Johannes (AMOLF)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 91

Type: **Talk**

## The Effect of Ice Type on Ice Adhesion

*Friday, January 12, 2018 9:40 AM (20 minutes)*

Ice formation is unavoidable at low temperatures. Ice and frost cause not only inconvenience but also danger in the daily life of human beings, especially in cold regions. For example, ice accumulation on roads or on aircraft wings causes accidents and ice accumulation on wind turbines or overhead power lines can affect the distribution of electricity, power losses and mechanical and electrical failures. To avoid such situations, icing mitigation methods using both anti-icing and deicing systems have been developed over the last decades, with differing efficacy depending on their application field.

There are three main pathways to achieve anti-icing surfaces, or icephobic surfaces. These three pathways are the removal of water before freezing, the delay of ice nucleation and the reduction of ice adhesion strength. The ideal icephobic surfaces have an ice adhesion so low that the ice formed on them would shed merely due to its own weight or a natural wind action. To achieve such a low ice adhesion, the fundamental mechanisms of ice adhesion need to be fully, or at least better, understood.

This investigation is the first study on the impact of different types of ice on the ice adhesion strength for the same substrate and the same temperature of formation. Ice is likely to behave in different manners depending on the conditions during freezing, and the type of ice is therefore an important factor of ice adhesion strength. The different ice types were formed and tested at the same temperature of -10 °C. The three ice types studied were impact ice generated in a wind tunnel, hard rime ice created in a cold room with water droplets raining from above, and glaze ice frozen directly on to the bars with silicon molds. The ice was frozen on similar aluminum 6061-T6 bars, and ice adhesion strength was measured with the centrifuge adhesion test at the AMIL facilities.

A total of 126 tests were performed. The mean ice adhesion strength was measured to  $0.78 \pm 0.10$  MPa for hard rime ice,  $0.53 \pm 0.12$  MPa for impact ice and  $0.28 \pm 0.08$  MPa for glaze ice. The ice adhesion strength for glaze ice is therefore more than 60% lower than for hard rime ice. A significant correlation was found between apparent density of the ice and ice adhesion strength, indicating that the ice adhesion strength decreases when the density of the bulk ice increases. The interface porosity of ice seems also to influence the ice adhesion strength.

The results indicate that ice adhesion models need to include a density factor of the ice in addition to the temperature to differentiate between different ice types. If correct, these observations may inspire a new strategy in icephobic surfaces.

### Significance statement

For the first time, it was shown that ice adhesion strength differs for different ice types generated at the same temperatures. The density of the ice showed significant correlation with ice adhesion strength. These observations may inspire a new strategy in icephobic surfaces to combat hazardous icing in cold climates.

**Primary author:** Ms RØNNEBERG, Sigrid (Norwegian University of Science and Technology)

**Co-authors:** Prof. LAFORTE, Caroline (Anti-icing Materials International Laboratory (AMIL), Uni-

versity of Québec in Chicoutimi); Prof. VOLAT, Christophe (Anti-icing Materials International Laboratory (AMIL), University of Québec in Chicoutimi); Prof. HE, Jianying (Norwegian University of Science and Technology); Prof. ZHANG, Zhiliang (Norwegian University of Science and Technology)

**Presenter:** Ms RØNNEBERG, Sigrid (Norwegian University of Science and Technology)

**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 92

Type: **keynote**

## Modelling mushy sea ice growth and brine convection

*Thursday, January 11, 2018 4:35 PM (45 minutes)*

More than 20 million square kilometres of the polar oceans freeze over each year to form sea ice. Sea ice is a mushy layer: a reactive, porous, multiphase material consisting of ice crystals bathed in liquid brine. The porosity of sea ice evolves in space and time, with important consequences for coupling to the oceans and sea ice ecosystems. Atmospheric cooling generates a density gradient in the interstitial brine, which can drive convection and rejection of dense brine from the sea ice to force ocean circulation and mixing. The resulting convective circulation also controls a nutrient supply to support biological activity, including sea-ice algae which grow within the liquid filled pores. This presentation will introduce the fundamentals of the multiphase behaviour of sea ice, with a particular focus on continuum phase-averaged models of sea ice thermodynamics using mushy-layer theory, and the generation of convective flows through the porous ice. I will present results from recent analysis of the transient growth of mushy layers. The cooling conditions provide a key control on the internal structure of the mushy layer during diffusive growth, with two regimes identified. A relatively porous mushy layer forms either for weak cooling, or early during growth when there are slow inefficient cooling rates. In contrast, strong and efficient cooling generates low porosity throughout much of the mushy layer, with a thin high-porosity boundary layer near to the mush-liquid interface. This localisation of porosity impacts the ice permeability, and provides a key control on the onset of convection in the mushy layer. I will conclude with a discussion of the nonlinear dynamics and the implications for the macroscopic ice structure, brine rejection and brine channel formation in growing sea ice.

### Significance statement

The growth of sea ice and resulting brine rejection have key implications for climate and polar ecosystems. Using mushy layer theory, we characterise the impact of the cooling conditions on the multiphase structure of porous sea ice, and the onset of convective drainage of dense brine into the underlying ocean.

**Primary author:** Dr WELLS, Andrew (University of Oxford)

**Co-authors:** Mr PARKINSON, James (University of Oxford); Mr HITCHEN, Joe (University of Oxford)

**Presenter:** Dr WELLS, Andrew (University of Oxford)

Contribution ID: 93

Type: **keynote**

## Amorphous ices and liquid states

*Tuesday, January 9, 2018 8:30 AM (45 minutes)*

The amorphous forms of water play an important role in the understanding of water's anomalous properties. Computer simulations suggest that the anomalous behaviour of ambient and supercooled water could be explained by a two state model of water [1]. Since the discovery of two distinct amorphous states of ice with different density (high- and low density amorphous ice, HDA and LDA) it has been lively debated whether and how this phenomenon of polyamorphism at high pressures is connected to the occurrence of two distinct liquid phases (HDL and LDL) [1]. Alternatively, amorphous ices have been suggested to be of nanocrystalline nature, unrelated to liquids.

The glass transition in both amorphous states, LDA and HDA, was investigated using different experimental techniques [2] and discussed controversially over the last years [3]. Our recent results using X-ray diffraction as well as X-ray correlation spectroscopy (XPCS) support the previous findings of HDA undergoing a glass-liquid transition at ambient pressure around 110 K and are consistent with the hypothesis of a liquid-liquid transition between HDL and LDL [4].

[1] P. Gallo, K. Amann-Winkel et al., Water a Tale of Two Liquids, Chem. Rev. 116, 7463-7500 (2016)

[2] K. Amann-Winkel, C. Gainaru et al., Water's second glass transition, PNAS 110, 17720 (2013)

[3] K. Amann-Winkel et al., Water's controversial glass transition, Rev. Mod. Phys. 88, 0110002 (2016)

[4] F. Perakis, K. Amann-Winkel et al., Diffusive dynamics during the high-to-low density transition in amorphous ice, PNAS 114, 8193 (2017)

### Significance statement

A liquid-liquid transition in water terminating in a hypothesized second-critical point is discussed controversially. Our x-ray experiments on water and amorphous ice shed light on this important debate.

**Primary author:** Dr AMANN-WINKEL, Katrin (Stockholm University)

**Presenter:** Dr AMANN-WINKEL, Katrin (Stockholm University)



Contribution ID: 95

Type: **Poster**

## Effect of rare gas matrix confinement on water nuclear spin conversion

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The properties of the nuclear spin isomers of the water molecule are of great interest in astrophysics since the ortho:para ratio (OPR) is assumed to provide insight into the formation mechanism and history of comets as well as other celestial bodies [1,2]. Technological advances are also foreseen for ortho-water enriched samples in magnetic resonance applications, in analogy with hyperpolarisation experiments relying on para-hydrogen. Motivated by these perspectives, technological bottlenecks need to be overcome: the development of an efficient separation methodology and the improvement in storage strategies through a better understanding of their inter-conversion mechanism [3-5]. Recent investigations of the inter-conversion kinetics in isolated water molecules, trapped in rare gas matrices at cryogenic temperatures, may provide important clues of the underlying mechanism [6]. In particular, the inter-conversion rates accelerate dramatically in the heavier water isotopologues H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O compared to normal water. This may provide insight into the role played by intramolecular (i.e., spin-rotation and spin-spin) as well as intermolecular (i.e., rotation-translation, inter-molecular spin-spin) couplings in the inter-conversion between the ortho and para-water nuclear spin isomers which are at play in the evolution of H<sub>2</sub>O nuclear spin states in all phases of water including ice.

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### Significance statement

First study of water isotopomers nuclear spin conversion confined in rare gas matrix.

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**Session Classification:** Poster & Lunch

Contribution ID: 96

Type: **Poster**

## Generation of pure H<sub>2</sub>O-ortho molecular beam with a Stern-Gerlach like experiment for nuclear spin conversion studies

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Water nuclear spin isomers properties are of great interest for astrophysicists regarding information they can potentially provide from celestial ice bodies and interstellar cloud formation [1,2]. Population ratio between magnetic (H<sub>2</sub>O-ortho;  $M_s=1$ ) and non-magnetic isomer (H<sub>2</sub>O-para;  $M_s=0$ ) at equilibrium is a thermodynamic constant related to the nuclear spin temperature ( $T_{spin}$ ). The very weak coupling occurring between H<sub>2</sub>O magnetic state and its others degrees of freedom like vibration and rotation states results in a lag time for  $T_{spin}$  to reach molecular thermal equilibrium. This lag time is seen as a memory effect potentially holding for millions of years according to some theoretical estimates. Understanding nuclear spin isomers interconversion mechanisms involving intramolecular phenomenon as well as interactions with their environment is crucial to adequately interpret anomalous spin temperature observations in some cometary comae ( $T_{spin}=30$  K) and in some star and planet forming regions ( $T_{spin}=10$  K). This talk will describe a methodology, developed by our team, that allows to separate H<sub>2</sub>O-ortho from H<sub>2</sub>O-para by their focalization in a molecular beam using a magnetic hexapole lens [3,4]. The molecular beam source is shown to be highly enriched in the H<sub>2</sub>O-ortho using rotationally-resolved REMPI-TOF mass-spectrometry techniques which opens the way to perform nuclear spin isomer conversion studies namely state-to-state ortho-H<sub>2</sub>O scattering on ice surfaces, heterogeneous chemical reactions involving proton exchange and resonant photo-desorption from ortho-ice.

1. Crovisier, J., et al., The spectrum of Comet Hale-Bopp (C/1995 O1) Observed with the Infrared Space Observatory at 2.9 Astronomical Units from the Sun *Science* 275, 1904-1907 (1997); Mumma, M.J. et al., Detection of water vapor in Halley's comet, *Science* 232, 1523-1528 (1986).
2. Hogerheijde, M.R., et al., Detection of the Water Reservoir in a Forming Planetary System, *Science* 334, 338-340 (2011).
3. Turgeon et al, Preparation, isolation, storage and spectroscopic characterization of water vapour enriched in the ortho-H<sub>2</sub>O nuclear spin isomer, *Phys.Rev.A* 86, 062710 (2012).
4. Kravchuk et al, A Magnetically Focused Molecular Beam of Ortho-Water, *Science* 331, 319-321 (2011).

### Significance statement

First magnetically enriched ortho-water molecular beam characterisation in gas phase

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**Presenter:** Dr VERMETTE, Jonathan (Université de Sherbrooke)

**Session Classification:** Poster & Lunch

Contribution ID: 97

Type: **Poster**

## **Methane dynamics and pressure induced hydrogen bond symmetrisation in filled ice methane hydrates**

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

We report the results of Raman spectroscopy and quantum thermal bath molecular dynamics simulations in methane and hydrate at pressures up to 150 GPa. We have found signatures of methane ordering, hydrogen bond symmetrisation and new high pressure phases.

### **Significance statement**

We have shown the stability of methane clathrate up to 150 GPa. Shown the presence of new ordered phase.

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**Co-authors:** Prof. FINOCCHI, Fabio (UMPMC); Mrs BOVE, Livia Eleonora (CNRS & Université P&M Curie, EPFL); Dr DEPOND, Philippe (UMPMC); Prof. GILLET, Philippe (EPFL); Mr SCHAACK, Sofiane (UMPMC); Mr RANIERI, Umberto (EPFL)

**Presenter:** Dr GAAL, Richard (EPFL SB ICMP EPSL)

**Session Classification:** Poster & Lunch

Contribution ID: 98

Type: **Talk**

## Upscaling microscopic crystal growth dynamics in snow

*Monday, January 8, 2018 3:30 PM (20 minutes)*

While the growth of single ice-crystals in the atmosphere is reasonably well understood, the microstructure dynamics of snow on the ground as the collective growth of aggregated crystals, is still lacking a unified treatment based on first principles of ice crystal growth. One of the key-challenges is the lack of models for the microstructure evolution of the bicontinuous ice matrix. To this end, we developed a rigorous microstructure upscaling scheme which takes common pore-scale (diffusion) principles of crystal growth to predict the volume-averaged evolution of the interface morphology. We derived a coupled set of evolution equations for the (volume averaged) ice volume fraction, specific surface area, Gaussian curvature and first and second moment of the mean curvature distribution, and demonstrate their correctness by a comparison to the evolution of different non-spherical grains under a prescribed growth law. In a second step, we use the model as a benchmark tool without a-priori assumptions for a comparison to experiments of snow microstructure evolution via interface tracking on 4D X-ray tomography data. The benchmarking allows us to quantify uncertainties in local estimates of crystal growth velocities. Finally, we demonstrate how the rigorous model facilitates a statistical assessment of common growth laws by combining 4D microstructure data with finite element numerics for heat transfer. The results e.g. show that a decay of the specific surface area cannot be explained by diffusion-limited growth models for the interface velocity. In addition, the evolution of microstructural parameters confirm a morphological asymmetry between growth and sublimation sites. Further conceptual insight is therefore needed to improve the link between volume averaged microstructural evolution in snow and ice crystal growth mechanisms.

### Significance statement

Most scientific problems involving physical properties of snow, depends highly on its microstructure. Given the range of scales of interest, there is a clear demand for a rigorous upscaling approach of objective and relevant microstructural parameters that connects recent advances in 4D X-ray tomography experiments and crystal growth theories.

**Primary author:** KROL, Quirine (WSL Institute for Snow and Avalanche Research SLF)

**Co-author:** Dr LÖWE, Henning (WSL Institute for Snow and Avalanche Research SLF)

**Presenter:** KROL, Quirine (WSL Institute for Snow and Avalanche Research SLF)

**Track Classification:** Ice Crystal Growth

Contribution ID: 99

Type: **Talk**

## Deposition Nucleation or Pore Condensation and Freezing? The role of pores on ice nucleation

*Tuesday, January 9, 2018 11:55 AM (20 minutes)*

Ice crystals in clouds play an important role in initiating precipitation and thus cloud lifetime which acts to moderate the Earth's radiative balance. As such, understanding the mechanisms responsible for ice formation is necessary to quantify the impacts of anthropogenic climate change. Pore condensation and freezing (PCF), is a proposed mechanism for ice formation below water saturation. During PCF, water condenses in pores or surface imperfections (herein referred to as pores) below water saturation, as predicted by the inverse-Kelvin effect. Thus, the ability of a pore to take up water strongly depends on the pore width and the contact angle of the pore wall. Once liquid water is present, ice can nucleate heterogeneously if an ice active site exists on the pore surface, or homogeneously if the temperature is below 235 K. However, the pore width must also be capable of accommodating the critical ice embryo for ice nucleation to occur. Therefore, the PCF mechanism is limited to particles with a critical pore size narrow enough to fill with water and wide enough to accommodate a critical ice embryo for a given temperature.

