Experimental report

30/09/2016

Proposal:	**INTER-311**	**Council:**	4/2015
Title:	Internal time on D4		
Research area:			

This proposal is a new proposal

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Experimental team:	Annalisa POLIDORI
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Samples: MgSiO3

Instrument	Requested days	Allocated days	From	To
D4	4	4	05/11/2015	09/11/2015

Abstract:

Characterization of a Ti-Zr pressure cell to investigate the structure of D_2O-NaCl via NDIS

Fluids as H_2O-NaCl and H_2O-CO_2 are commonly encountered in geological environments and are used in many industrial processes and chemical environmental engineering, including the use of CO_2 for enhanced oil and gas recovery, and CO_2-sequestration by mineral trapping. There is, however, a paucity of experimental information on the structure of these fluids at high pressure and temperature, which is a prerequisite for their understanding. Neutron diffraction with isotope substitution (NDIS) is a powerful method that can be used to investigate the structure of these systems under geological conditions.

A setup to perform experiments on the D_2O-NaCl system has been assembled on the D4c diffractometer at the ILL, and is shown in Figure 1. During the Exp.-No.6-02-547 we investigated

(i) water with H/D substitution spanning the phase-diagram over a pressure range from ambient to 0.2 GPa, and temperatures up to 150˚C,

(ii) The D_2O-NaCl system with ^{37}Cl-isotope substitution, up to 0.1 GPa and 150˚C.

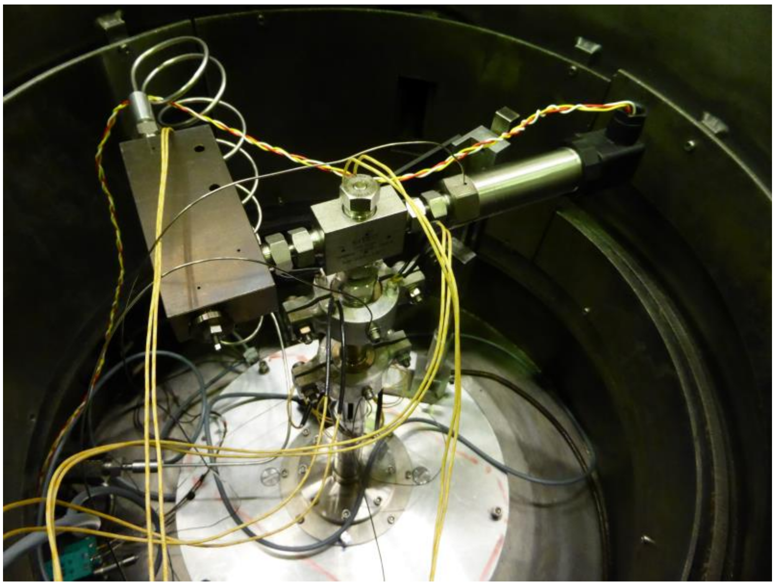

Figure 1 View of the D4c belljar once the setup is mounted. The neutron absorbing flags, made of B4C shield the setup by collimating the incident neutron beam. The orientation of the flags is kept constant for the different measurements. The separator is rotated horizontally and is connected to a pig-tail high pressure capillary. The cell is mounted on the candle stick, the heating-clamps are connected at the two ends, and the yellow wires of the cartridge heaters are suspended far from the can. The pressure transducer is to the right of the cross-union, while the separator is placed in a horizontal position and is connected to a pig-tail high pressure capillary to the left.

The setup worked well, but the data analysis, at a first order difference function $\Delta F(Q)$ level, revealed that we needed a better characterisation of the dependence of the background on the orientation of the clamps, in order to be sure that our samples were not affected from H/D exchange due to air-exposure of the sample while loading the cell. We thought in fact, that a small difference in the orientation of the clamps during the two measurements, as shown in Figure 2, might have given a different contribution to the diffraction patterns, similarly to the effect of a wrong ratio of H/D in the sample. The doubt arose from a discrepancy between the total structure factors $^{Nat}F(Q)$ for the D_2O-Na^{Nat}Cl sample and $^{37}F(Q)$ for the D_2O-Na^{37}Cl sample, in the range between 20-22 Å^{-1}, as shown in Figure 3. We therefore used the internal beam-time to characterise the background as a function of the orientation of the clamps as respect to the flags.

