



	<b>Experiment title:</b> Microscopic structure of water, D <sub>2</sub> O and aqueous NaCl solution at negative pressure	<b>Experiment number:</b> SC-5214
<b>Beamline:</b> ID20	<b>Date of experiment:</b> from: 26/10/2021 to: 31/10/21	<b>Date of report:</b>
<b>Shifts:</b> 6	<b>Local contact(s):</b> Christoph Sahle	<i>Received at ESRF:</i>
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### Report:

In this experiment, we aimed to test the feasibility of extracting the oxygen K-edge of water within a fluid inclusion (FI) from the signal of the surrounding quartz (SiO<sub>2</sub>) to study the microscopic structure of water under the influence of negative pressure. Thus, we performed X-ray raman scattering (XRS) measurements at the oxygen K-edge and silicon L-edge and extensively exploited the imaging capabilities of this experimental technique. Negative pressures can be applied by enclosing the water in a FI within a quartz matrix and cooling it to low temperatures after it has been brought in a metastable state with respect to vapor. The study of liquid water at negative pressure may have the potential to indirectly verify or falsify the hypothesized occurrence of two phases of liquid water along with the existence of a liquid-liquid critical point by examining the maxima of isothermal compressibility and density [*P. Gallo, et al., Chem. Rev. 116, 7463 (2016)*]. Two different quartz samples with FIs were investigated during the experiments. One sample was collected in the Alto Ligonha region, Mozambique and thus contained relatively thick (approx. 50 μm) naturally grown FIs with aqueous CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> solutions. For the other sample, rather thin FIs were synthesized with a thickness of less than 15 μm. The synthesis of FIs was achieved by sealing pre-fractured quartz prism together with deionized water in a gold capsule and exposing the capsules to temperatures between 420 °C and 520 °C at pressures between 710 MPa and 860 MPa for 46 to 94 hours in an internally heated pressure vessel [*C. Qiu, et al., Phys. Chem. Chem. Phys. 18, 28227 (2016)*]. During the experiment, the quartz was clamped into a Linkam-Stage to change the temperature and to homogenize the inclusions before each run. A camera was used to observe the inclusions during the experiments to improve the alignment of the beam on the sample and to determine the homogenization point. Due to the spatial requirements of the camera set-up, only three of the six spectrometer tanks were used at angles between 25° and 30° in forward scattering geometry with an analyzer energy of 9.689 keV and an overall energy resolution of 0.7 eV. The incident energy was scanned from 10.209 keV to 10.289 keV and from 9.789 keV to 9.824 keV for the O K-edge and the Si L-edge, respectively. A total of 6 spectra of the O K-edge were acquired with an acquisition time of about 10 hours for each spectrum with one half of them taken at the position of a FI at different conditions and the other half recorded of the pure quartz to determine and subtract its spectral changes under the influence of the changed temperature.