To investigate the PCF mechanism, spherical mesoporous silica particles with well-defined pore diameters of 3 to 4 nm are evaluated for their ice nucleation ability in the Zurich Ice Nucleation Chamber (ZINC). Within ZINC, the particles are exposed to temperatures ranging between 223 and 238 K and varying supersaturations with respect to ice. To further test the applicability of the PCF mechanism, the particles are functionalized with methyl and hydroxyl groups to alter the contact angle of the particles. We find that the contact angle of the particles helps determine the relative humidity at which pore condensation occurs and subsequently, ice nucleation. These results, combined with experiments performed with nonporous spherical silica, strongly support the proposed PCF mechanism.

### Significance statement

Ice nucleation below water saturation is conventionally viewed as the direct transition from water vapor to ice. However, our results suggest that supercooled liquid water contained in pores and surface imperfections is responsible for ice formation below water saturation.

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**Presenter:** Mr DAVID, Robert O. (Institute for Atmospheric and Climate Science, ETH Zürich)

**Track Classification:** Nucleation



Contribution ID: **100**Type: **Poster**

## Measuring the elastic modulus of snow

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The elastic modulus is a fundamental mechanical property of snow and key for the interpretation of seismic measurements, assessment of slope stability or development of constitutive models. However, literature values scatter by orders of magnitude due to visco-plastic peculiarities of ice and microstructural variability. Hitherto still no cross-validated measurement exists.

To this end we employ P-wave propagation experiments under controlled laboratory conditions on decimeter-sized snow specimen prepared from artificial snow and subjected to isothermal sintering, to cover a considerable range of densities ( $170 - 370 \text{ kgm}^{-3}$ ). The P-wave modulus was estimated from wave propagation speeds in transverse isotropic media and compared to microstructure-based finite element calculations (FEM) facilitated by X-ray tomography imaging of sub-sample microstructures. Heterogeneities and size differences between acoustic and FEM sample volumes were characterized by SnowMicroPen measurements, yielding an elastic modulus as a by-product. The moduli derived from the acoustic and FEM method are in very good agreement ( $R^2 = 0.99$ ) over the entire range of densities covering values from  $10 - 340 \text{ Mpa}$ . A remaining bias (24 %) between both methods can be explained by layer heterogeneities which systematically reduce the estimates from the acoustic method.

The consistency of these first-principle methods supports the validity of long-standing, published FEM moduli for various snow types and opens non-destructive routes to time-resolved elasticity measurements during fast sintering.

### Significance statement

The work contains the first cross-validated measurements of the elastic modulus of snow. Due to influences of visco-plasticity, commonly effective moduli are measured which is reflected by a considerable scatter of published values. Our results show that it is possible to measure the true elastic modulus of snow.

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**Co-authors:** Dr VAN HERWIJNEN, Alec (WSL Institute for Snow and Avalanche Research SLF); Dr LÖWE, Henning (WSL Institute for Snow and Avalanche Research SLF)

**Presenter:** Mr GERLING, Bastian (WSL Institute for Snow and Avalanche Research SLF)

**Session Classification:** Poster & Lunch

Contribution ID: 101

Type: Poster

## Inclusion of ammonium ion into clathrate hydrate in subsurface ocean of icy moons

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Clathrate hydrates are crystalline inclusion compounds composed of hydrogen-bonded water cages which incorporate hydrophobic gases called guest molecules. The clathrate hydrate could exist not only in the Earth but also in icy moons. One of the most likely candidate is Saturn's icy moon Enceladus, having a global ocean beneath the icy shell. INMS (Ion and Neutral Mass Spectrometer) aboard the Cassini spacecraft has investigated composition of the plumes that includes H<sub>2</sub>O (< 90 %), CH<sub>4</sub>, CO<sub>2</sub>, NH<sub>3</sub>, and other various organic materials. These results could reflect the composition of the subsurface ocean and imply the presence of clathrate hydrates in the ocean. Bouquet et al. (2015) suggests that the clathrate hydrate should be stable in the subsurface region deeper than 22 km. The clathrate hydrate formation in the ocean should affect concentrations of the ocean components by inclusion of guest and host molecules into clathrate structure. Here we especially focused the effect of inclusion of ammonium ion into clathrate hydrate on ammonium ion concentration in the ocean. Ammonium ion can be incorporated in the clathrate lattice by replacing a part of water cages. To evaluate the ammonium ion inclusion phenomenon in the subsurface ocean, we experimentally investigated the amount of ammonium ions included into clathrate hydrate when hydrate formed in ammonium salts aqueous solution.

As an analogue of CH<sub>4</sub> and CO<sub>2</sub> hydrate, tetrahydrofuran (THF) hydrate was synthesized in the ammonium chloride solution and the concentration of ammonium ion in the hydrate ( $C_s$  mmol/L) was measured. To assess the ammonium ion inclusion, K value which is ratio of  $C_s$  to initial concentration ( $C_0$  mmol/L) was determined. The K value was about 0.28 when  $C_0 \leq 10$  mmol/L, which was nearly three times higher than that of ice (=0.11). This K value about THF hydrate might be attributed to not only grain boundaries but also replacement with clathrate water cage because the K value was larger than that of ice. This result suggests that excluding ammonium ion from the ocean during clathrate formation is more effective than ice formation.

### Significance statement

We experimentally investigated the amount of ammonium ions included into clathrate hydrate when hydrate formed in ammonium salts aqueous solution. The ratio of concentration of ammonium ion in the hydrate to initial concentration was three times higher than that of ice.

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**Presenter:** Mr NISHITANI, Ryusuke (Department of Earth and Space Science, Graduate School of Science, Osaka University, Japan)

**Session Classification:** Poster & Lunch

Contribution ID: 102

Type: **Talk**

## Serrated flow of snow: Strain-rate softening in uniaxial compression

*Friday, January 12, 2018 9:20 AM (20 minutes)*

It is well known that the mechanical behavior of snow highly depends on strain-rate as a consequence of the visco-plastic nature of ice. Accordingly, the mechanical response of snow is commonly believed to undergo a single transition from ductile to brittle behavior at a critical strain rate. A recent analysis of snow compression has however revealed the relevance of another time-scale associated to healing effects (e.g. sintering) during compression. The competition of healing and visco-plastic effects gives rise to a rich mechanical behavior in an intermediate range of strain rates. To further elaborate these phenomena we have conducted deformation-controlled compression experiments of low-density snow in a micro-compression stage operated in an X-ray tomography scanner. By varying the imposed axial strain rate over three orders of magnitude, we find a transition regime where the stress response suddenly changes from a smooth to quasi-oscillatory behavior, reminiscent of the Portevin–Le Chatelier effect. This regime of serrated flow is accompanied by compaction bands that nucleate in the interior of the sample as revealed by the tomography analysis. Our experimental results can be well explained within a minimal, scalar model for a rate-dependent, elasto-plastic constitutive law with healing. The model shows a negative slope of the stress vs strain-rate characteristic (strain rate softening) and correctly predicts the range of instability as well as the amplitude and frequency of the serrations. This dynamical instability has an interesting practical consequence, since the results suggest a mechanism how an initially homogeneous snow layer may spontaneously develop a sub-layer structure under deformation.

### Significance statement

Serrated flow of snow resembles the Portevin–Le Chatelier effect where, in contrast, serrations are caused by competing dislocations. The observations demonstrate the importance of healing (sintering) which can fundamentally change the macroscopic mechanical behavior of snow.

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**Co-authors:** Prof. ZAISER, Michael (University of Erlangen-Nuremberg); Dr SCHLEEF, Stefan (WSL Institute for Snow and Avalanche Research SLF)

**Presenter:** Dr LÖWE, Henning (WSL Institute for Snow and Avalanche Research SLF)

**Track Classification:** Mechanics & Microstructure

Contribution ID: 103

Type: Talk

## Gas selectivity in mixed gas hydrates formed from pressurized ice.

*Monday, January 8, 2018 11:30 AM (20 minutes)*

In addition to their various applications in the environment, energy and technology fields, gas hydrates are supposed to be involved in the formation of planetesimals, comets and other planets, such as Titan or Enceladus, both being Saturn's moons. For instance, CO gas hydrate was one of the hydrates especially highlighted in the first work outlining this hypothetical hydrate formation in astrophysical conditions. Moreover, recent theoretical works suggest that the nitrogen depletion observed on the Jupiter family comet 67P/Churyumov-Gerasimenko might be due to N<sub>2</sub> encapsulation within hydrates and so assume that 67P agglomerated from these crystalline compounds. The preferential trapping of carbon monoxide with respect to nitrogen inside mixed gas hydrate allow to determine the temperature range of the cometary grains formation in the protosolar nebula. The present work is dedicated to the experimental investigation of such a preferential encapsulation by means of Raman scattering in various mixed gas (CO, CO<sub>2</sub>, N<sub>2</sub>) hydrates. Beyond the astrophysical interest, the molecular selectivity in mixed gas hydrate plays an important role in many areas such as process engineering or geoscience.

The investigation is based on the study of the gas selectivity in gas hydrates formed with high driving force, i.e. by ice exposure to different gaseous mixtures (in various pressure and temperature conditions). These studies have been carried out on the pure gas hydrates (CO, N<sub>2</sub> and CO<sub>2</sub>) as well as on the corresponding mixed gas hydrate. Such a series of gaseous molecules offer the opportunity to explore the impact of various physical-chemistry parameters onto the gas selectivity by forming hydrates. Many factors, such as steric hindrance or thermodynamic conditions of formation, govern this selectivity. CO<sub>2</sub> possesses a strong water affinity while CO and N<sub>2</sub> do not. CO and N<sub>2</sub> molecules have similar steric hindrance and close hydrate formation P-T conditions. CO is the only considered guest molecules possessing a dipolar moment. Raman spectroscopy results have put forward a clear preferred encapsulation of carbon monoxide molecules compared to nitrogen molecules during the mixed gas hydrate formation. Similar preferential encapsulation is observed in the case of CO<sub>2</sub> molecules with respect to CO and N<sub>2</sub> molecules. Moreover, neutron powder diffraction data have shown phase mixtures involving various structures (so-called type I and type II) and structural metastability. This whole set of results will be discussed in conjunction with DFT calculations, kinetic formation conditions and structural metastability properties evidenced in these gas hydrates.

### Significance statement

This work (Claire Petuya's PhD) provides the first experimental evidences of preferred gas trapping of CO in CO/N<sub>2</sub> mixed gas hydrate as well as of vibrational signatures of guest partitioning for the considered mixed gas hydrates, formed from pressurized ice.

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**Presenter:** Dr DESMEDT, Arnaud (CNRS)

**Track Classification:** Phases of Ice

Contribution ID: 104

Type: **keynote**

## Characterizing Key Features in the Formation Mechanisms of Ice

*Tuesday, January 9, 2018 10:50 AM (45 minutes)*

Ice crystallization is ubiquitous in nature and has numerous important roles, technological applications and implications. Yet, the ordering processes associated with the nucleation and growth of ice crystals have proven difficult to study directly with experiments, in part due to their stochastic nature of the underlying molecular processes. Consequently, a complete molecular-level picture of the details of ice formation has yet to emerge. Molecular simulations have afforded an excellent opportunity to investigate crystal nucleation and growth of ice at a molecular level, since they are able to probe directly the microscopic environment of a crystal during its nucleation or the interface of a growing crystal. In this presentation I will begin with a brief review of some key issues around simulations of crystallization, considering the attributes and limitation of various models and methods. I will describe some of the approaches that have been developed and utilized for the simulation of the formation and growth of crystals, both in the homogeneous and heterogeneous contexts. While specific results for ice will be a focus, the “simpler” case of gas clathrate hydrates will also be examined and compared. I will present results that will demonstrate that the process of crystallization is characterized by collective phenomena involving many molecules, where the organization can be seen to occur in stages. The nature of the structural topology and fluctuations that characterize a solid/liquid interface will be examined. I will show that defects can play key roles in observed behaviours. The lifetimes and transitions of specific structures will also be briefly discussed. Finally, I will consider how rugged funnel-shaped potential energy landscapes can provide a lens for understanding aspects of the phenomenological differences in the crystal nucleation of ice and gas hydrates.

### Significance statement

This is an invited presentation

**Primary author:** Prof. KUSALIK, Peter (University of Calgary)

**Presenter:** Prof. KUSALIK, Peter (University of Calgary)

Contribution ID: 105

Type: **Poster**

## Nitrogen trapping in amorphous ice and its transformation into clathrates

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Nitrogen-bearing clathrates, possibly mixed as gas hydrates also containing CO, H<sub>2</sub>, and CO<sub>2</sub>, are potentially important astrophysical constituents as they might take part in the formation of nebulae, comets and might have participated in the formation of the outer planets in the solar system.(1),(2)

The formation of clathrates in the solar system is often associated with vapor deposited amorphous solid water (ASW).(3)

Highly porous ASW has specific properties of adsorption, sintering and gas enclosure. It can enclose large amounts of gas which cannot be pumped off in vacuo. The enclosed gas enables the necessary pressure build-up for transformation of ASW into a crystalline form as temperature increases.

In the present work, ASW is obtained by vapor deposition at low temperature (~80 K). Nitrogen gas is admitted and the sintering process is observed between 80 K and 140K, as indicated by the removal of the Raman peak attributed to dangling OH. Formation of clathrates is characterized spectroscopically upon heating above 160K. The signature of enclosed nitrogen trapped in micropores of ASW and clathrate structure can be discriminated by high resolution Raman spectroscopy.

### References:

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- (2) Lunine, J.; Choukroun, M.; Stevenson, D.; Tobie, G. Titan from Cassini-Huygens; 2009.
- (3) Hallbrucker & Mayer, *Icarus*, 90, 176-180, 1991

### Significance statement

Formation of clathrates from amorphous solid water are of significant interest in astrophysical context, as they might take parts in the formation of nebulae, comets or small planets. Laboratory studies are relevant to study the ASW to clathrate transformation using vibrational spectroscopy of the guest trapped into the solid structure

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**Presenter:** Prof. CHAZALLON, Bertrand (Laboratoire PhLAM, Bât. P5, UMR CNRS 8523, Université de Lille, 59655 Villeneuve d'Ascq, FRANCE)

**Session Classification:** Poster & Lunch



Contribution ID: 106

Type: PICO talk

## Modelling phase diagrams of crystalline ice structures - a comparison of force fields and density functional theory

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Solid water comprises the most abundant form of ice in the universe and is believed to have played an important role in catalysing the formation of those prebiotic molecules that were essential for the development of life on earth. Apart from amorphous structures solid water also appears in a plethora of ordered structures under different temperature and pressure conditions. The corresponding phase diagram have been well studied in numerous experiments. On the other hand, despite 30 years of computer simulations of water, computer simulations of this phase diagram based on atomistic chemical interaction models are still challenged by accurately for hydrogen bonding and van-der-Waals interactions. The quantum mechanical interaction of electrons is at the heart of these interactions, but this is not explicitly included in well-established empirical force fields – which have commonly been parameterized for liquid water. Given this situation, it is an interesting question how recently developed density-functional theory (DFT) methods perform in comparison.

In this work, we focus on the well-known ordered crystalline ice structures (Ih, II, VIII, IX, XIII, XIV, XV), which capture a wide range of local coordination and thus bonding scenarios between individual molecules in solid water. For these structures, we calculate the corresponding (sub-part of the overall) phase diagram based on various different empirical force fields (SPC/E, TIP3P, TIP4P/2005, TIP4P/ice, q-TIP4P/F) and systematically compare to results of state-of-the-art DFT including an explicit account for van-der-Waals interactions. We start from the experimentally determined crystal structures and perform space-group-constrained structural relaxations individually for each different chemical interaction model. This yields the internal energy of the solid and allows us to calculate well-defined phononic properties by means of lattice dynamics. Using the quasi harmonic approximation allows us to compute the free energy contribution as an analytical function of the temperature and volume for a given potential. We will compare the so-obtained phase diagrams to available experimental data and discuss the influence of different bonding contributions within the investigated atomistic chemical interaction models – potentially also including a detailed analysis of the phononic band structure.

