Experimental report

30/10/2025

Proposal: **6-07-117** **Council:** 4/2023

Title: Phase diagram of water confined inhydrophilic mesoporous silica: Effects of pore filling and pore size at high pressures.

Research area: Materials

This proposal is a new proposal

Main proposer: **Christiane ALBA SIMIONESCO**

Experimental team: Florence PORCHER
Oriana OSTA RANGEL
Thomas MARESCOT
Christiane ALBA SIMIONESCO

Local contacts: Viviana CRISTIGLIO

Samples: SiO_2 mesoporous + D_2O

Instrument	Requested days	Allocated days	From	To
D16	7	7	14/11/2023	20/11/2023
			08/03/2024	11/03/2024

Abstract:

With this experiment, we will formally assess the question of the melting transition line of D_2O in hydrophilic confinement under pressure, and its relationship with the crystalline form of ice. We will study two factors that might have a great influence in the crystalline phases formed: the dynamics of intrusion and the pore size.

The aim of this study is to investigate the phase diagram of water when confined within a hydrophilic matrix. The primary objective is to evaluate the validity of the Gibbs-Thomson equation under high pressure using slow compression.
To achieve this, we conducted experiments over a total of ten days: seven days were attributed in November 2023 and three additional days in March 2024, because of few experimental problems resolved by the ILL support and the local contact. Water was confined within two different samples: a SBA-15 (D~ 6 nm) and a MOF a metal-organic framework with well-defined porosity. These materials were selected for their distinct structural and surface properties, enabling a comparative analysis of confined water behavior, and fully characterized in our lab.

To explore the phase diagram of confined water under pressure, two different compression methods were employed requiring a long installation time and calibration:

1. Gas Compression with Helium: A pressure bench utilizing helium gas was used to ensure uniform compression across all samples. Helium was selected due to its small molecular size, which allows efficient pressure transmission within the porous matrix.
2. Liquid Compression: In this method, pressure was increased by adding more water to the sample.

The two compression modes provided by the SANE group (James MAURICE, Pascal MOUVEAU) allow comparing different confined water P-T phase diagrams. We monitored various thermodynamic paths: i- an isotherm at Troom increasing pressure up to 4kbar, and ii- several isobars between 0-2kbar in a T range of 295–180 K. Then these diagrams are then compared to bulk water.

The collected data covered a scattering vector range of 0.05–2.5 $Å^{-1}$ with two detector positions. Accordingly we could focus, on one side, on the structure of the matrices, (0.05–1 $Å^{-1}$, used to study the impact of filling and pressure on the structure of the matrices), and on the other side, at higher Q's (1–2.5 $Å^{-1}$) on the changes of the confined water and external water surrounding the sample and ensuring the compression. The raw data were first processed and subsequently analyzed through fitting procedures and Rietveld refinement. This allowed us to track variations in the matrix peaks at low Q for the SBA and follow the evolution of the structure of the MOF. After background subtraction, these intensity variations of the peak of the SBA were used to calculate the density of confined water and assess the impact of pressure on compressibility. Contrast matching was performed using the differences in scattering length densities between D_2O and SiO_2.

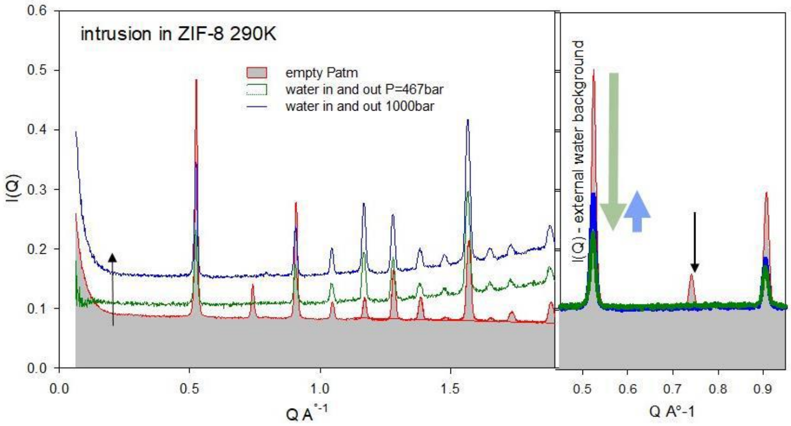

Figure 1: Structural changes of ZIF-8(MOF) during the Water intrusion process at room temperature. As pressure increases, the amount of water in the cell around the material increases leading to an increase of background and the structure of free water can be seen close at higher Q's. When water enters the pores, then the Bragg peak intensities of ZIF8 are modified: In red, structure of the crystalline ZIF-8, empty; in green just above the intrusion pressure water inside and outside the pore, the intrusion is indicated by the change in intensity of several peaks (see zoom); in blue at higher pressure. The crystalline structure of the material is strongly affected as well (disappearance of peaks, and special Tdependence not shown here)

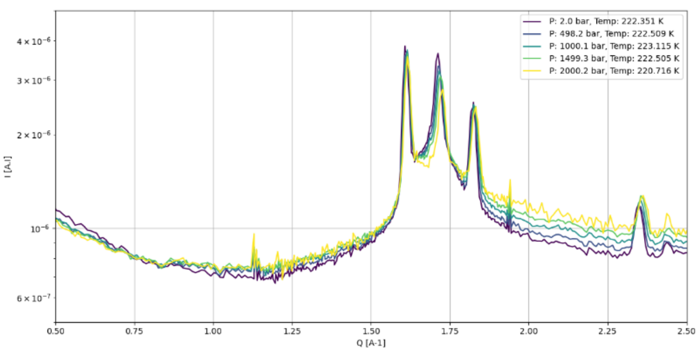

Figure 2 : Water Ice (Isd) under high pressure in a SBA15 of pore diameter of 6nm with gas compression

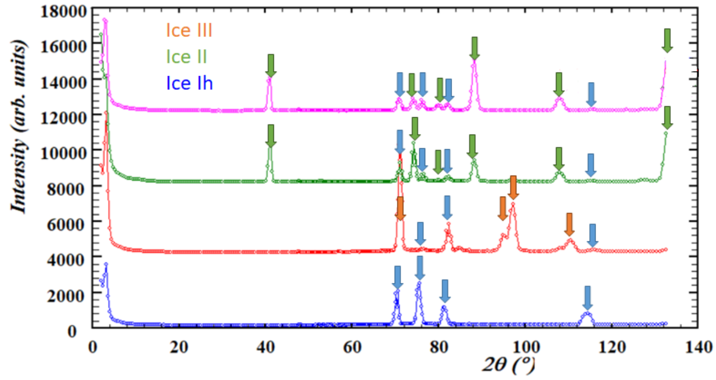

Figure 3 : Water Ice under high pressure in a SBA15 of pore diameter of 6nm with liquid compression