ESRF	**Experiment title:** Revisiting water phase diagram to better constrain extraterrestrial habitability: in-situ single crystal X-ray diffraction of ices II, III and V.	**Experiment number**: ES-640
Beamline: ID15b	**Date of experiment**: from: 21/02/2018 to: 25/02/2018	**Date of report**: 1/03/2018
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Scientific background

The study of water-rich planetary bodies like icy moons (e.g. Europa, Ganymede, Titan), trans-neptunian objects (e.g. Pluto, Charon) or water-rich exoplanets is the next frontier in planetary exploration. This momentum is being mainly built by the astrobiology potential of these bodies that could host a global liquid water ocean, possibly sandwiched between high-pressure ices. Nevertheless, very few basic physical properties are known on the high-pressure ice polymorphs (elasticity, PVT-EOS, solute incorporation), which represent an important constraint on accurate interior modelling and data interpretation of space missions. Furthermore, recent experimental work has shown that salts (e.g. NaCl, LiCl, RbI) and small volatile molecule (CH_3OH) are moderately incompatible with ice VI and VII, and can be incorporated up to few mol/kg. The behaviour of T<300K high-pressure ices toward solute incorporation remains yet unexplored. We therefore proposed to perform (i) accurate *in-situ* single crystal X-Ray diffraction refinement of their structure for pure water and for NaCl and $MgSO_4$ aqueous solutions, (ii) acquire multiple data points in a 220 to 290K and 0.2 to 0.65 GPa range to constrain the thermal equations of states of pure and NaCl and $MgSO_4$ salty ice II, III and V at conditions relevant for planetary science.

Experimental procedure

Pure H_2O (MiliQ), along with ruby spheres (pressure gauge), were loaded in low temperature HP diamond anvil cells (DAC) from the ESRF pool. The DAC was then mounted inside the cryostat on ID15b beamline. The pressure was then rose using an automated membrane pressure controller, and the temperature was slowly decreased (~2.5K/min) to reach the stability field of different ice polymorphs (ice III, V, and VI).

Ice polymorph formation proved to be more difficult than initially thought, especially for ice III, because of very important supercooling effect (up to 50-70K). Often another phase was reached because of too low temperature or variation of the membrane pressure due to the temperature variation in the membrane capilary. Nevertheless, we were able to from ice Ih, II, III, V and VI, for which both powder diffraction and single crystal acquisitions were obtained, as well as a few melting points for calibration. Pressure was then measured using ruby fluorescence and temperature was read from the cryostat control system. Corrections for both pressure and temperatures were applied based on the measured melting points.

Due to the challenging formation of certain polymorphs, the time necessary to select ice single crystals that can only be grown in-situ in DACs, and the necessity to obtain many accurate pure H_2O data at this range, we were not able to study the NaCl-H_2O or $MgSO_4$-H_2O systems, as initially planned.

Preliminary results

We were able to obtain accurate volume data points for ice III, V and VI along several isotherms (more than 100 data points) which will enable the determination of accurate P-V-T equations of state for all these polymorphs (example for ice III in fig. 1). It should be underline that it is the first time that ice III, ice V and ice VI have been measured in-situ at T < 300K with so many data points and also using single-crystal diffraction to resolve their structure. There is no doubt that these results will have a strong impact in the planetary science community and serve as a solid base for future measurements including ice polymorphs growing in equilibrium with salts.

We also report the measurement of potential new phases of orthorhombic H_2O ice polymorphs. These have different lattice parameters from reported structure of both stable and metastable structures in this range of pressure and temperature (ice Ih, II, III, IV, V, VI & XII). Powder and single crystal diffraction measurement where obtain for those and their structure are going to be refined.

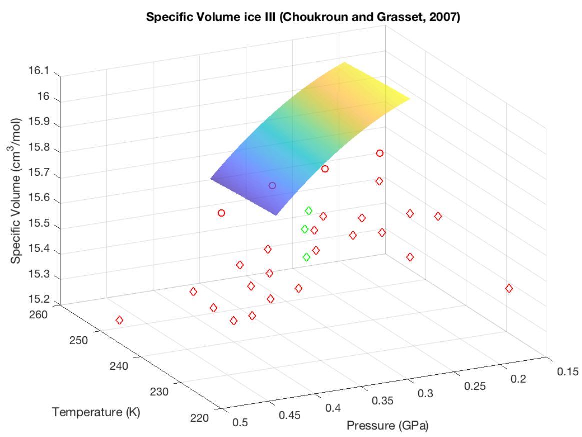

Figure 1 : Examples of volume data for ice III . Our data (red diamonds) are in very good agreement with the few data points from Bridgman (1912) (red circles) and Londono (1993) (green diamonds). The colored surface is from the theoretical volumes from Choukroun and Grasset (2007) and show the large discrepancies with experimental data, as well as unrealistic compression behavior (negative bulk modulus).

References

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