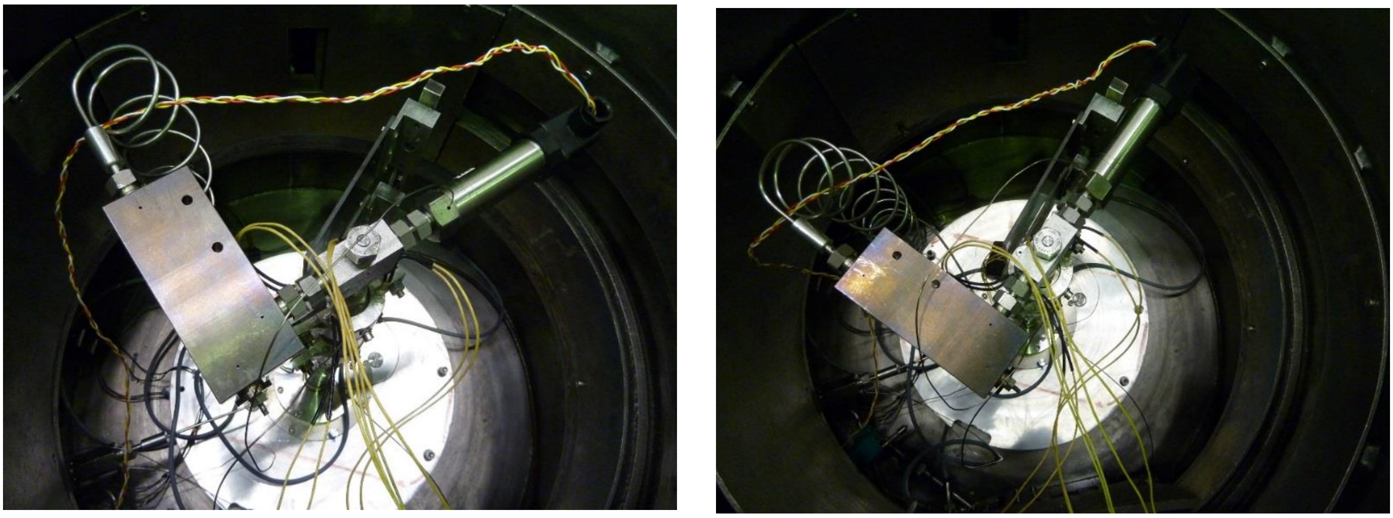

Figure 2. The different orientation of the clamps as respect to the flags during the measurements for D_2O-$Na^{Nat}Cl$ and D_2O-$Na^{37}Cl$, respectively. Note, in Figure 1, that the clamps are oriented in the same direction as the pressure transducer.