### Significance statement

We present a systematic comparison of simulated phase diagrams of crystalline ices based on a variety of atomistic interaction models, ranging from commonly used force fields to recently developed density-functional theory methods and including a detailed account of vibrational properties. This scrutinizes different chemical bonding contributions in solid water.

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versity)

**Session Classification:** Poster & Lunch

Contribution ID: 107

Type: Talk

## The Structural Origins of Dynamical Heterogeneity in Water Pinpoint the Source of Ice-Nucleation

*Tuesday, January 9, 2018 2:45 PM (20 minutes)*

The dynamical properties of liquid water play a role of great importance in the context of hydrophobic interactions, where the mobility of water molecules affects e.g. both the thermodynamics and the kinetics of ionic and proton transfer, as well as the mass diffusion of molecular species in aqueous environment. Not least, the ubiquitous phenomena of the glass transition and, as we argue in this work, of ice nucleation are intimately connected to the dynamics of supercooled water. For most atomic and molecular liquids it has been shown that their dynamics are heterogeneous in nature: different regions of the system are characterized by different degrees of mobility, yielding macroscopic effects such as e.g. the breakdown of the Stokes-Einstein relation. This dynamical heterogeneity is at the heart of phenomena of practical relevance such as the formation of ice in clouds, ruling the water cycle on Earth, and low-temperature science including cryobiology.

However, obtaining experimental insight into the microscopic details of water dynamics within its supercooled regime is a most challenging task. For instance, how exactly the dynamics of water molecules at low temperatures influences solvation processes is still largely unknown. Most importantly, it is presently unclear whether there exists a specific correlation between the heterogeneous dynamics of supercooled water and the molecular-level details of its structure.

In this work [1], we assessed the structural origins of dynamical heterogeneity in supercooled water by means of molecular dynamics simulations, using coarse-grained and fully atomistic water models. We described the emergence of heterogeneous dynamics in terms of domains of slow and fast moving water molecules identified by iso-configurational analysis. We found that slow moving regions are on average less defective in terms of the hydrogen bond network, which translates into more “tetrahedrality” in agreement with the existing literature. Most importantly we could pinpoint a specific hallmark of these slow-moving regions, namely the abundance of five, seven, and most prominently six-membered rings. Interestingly, most of the water molecules belonging to these rings cannot yet be labelled as ice-like per common topological criteria.

We argue that the substantial presence of six-membered rings within slow-moving domains has the potential to facilitate ice nucleation. This is because the building blocks of ice (six-membered hydrogen bonded rings of water molecules) are already present in the slow-moving domains, hence a spatial re-arrangement of this topological feature can very well result in the onset of crystallization. This in turn means that a change of dynamical order parameters could precede the structural ordering – a fresh point of view on ordering phenomena such as ice nucleation. Our results provide a new link between two of the most fundamental aspects of water and other tetrahedral liquids.

[1] M Fitzner, GC Sosso, SJ Cox and A Michaelides, in preparation

### Significance statement

Dynamical heterogeneity affects many interactions of supercooled water like mass diffusion and solvation whilst ice nucleation is ubiquitous (e.g. cloud formation or cryobiology). Our results uncover the structural origins of dynamical heterogeneity in water and suggest a fundamental connection with ice nucleation, opening new avenues to understand the latter.

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**Presenter:** Mr FITZNER, Martin (Department of Physics and Thomas Young Centre, University College London)

**Track Classification:** Nucleation

Contribution ID: 108

Type: Talk

## Deliquescence and Ice Nucleation at near- and sub-Eutectic Temperatures

*Tuesday, January 9, 2018 1:45 PM (20 minutes)*

The phase state and role of aerosol particles in the radiative budget of the planet are important sources of uncertainty for climate modeling and prediction. The phase behavior of atmospheric particles depends on both environmental conditions and particle properties and can influence surface and bulk processes in both physical and chemical contexts. In the atmosphere soluble particulate is primarily considered to occur in one of two phase states. Either as dry particulate at low relative humidity (RH) conditions or as dissolved solution droplets at higher RH; and the limiting deliquescence RH (DRH) when the soluble material dissolves from one state to another is considered to have sudden discontinuous phase transition like character. A more realistic model of the meta-stable continuous deliquescence of particles has implications for liquid availability at RH smaller than DRH. Furthermore, it raises the question of soluble particles acting as ice nucleating particles in low temperature environments. Here we discuss theoretical developments and experimental observations related to sub-eutectic deliquescence and ice nucleation. Implications for atmospheric processes such as mixed-phase cloud longevity will be discussed.

### ACKNOWLEDGEMENTS

This work was supported by the Swedish Research Council, the Swedish Foundation for International Cooperation in Research and Higher Education (IB2016-6612), and the US National Science Foundation (AGS-1461305, AGS-1461347).

### Significance statement

Water adsorption and continuous deliquescence from low RH through saturation may have significance for cloud processes including hydrometeor formation, and mixed phase cloud formation and evolution. Furthermore, sub-eutectic metastable liquid may be a reservoir for atmospheric ice nucleation.

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**Presenter:** Dr THOMSON, Erik S. (University of Gothenburg)

**Track Classification:** Nucleation

Contribution ID: 109

Type: **Talk**

## Ice-binding proteins from a sea-ice diatom, their effect on ice growth and physical properties

Thursday, January 11, 2018 3:00 PM (20 minutes)

Ice-binding proteins (IBPs), produced by polar and cold-tolerant organisms, have the ability to bind to ice, affecting its growth. They are key elements in biological adaptation to cold environments, and no other particles, neither natural nor synthetic, show comparable effect in controlling ice growth. However, the details of the protein-ice interactions have not been clarified yet. Different IBP families affect ice in different ways, and the relevant common traits, as well as the differences of the ice binding mechanisms, are still under investigation.

Here we present the IBP from the polar sea-ice diatom *Fragilariopsis cylindrus* (fcIBP). It belongs to a protein family defined by a domain (DUF 3494) extremely successful among polar microorganisms. We studied the effects of the fcIBPs on single crystal free growth using optical bright field and interferometric microscopy. We studied crystal morphology changes and growth rates dependent on supercooling and protein concentration. We saw differential effects of the protein on the growth of crystallographic planes, dependent on fcIBP dynamics in the different directions. We relate this to differential affinity and adsorption time of the protein to the basal and prismatic planes. Switching to a more macroscopic level, we analyzed the effect of the proteins to physical properties of polycrystalline ice. We show the strong inhibition of fcIBPs on grain growth. We observed the evolution of microstructure in fine-grained samples over several weeks, instead of the hours often used for annealing experiments with IBPs. Furthermore, we show that the effect of IBPs on the driving factors for ice deformation during creep, i.e. on internal dislocations due to incorporation within the lattice and on the mobility of grain boundaries due to pinning, make these proteins particularly interesting in studying the process of ice deformation.

### Significance statement

Our results of single crystal growth morphology and rates contribute to a better understanding of ice growth mechanisms and interaction with nanoparticles. We also show the effects of fcIBPs on polycrystalline ice physical properties, providing relevant results for basic research on fcIBP-ice interaction mechanisms and for potential fcIBPs applications.

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**Presenter:** Dr BAYER-GIRALDI, Maddalena (Alfred-Wegener-Institute Bremerhaven (Germany))

**Track Classification:** Ice Binding Proteins

Contribution ID: 110

Type: Talk

## Air cavity migration in ice as a case study for temperature gradient metamorphism of snow: time-lapse X-ray microtomography observation and phase-field simulations.

Thursday, January 11, 2018 5:40 PM (20 minutes)

Temperature gradient metamorphism of snow is a mechanism of snowpack transformation resulting from the coupling of elementary physical processes: heat conduction, vapour transport in the pore space and phase change at the ice/air interface. An important feature of this mechanism is that it produces a faceted microstructure with sufficiently strong gradient, as a consequence of the anisotropy of the kinetic coefficient of ice.

To model this mechanism at the pore scale, the phase field method appears to be a relevant choice. Indeed, this method is well suited to describe interface evolution problems coupling phase change to other physics. In the case of snow, Kaempfer and Plapp (2009) developed such a model so that temperature gradient metamorphism could be addressed, with however an isotropic kinetic coefficient. Now, a desirable extension of this model is to add the ability to reproduce faceting. This asks for further model developments.

For this, one needs suited experimental data to guide modelling and perform validations. Experiments using real snow are ideal to establish correlations between macroscopic conditions and properties. However, these present variability and complex geometry, which makes interpretation of comparison with microstructural model difficult. Instead, for microstructural modelling, it is practical at first to dispose of experimental data that imply all targeted processes but on a simpler case and, if possible, on which computationally light simulations can be performed.

To that purpose, we submitted a monocrystalline ice block containing a spherical air cavity of 190  $\mu\text{m}$  in diameter to an external temperature gradient of 45 K/m, parallel to the *c*-axis of the ice, with a mean temperature of  $-4^\circ\text{C}$  using CellDyM cryogenic cell (Calonne et al 2015). We followed the evolution of the cavity using time-lapse X-ray microtomography for 4 days, scanning every 3 hours, with a resolution of about 7.4  $\mu\text{m}$ . The cavity migrates in parallel to the gradient, towards the warm side. The speed of the bubble is constant to 0.00046  $\mu\text{m/s}$ . Hexagonal faceting is observed on the sublimating part of the interface while the condensing part remains rounded.

Then, simulation of this problem has been carried out using a COMSOL multiphysics implementation of Kaempfer and Plapp's model (2009). First, the overall migration of the cavity could be retrieved, underlying the facts that the core physics is captured. Next, as expected, differences in terms of shapes appear clearly so that faceting can be studied. Finally, valuable information on temperature gradient metamorphism get out of these works, and constitutes the first steps for addressing the faceting problem in further modelling investigations.

Kaempfer, T. U., & Plapp, M. (2009). Phase-field modeling of dry snow metamorphism. *Physical Review E*, 79(3), 031502.

Calonne, N., Flin, F., Lesaffre, B., Dufour, A., Roulle, J., Puglièse, P., Philip, A., Lahoucine, F., Geindreau, C., Panel, J.M., Rolland du Roscoat, S. & Charrier, P. CellDyM: A room temperature operating cryogenic cell for the dynamic monitoring of snow metamorphism by time-lapse X-ray microtomography. *GRL* 2015. DOI : 10.1002/2015GL063541

### Significance statement



Air cavity migration in ice under a temperature gradient has been followed by time-lapse X-ray microtomography and simulations have been performed using a phase-field model. This study implies the same physical processes as temperature gradient metamorphism of snow, these are works towards improvement of snow metamorphism modelling.

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**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 112

Type: **Poster**

## Modeling and field study of the influence of bauxite mining residues tailings on snow albedo

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Mining residues tailings are a major environmental problem facing mining industries. These phenomena are a greater source of preoccupation during winter conditions since wind-borne dust emissions are less predictable; it is thus more difficult to prevent them. Also, mining residues tailings cause greater modulation of the albedo on permanently or seasonally snow-covered regions. Their potential impact is most acute on air quality but also on the visual aspect of snow which is an immediate concern to neighboring urban communities. A recent collaboration with a bauxite residue management center in Quebec made it possible to benchmark the Two-stream Radiative Transfer in Snow (i.e., TARTES) model using the bauxite mining residues tailings disseminated on snow at the management site. We report optical albedo and reflectivity measurements performed on snow showing strong dependency on its bauxite residues content. Those experimental data are compared to the TARTES model,[1] allowing a critical evaluation of the optical parameters, particle size distributions and physical properties of the bauxite residues and of the snow that are used as inputs. Deficiencies in the model indicate better account for particles size distributions, optical properties and abundances are essential to better describe and understand the effect of mining residues tailing on snow properties. Ongoing efforts towards the characterization of mining residues physico-chemical properties highlight a correlation between the different populations of the size distribution and the chemical composition of the bauxite residues as revealed by dynamic light scattering (DLS) and X-ray diffraction (XRD). The experimental characterization of the bauxite residues will therefore provide us with precise inputs to use in the TARTES model which will be validated with field measurements. The improvement of the theoretical model will make it possible to describe and have a better understanding of the alteration of various mine tailings on snow albedo.

[1] Q. Libois, G. Picard, J. France, L. Arnaud, M. Dumont, C. Carmagnola, and M. D. King, Influence of grain shape on light penetration in snow, *The Cryosphere*, 7, 1803-1818, (2013).

### Significance statement

This study suggests that characterization of mine residues tailings allows optimization of a theoretical model describing their modulation on snow albedo

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**Session Classification:** Poster & Lunch

Contribution ID: 114

Type: **Poster**

## Quasi-continuous generation and rheological characterisation of CO<sub>2</sub>-gas hydrate ice crystal slurries

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

CO<sub>2</sub> gas hydrates are non-stoichiometric crystalline structures consisting of CO<sub>2</sub> molecules entrapped in a 3D lattice of polyhedrals formed from water molecules. These structures, stable under moderate pressures and low temperatures, play a crucial role in many environmental and energy sectors. Understanding and controlling the flow of hydrate slurries can bring rapid solutions for some applications in these areas.

In this study, a robust methodology for clathrate slurry generation and flow/rheology control is discussed. An in-house built high-pressure loop with an embedded surface scraped heat exchanger enhancing hydrate crystal formation kinetics and high-pressure rheology were used to study CO<sub>2</sub> gas hydrate slurry flow properties during hydrate nucleation, growth and decomposition processes. The slurries were formed from high water cut sugar solutions. The aim of the study was to investigate the clathrate slurry flow behaviour and apply high-pressure pipeline (in-line) and rotational (off-line) rheometry at specific positions in the CO<sub>2</sub> hydrate phase diagram, relevant for technological applications.

CO<sub>2</sub> gas hydrate slurries were formed in situ (i) in a high-pressure loop reactor (4.5 L, pipe diameter ½") with a built-in Coriolis flowmeter recording density and viscosity or (ii) in a high-pressure rheometric cell (25 ml) of a rotational rheometer (MRC 200) equipped with a four-blade vane mixer geometry. The vane mixer elucidated the formation of hydrates in situ allowing for a well-mixed system throughout the whole measurement. From the flow rate-pressure drop trends in the loop-reactor pipeline apparent flow functions were derived and compared to such received from the rotational rheometer measurements. A robust flow model coupling the strain rate - shear stress responses of the non-Newtonian slurries was derived. This simple approach to compare clathrate slurry flow in a quasi-continuous loop reactor to related, well-defined laboratory scale precision measurements, exhibits new insights into flow assurance relevant characterisation of hydrate suspensions.

### Significance statement

The introduced methodologies offer new possibilities for gas hydrate slurry flow characterisation from analytical and process application perspectives.

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**Co-author:** Prof. WINDHAB, Erich J. (ETH Zurich)

**Presenter:** SEDIVA, Zuzana (ETH Zurich)

**Session Classification:** Poster & Lunch

Contribution ID: 116

Type: **Talk**

## **BIRCH TREES - SOURCES OF ICE-NUCLEATING MACROMOLECULES**

*Tuesday, January 9, 2018 3:05 PM (20 minutes)*

Aerosol-cloud interaction is an important part in understanding the Earth radiation balance and thus global climate. The IPCC indicates the level of understanding of this issue as rather low. This is particularly true for mixed phase clouds and ice clouds. In the recent past a broad variety of aerosols has been test for ice nucleation ability. However, there is still little knowledge about the impact of biological ice nuclei.

In particular, biological macromolecules have for a long time been neglected by atmospheric scientists. However, plants are known by biologists to produce macromolecular ice nuclei as a part of their low-temperature survival strategy. In the past, it has been shown by us that birch pollen exhibit ice nucleation active macromolecules at their surface. These molecules can be washed off from the pollen grains and nucleate ice independently. Only recently, we found the same ice nuclei also on secondary and primary wood and on leafs of birch trees. The question remains if these biological ice nuclei can be dispersed through the atmosphere and can impact cloud glaciation processes.

Here we apply different spectroscopic and microscopic techniques to gain insights into the nucleation mechanisms and into the chemical signatures of the molecular ice nuclei.

