ESRF	**Experiment title:** Structural changes of water at high pressure and high temperature	**Experiment number**: HE-3591
Beamline: ID16	**Date of experiment**: from: 15 Jun 2011 to: 21 Jun 2011	**Date of report**:
Shifts: 18	**Local contact(s)**: Laura Simonelli	*Received at ESRF:*

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Report: The purpose of the experiment HE-3591 was to study the changes in the local atomic environment of the oxygen atoms in water under high temperature and high pressure conditions. This particular question has been discussed rigorously and so far neither experimental methods such as x-ray and neutron scattering, optical Raman, and NMR spectroscopy or molecular dynamics simulations were able to shed unambiguous light on the matter. However, the question of the structural details of water under these conditions is of great importance for e.g. geoscientists as water plays a key role in heat and mass transfer as well as element fractionation processes in the Earth's lithosphere.[Keppler1996] Moreover, supercritical water is used as a reaction medium for chemical and material synthesis, waste destruction, plastics recycling, and biomass processing.[Akiya2002]
High temperature and high pressure conditions were achieved using an externally heated hydrothermal diamond anvil cell (HDAC). The pressure was determined from the liquid-vapor homogenization temperature before and after the experiment, the composition, and the equation of state [Wagner2002] or correlation formulae for phase relations [Schmidt2007]. The HDAC had a recess in the culet of the lower diamond and other modifications to adapt it to the unique experimental setup of beamline ID16, which allows to exploit the imaging properties of the analyzer crystals by means of a 2D pixel counting Maxipix detector and grants excellent background signal discrimination.
Measured spectra of water at and p/T conditions above vapor pressure are depicted in Fig. 1. From ambient to supercritical conditions, systematic changes in the shape of the oxygen K-edge with temperature and pressure are evident. At ambient conditions, the oxygen K-edge exhibits a prominent post-edge in the energy loss range 538-546 eV energy loss and a pre edge feature at 535 eV energy loss. With increasing temperature and pressure, spectral weight is

systematically shifted from the post edge region into the region of the pre edge. At the same time, the position of the pre edge shifts towards smaller energy losses. Contrary to a preceding study [Wernet2005], the spectrum of water under supercritical conditions cannot be modeled by a simple superposition of a spectrum of liquid at ambient p/T and a gas phase spectrum and a more homogeneously disordered structure than previously suspected must be assumed.
In addition to the study on water, the oxygen K-edge of a 4.4 molal HCl solution was measured at some similar p/T conditions. These spectra are compared in Fig. 2. In comparison to the influence of increasing temperature and pressure, addition of HCl has a reversing effect on the K-edge shape. The pre-edge is less pronounced and the post-edge more pronounced than in water at the same p/T conditions. Comparison to spectra of water at 400 °C and 0.54 and 0.86 g/cm^3 shows that the influence of ions in solution is similar to that of an this increase in pressure, which is in line with earlier neutron diffraction data.[Leberman1995]
To complement this study, calculations of the spectra from snapshots resulting from ab initio Molecular Dynamics have been performed.
The results of the presented study are presented in detail in [Sahle2013].

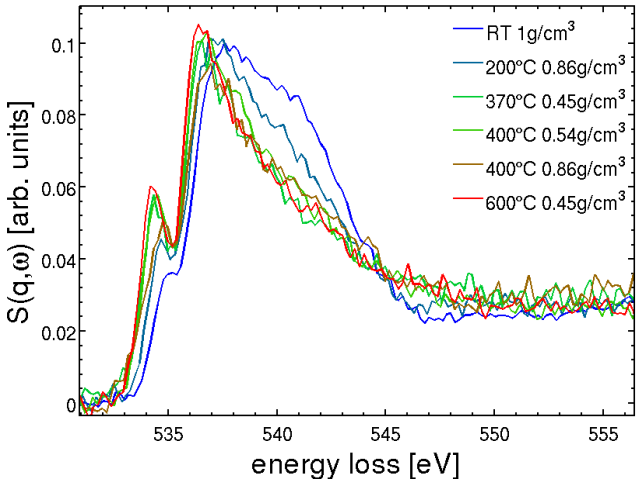

Fig. 1: Oxygen K-edges of water under ambient conditions and at elevated temperatures and pressures.

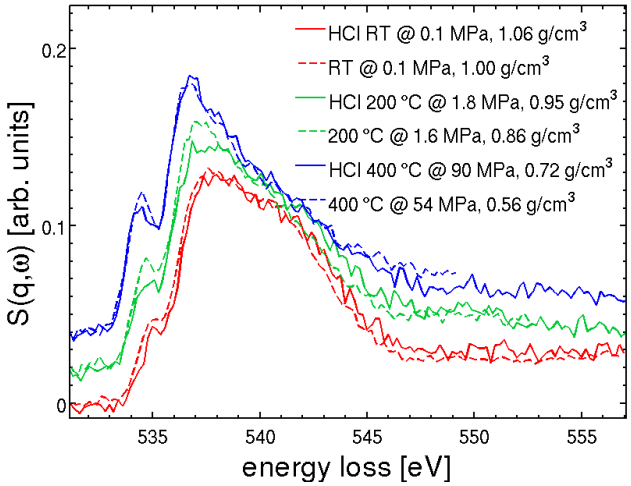

Fig. 2: Oxygen K-edges of water compared to oxygen K-edges of HCl solutions for ambient and high T/p conditions.

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