ESRF	**Experiment title:** Electronic properties and local structure of haplobasaltic glasses at pressure: The role of iron coordination and valency	**Experiment number**: ES-1172
Beamline: 20,18	**Date of experiment**: from: 21.06.2022, 23.06.2022 to: 27.06.2022, 27.06.2022	**Date of report**:
Shifts: 18,12	**Local contact(s)**: Christoph Sahle, Sergey Yaroslavtsev	*Received at ESRF:*

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Report:

The purpose of the experiment ES-1172 was to reveal the iron's spin state and electronic structure depending on the Fe^{3+}/Fe_{tot} ratio of haplobasaltic glasses up to pressure conditions of the deep Earth's mantle and to correlate this with changes in the silicate network structure. The applied methods were X-ray emission spectroscopy (XES) of the Fe $K\beta_{1,3}$ and valence-to-core (vtc) emission as well as 1s2p resonant X-ray emission spectroscopy (RXES) at the iron K-edge performed at beamline ID20 combined with parallel synchrotron Mössbauer spectroscopy (SMS) measurements at beamline ID18. All samples contained in diamond anvil cells (DACs), were circulating between both beamlines in order to measure at the same conditions. The basalt composition (SiO2 (48.56 wt%), Al2O3 (15.98 wt%), FeO (8.00 wt%), MgO (7.82 wt%), CaO (19.09 wt%)) was the basis to synthesize three glasses with Fe^{3+}/Fe_{tot} ratios of 0.13, 0.47 and 0.61. The samples were measured *ex situ* as well as *in situ* loaded as powder in DACs, which allows to reproduce high-pressure conditions and enabled measurements up to 120 GPa. The pressure was determined by optical Raman spectroscopy of the diamond culet. In the following, preliminary results of a haplobasaltic glass with Fe^{3+}/Fe_{tot} ratios of 0.47 and 0.61 are presented while the measurements of the glass with 0.13 composition at higher pressures still need to be completed in a further experiment. The Kβ XES and vtc spectra were measured at beamline ID20 using the new von Hámos spectrometer exploiting two Si(110) analyzer crystals. The incident beam was monochromatized by the Si(111) monochromator and focused to 20 x 20 µm² (v x h) at an incident energy of 10200 eV. About 10 pressure steps per sample were taken and allow an *in situ* pressure dependent spin state analysis (see fig. 1). At selected pressures, vtc spectra were taken. 1s2p RXES was measured via a Si(111) analyzer crystal installed at the spectrometer scanning the incident energy between 7090 and 7300 eV at the iron K-edge at about 60, 90 and 120 GPa for the samples. The high-energy-resolution fluorescence detected (HERFD) pre-edge spectra were extracted from RXES maps and are shown in figure 2 for both samples. Further we were able to track changes of the Fe^{3+}/Fe_{tot} ratio and spin state via synchrotron Mössbauer spectroscopy

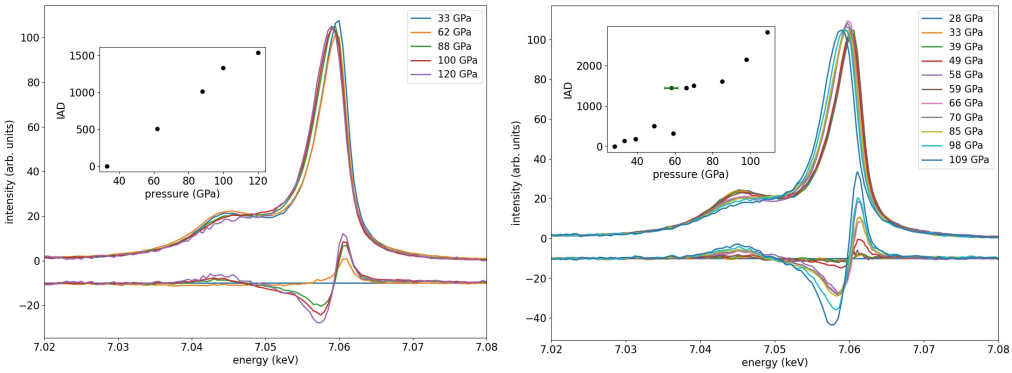

***Fig. 1**: Pressure dependent XES spectra and the differences to the lowest pressure as well as calculated integral of absolut difference (IAD) values in the inset **left)** 61% Fe^{3+} glass **right)** 47% Fe^{3+}glass. The green bar indicates the pressure uncertainty.*