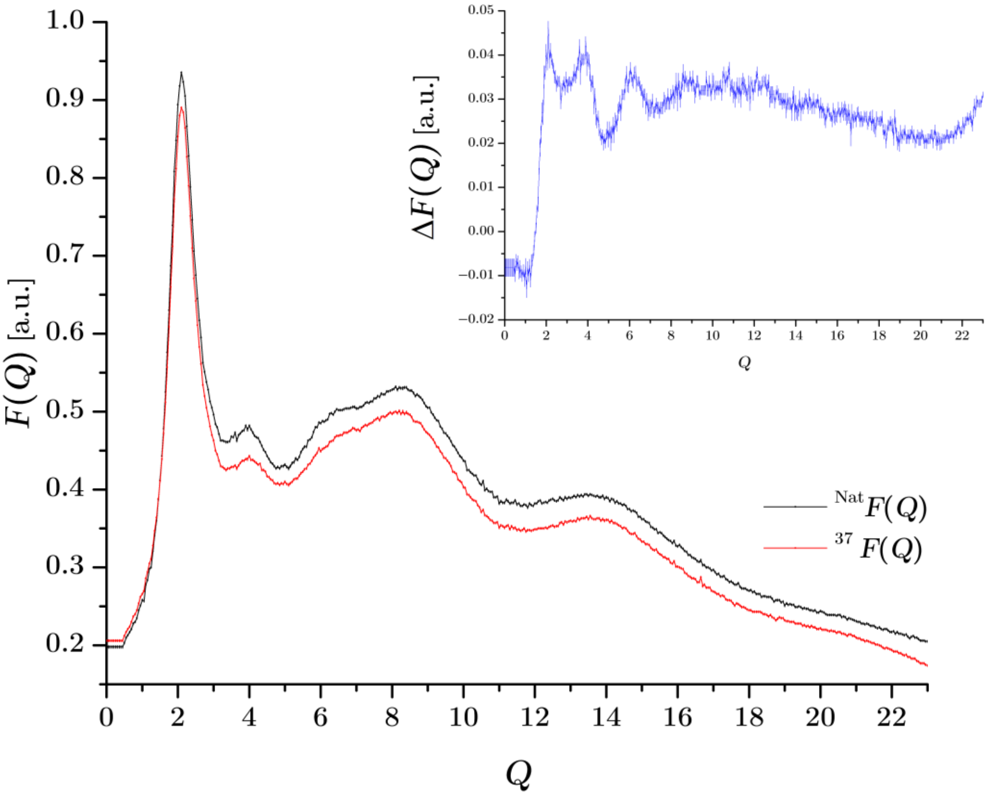

Figure 3 The total structure factors $^{Nat}F(Q)$ for the D_2O-$Na^{Nat}Cl$ and $^{37}F(Q)$ for the D_2O-$Na^{37}Cl$ samples. In the inset the first order difference function $\Delta F(Q)$ obtained by the subtraction of the two $F(Q)$ is shown .

During the internal beam-time on D4c INTER-311 we measured the empty Ti-Zr cell with the clamps oriented in two different positions, similarly to what happened during the experiment. In Figure 4 the two diffraction patterns we obtained are presented in reciprocal space. These show a difference in the intensity in the range between 20-22 Å^{-1}. Also, the difference between the two diffraction patterns has a shape very similar to the first order difference function $\Delta F(Q)$ shown in the inset in Figure 3.

