



## **The structure of amorphous GeO<sub>2</sub> up to 100 GPa by X-ray emission spectroscopy: Implications for magmas in the lower mantle.**

Max Wilke (1), Georg Spiekermann (1), Sylvain Petitgirard (2), Keith Gilmore (3), Manuel Harder (4), Christoph Sahle (3), and Christian Sternemann (5)

(1) Universität Potsdam, Geowissenschaften, Potsdam, Germany (max@geo.uni-potsdam.de), (2) ETH, Erdwissenschaften, Zürich, Switzerland, (3) ESRF, Grenoble, France, (4) DESY, Hamburg, Germany, (5) TU Dortmund, Germany

The application of valence-to-core X-ray emission spectroscopy (vtc-XES) to high pressure experiments with diamond anvil cells is a recent development, which allows for insight to the structure of amorphous material. Glasses serve as analogue for melts or magmas and help constraining the properties of magmas at conditions of the lower mantle. Magmas are postulated for the lower-most mantle to explain anomalies in seismic velocities detected by seismic tomography.

The structure of compressed amorphous GeO<sub>2</sub> above 40 GPa is uncertain, but is of particular interest due to its similarity to SiO<sub>2</sub>, one of the main components of the Earth's mantle. A study on the density has postulated a density crossover of amorphous GeO<sub>2</sub> relative to crystalline GeO<sub>2</sub> phases (Hong et al. 2007). This would probably require an average Ge coordination number above six, which is the coordination number in known stable GeO<sub>2</sub> polymorphs at mantle pressures. A recent X-ray diffraction study reported an average Ge coordination number of seven at 60 GPa (Kono et al. 2016). This contrasts results of ab initio molecular dynamics, which postulate deviation of sixfold coordination not below 80 GPa (Du et al. 2017).

We compressed amorphous GeO<sub>2</sub> up to 100 GPa in diamond anvil cells and measured germanium valence-to-core X-ray emission spectra. Bethe-Salpeter spectral calculations of GeO<sub>2</sub> polymorphs guide the interpretation of measured spectra. Our results show that there is no necessity to invoke Ge coordination numbers above six to explain the observed spectra up to 100 GPa. Therefore, it is unlikely that compressed GeO<sub>2</sub> glass exceeds the density of sixfold coordinated GeO<sub>2</sub> polymorphs at the pressure conditions of the Earth's mantle. In analogy, the coordination number of Si in magmas at pressures of the lower mantle will likely not exceed six, either as found recently by spectroscopy on Si in compressed amorphous SiO<sub>2</sub> (Petitgirard in revision). Consequently, magmas with higher density than the surrounding matrix and negative buoyancy close to the core-mantle-boundary must be related to compositional parameters and not to differences in the structural compaction mechanism of Si or Ge polyhedra in melts compared to polyhedra in crystalline solids.

Du et al. 2017 J Phys Chem 121, 10726-10732; Hong et al. 2007 Rev Sci Instr 78, 103905; Kono et al. 2016 PNAS 113, 3436-3441