### **Significance statement**

We are searching for the perfect heterogeneous ice nucleus

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**Presenter:** Prof. GROTHE, Hinrich (TU Wien)

**Track Classification:** Ice Binding Proteins

Contribution ID: 117

Type: PICO talk

## Crystallization of ice in AFP-III solutions

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The purpose of our research is to explore how type III AFP modifies the morphology and growth kinetics of ice crystals, and to reveal the action mechanisms of AFP-III.

In a glass capillary seed crystals of ice of hexagonal modification were formed in supercooled water with AFP-III concentrations of 0-0.8 mg/ml. Measurements of growth rates were performed by Mach-Zehnder interferometry at supercoolings from 0 to 1.0 K. We have found that AFP-III exhibits an extremely high activity. Even at a concentration of 0.001 mg/ml it changes the morphology of ice crystals, and prismatic faces appear in the a-axis directions instead of circular disk-like shapes typical for growth in pure water. Our measurements of the growth rates have shown that AFP-III molecules can act both as an inhibitor for the prismatic faces and as a promoter for the basal faces of ice crystals, and cause the formation of macrosteps on the basal faces. The value of growth thermal hysteresis rises non-linear with the increase in AFP-III concentration. The influence of AFP-III on the crystallization of ice was explained by adsorption of the protein molecules on the crystal surface. Retardation of ice growth in the presence of AFP-III occurs due to blocking of the surface by adsorbed protein molecules. From thermodynamics, it can be expected that an ice surface covered by the protein molecules will be able to grow when the inter-molecule distance exceeds the critical value predicted by the Gibbs-Thomson law. Direct observations by confocal fluorescent microscopy of the protein molecules labeled with a fluorescent isocyanate allowed to estimate the average distance between AFP-III adsorbed on the prismatic surface of ice crystals. The theoretical values of the freezing point depression in the presence of AFP-III corresponded with the experimental data when we assumed that AFP-III decreased the surface free energy of the faces of the ice crystal.

D.V. is grateful for the support from the Japan Society for the Promotion of Science (Grant No. L17515).

### Significance statement

Antifreeze proteins (AFPs) exhibit a strong ability to control the nucleation and growth of ice. The inhibition effect of AFPs on the recrystallization and growth of ice is very common in nature, and it helps living organisms (sea fish, plants, insects) to survive in a subfreezing environment.

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**Presenter:** Prof. FURUKAWA, Yoshinori (Institute of Low Temperature Science, Hokkaido University)

**Session Classification:** Poster & Lunch

Contribution ID: 118

Type: **Talk**

## Investigating the Microscopic Location of Trace Elements in Glacier Ice

*Wednesday, January 10, 2018 11:05 AM (20 minutes)*

Past changes in atmospheric pollution can be reconstructed from high-alpine ice core trace element records (Schwikowski et al., 2004). Eichler et al. (2001) suggested that the preservation of major ions with respect to meltwater percolation depends on their location in the ice crystal lattice. Species predominately segregated at grain surfaces during snow metamorphism were more efficiently scavenged by percolating meltwater compared to others incorporated into the ice lattice. Here, we present for the first time a comprehensive study on the microscopic location of anthropogenic, dust and volcanic related trace elements in glacier ice using two different approaches. Moreover, we link the outcome of the study to the tendency of crystalline ice to embed dopants. On the one hand we assessed the microscopic location of trace elements indirectly by analyzing their concentration records in a high-alpine ice core from Grenzgletscher in the southern Swiss Alps using inductively coupled plasma mass spectrometry (ICP-MS). A 13 m w.eq. part of the ice core has been shown to be affected by an inflow of meltwater. Our results demonstrate for the first time that a variety of trace element records, such as Fe, Pb or Cu are not significantly altered by meltwater percolation, indicating a higher solubility of these species in ice. Other trace elements (e.g. Cd, Mn or Zn) are significantly depleted in the affected section of the ice core, presumably due to their initial segregation at grain boundaries.

In a second approach we examine the outcome of the indirect analysis by direct spatial analysis of trace elements in Grenzgletscher ice samples. We developed a method based on cryocell laser ablation (LA) ICP-MS, which is the method of choice for the direct in situ chemical analysis of trace elements at a sub-millimeter resolution in glacier ice (Della Lunga et al., 2014, Sneed et al., 2015). The setup is currently tested to analyze concentration differences of accessible trace elements (e.g. Al, Fe, Pb or Mn) within grains and along grain boundaries in ice core samples from Grenzgletscher.

Results of both approaches will be presented. Based on these findings we will discuss possible driving forces causing the observed incorporation of trace elements (such as size and concentration levels) and address how the capability of the ice crystal to form solid solutions responds to size and concentration levels of solutes. This will not only help to evaluate the potential of trace elements as environmental proxies in glaciers partially affected by melting, but also involves the fundamental aspect of how dopants are incorporated into an ice lattice.

### Significance statement

The microscopic location of trace elements is a key factor for their potential post-depositional relocation in glaciers affected by melting. Our study provides new insights into the nature of impurity location in glacier ice and into the solubility of dopants in single crystalline ice.

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**Presenter:** Mr AVAK, Sven Erik (Laboratory of Environmental Chemistry, Paul Scherrer Institute, Switzerland)

**Track Classification:** Mechanics & Microstructure



Contribution ID: 119

Type: Talk

## Freezing-induced pH jump is proved to be an important degradation factor for proteins being frozen

*Thursday, January 11, 2018 2:40 PM (20 minutes)*

The freezing of aqueous solutions leads to the separation of ice crystals and the remaining solutes into microscopic veins and pockets; these regions are known as the freeze concentrated solution (FCS). The interactions between the molecules present within this phase are of key importance for the stability or reactivity of compounds in both natural and human-controlled freezing. Pharmaceutical stabilization often involves two steps, namely, freezing and freeze-drying; as each of the procedures can have deleterious effects on active pharmaceutical ingredients (API), we examined them closely.

We investigated the stability of proteins in terms of the enzymatic activity after exposure to repeated freezing and thawing. The most significant losses in enzyme structure and functionality were found in very fast cooling or when the apparent pH had changed markedly. Besides the simple freeze-concentration effect, the two main causes of acidity variation in FCS are as follows: a) preferential crystallization of one buffer component, letting the other one interact with API; b) uneven distribution of ions between the ice and FCS to be later neutralized by the flow of protons. The latter effect is also connected to the Workman-Reynolds freezing potential. The two effects are approximately additive, and we demonstrated that the pH jump induced by the former one can be neutralized by the latter. Moreover, we proved experimentally that when a pH jump was avoided, the fully preserved enzyme activity after reconstitution was sustained. Thus, we proposed a new protein stabilization strategy: adding a neutral salt to the buffer to minimize the pH after freezing. The method was named ionic cryoprotection.

Next, we studied the effects of freeze-drying on the pH in FCS. The apparent pH change after freezing was substantial, but it was found to be much less pronounced after the lyophilization step. This is explainable by additional crystallization of its components. Thus, we consider misleading to assess the pH stress accompanying the lyophilization cycle solely by monitoring the pH of the lyophiles (as practised previously). The unexpected negative dependence between initial pH of the solution and the acidity of the lyophiles further demonstrates the remaining unpredictability accompanying the freezing process.

The pH jump was assessed via the Hammett acidity function by measuring the amount of protonation in sulfonephthalein acid-base indicators. At this stage, sodium and potassium phosphate buffers and several common salts were examined in detail.

In conclusion, we show that a freezing-induced pH change can be harmful to the compounds present in FCS but is easily avoidable if the salts are chosen rationally. The good correlation between the Hammett acidity function in the frozen and lyophilized states and the enzyme recovery activity suggests that the indicator method for the pH assessment exhibits sufficient functionality and can be applied also in other research fields dealing with frozen aqueous solutions.

### Significance statement

The degradation of proteins during freezing often accompanies (pharmaceutical) stabilization steps and occurs in natural conditions too. The substantial apparent pH changes were identified as the most detrimental factors. Therefore, we focused on the method of cryoprotection by ionic

compounds, which preserves the original enzymatic activity.

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**Presenter:** Dr HEGER, Dominik (Masaryk Univerity)

**Track Classification:** Ice Binding Proteins

Contribution ID: 120

Type: **Talk**

## Increased Acidity of Trifluoroacetic Acid in Amorphous Solid Water and Charge-Delocalized Hydroniums

*Thursday, January 11, 2018 11:50 AM (20 minutes)*

We studied the ionic dissociation of trifluoroacetic acid (TFA) in amorphous solid water (ASW) using reflection absorption infrared spectroscopy, low energy sputtering, and H/D isotopic exchange experiment. TFA readily dissociated to hydronium and counter ions in ASW at 60 K, which indicates a significant increase of the acidity as compared to that in aqueous solution at room temperature. The acid dissociation in D<sub>2</sub>O-ASW produced a Zundel continuum band in the 1000–3000 cm<sup>-1</sup> region and an accompanying lowered intensity of the O–D stretching band of D<sub>2</sub>O. The reduced intensity of D<sub>2</sub>O was several times larger than that expected for 1:1 stoichiometric proton transfer from TFA to water. Excess protons released from the acid migrated through as many as 20 water layers in ASW. These observations indicate that excess protons are highly mobile and dynamically delocalized in the hydrogen-bonded water chain. Such characteristics of excess protons may be related to the increased acidity of TFA and the appearance of the Zundel continuum absorption in IR spectra.

### Significance statement

The observation of efficient ionization of trifluoroacetic acid in amorphous solid water leads to an intriguing question: “can acids be more acidic in ASW than in liquid water?” The highly mobile nature of excess protons in ASW and its entropy-increasing effect may provide a clue to answer this question.

**Primary author:** Prof. KANG, Heon (Seoul National University)

**Co-author:** Dr SHIN, Sunghwan (Department of Chemistry, Seoul National University)

**Presenter:** Prof. KANG, Heon (Seoul National University)

Contribution ID: 121

Type: **Talk**

## Time dependent change of tip velocities of a dendritic ice crystal in growing from supercooled water

*Monday, January 8, 2018 3:10 PM (20 minutes)*

We measured the growth rates of secondary branches of a dendritic ice crystal growing from supercooled heavy water in both microgravity and 1g conditions. We have analyzed recorded sequences of images of microgravity experiments that were carried out 134 times in the International Space Station (ISS) and measured the growth rates of both the tip of a primary dendrite and the basal faces of an ice crystal growing from supercooled heavy water in the range of supercooling from 0.03 to 2.0 K and found that the steady state primary tip velocity agrees with the dendritic growth theories [1,2] of dimensionless supercooling for  $\Delta > 0.002$  (=0.16 K) when the growth on the basal face is not zero [3]. In contrast to steady-state primary tips motion, the measured data show that the tip growth rates of secondary branches are not constant with time and almost half of that of the primary tip in the initial stages and subsequently decrease with time for the small undercooling region  $< 1.0$  K. The time dependency of tip growth rates of secondary branches is different for microgravity and 1g conditions. For the larger undercooling, the time dependency can depend on the position on the main stem.

Furthermore, we extracted the contour images of a dendritic ice crystal from images and examined the pattern matching of extraction contours around the tips of both primary and secondary branches. The dendrite tip of the ice crystal is composed of two distinct tip radii, R1 and R2. The tip radius R1 is parallel to the basal plane, while the tip radius R2 is perpendicular to the basal plane. The contour images corresponding to R1 show that the radii do not change with time and the radii tips of secondary branches agree with that of the primary tip. As a result, we expect that all radii R1 of dendritic tips have the same value and determined by supercooling, nevertheless the tip velocities of secondary branches are different from the primary tip velocity.

Finally, we calculate a critical value of the interfacial stability parameter [2,4] using the data obtained from both the ISS experiments and 1g experiments and show these two sets of the values are fairly separated. The critical value in 1g decreases with increasing dimensionless supercooling, while the value in microgravity is almost constant because of no natural convection. This result is almost the same as the analysis for succinonitrile experiments having four fold symmetry [4] and agrees with the Interfacial Wave (IFW) Theory [2]. We also discuss the occurrence of side branches and the asymmetric with respect to the main stem.

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### Significance statement

The growth rates of secondary branches of a dendritic ice crystal growing from supercooled water are not constant with time. On the other hand, the radii of secondary branches parallel to the basal plane do not change with time and they agree with the primary tip radius.

**Primary author:** Prof. YOKOYAMA, Etsuro (Computer Centre, Gakushuin University)

**Co-author:** Prof. FURUKAWA, Yoshinori (Institute of Low Temperature Science, Hokkaido University)

**Presenter:** Prof. YOKOYAMA, Etsuro (Computer Centre, Gakushuin University)

**Track Classification:** Ice Crystal Growth

Contribution ID: 122

Type: **Poster**

## Transport properties of sea ice from X-ray microtomographic imaging - evidence for directed percolation

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Percolation theory describes the properties of a large number of objects related to their connectivity. The spreading of fluid through a porous medium is, among other applications, a percolation process that was first described by Broadbent and Hammersley (1) in terms of percolation theory. During the past decades this theory has been formulated and many different applications, like forest fires and soil physics, have been linked and compared to it (2,3). Within cryospheric sciences percolation theory has been discussed for the connectivity of sea ice pore networks (4,5,6). A frequently mentioned conclusion of these studies is that the sea ice pore space undergoes a percolation phase transition at a porosity of 5%, which since has been adopted to model sea ice (e.g., 5,7). However, the conclusions have been largely based on laboratory experiments, limited sample sizes and resolution.

The present work presents new insight into sea ice pore space percolation based on 3-d X-ray micro-tomographic imaging (XRT) of natural sea ice and an analysis in terms of directed percolation - a class of non-equilibrium phase transitions (9) that differs from isotropic variants employed in earlier studies (4,5,6). From XRT images of young sea ice at different temperatures we derive pore characteristic length scales, open and closed porosity, connectivity and simulate conductivity and permeability numerically. The results are evaluated in terms of critical exponents of percolation properties. The critical exponent of the strength of the percolating cluster was within a few percent of 0.81 known from numerical predictions for directed percolation (9). This finding of directional percolation behavior of sea ice is consistent with its unidirectional growth and desalination driven by gravity. However, while such directional percolation behavior of natural porous media had already been suggested by Broadbent and Hammersley (1), only a few experimental demonstrations of it in nature are known (9), indicating the potential of sea ice studies to advance general knowledge in this field. The phase transition porosity threshold is found close to 2%, considerably lower than 5% estimated in previous work (6). A closer look on pore scale characteristics indicates that the latter was overestimated due to insufficient spatial resolution.

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### Significance statement

Sea ice, microstructure, X-ray tomography, phase transition, percolation

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**Presenter:** Dr MAUS, Sønke (Norwegian University of Science and Technology (NTNU))

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 123

Type: **Poster**

## Frosts on cooling glass surfaces with micro-scale lattice-patterned grooves

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The growth of frost crystals and frost layers on solid surfaces causes serious troubles, such as poor visibility through automobile windshields and a deterioration of the performance of heat exchanger in the air. Thus, the growth controls of frost crystals and frost layers are very important for reducing these troubles. Many experiments for these controls have been conducted using grooved metals. However, frosts on micro-scale, grooved surfaces or non-metal surfaces have not yet been fully investigated. Thus, we have conducted experiments for glass plates with micro-scale lattice-patterned grooves. The width of grooves was half the pitch of pattern. Thus, 25% of the original surfaces remained regardless of the pitches (60 $\mu\text{m}$ , 80 $\mu\text{m}$  or 100 $\mu\text{m}$ ). A hydrophobic surface was obtained by coating a silane coupling agent on the glass surface. Each glass plate was set on a cooling stage. The stage was closed and the nitrogen gas was filled before the experiments started. After the temperature reached -20°C, the stage was opened. The surfaces were observed with a digital video microscope, and the surface temperature was measured with a thermocouple.