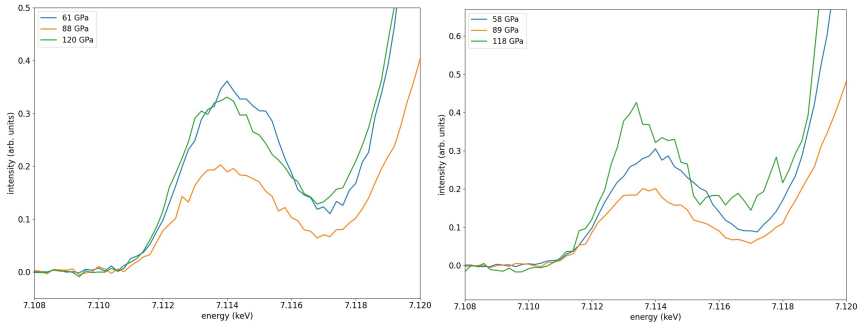

***Fig. 2**: HERFD pre-edge spectra extracted from RXES data at 3 selected pressures for haplobasaltic glass containing **left)** 61% $Fe^{3+}$and **right)** 47% Fe^{3+}.*

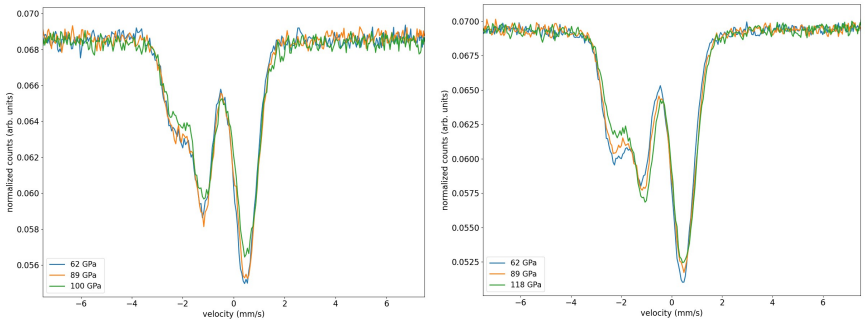

***Fig. 3**: SMS spectra of haplobasaltic glass for selected pressures with **left)** 61% Fe^{3+} **right)** 47% Fe^{3+}.*

(SMS) carried out at beamline ID18 (see fig. 3 for selected pressures). The XES spectra indicate a change in spin state at around 60 GPa as well as another change at around 100 GPa. For a preliminary analysis we calculated from these differences the integral of absolute difference (IAD) values as a quantification of spin state change shown in the inset. Details of changes in covalency require a more detailed analysis. The 1s2p RXES data supports changes in the electronic structure of iron in both regimes. This is exemplified by the extracted HERFD pre-edge spectra (see figure 2) and confirmed also by subtle changes in the SMS spectra as presented in figure 3. However, the data analysis is still ongoing. To conclude, we have measured a unique consistent data set to obtain *in situ* information on spin state and electronic structure of haplobasaltic glasses with different Fe^{3+}/Fe_{tot} ratios up to 120 GPa. Although we aimed for complementary information on the network structure by X-ray Raman scattering (XRS) at the O K-edge and Si as well as Ca L-edges, due to time constraints we needed to focus on XES and RXES during this experiments, which was conducted for the first time at this beamline for such systems. Hence, we plan to complement the whole data set in a follow up experiment which will provide required data by XRS for all samples. While we obtained solid results for the two samples with dominating Fe^{3+} content we need to perform additional XES and SMS measurements for the sample with dominating Fe^{2+} contribution in order to distinguish between Fe^{2+} migration or X-ray induced oxidation.