Structural changes of water at high pressure and high temperature: information from X-ray Raman scattering at the oxygen K-edge

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We present a study of the local structure of water at high pressure and high temperature conditions using x-ray Raman scattering (XRS) at the oxygen K-edge. The use of this energy loss technique enables one to acquire bulk sensitive information and thus understand the structural changes of water under supercritical conditions, which are highly relevant in geosciences.
Besides the prevailing general scientific interest in the structure of water across its extensive phase space, water plays a key role in heat and mass transfer and in element fractionation processes in the Earth's lithosphere, such as volcanism and ore deposit formation (Keppler 1996). This is largely due to its polar character and greater tendency to dissociate, which make it a substantially more powerful solvent than other volatiles (Manning 2004). The solvent properties of H_2O depend not only on density and dissociation, but also on structural parameters. However, this is poorly understood particularly at the supercritical conditions prevalent in the Earth's interior. Supercritical water is thought to be largely disordered, with a disrupted hydrogen-bond network (Soper 2000). On the other hand, Raman spectra in the O–H stretching region of water suggest that the fraction of network water increases with pressure and its fraction can be signficant to temperatures of at least 600 °C, even at high solute concentrations (Schmidt 2010, Mysen 2009). XRS yields similar information as soft x-ray absorption and electron energy loss spectroscopy and is sensitive to changes in the electronic and local atomic structure. As it is an energy loss technique XRS allows one to choose the energy of the incident x-ray beam freely and thus makes the study of low lying absorption edges in highly absorbing sample environments feasible. Supercritical conditions were achieved using a hydrothermal diamond anvil cell (HDAC), which was modified to meet the specific requirements of XRS. Changes in the shape of the oxygen K-edge with P and T are observed as a fingerprint for changes in bonding and local structure. The measured spectra are compared with results of oxygen K-edge spectra of different ice phases (Pylkkänen 2010) and *ab initio* calculations from molecular dynamics simulations.

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