ESRF	Local structure in silicate melts and glasses at Earth's lower mantle conditions	**Experiment number**: ES 868
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Shifts: 12	**Local contact(s)**: Angelika Rosa	

Names and affiliations of applicants (* indicates experimentalists):

Max Wilke*, University of Potsdam, Potsdam, Germany
Marija Krstulovic*, European Synchrotron Radiation Facility (ESRF), Grenoble, France
Angelika Rosa*, European Synchrotron Radiation Facility (ESRF), Grenoble, France
Lelia Libon*, University of Potsdam, Germany
Christian Albers*, University of Dortmund, Germany

Report:

This study aims at understanding the structural properties of silicate melts relevant to magmatic processes in the deep Earth [1], [2], [3]. Silicate melts represent major component of the Earth's interior and as such, they are responsible for most geodynamical processes. Understanding the structural properties of silicate melts is fundamental to explain their chemical and physical behavior as well as the processes operating in the deep Earth. This study focuses on elucidating the local structural environment of network forming cations in silicate melts in the joint albite-diopside eutectic system at the relevant pressure and temperature conditions prevailing in the deep Earth's interior (> 2000 K and up to 40 GPa). The objective was to study in detail the effect of temperature and pressure on the structure of silicate melts, and in particular the coordination change from 4- to 6-fold coordinated network former cations.

Such extreme conditions are experimentally accessible only using the laser-heated diamond anvil cell coupled to micro-focused X-ray beams and fast detection techniques. Experiments have therefore been conducted at the energy dispersive XAFS beamline ID24 of the European Synchrotron Radiation Facility (ESRF) which is presently worldwide the only beamline offering all these requirements.

We used synthetic silicate glass samples doped with Ge (26 wt%) that partially substitutes Si and mimics its role as network former. The glass was additionally doped with 1 to 2 wt% Fe_2O_3 serving as an absorber of the infrared laser and therefore ensuring a homogenous heating of the sample.

The experiment was performed at the S-branch of the ID24 beamline which allows a high-focusing of the beam as it is equipped with a set of horizontal and vertical mirrors in a Kirkpatrick-Baez configuration. The beam energy was tuned to the Ge-Kedge (11.2 keV) using two undulators (U32) closed to a gap of ~ 14.6 mm providing an energy range over 1000 eV after the edge. Fine vertical focusing was achieved using a second horizontal mirror coated with silicon and inclined to 4 mrad. Fine horizontal focusing on the sample was achieved by an elliptically bent Si(111) crystal polychromator crystal. A Hamamatsu camera equipped with an energy-position sensitive chip was used to acquire the I1 signal after the sample. I0 was taken before and after I1 outside the diamond anvil cell, as the sample chamber was entirely filled with the glass. At the 11.2 keV the highest focusing of 4.8 x 4.8 μm^2 at the Ge K-edge is achieved only for a restricted energy range of about 100 eV because beam penetration into the polychromator crystal becomes significant at this energy and leads to tails for the focus of the X-ray beam. In the present experiment we therefore acquired only XANES data.

High pressure in the sample was reached by increasing the membrane pressure in the diamond anvil cell (DAC) equipped with nano-polycrystalline diamonds of the Le Toullec type. The sample was loaded in a small hole (hole diameter 120, 150 and 200 µm respectively) drilled in the Re-gasket, placed between the two diamonds. A micrometric ruby crystal was loaded into the sample chamber close to the rim of the Re-gasket. The pressure in the sample was accurately determined by measuring the fluorescence line of the ruby, excited by a green laser (532 nm). Pressure was determined before and after each heating run and for the pressure calculation the non-hydrostatic ruby scale was used [4].

Temperature was generated in the sample using two infrared 120WNd:YAG fiber-coupled lasers (1064 nm wavelength) that were focused onto the sample using lenses. The sample was heated from both sides in order to reduce axial temperature gradient in the sample. The laser beams enter the sample with an angle of 30 degrees with respect to the direction normal to the sample allowing the generation of large (20-30 µm) heating spots, ensuring a flat temperature profile in the central hot-spot region. The temperature in the central portion of the hot-spot was determined in-situ using the spectral radiometry and optical lens systems to collect the emitted light.