We found that the scenario of growth of frost crystals and frost layers depended on the dimension of grooves and surface hydrophobicity: (1) In the case of the shortest pitch, condensation droplets appeared only on the protrusions of the surface first. Secondly, almost all the droplets grew. Thirdly, many droplets froze, and some droplets coalesced during the freezing. Also, small frost crystals grew from the edge of the protrusions. Next, a wide, thin, frost-layer grew. (2) In the case of the hydrophobic surface 60 $\mu\text{m}$  in pitch, small droplets appeared on the protrusions first. Next, many droplets coalesced and small frost crystals grew from the edge of the protrusions. These changes occurred quicker than those occurred in the case without the coating. Thirdly, a narrow, thick frost-layer appeared in a region, while small frost crystals with hexagonal-prism shapes were observed to stand on the protrusions in another region. After that, the frost layer grew rapidly, while the frost crystals grew slowly. (3) In the case of 80 $\mu\text{m}$  in pitch, many droplets on the protrusions started to freeze first. Also, small frost crystals grew from the peripheral of the protrusions. Secondly, the frost crystals grew rapidly, while some other crystals grew from the tops of the droplets. Thirdly, narrow, thin, frost-layers appeared in some small regions, while small frost crystals with hexagonal-prism shapes were observed to lay horizontally on the protrusions in another region. After that, both the frost layer and frost crystals grew gradually. Next, the frost layer covering the laid crystals grew. All the scenarios are different from those in the case of metal surfaces with large grooves. It is expected that the frost crystals and the frost layers seems to remove easily in our cases. Thus, the glass surfaces with micro-scale grooves are effective for attenuating the growth of frost crystals and frost layers.

### Significance statement

The glass surfaces with micro-scale lattice-patterned grooves are effective for attenuating the growth of frost crystals and frost layers. All the scenarios for the frost growth are different from those in the case of metal surfaces with large grooves.



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**Presenter:** Prof. HAGIWARA, Yoshimichi (Kyoto Institute of Technology)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 124

Type: **keynote**

## Towards a molecular-level understanding of heterogeneous ice nucleation by direct surface deposition of water vapor

*Wednesday, January 10, 2018 5:05 PM (45 minutes)*

Ice nucleation research is currently booming and much of the attention is motivated by the need to improve the description of aerosol and cloud processes in the atmosphere. The formation of clouds has important effects on the water cycle on Earth and on the radiation budget of the atmosphere. The formation of liquid cloud droplets is comparatively well described by existing theory, while the formation of ice particles remains poorly understood. This is a major concern since it introduces uncertainties in our ability to model and project changes in climate.

In the atmosphere water droplets tend to remain in a super-cooled state far below the melting point of water with temperatures of about 235 K required to homogeneously freeze pure cloud droplets. Alternatively, ice formation may be enhanced by heterogeneous nucleation that may occur, either when supercooled liquid water contacts an insoluble aerosol particle and subsequently freezes, or when water vapor is directly deposited as ice onto a particle surface.

Here we focus on the latter mechanism that is commonly referred to as deposition freezing. This ice nucleation mode primarily contributes to nucleation at temperatures below approximately 243 K, and is more important than other heterogeneous ice nucleation modes at temperatures below 235 K. Deposition freezing is thus of particular relevance for clouds in the upper troposphere. Similar to other heterogeneous ice nucleation modes, deposition freezing remains poorly understood, and parameterizations currently used in cloud models are mainly based on empirical data from laboratory and field studies.

Although we know that several different types of solid material may act as deposition freezing ice nuclei, we do not yet have a theoretical description that can be used to predict the outcome. Defects in the substrate, the type of bond that the adsorbing water molecules form with the substrate, and the type of atoms exposed on the substrate all appear to affect heterogeneous nucleation.

This paper takes a molecular-level perspective and surface science-based approach to investigating deposition freezing phenomena. We summarize the current understanding of the ice formation process based on recent results obtained with several methods, including environmental molecular beam experiments, molecular dynamics simulations and kinetic modelling. Existing models are critically reviewed and outstanding questions are discussed.

### Significance statement

This paper will review the current molecular-level understanding of heterogeneous ice nucleation in the deposition freezing mode, based on recent experiments and theory using methods adopted from the fields of surface and aerosol science. Existing models are critically reviewed and outstanding questions are highlighted and discussed.

**Primary author:** Prof. PETTERSSON, Jan B. C. (University of Gothenburg)

**Co-author:** Dr THOMSON, Erik S. (University of Gothenburg)

**Presenter:** Prof. PETTERSSON, Jan B. C. (University of Gothenburg)

Contribution ID: 125

Type: **Talk**

## Fundamentals of acid-base chemistry at and in the quasi-liquid-layer

*Thursday, January 11, 2018 10:50 AM (20 minutes)*

Earth's surface snow plays an active part in atmospheric chemistry. Research over the past decades has provided an impressive observational basis of the resulting large scale effects, such as substantial modification of the composition and of the chemical reactivity of the lowermost atmosphere in polar regions.

Here, I present details on the chemical mechanisms operating in environmental snow and ice derived from well controlled laboratory based experiments. The research is taking full advantage of the Near Ambient Pressure Photoelectron spectroscopy (NAPP) end station at PSI/SLS reveals the ability of atmospheric trace gases to modify the structure of ice at the upper few nanometers at the air-ice interface upon adsorption. Using near ambient pressure core level X-ray photoelectron spectroscopy, we directly detected depth profiles and dissociation degree of adsorbed acidic trace gases at 230 - 255 K at low surface coverage. Complementary X-ray absorption measurements (NEXAFS) show how the presence of acid induces changes to the hydrogen bonding network in the interfacial region.

We interpret the data as

\* a Janus-type character of physisorbed molecular acid at the outermost ice surface and dissociation occurring upon solvation deeper in the interfacial region.

\* a non-uniform of chemical and physical properties of the hydrogen bonding network along the depth of the QLL

Even with a focus of this presentation on adsorption of acidic trace gases (HCl, HNO<sub>3</sub>, formic acid, acetic acid) to ice and on the molecular structure of the hydrogen bonding network at the air-ice interface, the details on chemistry at extreme concentration and temperature conditions at interfaces might be of high relevance not only in environmental science but also in general chemistry, material science, catalysis, cryobiology, and astrophysics.

### Significance statement

These data describe the chemical properties of the air-ice interface and question the general applicability of the acid-base concept across interfaces.

**Primary author:** BARTELS-RAUSCH, Thorsten (Paul Scherrer Institut)

**Presenter:** BARTELS-RAUSCH, Thorsten (Paul Scherrer Institut)

**Track Classification:** Chemistry

Contribution ID: 126

Type: **Poster**

## **Bulk and Surface reactivity in frozen salt-organic-ice mixtures.**

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Tropospheric ozone depletion events (ODEs) via halogen activation are observed in both cold and warm climates [1-3]. Very recently, it was suggested that this multiphase halogen activation chemistry is the dominant in the tropical and subtropical upper troposphere. These occurrences beg the question of temperature dependence of halogen activation in sea-salt aerosol, which are often mixtures of sea-salt and organic molecules.

With the application of flow-tubes, the aim of this study is to investigate the temperature dependence of bromine activation via ozone interaction in a bromide containing film as a proxy for mixed organic – sea-salt aerosol. Citric acid is used in this study as a hygroscopically characterized matrix and a proxy for oxidized organics, which is of relevance to atmospheric chemistry. Here, we present reactive ozone uptake measured between 258 and 289 K. The data show high reproducibility. With available knowledge, we have reproduced the measured uptake with modelled bulk and surface uptake while accounting for temperature dependence of the substrate's properties as diffusivity, viscosity, and gas solubility.

The data give evidence of the importance of surface and bulk processes in frozen systems. Further, the modelling of the bulk chemistry in these cold and viscous matrixes is discussed in detail.

This work is part of a cross-disciplinary project with the aim to investigate the impact of metamorphism on impurity location in aging snow and its consequences for chemical reactivity. Metamorphism drastically shapes the structure and physical properties of snow, which has impacts on heat transfer, albedo, and avalanche formation. Such changes can be driven by water vapour fluxes in dry metamorphism with a mass turnover of as much as 60% per day - much greater than previously thought. The consequences for atmospheric science are a current question of research. Here, we also aim at addressing how the re-distribution of solutes during snow metamorphism in artificial snow impacts chemical reactivity.

### **Significance statement**

Sea salt aerosol contain organics. Little is known about their reactivity to release halogens at Polar temperatures.

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**Presenter:** BARTELS-RAUSCH, Thorsten (Paul Scherrer Institut)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 127

Type: **Talk**

## The skeletal layer of sea ice: X-ray microtomography and modeling

*Wednesday, January 10, 2018 11:25 AM (20 minutes)*

When columnar sea ice forms on seawater by unidirectional freezing its interface is known to have a lamellar microstructure, consisting of vertically oriented plates with largely horizontal c-axis orientation, parallel within each grain. Away from the interface these plates thicken by lateral freezing, driven by (i) a decrease in temperature and (ii) intermittent convective exchange of brine against seawater. This convection is the main process that drives the desalination of sea ice, and takes place within a layer of a few centimeter thickness that often is called “skeletal layer” (1,2,3). The skeletal layer is not only relevant for convective desalination, but also shapes an important habitat for life near the sea ice bottom (4) and is critical for pollution issues like oil uptake by sea ice (5). As the skeletal layer has high porosity and is, due to its fragile nature, difficult to sample, relatively little is known about its 3-d structure and transport properties like permeability and thermal conductivity. A conceptual model that involves the bridging of plate-like crystals at some distance from the interface, setting the upper boundary of the skeletal layer, has been suggested half a century ago based on thin-section analysis (1,2), but still remains unvalidated. In the present study first different observations of the sea ice skeletal layer are reviewed, followed by an in-depth analysis of the skeletal layer from 3-d microtomographic imaging (XRT) of natural sea ice and laboratory-grown saltwater ice. The XRT images are analysed with emphasis on the process of necking of lamellar ice plates, changes in grain sizes, and the evolution of pore structure and permeability within the skeletal layer. The determined porosity-permeability relationship is used to model and predict the onset of convection and skeletal layer thickness and compare them to previous work (6,7). The present analysis highlights the importance of crystal structure for sea ice property evolution.

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### Significance statement

Sea ice, interface, crystal growth and structure, X-ray microtomography

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**Presenter:** Dr MAUS, Sønke (Norwegian University of Science and Technology (NTNU))

**Track Classification:** Ice Crystal Growth

Contribution ID: 131

Type: **Poster**

## Investigation of Ice-Binding Proteins using Heterodyne-Detected Vibrational Sum-Frequency Generation Spectroscopy

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Antifreeze proteins (AFPs) and Antifreeze Glycoproteins (AFGPs) collectively abbreviated as AF(G)Ps are a unique class of proteins that modify ice crystal growth and enable the survival of organism in freezing and subfreezing habitats. The molecular working mechanism behind AF(G)Ps freezing inhibition is not well understood, because, as yet, there are few experimental techniques that allow obtaining molecular details on how antifreeze proteins function directly at the surface of ice. Here we use surface specific heterodyne-detected vibrational sum-frequency generation spectroscopy (HD-VSFG) to study the properties of antifreeze proteins directly at the ice surface and at the molecular level.

### Significance statement

Antifreeze proteins (AFPs) and Antifreeze Glycoproteins (AFGPs) collectively abbreviated as AF(G)Ps are a unique class of proteins that modify ice crystal growth and enable the survival of organism in freezing and subfreezing habitats.

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**Presenter:** Ms MOLL, Carolyn (AMOLF)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 132

Type: **Poster**

## **Isothermal metamorphism of snow: measurement of interface velocities and phase-field modeling for a better understanding of the involved mechanisms**

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Once deposited on the ground, snow forms a complex porous material whose microstructure constantly transforms over time. These evolutions, which strongly impact the physical and mechanical properties of snow (e.g. Srivastava et al, 2010; Calonne et al, 2014; Wautier et al, 2015) need to be considered in details for an accurate snowpack modeling. However, some of the physical mechanisms involved in metamorphism are still poorly understood. To address this problem, several investigations combining X-ray tomography and 3D micro-modeling have been carried out over the past decade (e.g. Flin et al, 2003; Kämpfer and Plapp, 2009; Pinzer et al, 2012) but precise comparisons between experimentation and modeling remain difficult. One of the difficulties comes from the lack of high resolution time-lapse series for experiments occurring with very well-defined boundary conditions, and from which precise measurements of the interfacial growth rates can be done.

Thanks to CellDyM, a recently developed cryogenic cell (Calonne et al, 2015), we conducted in situ time-lapse tomographic experiments on several snow and ice samples under various conditions. We focus here on a 28 h experiment of isothermal metamorphism at  $-7^{\circ}\text{C}$ . The non-destructive nature of X-ray microtomography yielded a series of 8 micron resolution images that were acquired with a 2 to 12 h time step. An image analysis method was implemented to estimate the normal growth rates on each point of the ice-air interface and applied to the series obtained. In addition, a curvature-based phase-field model (Bretin et al, 2015) was used on the first image of the experimental series to compute the snow evolution under a pure sublimation-condensation mechanism: the numerical morphologies were then compared to the experimental ones.

The analysis of all the results gives interesting outlooks for the understanding of the physical mechanisms involved in snow isothermal metamorphism. In particular, our measurements tend to confirm the recent observations of Krol and Löwe (2016) that suggest the sublimation-condensation might be predominant over the vapor diffusion mechanism.

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### **Significance statement**

This study presents an analysis of an experiment of snow isothermal metamorphism monitored by time-lapse tomography. Measurements of interfacial velocities as well as phase-field modeling are used to investigate the physical mechanisms involved.



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**Presenter:** FLIN, Frederic (Meteo-France CNRS / CNRM UMR 3589 / CEN)

**Session Classification:** Poster & Lunch

Contribution ID: 138

Type: **Talk**

## Gas Nucleation Processes In Sea Ice Brines Inclusions

*Thursday, January 11, 2018 5:20 PM (20 minutes)*

Past and recent literature have highlighted that sea ice might play a crucial role in controlling and contributing to the exchange of significant climatically active biogases between the ocean and the atmosphere in polar areas. However, the formation of air inclusions and the transport of gases within sea ice cover are still poorly understood. In its pure form sea ice is a multi-phase system formed by the freezing of seawater, which consists of ice, salt precipitates, liquid brine, and air bubble (WMO, 1970). As the ice grows under cooling conditions, each brine inclusion shrinks in size until the internal salinity of the inclusion is high enough to compensate further cooling. In these smallest inclusions, the concentration of salts as well as other solutes (e.g. gases, dissolved inorganic carbon) can increase to a point where the solution is supersaturated (concentration effect). Conversely, if the temperature of the ice cover increases under warming conditions, some of the pure ice along the inclusion walls melts, expanding the brine inclusions and diluting the brine, which lowers the brine salinity. Gases are incorporated in dissolved phase in the brine during ice growth and literature suggests that bubble nucleation further happened in supersaturated brine inclusions. Recent modelling study concluded that the partitioning between dissolved and gaseous phases can play a critical role in gas transport in sea ice, since the transport of gas in air bubble might be decoupled from brine motion. Since there is no analytical method to assess the partitioning of gases between dissolved and gaseous forms in brine, the brine saturation state is commonly used as a proxy to estimate the fraction of gas residing in bubble. According to the reasoning therein, bubble formation should increase as temperature decreases due to the concentration effect in winter (cooling). However, recent experiences using both traditional (crushing and gas chromatography) and new sea ice analytical techniques (CT-Imaging and Raman spectrometry) show that nucleation is not a linear function of the saturation state and that bubbles may shrink in size or disappear during cooling. Our results suggest that surface tension and brine internal pressure might control gas nucleation processes in brine. Results from this work are a valuable addition to limited studies available on gas content dynamics in sea ice, and provide new methodology for the interpretation and characterization of sea ice porosity as well as new knowledge for sea ice modelling.

### Significance statement

The findings of this research contribute to the field of sea ice physics as they provide new suitable techniques to characterize air bubbles and new discussions on processes controlling sea ice gas content and transport.

