ESRF	**Experiment title:** In-situ study of the local structure in hydrous sodium silicate melts by x-ray Raman scattering	**Experiment number**: EC596
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Report: We report on the first in situ high-temperature and high-pressure study of absorption edges of hydrous silicate melts using non-resonant x-ray Raman scattering (XRS). This experiment shows the feasibility of such in situ studies utilizing XRS and provides insight into the changes in silicate melts inferred by the dissolution of H_2O at high pressure and high temperature.

The substantial amounts of H_2O, which is taken up by silicate melts at high pressure, has strong influence on their physical properties, e.g. viscosity. These effects of H_2O dissolution are of fundamental importance for geological processes involving melts and magmas and thus for the formation and evolution of the Earth's crust. There are many studies on the structural changes of silicate melts by dissolution of H_2O. However, most studies were performed on quenched samples, which might be the source for some of the controversy in the discussion of this topic. Here, XRS provides a unique bulk sensitive technique to probe shallow absorption edges under extreme temperature and pressure conditions.

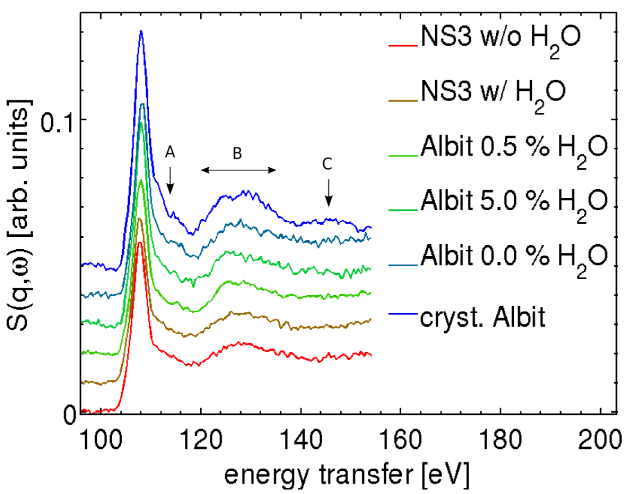
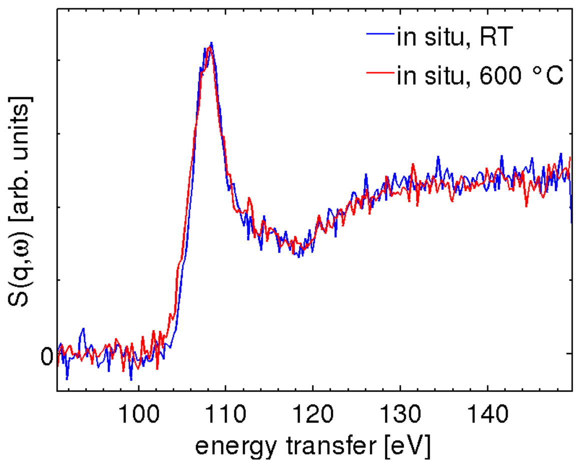
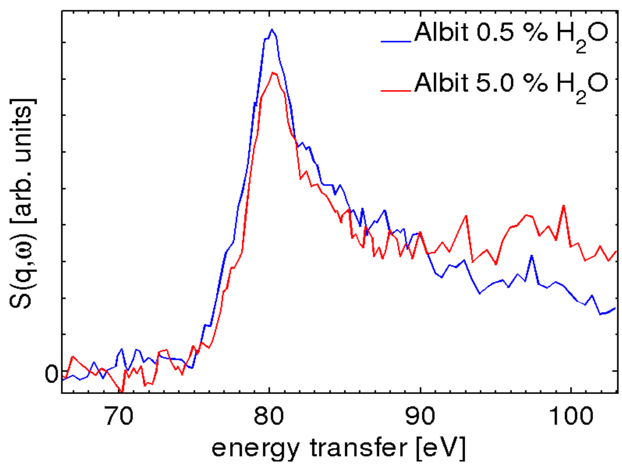


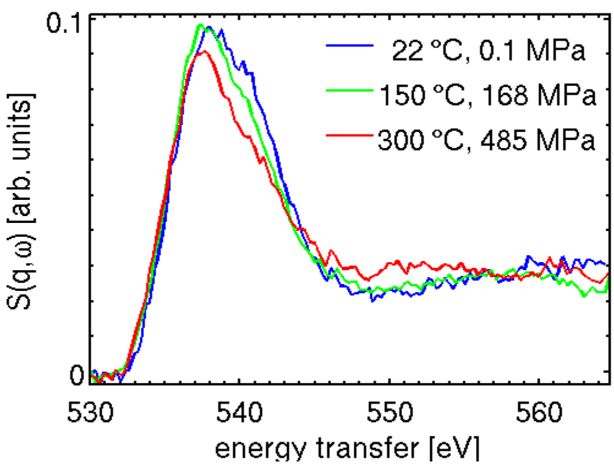
Figure 1 shows the Si L23-edges of various glasses (NS3: $Na_2Si_3O_7$, Albite: $NaAlSi_3O_8$) and an albite crystal, all measured ex situ as reference samples. These were recorded to prove that changes in the local structure of Si

melts are visible at the Si L-edge. In these spectra, a modulation of feature A and B can be observed.
Figure 2 shows the Si L_{23}-edge of hydrous NS3 melt at room temperature and a pressure of 0.1 MPa as well as at 600 °C and a pressure of about 230 MPa. Differences in the two spectra are hardly visible. This is quite expected, though, since the Si-O bond is rather rigid and more prominent structural changes due to the dissolution of H_2O are expected to occur in the vicinity of the sodium atoms (e.g. Farges et al. 2009). The Na L_{23}-edge, however, was heavily superimposed by valence electron excitations and a clear extraction of the Na L_{23}-edge proves very difficult and is thus in an early stage, yet. A more straightforward extraction should be possible for the Na K-edge, but the experimental setup was not optimized for energy losses beyond some 100 eV. Such measurements are strongly recommended.
In order to prove that more drastic changes in the absorption edge's shape occur with the dissolution of water, we also measured the Al L_{23}-edge in two albite glass samples with different H_2O content. The results are shown in figure 3. Here, significant changes in the shape of the near edge structure are clearly visible. Structural information will be gained by comparison with spectra calculated using the FEFFq program package. An in situ experiment with albite melt could not be carried out due to time constraints.



For the improvement of future experiments, a new HDAC cell design was developed and could be tested during this experiment. Using this cell, XRS spectra of the oxygen K-edge of pure water were recorded at room temperature (0.1 MPa), 150 °C (168 MPa), and 300 °C (485 MPa). With this new setup, the signal to noise ratio could be improved by a factor of 3 which results in higher quality data at reduced scan duration times. The results are shown in figure 4 where strong changes in the shape of the oxygen K-edge are visible. In particular, not only changes in the main edge but also the post edge region are obvious. The water pre-edge feature, however, could not be resolved since the experimental setup was not optimized and an energy resolution of only 2.2 eV could be achieved (E0=12.9 keV).





The results obtained in these test experiments are very promising. They indicate that new measurements of the Na K-edge and the Al L-edge should significantly contribute to a better understanding of the structural changes in hydrous silicate melts under high pressure and high temperature conditions.