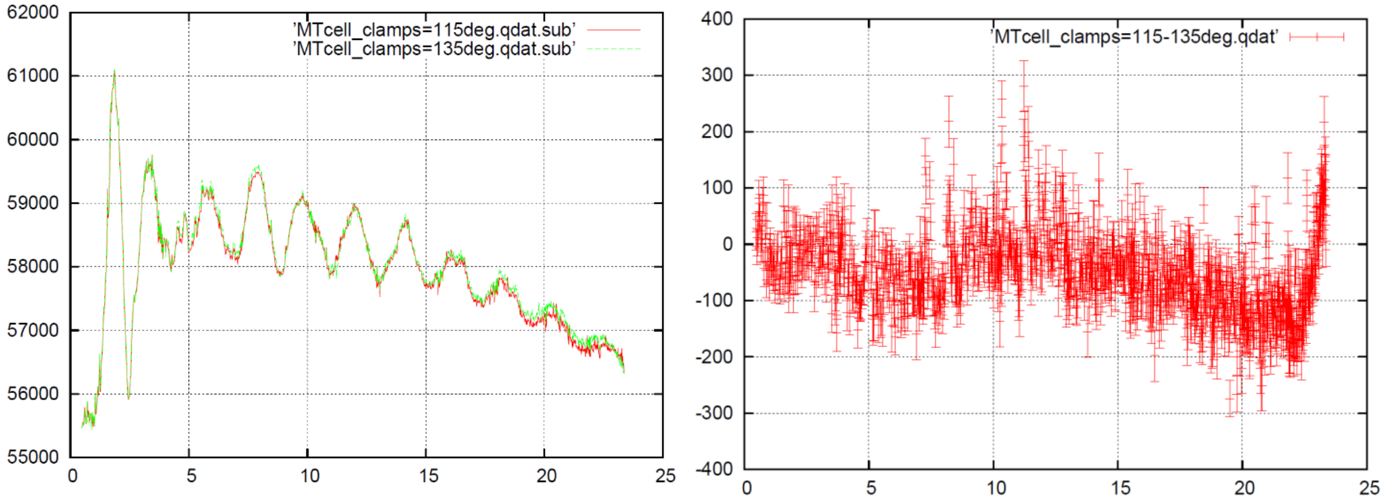

Figure 4. On the left: the diffraction patterns, in reciprocal space (in arbitrary units), for the empty cell measured with the clamps in two different orientations, after the background has been subtracted. On the right: the difference between the diffraction patterns on the left.

We then filled the cell with H_2O and the two diffraction patterns measured were obtained by placing the clamps in the most reproducible positions than those used for the empty measurements. The difference between the measured diffraction patterns is shown in Figure 5a, and clearly confirms that the tail in the range between 20-22 Å^{-1} is due to the difference in the orientation of the clamps. Therefore, we could confirm that our data are not affected by a contamination of the sample, but also that having a fixed orientation of the clamps is crucial. Figure 5b shows that if the data for H_2O are corrected by using the empty cell measurements with the right orientation of the clamps, the tail do not appear.

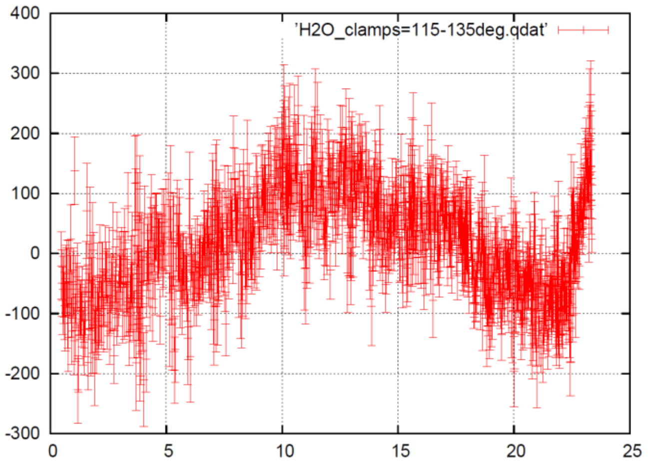

Figure 5a. Difference between the diffraction patterns measured for the cell filled with H_2O, with two different orientation of the clamps. The data are shown in reciprocal space and arbitrary units.

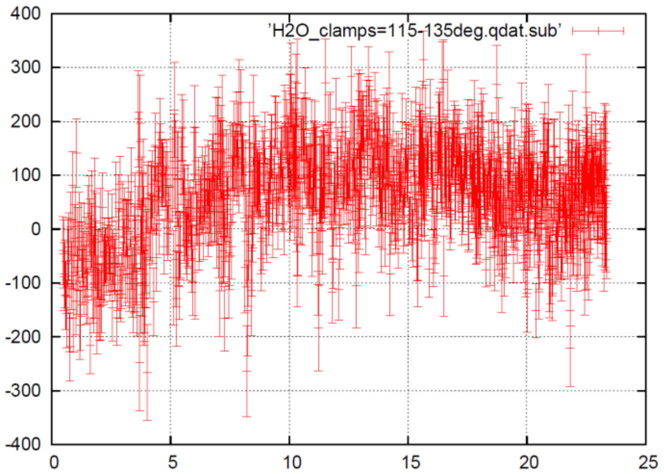

Figure 5b. Difference between the diffraction patterns measured for the cell filled with H_2O, with two different orientation of the clamps, but after the empty-cell measurement has been subtracted. The data are shown in reciprocal space and arbitrary units.