Data were collected in a P/T domain of 3-37 GPa and 1500 to 5000 K. The integration time of the beam on the sample was set to 4 ms during the heating runs. The sample temperature was raised on the sample continuously through adjusting the laser output power. The laser hotspot to X-ray position was adjusted for each heating step to ensure that XAS data were acquired in the central hot-spot region that exhibits a flat and homogeneous temperature profile.

Typical Ge K-edge XANES spectra obtained during the experiment are shown in figure 1.

The figure shows the evolution of XANES features at constant pressure (19 GPa) over a temperature range of 1500 to 5000 K. The decreasing intensity of the first XAENS peak at given pressure and along the temperature range between 1500 and 5000 K it seems that the tetrahedral to octahedral coordination was completed bellow 1500 K and the broadening of the white line visible at the three spectra at 3900 K and beyond indicate that the sample is fully molten.

Our previous EXAFS results from cold compression runs have revealed that the evolution of the second XANES peak shape can be interpreted in terms of the tetrahedral to octahedral coordination change (ES706). Our previous EXAFS experiments showed that the 4-6 fold coordination change can be clearly monitored through the variation of the nearest neighbor bond length. These results allow interpreting also the XANES spectra evolution (edge position variation, second XANES peak intensity change) in terms of the underlying structural changes

Based on this approach we find that the 4-6 fold coordination change was completed already below 19 GPa and 1500 K. This is a much lower pressure than observed in the previous cold compression and resistive heated DAC experiments at 515 °C that demonstrate that the octahedral configuration was not reached at 23 GPa (ES706).

A very first analysis of XANES spectra evolution allowed us to distinguish different P/T domains and coordination states of Ge. Below 5 GPa we observe 4-fold coordination at ~ 4000 K, whereas beyond 5 GPa Ge converts to an intermediate (mixed 4-, 5 and 6-fold) coordination. Mixed coordination prevails over the pressure interval from 5 GPa < p < 20 GPa and in the temperature range between 300 and 5000 K. Beyond 20 GPa Ge is in 6-fold coordination at all measured temperatures (Fig. 2).

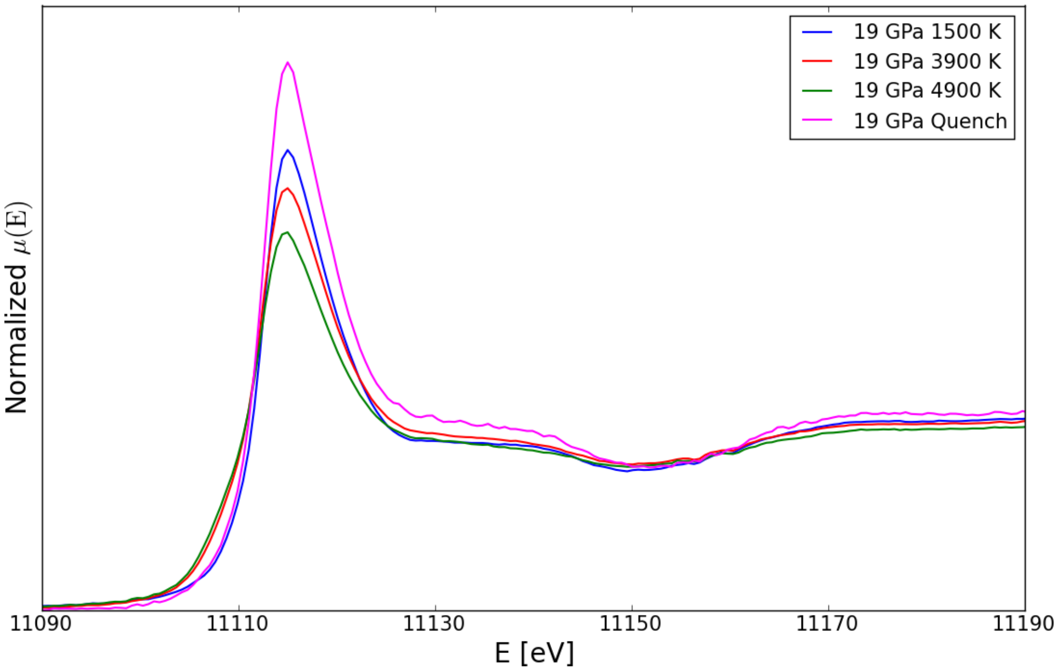

Figure 1. Figure 1. Normalized Ge K-edge XANES spectra collected at 19, GPa and 1500 K, 3900, 4900 K and on quenched amorphous $Na_{0.45}Ca_{0.1}Mg_{0.05}Sr_{0.5}Si_{1.95}Ge_{0.5}O_{7.8}$ *doped with 2 wt% Fe2O3*