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**Presenter:** Dr CRABECK, Odile (University of Manitoba)

**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 139

Type: **Poster**

## Quantifying black carbon deposition to Greenland surface snow from forest fires in Canada

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Black carbon (BC) concentrations has been observed in 22 snowpits sampled in the northwest sector of the Greenland ice sheet in April 2014. The pits contain a strong and widespread BC aerosol deposition event, which accumulated in the pits during two snow storms between 27 July and 2 August 2013. This event comprises a significant portion (57% on average across all pits) of total BC deposition measured in the snowpits (~10 month record). We link this deposition event to forest fires burning in Canada during summer 2013 using modeling and remote sensing tools. Specifically, we use high-resolution regional chemical transport modeling (WRF-Chem) combined with high-resolution fire emissions (FINNv1.5) to study aerosol emissions, transport, and deposition to Greenland snow during this event. The model captures the timing of the BC deposition event and shows that fires in Canada were the main source of deposited BC. The implications for understanding the influence of BC originating from fires on the optical properties of snow is discussed.

### Significance statement

The 57% of black carbon aerosol deposition in 2013 in northwest Greenland measured in snowpits is linked to a specific event in late July/early August 2013. The origin of this event is emissions from forest fires burning in Canada.

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**Presenter:** Dr THOMAS, Jennie (LATMOS/IPSL, UPMC Univ. Paris 06 Sorbonne Universites, UVSQ, CNRS, Paris, France)

**Session Classification:** Poster & Lunch

Contribution ID: 140

Type: Talk

## **Ice growth and air/water interface motion of water droplets impinged on a horizontal cooling surface**

*Thursday, January 11, 2018 8:55 AM (20 minutes)*

The formation of ice layer by water droplets on surfaces causes many troubles, such as poor visibility through the windshields of aircraft, trains and automobiles; the breaking of power transmission lines; a deterioration of the aerodynamic performance of aircraft wings. Thus, many studies have been carried out. However, the details of heat transfer during the freezing have not yet been clarified. We have carried out experiments and numerical simulation to elucidate the detailed mechanism of droplet freezing. In this report, we have focused on time changes in the freezing fronts and air-water interfaces for impinged water droplets on a horizontal cooling surface. In this research, we carried out two-dimensional numerical simulation on the droplets. The time advancements of the air-water interfaces and ice-water interfaces for the droplets were predicted using Phase-field methods. The ice area was expressed with an immersed boundary method. The velocity fields of air and water were predicted by solving the Navier-Stokes equations. The temperature field in the whole domain was predicted by solving the energy equation. The surface tension force and the properties of ice, water and air at around 0 degrees were adopted. The temperatures of air and the cooling surfaces and the droplet impact velocity were varied. The Reynolds number and Weber number of the droplets were in the range of 35 - 129 and 1.6 - 22, respectively.

The computational results showed that the height of the impinged droplets on the symmetrical axis started to oscillate as a result of the impact of the collision of droplets with the surfaces in all the cases that we investigated. The oscillations converged rapidly in all impinged water droplets that froze on the cooling surface. This is due to the fact that ice layer, developed along the cooling surface, reached the air-water interface of the droplet on the cooling surface and that the contact area of the droplet was fixed. The ice layer was downward convex during the growth of the layer. This is partly because the water temperature in the central part of droplets was slightly high as a result of the convection and conduction of the latent heat, and partly because the water temperature near the air-water interface was slightly low as a result of low temperature of the air near the cooling surface. When we also took account of the homogeneous ice nucleation, we introduced many ice nuclei into the sub-zero degree region inside the droplets. These nuclei melted by the latent except for the region adjacent to the air-water interface. The predicted oscillation frequency of the air-water interface during the freezing was much lower than the measured frequency, while the maximum amplitude and convergence time of the oscillation were reasonably predicted. This discrepancy was due to the difference in the freedom of oscillation in the two-dimensional computation and the three-dimensional measurements. Thus, our computational results were consistent and reasonable.

### **Significance statement**

We have focused on time changes in the freezing fronts and air-water interfaces for impinged water droplets on a horizontal cooling surface. Our computational results show that our simulation is reasonable.

**Primary author:** Mr TOYOHARA, Kazumasa (Kyoto Institute of Technology)

**Co-author:** Prof. HAGIWARA, Yoshimichi (Kyoto Institute of Technology)

**Presenter:** Prof. HAGIWARA, Yoshimichi (Kyoto Institute of Technology)

**Track Classification:** The surface and interface of ice

Contribution ID: 143

Type: **Poster**

## Molecular dynamic simulation on the interaction between 'antifreeze' polypeptide, water and an ice

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The inhibition of ice growth is an important issue in various fields, such as the maintenance of the quality of food texture in food preservation, and cryosurgery. Antifreeze protein (AFP) and antifreeze glycoprotein (AFGP) have been investigated in relation to the inhibition of ice growth. This is because the AF(G)P solutions have the following properties: (a) the freezing point drops noticeably, (b) the melting point is retained, (c) the osmotic pressure does not significantly increase, and (d) specific facets are observed on the surfaces of ice crystals. Therefore, AFP and AFGP are promising additives for the applications. On the other hand, the denaturation of these proteins occurs inevitably. Also, these proteins are expensive regardless of synthetic one or natural one. Kun and Mastai (Peptide Science, vol. 88, 2007, pp. 807-814) synthesized a twelve-residue polypeptide based on a part of winter flounder AFP. They showed that this polypeptide has the aforementioned two properties; (a) and (b). Our research group expects that denaturation of the polypeptide does not occur in this case because the short helical structure of the polypeptide, which includes many hydrophobic residues, is maintained with strong hydrophobic interaction and the hydrogen bonds. However, as far as the present authors know, no report has been published concerning the mechanism of ice-growth inhibition for the polypeptide.

Thus, we have carried out molecular dynamics simulation for the mixture of the polypeptide, water and an ice layer in the present study. We adopted the Canonical ensemble. The Newton-Euler equations for the translational and rotational motions of the molecules were solved at each time step, and were integrated with respect to time by using the Gear algorithm. The TIP4P/Ice potential function was used for the interaction between two water molecules. The Ewald method was used for the Coulomb potential in order to reduce the electrical force of distant molecules. The OPLS parameters were adopted as the potential parameters of each site of the peptide. The results of the simulations showed that the presence of the polypeptide inhibits the hydrogen bonding among water molecules and shortens the period of the hydrogen bonding. Consequently, the presence of the polypeptide attenuated the formation of tetrahedral networks of water molecules near the ice surface. This is a reason for the ice growth inhibition by the polypeptide. When the polypeptide was adsorbed on the ice surface, the motion of the peptide is more noticeable compared with that of the winter flounder antifreeze protein. This is the reason for the necessity of higher concentration of the polypeptide than the winter flounder antifreeze protein for the inhibition of ice growth. All these results are consistent with the experimental results. In addition, we examined the polypeptide bound with hydrophobic glutaraldehyde, which can be a linker of the polypeptide to cooling surfaces. The results showed that the ice growth was further inhibited. It can be concluded that the coating of glutaraldehyde-linked polypeptide might be effective for producing ice-phobic surfaces.

### Significance statement

We have carried out molecular dynamics simulation for the mixture of the polypeptide, water and an ice layer in the present study. All the results are consistent with the experimental results. We also examined the polypeptide bound with hydrophobic glutaraldehyde.



**Primary author:** Mr KAIJIMA, Tadashi (Kyoto Institute of Technology)

**Co-authors:** Mr TERAJ, Kou (Kyoto Institute of Technology); Prof. HAGIWARA, Yoshimichi (Kyoto Institute of Technology)

**Presenter:** Mr KAIJIMA, Tadashi (Kyoto Institute of Technology)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 144

Type: **Poster**

## Freezing of sessile droplets on glass surfaces coated with antifreeze polypeptides by a silane coupling agent

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

To develop icephobic surfaces is an urgent issue because ice-covering surfaces cause serious troubles, such as (1) poor visibility through the windshields of aircraft, trains and automobiles; (2) poor visibility of traffic lights in snowy winter, (3) the breaking of power transmission lines; (4) a deterioration of the aerodynamic performance of aircraft wings. To date, many studies proposed icephobic surfaces. However, as far as the present authors know, there has not yet been proposed for the icephobic transparent surfaces, necessary for reducing the first two troubles. Concerning the ice growth on a transparent glass, the antifreeze protein type I bound on the glass surface was studied by Esser-Kahn et al. However, the denaturation of the antifreeze protein was not discussed. The present authors have looked for alternatives for icephobic surface coating because of the protein denaturation. Kun and Mastai synthesized three polypeptides inspired from antifreeze protein. Using an osmometer, they measured freezing point depression for a solution of one of these polypeptides. The amino-acid residues of this polypeptide were identical with the first twelve amino-acid residues of winter flounder antifreeze protein. We have expected that denaturation of the polypeptide does not occur in this case because the short helical structure of the polypeptide, which includes many hydrophobic residues, is maintained with strong hydrophobic interaction and hydrogen bonds. We showed the increase in the supercooling at the ice/solution interface and decrease in the ice growth rate for the polypeptide solution in the unidirectional freezing. However, we have not yet tried the adhesion of the polypeptide on a solid surface. Based on these results, we have conducted experiments on the freezing of sessile pure-water droplets on cooling glass surfaces. The polypeptides were adhered on the glass surfaces with coupling agents and linkers. We measured supercooling temperature inside the droplets using a fine thermocouple. Also, we measured the surface adhesion strength of frozen droplets. In addition, we observed the surfaces using an atomic force microscope. The cooling rate of the surfaces was  $-2.0$  °C/min. It was found that the supercooling temperature in the case coated with the silane coupling agent was lower than that in the case of untreated surface. This is because the droplet contact area became small due to the hydrophobicity of the silane coupling agent. The supercooling temperature in the case with the polypeptides was the lowest. Also, the adhesion strength of frozen droplets in the case with the polypeptides was found to be lower than that in the other cases. In addition, it was observed with the atomic force microscope that many aggregates of the polypeptides in various size were adhered on the surfaces randomly. It can be surmised that the hydrophobic residues of the polypeptides are exposed in the aggregates, and that the hydrophobic hydration of water molecules occurs by the hydrophobic residues on the aggregates. This can be the reason for the decreases in the supercooling temperature and adhesion strength.

### Significance statement

We conducted experiments on the freezing of water droplets on cooling glass surfaces. The polypeptides were adhered on the surfaces with coupling agents. The hydrophobic residues of the polypeptides in their aggregates can be the reason for decreases in the supercooling temperature and adhesion strength.

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**Presenter:** Prof. HAGIWARA, Yoshimichi (Kyoto Institute of Technology)

**Session Classification:** Poster & Lunch

Contribution ID: 146

Type: **Talk**

## Microscale distribution of major ions in snow

*Wednesday, January 10, 2018 11:45 AM (25 minutes)*

Impurity records of an ice core are used as a proxy for past climate change. However, the processes leading to the embedding of chemical compounds are not completely understood: The compounds from the atmosphere are deposited on the ground during snowfall. If the snow does not completely melt, like on polar and alpine glaciers, the impurities will be preserved in the snowpack and later incorporated into the glacier ice.

Especially the recrystallization of the snowpack during metamorphism processes can cause a redistribution of embedded compounds. We therefore investigated the transport of major ions of  $(\text{NH}_4)_2\text{SO}_4$ , NaF and  $\text{CaCl}_2$  in the dynamic snow.

In an elution experiment, chemically homogeneous ice droplets were metamorphosed and rinsed with zero-degree water to determine the redistribution of ions. Hereby, we concentrated on the accumulation of ions on the surface of the ice crystals and their inclusion in the ice. This experiment was repeated with natural snow from a field site above Davos, Switzerland. Further, from January to June 2017, we monthly sampled the vertical distribution of major ions in the natural snowpack at the same field site.

First results show a strong separation of the ions during snow metamorphism. The concentration of sulfate and calcium on the outside of the ice crystals increased of up to 6 times with storage time. This project is a joint project between the Paul Scherrer Institute (PSI) and the WSL Institute for Snow and Avalanche Research (SLF).

### Significance statement

Impurity records of an ice core are used as a proxy for past climate change. However, the processes leading to the embedding of chemical compounds are not completely understood: Metamorphism processes in snow can cause a redistribution of embedded compounds.

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**Presenter:** Mr TRACHSEL, Jürg (WSL Institute for Snow and Avalanche Research SLF)

**Track Classification:** Mechanics & Microstructure

Contribution ID: 148

Type: PICO talk

## Brownian ratchet model - particle and ice front interaction

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

When a moving solidification front encounters a foreign particle in the melt for example during freezing, it can either engulf it, or push and reject it. This interaction takes place in freezing of any colloidal suspension and is basic in metallurgy, freeze casting, frost heave, and cryopreservation. In this work we show that the interaction of the particles with the freezing front can be explained by displacement of the particle that undergoes Brownian fluctuations near a moving wall which is the freezing front. Movement of the ice front limits the space where the randomly fluctuating particle can diffuse, resulting in a ratchet mechanism that allows the particle to move only in the direction of the growth of the ice. The model reproduces the known and established result that the critical velocity for engulfment scales as  $1/(n r)$ , where  $n$  is the viscosity of the fluid and  $r$  is the particle radius. The Brownian ratchet model also explains the independence of the critical velocity on the particle size, for small particles, which was observed in early work in the field. Numerical simulation based on our model predict that the dragging distance of the particle being pushed by the ice front scales as  $\exp(1/v r)$  where  $v$  is the ice growth velocity. Experimental data obtained by us and published by others is in agreement with predictions of our model.

The scaling of the dragging distance for a single particle, once developed for a multi particle system can allow the calculation of the length scales of patterns being formed during freezing such as ice lenses and freeze casting.

This work was supported by a grant from the Israel Science Foundation and the Rudin fellowship.

### Significance statement

We present a novel and intuitive model explaining the particle rejection phenomenon. It explains existing data and predicts the particle dragging distance by the ice front. Model implication to multi-particle systems can be the framework to develop a theory explaining the length scales in patterns formation during solidification.

**Primary author:** Mr CHASNITSKY, Michael (The Hebrew University of Jerusalem)

**Co-authors:** Prof. BRASLAVSKY, Ido (The Hebrew University of Jerusalem); Dr YASHUNSKY, Victor (Institut Curie, Paris)

**Presenter:** Mr CHASNITSKY, Michael (The Hebrew University of Jerusalem)

**Session Classification:** Poster & Lunch

Contribution ID: 149

Type: **Poster**

## Na<sup>+</sup>, F<sup>-</sup>, Br<sup>-</sup> and Cl<sup>-</sup> Adsorptions and Penetrations on Ice Surface

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

With the help of our QM/EFP scheme, the adsorptions of Na<sup>+</sup>, F<sup>-</sup>, Br<sup>-</sup> and Cl<sup>-</sup> ions on Ih ice surface were theoretically studied. Drastically different adsorption behaviors depending on ion signs and surface heterogeneity were observed. The positive Na<sup>+</sup> ion forms 4 ~ 5 Na<sup>+</sup>-O interfacial bondings regardless of the numbers of hydrogen dangling bonds (HDB), yielding consistent adsorptions with large stabilization energies of -49.2 ~ -65.6 kcal/mol. On the other hand, the binding strengths of negative ions are sensitive to the numbers of HDB. In the particular binding sites where there is no HDB, both Cl<sup>-</sup> and Br<sup>-</sup> cannot form a stable surface adsorption product. At the same binding site, more reactive F<sup>-</sup> can undergo insertion reaction into surface hydrogen bonding. A molecular HF and a hydroxide is formed on a site with one HDB, showing that the surface acid-base chemistry may depend on the surface heterogeneity. In general, the versatile bonding ability of Na<sup>+</sup> through s and empty p orbitals provides strong interactions with the ice surface by disrupting surface hydrogen bonding network, which in turn reduces its initial penetration barriers into bulk. However, the ice surface structures are intact in the case of negative ion adsorptions, making their penetrations into bulk difficult.

