ESRF	**Experiment title:** Revealing the microscopic structure of hydrothermal aqueous fluids: The case of sodium chloride solvation	**Experiment number**: ES-863
Beamline:	**Date of experiment**: from: 03.10.18 to: 08.10.18	**Date of report**: 23.01.2020
Shifts:	**Local contact(s)**: Christoph Sahle, Blanka Detlefs	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

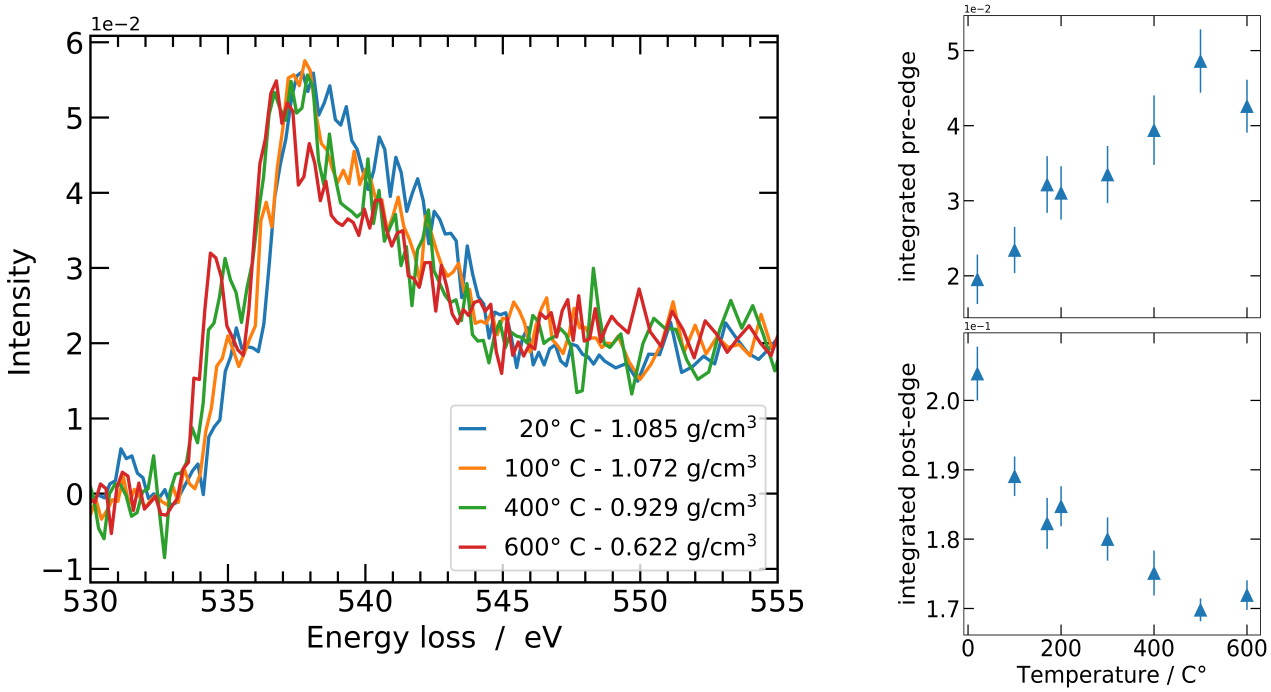
Christian Schmidt (GFZ Potsdam), Mirko Elbers (TU Dortmund/DELTA), Robin Sakrowski (TU Dortmund/DELTA), Christoph Sahle (ESRF), Christian Sternemann (TU Dortmund/DELTA), Max Wilke (Universität Potsdam)

Report:

In this experiment, we performed x-ray raman scattering (XRS) measurements at the oxygen K-edge on aqueous sodium chloride (NaCl) solutions in a wide range of temperature, pressure and density. Aqueous NaCl solutions are of special interest, since NaCl is one of the major solutes in aqueous fluids in Earth's crust and is also involved in many geochemical processes e.g. formation of ore deposits [1]. Therefore, we aimed to reveal the influence of this highly important solute on the microscopic water structure, particularly on the hydrogen bond network, up to the supercritical regime.