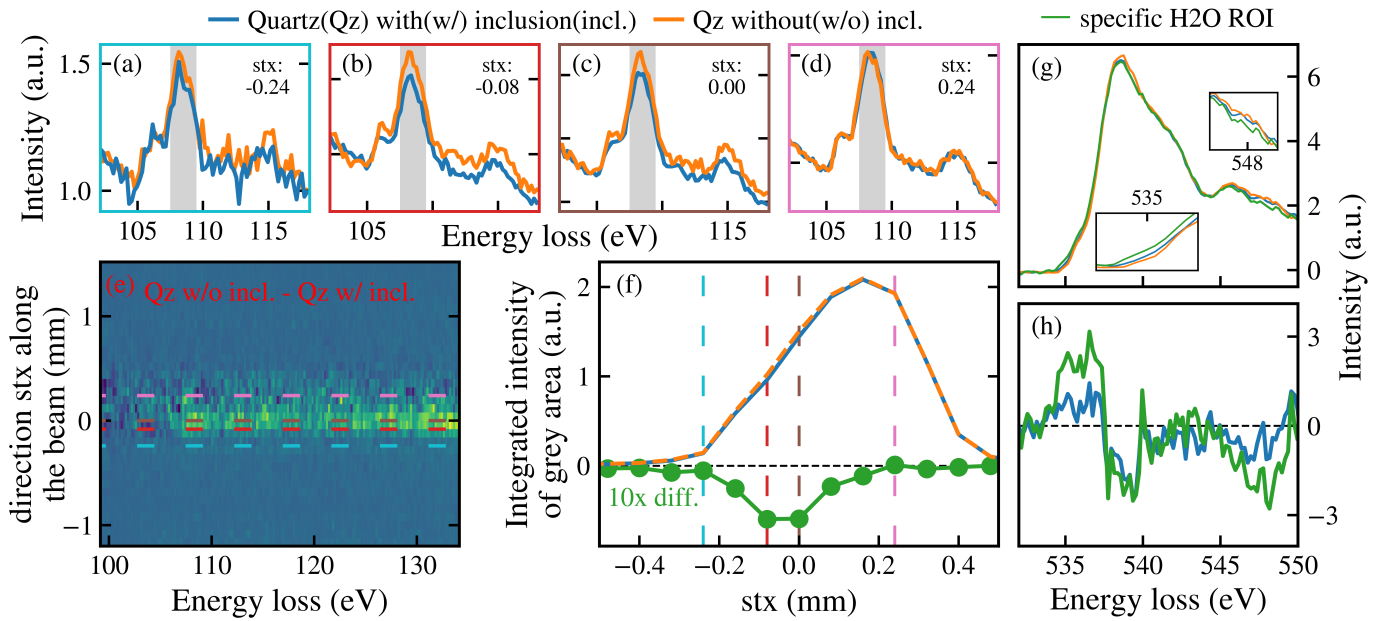


Figure 1: [a-d] Si L-edge spectra of quartz with (w/) and without (w/o) inclusions at different positions (stx) along the beam. [e] 3D-Plot depicting the differences in intensity between w/o and w/ inclusion as a function of energy loss and stx. [f] Orange and blue lines show the integrated intensity of the gray area in plot a-d as a function of stx while the green line is the corresponding difference times 10. [g] The O K-edge spectra for the pure quartz and the inclusion calculated based on a wide (stx: -0.16 to 0.48) range in stx and on only two specific stx values (plot e, red and brown). [h] Difference spectra of plot g with regards to the pure quartz.

In order to fully utilize the imaging capabilities of the XRS technique, detector images at the elastic line were recorded of scotch tape at several positions along the beam to map each pixel of every crystal to its respective distance value along the beam axis. This way, a unified positional axis for every crystal can be established which is crucial to facilitate the extraction of the inclusions O K-edge signal.

The Si L-edge is used to determine the position of the FIs as it provides a larger contrast between the Si bearing quartz and the Si free inclusions. This approach is depicted in Fig.1 (a-d) where Si L-edge spectra of the naturally grown sample at different positions along the beam exhibit a decrease in intensity at the position of the FI (Fig.1 e+f, see caption). The final O K-edge spectrum (Fig.1 g+h) exhibits spectral changes with regards to the pure quartz as expected from the spectrum of water. Thus, a slight increase and decrease of spectral intensity at 535 eV and 548 eV is observed, respectively, where the spectrum of pure water shows more spectral intensity due to the additional pre-edge feature and less due to its lower intensity in the outgoing tail. The selection of the detector signal with regards to the exact location of the FI position along the beam increases the overall water signal by a factor of more than two, as can be nicely seen in the difference spectra. This impressively underlines the ability of this experimental set-up to extract signals of small samples that are heavily contaminated with an undesired background. However, for the even smaller synthesized FI with a thickness of less than 15  $\mu\text{m}$ , the contrast between the FI and the quartz signal (for both Si L-edge and O K-edge) proved to be too low to extract the former. Thus, the detailed analysis of Fig. 1 could not be performed to localize the thin FIs and the whole detector images had to be used. The resulting spectra are shown in Fig. 2 and reveal no difference between pure quartz and FI containing quartz, regardless of the applied temperatures. This indicates that the signal from the thin FI is too small to make a significant contribution, thus rendering the investigation of the local water structure unfeasible. Consequently, future experiments require thicker FIs or a higher spatial resolution as achieved from e.g. smaller detector pixels to further enhance the imaging capabilities and the extraction of the signal from a wide range of minute samples.

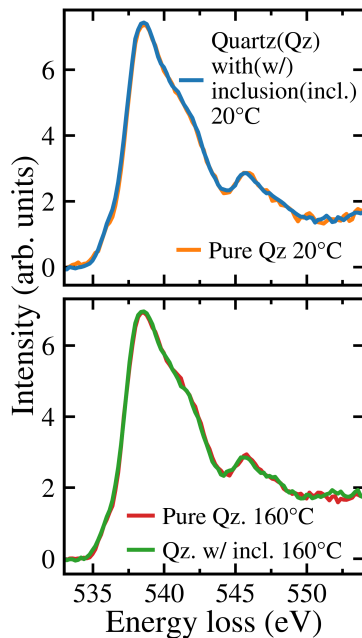


Figure 2: O K-edge spectra of quartz with synthesized inclusions taken without and (presumably) with a fluid inclusion along the X-ray beam at a temperature of 20°C [top] and 165° [bottom], respectively.