### Significance statement

Detailed binding structures and characteristics of ions on ice surface.

**Primary author:** Prof. CHOI, Cheol Ho (Kyungpook National University)

**Presenter:** Prof. CHOI, Cheol Ho (Kyungpook National University)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 151

Type: **keynote**

# The influence of subglacial water on glaciological friction

*Friday, January 12, 2018 10:35 AM (45 minutes)*

The movement of continental and mountain-scale ice masses is usually modelled as a problem of viscous creep. The viscosity arises from temperature- and stress-dependent migration of defects through the polycrystalline structure of the ice, and the rheology is usually described as a power law fluid for the purposes of large-scale ice-sheet models. Much of the ice motion arises from effective slip at the bed. This may arise from actual sliding at the ice-bed interface, from enhanced ice deformation close to the bed, or from deformation of the bed itself (where it comprises deformable glacial sediments). The slip is described mathematically by a glaciological sliding or friction law.

This presentation will review classical descriptions of the friction experienced by the flow of glacial ice over a hard bed, will highlight more recent work on the subject, and discuss opportunities for further understanding.

The ice-rock interface is typically close to the pressure-dependent melting point and a thin film of water resides between ice and rock. At a small (~mm) scale, there is therefore little resistance to shear, and the macroscopic friction experienced by the glacier is thought to be primarily due to the requirement for ice to flow over or around roughness elements in the bed; effectively a type of form drag. Low stresses downstream of bumps in the bed can result in cavitation, with the ice peeling off from the bed to leave a water-filled cavity. Such cavitation on a large scale effectively reduces the ice-bed contact area and can result in a reduction of friction. We discuss conceptual models of this process and their implications in terms of the dependence of friction on ice speed, cavity pressure and volume. A crucial and unresolved question is the extent to which such cavities are hydraulically connected and can therefore evolve in response to meltwater that enters glaciers from the surface during the melt season. We will discuss observations of how glacier sliding varies in time, and hypotheses for the small-scale dynamics at the bed that give rise to these changes. We also discuss the role of bed deformation and the thermodynamic effects of regelation and viscous dissipation.

## Significance statement

Glaciers and ice sheets are losing mass in response to climate change. The rate at which this happens is strongly controlled by how fast the ice can move. This talk reviews current knowledge about the glacial friction that controls this movement, and how it may change in the future.

**Primary author:** Prof. HEWITT, Ian (University of Oxford)

**Presenter:** Prof. HEWITT, Ian (University of Oxford)

**Track Classification:** Fundamentals of the Cryosphere

Contribution ID: 152

Type: **Poster**

## Nucleation and deposition growth of ice crystals on mineral substrates

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

We report measurements of growth rates of ice crystals that were nucleating on feldspar mineral substrates in the environmental scanning electron microscope (ESEM) filled with the mixture of nitrogen and water vapor [3]. The linear growth velocity of prismatic and basal faces of ice crystals has been estimated from the sequence of individual ESEM frames recorded every second. Using the theoretical framework formulated by Yokoyama and Kuroda [2] and Libbrecht [3], we have been able to calculate the local values of water vapor supersaturation at ice nucleation onsets. We show that growth rates of individual crystals are extremely sensitive to local fluctuations of vapor pressure which can be affected by the presence of ice crystals in the vicinity. Using this method, we compare on-set supersaturation values for two different feldspar specimens, feldspar treated with a weak aqueous solution of H<sub>2</sub>SO<sub>4</sub>, and different cooling rates. Exemplary crystal features that could imply a memory effect induced at nucleation stage (stacking disorder, screw dislocation, etc.) will be demonstrated and discussed as well.

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2. E. Yokoyama and T. Kuroda, Pattern formation in growth of snow crystals occurring in the surface kinetic process and the diffusion process. *Phys. Rev. A*. 41, 2038–2049 (1990).
3. K. G. Libbrecht, Growth rates of the principal facets of ice between -10C and -40C. *J. Cryst. Growth*. 247, 530–540 (2003).

### Significance statement

ESEM is a powerful tool allowing studies of ice nucleation and characterization of ice nucleating particles in one instrument. We demonstrate its ability to measure ice growth rates under precisely controlled relative humidity conditions. Our observations suggest that ice can possess stacking disordered structure even if nucleation occurred at -30C.

**Primary author:** Dr KISELEV, Alexei (Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research)

**Co-author:** Prof. LEISNER, Thomas (Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research)

**Presenter:** Dr KISELEV, Alexei (Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)



Contribution ID: 153

Type: **Poster**

## The vapor pressure over nano-crystalline and amorphous ice

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

It is known that at ambient pressure the crystallization of amorphous ices proceeds via the formation of nano-crystallites. This fact, however, is not considered in many studies on amorphous and crystalline ices formed from the amorphous phase even though it has important implications on various ice properties. As an example, we show in this contribution, that the saturation vapor pressure over nano-crystalline ice is elevated by a factor of two to three compared to the assumed saturation vapor pressure of cubic/hexagonal ice between 135 K and 160 K due to the high curvature of the nano-crystallites. We then analyze heat capacity measurements of amorphous and crystalline ices from the previous five decades on the premise of nano-crystallite formation. We show that heat capacity data has to be re-interpreted and that the free energy difference between amorphous and hexagonal ice is substantially higher than previously assumed. Taking these findings we propose a new parameterization for the saturation vapor pressure over amorphous ice for temperatures below 200 K.

As nano-crystalline ice and amorphous solid water are stable for hours below 160 K and 135 K, respectively, both phases have to be considered for ice cloud processes occurring at or below these temperatures in planetary atmospheres, for instance in the mesospheres of Earth and Mars.

### Significance statement

We present a new and substantially higher parameterization for the vapor pressure over amorphous solid water below 200 K which is based on own measurements of nano-crystalline and amorphous ice and studies from the last five decades. The result has important implications on processes in cold ice clouds.

**Primary author:** NACHBAR, Mario (Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany)

**Co-authors:** Dr DUFT, Denis (Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany); Prof. LEISNER, Thomas (Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany)

**Presenter:** Dr DUFT, Denis (Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 154

Type: **Poster**

## The Cryosphere and Atmospheric Chemistry (CATCH): Research challenges and opportunities for collaboration

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The cold regions on Earth are undergoing significant climate change. Yet many underlying chemical, biological, and physical processes and feedbacks are still poorly understood strongly motivating continued research in cold regions. Such research inherently requires cooperation among researchers and programs across national boundaries to achieve science objectives. CATCH is an emerging activity of the IGAC (International Global Atmospheric Chemistry) project and is endorsed by SOLAS (Surface Ocean-Lower Atmosphere Study). CATCH facilitates interdisciplinary and international research with a focus on interactions between snow, ice, ocean, aerosols, and clouds in cold regions. CATCH science addresses cold region research challenges to help reduce model uncertainties and improve climate predictions. Here we give an overview of scientific aims and strategy to develop collaborative research teams and projects. Particular areas of interest include: sea ice changes, atmosphere-ice-ocean interactions and their impacts on atmospheric chemistry; feedbacks between climate change and atmospheric chemistry mediated by changes in the cryosphere; the production, processing and climate impacts of aerosols and cloud precursors; ice cores as archives of past environmental change, and the influence of background atmospheric chemistry on the fate of pollution. CATCH seeks to link research on a fundamental, molecular level with larger scales targeted by field and satellite observations, as well as modeling.

### Significance statement

CATCH is an international activity that aims to link fundamental knowledge of snow/ice processes to knowledge of atmospheric chemistry in cold regions

**Primary author:** Dr THOMAS, Jennie (LATMOS/UCLA)

**Co-authors:** CATCH IMPLEMENTATION TEAM, - (-); Dr FREY, Markus (British Antarctic Survey); BARTELS-RAUSCH, Thorsten (Paul Scherrer Institut)

**Presenter:** Dr THOMAS, Jennie (LATMOS/UCLA)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 155

Type: PICO talk

## Quantum dynamics of H<sub>2</sub> molecules confined in ice XVII

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Ice XVII is a newly discovered solid form of pure water, which is metastable at ambient pressure if maintained below 130 K. It is obtained from the so-called C0-phase of the H<sub>2</sub>-H<sub>2</sub>O binary compound, quenched at a temperature  $T=77$  K, after letting the hydrogen molecules diffuse out of the crystal [1]. It is intrinsically porous and can absorb again molecular hydrogen and release it repetitively, showing a larger or smaller hysteresis depending on the temperature. By means of neutron diffraction, we have recently determined the structure of ice XVII, (hexagonal, with space group P6122) [2]. It presents accessible spiraling channels, where hydrogen molecules have been located during the production and where other molecules (belonging to hydrogen or another gas) can be absorbed again, confined in an essentially one dimensional geometry [2]. This is the second form of metastable ice experimentally obtained by removing weakly-interacting guests (the first being ice XVI, obtained from a neon clathrate [3]), but many low density ice structures have been theoretically studied and found to be possibly stable [4,5]. We present here the results of a new high-resolution inelastic neutron scattering experiment on ice XVII, containing molecular hydrogen with different ortho/para ratio, and with molecular dynamic results. We have unequivocally assigned the measured spectral bands to rotational and center-of-mass translational transitions of either para- or ortho-H<sub>2</sub>. Reported data demonstrate that H<sub>2</sub> molecules rotate almost freely in these nanometric channels, though showing larger perturbation than in clathrate hydrates, and perform a translational motion exhibiting two low frequency excitations. The comparison between the measured spectra and the MD calculations supports the identification of the lowest frequency band as the vibration along the channel direction, while the higher mode corresponds to the motion across the spiral channel. These measurements clearly enable to portray a picture of the confined motions of a hydrophobic guest in this novel inclusion compound [6].

### References

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### Significance statement

Ice XVII has a unique porous structure. This experimental study of the quantum dynamics of H<sub>2</sub> molecules, confined in ice XVII nanometric one-dimensional channels, opens new perspectives for both the modelling of the solid water-hydrogen mixture and for understanding quantum one-dimensional diffusion.

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**Presenter:** Dr ULIVI, Lorenzo (IFAC-CNR)

**Session Classification:** Poster & Lunch

Contribution ID: 156

Type: **Poster**

## Towards the surface science of ice nucleation on aqueous organic solutions and solid substrates

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

The nucleation of ice is an important process in chemistry, physics and atmospheric science. Although ice nucleation has been studied since long, our understanding of ice nucleation is still far from complete, particularly from a molecular point of view. The hydrogen bonding structure of H<sub>2</sub>O ice can be significantly different between liquid water to ice, which is responsible for most of the difference in physical and chemical properties between the different aggregation states of water. The difference between the hydrogen bonding structure of liquid water and ice can be experimentally observed by near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge, because it involves resonant transitions into unoccupied molecular orbitals, which are very sensitive to the nearest neighbors of oxygen atoms. NEXAFS spectroscopy can be performed in electron yield mode, in which Auger electrons emitted upon initial core hole excitation are detected, which provides a surface sensitive NEXAFS spectrum. Experiments reported in this work were performed at the near ambient photoelectron spectroscopy endstation (NAPP) at the SIM and NANOXAS beamline at the Swiss Light Source (SLS).

Since it has been suggested that some organic compounds have the potential to modify the structure of water that influences the nucleation of ice, we have measured electron yield NEXAFS spectra from a liquid jet of aqueous solution containing tetrabutylammonium bromide (TBAB). The O K-edge NEXAFS spectra of these organic solutions exhibit a clear change in the relative features. These features represent hydrogen bonding at different level, indicating that the cationic head group of TBAB induces a significant variation of the hydrogen bonding network near the surface of the aqueous solution.

On the other hand, the hydrogen bonding structure of adsorbed water on a solid substrate may control deposition nucleation, which is another pathway of heterogeneous ice nucleation. The hydrogen bonding structure may be affected by short and long range interactions between the substrate and the adsorbed water molecules. As a first approach, we have measured electron yield NEXAFS spectra of adsorbed water on graphite and titanium dioxide (TiO<sub>2</sub>) under subsaturated conditions with respect to ice. Under isobaric conditions and by varying the temperature of the sample, we can change the relative humidity, which leads to varying amounts of adsorbed water in equilibrium between the substrate and water vapor. Preliminary results show that, under different relative humidity, the weakly and strongly coordinated OH bond of adsorbed water on TiO<sub>2</sub> and graphite show different contributions to the Auger electron yield NEXAFS spectrum, that is, the resonant transitions near the oxygen K-edge vary with relative humidity and temperature. We attribute this to the modification of the organization of water molecules in response to the interactions with the solid substrate. In view of the application of the NEXAFS technique, we believe it opens up a powerful tool to address the surface science of ice nucleation in the future.

### Significance statement

Investigation of organic compounds which have the potential to modify the structure of water that influences the nucleation of ice, and the water adsorption on solid substrates that shows ice like structure.

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**Presenter:** Mr YANG, HUANYU (Paul Scherrer Institut)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 157

Type: **Poster**

## **Brittle and Elastic Ice Shelves: Coupling fracture and wave propagation**

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Distant storms, tsunamis, and earthquakes generate waves in floating ice shelves. In several instances, seismic observations have clearly demonstrated a mechanistic link between periods of elevated wave activity and iceberg calving. The detailed mechanical interpretation of observed seismograms is complicated, however, by the existence of numerous types of waves that propagate in the coupled ice–ocean–earth system. Here, I describe wave propagation in an elastic, finite-thickness, buoyantly floating ice layer above a uniform and inviscid water layer. I place particular focus on waves with wavelength greater than the ice thickness, as have recently been observed on the Ross, Pine Island, and Amery Ice Shelves. I show that mode uncoupling occurs at long period such that waves occur as either symmetric or flexural modes. I calculate the stresses associated with the seismically observed wave field on the Ross Ice Shelf. In the second part of this work, I place these stresses the context of linear elastic fracture mechanics. I show that long rifts in buoyantly floating ice shelves experience stabilization due to the inability of a thin elastic layer to effectively transmit stresses over long distances. I derive a rift tip equation of motion that shows excellent agreement with observed rift tip propagation velocities. The theory presented here paves the way to an improved depiction of ice shelf calving in predictive ice sheet models.

### **Significance statement**

Ice shelves provide a net resistive force to grounded ice sheets and therefore permit a greater terrestrial ice volume than would be possible in their absence. Ice shelves are limited in extent by 100 km long fractures called rifts. This work explores the formation and propagation of these rifts.

**Primary author:** Dr LIPOVSKY, Bradley Paul (Harvard University)

**Presenter:** Dr LIPOVSKY, Bradley Paul (Harvard University)

**Session Classification:** Poster & Lunch

Contribution ID: 158

Type: **Poster**

## The heterogeneous formation process of clouds below 150K

*Wednesday, January 10, 2018 6:10 PM (3h 5m)*

Heterogeneous H<sub>2</sub>O nucleation studies below 150K are rare, but important to understand the formation of cold ice clouds in terrestrial atmospheres, e.g. polar mesospheric clouds on Earth or water ice clouds on Mars. We use a time-of-flight mass spectrometer to study H<sub>2</sub>O adsorption, critical saturation and subsequent growth on sub 4nm iron oxide and silica particles levitated in a modified ion trap where the particles are exposed to a well-defined H<sub>2</sub>O supersaturation between 125K and 150K. In this contribution, we determine the binding energy/desorption energy of water molecules on the particle material, which allows us to parameterize the amount of water molecules which are adsorbed on a surface as function of temperature and saturation. In addition, we are able to evaluate for the temperature dependent sublimation flux of water molecules from the particle and conclude that the deposited ice polymorph is amorphous solid water (ASW). We show that for all temperatures under investigation, H<sub>2</sub>O growth is activated as soon as the equilibrium saturation over the curved particle surface including the amount of adsorbed water molecules (Kelvin effect) is exceeded. We present a method to predict critical saturations needed for cloud formation below 150K.

### Significance statement

We present measurements of H<sub>2</sub>O adsorption, critical saturation and growth on small nanoparticles below 150K in order to understand the formation of cold ice clouds. We show that ASW is deposited as soon as the equilibrium saturation over the particle surface including the amount of adsorbed water molecules is exceeded.