In order to reach temperature and pressure conditions up to 600 °C and 250 MPa, respectively, we used a hydrothermal diamond anvil cell (HDAC), modified to facilitate XRS spectroscopy measurements [2,3]. The heating of the sample is realized via NiCr heating wires, which are coiled around the tungsten carbide seats of the two diamonds. To measure the temperature, we used K-type thermocouples which are attached to the surface of the diamonds close to the sample, whereas the pressure was determined using appropriate equation of states and the visual determination of the liquid-vapor homogenization temperature with a microscope. The diamonds had a culet diameter of 1 mm and one of them had an additional laser drilled recess. We enclosed the sample using the two diamonds without gasket so that the recess functioned as sample volume, leading to a higher measurable intensity at least by a factor of two due to the larger usable solid angle for the XRS spectrometer. Due to restrictions regarding the sample cell setup, only one of the six spectrometer modules was used at an angle of 30° in forward scattering with an analyser energy of 9.689 KeV and an overall energy resolution of 0.7 eV. Hence, the incident energy was scanned in a range from

10.207 to 10.278 KeV to record spectra of the oxygen K-edge. In total, we acquired twelve spectra with an acquisition time of 6-8 hours for each spectrum in a concentration and temperature range of 13.18 wt.% to 15.96 wt.% and 20 °C to 600 °C, respectively. Leading to a maximum pressure of 250 MPa and a minimal density of 0.56 g/cm³. The 2D detector images were processed pixel-wise to properly subtract the background signal of the diamonds surrounding the sample for an optimal signal to noise ratio. Several extracted spectra, subtracted from the remaining background and area normalized, are shown in Figure 1 (left) at different temperatures. The spectra exhibit a systematic temperature dependent change: The pre-edge region around 535 eV gains more spectral weight with increasing temperature and shifts to lower energy losses whereas the post-edge at around 541 eV is dominant at ambient temperature but loses intensity when the temperature is increased. This temperature dependence can be seen especially in the integrated spectral intensities in Figure 1 (right). According to [4], the intensity of the pre-edge feature is anti-correlated to the number of hydrogen bonds and correlated to a deviation from a tetrahedral structure whereas a similar but opposite correlation can be observed for the post-edge region. Translated to our spectra, that points toward a reduction in the total number of hydrogen bonded molecules with increasing temperature possibly accompanied by a general loss of tetrahedral order. Currently, these effects are further analysed by comparing the experimental spectra with calculated ones based on structures extracted from ab initio molecular dynamics simulations. In order to reveal the influence of the sodium chloride on the stability of water structure up to the supercritical regime, the results will further be compared with pure water as well as NaOH and HCl aqueous solutions [5,6].



[1] E. Roedder, Reviews in Mineralogy, Vol 12. Mineralogical Society of America (1984); [2] W.A. Bassett, A.H. Shen, M. Bucknum and I-M. Chou, Reviews of Scientific Instruments, 64, 2340-2345 (1993) [3] C. Schmidt and K. Rickers, American Mineralogist, 88, 288-292 (2003) [4] J. Niskanena, M. Fondell, C. J. Sahle, S. Eckert, R. M. Jay, K. Gilmore, A. Pietzsch, M. Dantz, X. Lu, D. E. McNally, T. Schmitt, V. Vaz da Cruz, V. Kimberg, F. Gel'mukhanov, and A. Föhlisch, PNAS, 10, 4058-4063 (2019) [5] C.J. Sahle, C. Sternemann, C. Schmidt, S. Lehtola, S. Jahn, L. Simonelli, S. Huotari, M. Hakala, T. Pylkkänen, A. Nyrow, K. Mende, M. Tolan, K. Hämäläinen and M. Wilke, PNAS, 16, 6301-6306 (2013) [6] C.J. Sahle, J. Niskanen, C. Schmidt, J. Stefanski, K. Gilmore, Y. Forov, S. Jahn, M. Wilke and C. Sternemann, Journal of Physical Chemistry B, 50, 11383-11389 (2017)