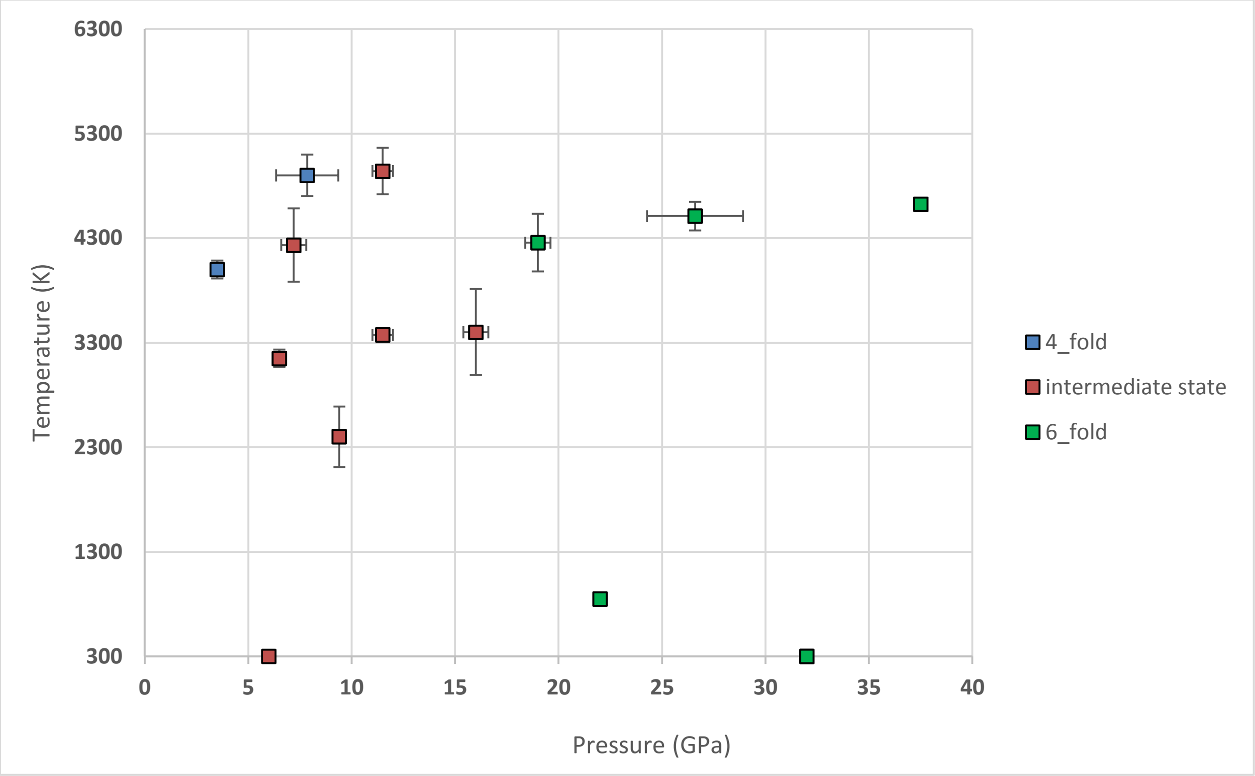

Figure 2. Extracted coordination number as a function of pressure and temperature collected at pressure between 3 and 38 GPa and temperature between 300 and 5000 K on amorphous $Na_{0.45}Ca_{0.1}Mg_{0.05}Sr_{0.5}Si_{1.95}Ge_{0.5}O_{7.8}$ *doped with 2 wt% Fe2O3*

A more detailed analysis of the XANES spectra is presently in progress.

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