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**Presenter:** Mr NACHBAR, Mario (Institute of Environmental Physics, University of Heidelberg)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)



Contribution ID: 159

Type: Poster

## Structural change of amorphous ice with warming

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Water exists as amorphous ice in interstellar molecular clouds. Because molecules undergo chemical evolutions through various processes on amorphous ice, the structure and properties of amorphous ice is one of the important factors govern the chemical evolutions of organic molecules in the universe. Amorphous ice is formed by various methods; vapor deposition of water on cold substrates under vacuum, droplet quenching of liquid water, pressurization of crystalline ice Ih, and matrix sublimation method [1]. The formation process of the deposition method is similar to the situation of amorphous ice formation in interstellar molecular clouds. The amorphous ice is mainly classified into two types: low-density amorphous (LDA) and high-density amorphous (HDA) ice, although the structure and properties dependent on formation conditions and thermal history. In the present study, to investigate the structural change of amorphous ice with warming, we measured infrared spectra and performed molecular dynamics (MD) calculations.

Amorphous ice was prepared with vapor deposition of distilled and degassed water on a substrate of oxygen-free copper at 42 K. The total pressure in the vacuum chamber was kept at about  $3.5 \times 10^{-5}$  Pa during the deposition. After the deposition of amorphous ice, the substrate was warmed to 180 K with a rate of 2 K/min. The IR spectra were measured using Shimadzu IRPrestage-21 at 2 K intervals during warming.

Because several peaks exist in the IR spectra in the region of the O–H stretching band (2800–4000  $\text{cm}^{-1}$ ), the peak positions were analyzed by fitting the data using five Gaussian functions. For four modes in the lower wave numbers are assigned to the in-phase mode of the O–H symmetric stretching, TO and LO modes of the O–H asymmetric stretching, and out-of-phase mode of the O–H symmetric stretching [2]. The mode at the highest wave number is assigned to less coupled H<sub>2</sub>O [3]. The result shows that the vibrational frequency of the five modes discontinuously change at around 110 K. To analyze the detailed structural change without effects of thermal expansion and pore collapse, the IR spectra of the annealed samples at a temperature in 50 – 150 K were measured. The result shows that the vibrational frequencies of the five peaks significantly change at around 80 – 120 K. This indicates that the HDA ice is transformed into LDA ice via few types of intermediate structures in 80 – 120 K. The existence of the intermediate structures was also confirmed from the MD result.

### References

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### Significance statement

To investigate the structural change of amorphous ice with warming, we measured infrared spectra and performed molecular dynamics calculations. The result show the HDA ice is transformed into LDA ice via few types of intermediate structures.

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**Presenter:** Mr KINJO, Akimichi (Department of Applied Chemistry, Meiji University, Japan)

**Session Classification:** Poster & Lunch

Contribution ID: 160

Type: PICO talk

## The self-preservation effect in CO<sub>2</sub> clathrate hydrates at low driving forces

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Clathrate hydrates of CO<sub>2</sub> are crystalline inclusion compounds composed of CO<sub>2</sub> and water. They are expected to occur in vast amounts on comets, icy moons, and the Martian ice caps, where they play a significant role in the planetology. On earth, they are considered for usage in carbon capture and storage technologies due to their high mass density of CO<sub>2</sub> [1,2].

Particularly, in the case of carbon storage good knowledge of stability conditions is crucial. Although equilibrium temperatures and pressures are well known and can be modeled with high accuracy [3], decomposition kinetics of some clathrate hydrates, including CO<sub>2</sub> clathrate hydrates, show an anomaly called “self-preservation”. Self-preservation refers to the clathrate hydrates ability to protect itself from decomposition by showing strongly reduced dissociation rates when placed outside the stability region. This is best seen in rapid depressurization experiments, where the clathrate hydrate is forced isothermally from stable pT-conditions to unstable pressures within seconds [1]. The formation of a protecting ice shield after an initial phase of dissociation is a popular hypothesis to explain this phenomenon [1]. However, until today there is no complete model which could explain the variety of pT-conditions for self-preservation as well as its dependence on particle size, clathrate preparation method, and experimental apparatus.

In contrast to generally high driving forces in rapid depressurization experiments, here we studied the self-preservation effect at very low driving forces in temperature-ramping experiments in a closed system. Samples with diameters of 0.5-2 mm were produced following a CO<sub>2</sub>-H<sub>2</sub>O vapor deposition process as described by Mitterdorfer et al. [4], and stored in liquid nitrogen afterwards. They were then loaded into a precooled sample cell containing dry nitrogen gas at 203 K and barometric pressure. The cell was tightly closed, and the pressure was monitored. After an initial waiting period at 203 K an equilibrium CO<sub>2</sub> partial pressure of approximately 200 mbar was attained by gas release of the decomposing clathrate hydrate. Subsequent heating of the sample at a rate of 1 K/min resulted in further dissociation. Gas release rates were high enough to attain equilibrium pressures at all temperatures until a significant decrease in gas release rates indicated the advent of self-preservation conditions. Remarkably, these conditions were found at several different temperatures in the range of 230-250 K corresponding to the sample size. That is, the larger the sample, the higher the temperature at which the gas release rate dropped to zero. Complete decomposition of the samples between 270-273 K showed that only about 10 wt% of the initial clathrate mass survived until melting. This is in contrast to the results obtained by Circone et al. [2], where 80 wt% of the clathrate hydrates survived until 270 K in similar experiments.

[1] Falenty et al., J. Phys. Chem. B, (2009)

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[4] Mitterdorfer et al., Phys. Chem. Chem. Phys. (2011)

### Significance statement

Our results show the existence of the self-preservation effect at low driving forces. Furthermore, a particle size dependence of the self-preservation effect in CO<sub>2</sub> clathrate hydrates, not in accordance with the general notion that larger particles exhibit stronger self-preservation, was observed.

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**Co-authors:** Prof. OSTERMANN, Alexander (University of Innsbruck); Dr PETRASCH, Joerg (Illwerke VKW Professorship for Energy Efficiency, Vorarlberg University of Applied Sciences); Dr RAHMATIAN, Nima (Vorarlberg University of Applied Sciences); Prof. LOERTING, Thomas (Institute of Physical Chemistry, University of Innsbruck)

**Presenter:** Mr ARZBACHER, Stefan (Illwerke VKW Professorship for Energy Efficiency, Vorarlberg University of Applied Sciences)

**Session Classification:** Poster & Lunch

Contribution ID: 161

Type: **Poster**

## Location and composition of micro-inclusions in deep ice from the EDML ice core (Antarctica) using optical microscope and cryo-Raman spectroscopy.

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

The impurity content in meteoric ice from polar regions is relatively low compared to other natural materials. However, it controls a variety of physical properties of ice - from dielectric response to its mechanical behaviour. Links between impurity concentration, changes in ice micro-structure and deformation rate have been reported on several scales. In order to approach the responsible mechanisms, a better understanding is needed regarding the in-situ form, location, and distribution of the different species within the polycrystal.

We used an optical microscope to generate high-resolution 2D-maps of micro-inclusions in deep ice from the EDML ice core (Antarctica). Superposition of the grain boundary network and micro-inclusion distributions shows no significant correlations between grain boundaries and micro-inclusions. Implications for the relevance of Zener pinning during grain boundary migration and redistribution of impurities by grain boundary drag are discussed. Raman spectra of micro-inclusions in selected regions were obtained using a confocal cryo-Raman system. Comparison with ion chromatography shows that most of the available ions in ice precipitate in form of micro-inclusions. However, indications were found that some of the residual components could coexist in form of solid solution.

### Significance statement

Ice cores serve as archives of atmospheric aerosols from the past. Furthermore, these impurities control physical properties of ice in polar ice sheets. A better understanding of impurity-related processes on micro- and nano-scale is needed to properly model ice flow.

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**Presenter:** Mr EICHLER, Jan (Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research)

**Session Classification:** Poster & Lunch

Contribution ID: 162

Type: Poster

## EBSD analysis of subgrain boundaries and dislocation slip systems in Antarctic and Greenland ice

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Ice has a very high plastic anisotropy with easy dislocation glide on basal planes while glide on non-basal planes is much harder. Basal glide involves dislocations with Burgers vector  $b=\langle a \rangle$ , while glide on non-basal planes can involve dislocations with  $b=\langle a \rangle$ ,  $b=\langle c \rangle$  and  $b=\langle c+a \rangle$ . During natural ductile flow of polar ice sheets most of the deformation is expected to occur by basal slip accommodated by other processes including non-basal slip and grain boundary processes, however the importance of different accommodating processes is controversial. The recent application of micro-diffraction analysis methods to ice such as X-ray Laue diffraction [1] and electron backscattered diffraction (EBSD) [2] has demonstrated that subgrain boundaries indicative of non-basal slip are present in naturally deformed ice, although, so far the available data sets are limited. In this study we present an analysis of a large number of subgrain boundaries in ice core samples from one depth level from two deep ice cores, from Antarctica (EPICA-DML deep ice core at 656 m depth) and from the Greenland (NEEM deep ice core at 719 m depth).

EBSD provides information for the characterization of subgrain boundary types and on the dislocations that are likely to be present along the boundary. EBSD analyses, in combination with light microscopy measurements, are presented and interpreted in terms of the dislocation slip systems [3]. The most common subgrain boundaries are indicative of basal  $\langle a \rangle$  slip, with an almost equal occurrence of subgrain boundaries indicative of prism  $\langle c \rangle$  or  $\langle c+a \rangle$  slip on prism and/or pyramidal planes. A few subgrain boundaries are indicative of prism  $\langle a \rangle$  slip or slip of  $\langle a \rangle$  screw dislocations on the basal plane. In addition to these classical polygonization processes that involve recovery of dislocations into boundaries, alternative mechanisms are discussed for the formation of subgrain boundaries that are not related to the crystallography of the host grain.

The finding that subgrain boundaries indicative of non-basal slip are as frequent as those indicating basal slip, is surprising. Our evidence of frequent non-basal slip in naturally deformed polar ice core samples has important implications for discussions of crystal plasticity descriptions for ice, on rate-controlling processes which accommodate basal glide and on subsequent discussions of anisotropic ice flow descriptions of large ice masses, with the wider perspective of sea-level evolution.

[1] doi: 10.3189/002214311795306628

[2] doi: 10.1111/j.1365-2818.2010.03471.x

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### Significance statement

The potential significance of non-basal dislocations in natural ice shown for the first time in 2011 [1] is confirmed by this study on a large number of subgrain boundaries in ice core samples from both poles' ice sheets.

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**Presenter:** Mr EICHLER, Jan (Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research)

**Session Classification:** Poster & Lunch

Contribution ID: 163

Type: **Poster**

## Calorimetric determination of the unfrozen water content in glacier ice

*Tuesday, January 9, 2018 12:35 PM (1h 30m)*

Glacier ice at the melting temperature may contain up to 6% of unfrozen water, as was inferred with indirect methods such as ice-penetrating radar. This inter-grain water influences ice deformation, the thermal structure of ice sheets, and subglacial hydrology.

We determined by the content of free water in-situ in ice caves and at the base of several temperate glaciers. The calorimeter consists of an active cooling system in a central borehole and a set of thermistors which are placed in several distances from the center. We thus measure the velocity of the freezing front as well as the cooling rates. With help of a 3D finite element heat flow model synthetic freezing curves are obtained for various initial water contents. Matching these synthetic curves to the measurements yields in-situ water contents between 0 and about 3% in basal ice. These values confirm the indirectly derived free water contents within the ice matrix of Alpine glaciers.

### Significance statement

We present unique in-situ measurements of free water within the ice matrix of Alpine glaciers.

**Primary author:** Dr LUETHI, Martin (University of Zurich, Geography)

**Presenter:** Dr LUETHI, Martin (University of Zurich, Geography)

**Session Classification:** Poster & Lunch



Contribution ID: 164

Type: **keynote**

## Ice surface chemistry studied by core level spectroscopy

*Tuesday, January 9, 2018 4:55 PM (45 minutes)*

Ice surfaces play a major role in many environmental processes and heterogeneous chemical reactions in the atmosphere. The properties of ice surfaces under environmental and atmospheric conditions, in particular the presence of a liquid-like layer at the ice surface at temperatures close to the melting point, are still far from being understood. For instance, reported thicknesses of the liquid-like layer at temperatures close to the melting point vary widely. This might partly be due to the influence of adsorbates, which most likely alter the onset temperature for pre-melting. The interaction of trace gases with ice has also attracted considerable attention over the past decades due its relevance for atmospheric and polar chemistry. Core level spectroscopies such as X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy are promising tools to investigate simultaneously the surface chemistry and premelting transition at ice surfaces. While NEXAFS is highly sensitive to small changes in the structural order at the ice surface, XPS is well suited for the characterization of the chemical composition of the ice surface, including the presence of adsorbates and reaction products. In this presentation we will discuss the current status of XPS and NEXAFS measurements of ice surfaces and give an outlook on future opportunities for core-level spectroscopy-based research of the heterogeneous chemistry of ice.

### Significance statement

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**Primary author:** BLUHM, Hendrik (Lawrence Berkeley National Laboratory)**Presenter:** BLUHM, Hendrik (Lawrence Berkeley National Laboratory)

Contribution ID: 165

Type: Poster

## Depth Profiles of Solutes at the air-ice Interface

Wednesday, January 10, 2018 6:10 PM (3h 5m)

The pre-melting at the surface of ice crystals in surface snow or ice clouds has been proposed to explain a number of large-scale environmental effects ranging from electrification of thunder clouds and the scavenging of atmospheric trace gases to the flow of glaciers<sup>1</sup>. There is now general agreement on the appearance of this quasi-liquid layer (QLL) when temperatures approach the melting point and on its enhancement in presence of impurities<sup>2</sup>. In particular, McNeill showed that the extended quasi-liquid layer increases the solubility of trace gases leading to a larger capacity for scavenging from the gas-phase and that it accelerates chemical reaction rates of atmospheric importance<sup>3</sup>. While this is an eminent example of how anthropogenic emissions can alter the properties of clouds and surface snow, the precise on-set temperature of this impurity induced QLL, its properties and extend remain controversial.

Here, we present experimental results directly showing how deep a number of formic acid, nitric acid, and hydrochloric acid enter the upper few nanometre of the air – ice interface and to which extend their presence is accompanied by the formation of a QLL. These findings using a combination of near ambient pressure X-ray photoelectron spectroscopy (XPS) <sup>4,5</sup> and partial electron yield near edge X-ray absorption fine structure (NEXAFS) <sup>4,5</sup> spectroscopy reveal that the ability of these acids to induce a QLL is a function of temperature and scales with room temperature solubility. Direct comparison of the thickness of the QLL as interfered by the NEXAFS measurements with the depth of the acids within the QLL indicate that the QLL is not a homogeneous layer. Rather, we propose that the acids induce solvation shells in their vicinity. The observed extend of QLL, or hydration shell formation, is then a balance of the individual acid's water demand to satisfy their hydration needs and the liquid-like properties of the ice surface which is a function of temperature and impurity content. Further, the dissociation degree of acids in the QLL is discussed.

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Further information:

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### Significance statement

Overall, this study shows how trace gases can alter the properties of ice and snow on a molecular level in the Anthropocene with implications for multiphase chemistry, nucleation, and physical

properties of surface snow and ice clouds.

**Primary author:** BARTELS-RAUSCH, Thorsten (Paul Scherrer Institut)

**Presenter:** BARTELS-RAUSCH, Thorsten (Paul Scherrer Institut)

**Session Classification:** Poster Session & Apéro Riche (apéro dîner)

Contribution ID: 166

Type: **not specified**

## **Snow and Ice Chemistry: Motivations and Key Questions**

*Thursday, January 11, 2018 10:30 AM (20 minutes)*

**Presenter:** Dr HULLAR, Ted (University of California at Davis)