



	<b>Experiment title:</b> Local structure of haplobasaltic glasses at pressure: The role of iron in the silica network	<b>Experiment number:</b> ES-1324
<b>Beamline:</b> ID 20	<b>Date of experiment:</b> from: 25.04.2023 to: 02.05.2023	<b>Date of report:</b> 26.05.2023
<b>Shifts:</b> 18	<b>Local contact(s):</b> Christoph Sahle	<i>Received at ESRF:</i>
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## Report:

Aim of experiment ES-1324 was to complement the data of the previous experiment (ES-1172) in order to systematically investigate the electronic and local structure of haplobasaltic glasses with different  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratios for pressures up to 120 GPa to link changes in the iron's spin state and electronic structure to local changes of the silica network, focusing on the role of  $\text{Fe}^{2+}$ . The methods used were Fe-K $\beta_{1,3}$  and valence-to-core (vtc) X-ray emission spectroscopy (XES) and X-ray Raman scattering (XRS) at the oxygen K-edge. In this experiment we studied the two endmembers, purely  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , basaltic glasses as well as two glasses with a 61%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  and a 13%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratio. All four samples were measured from ambient conditions up to pressures of 120 GPa *in situ* loaded as powder in diamond anvil cells (DACs). Pressure determination was performed via optical Raman spectroscopy of the diamond culet.

In the following, preliminary results of the XES experiment for 13%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  and for both endmembers are presented. The XES measurements of the K $\beta$  and vtc emission were conducted using the von Hámos spectrometer equipped with three Si(110) analyzer crystals. A Si(111) monochromator was used to monochromatize the incident beam to an energy of 10200 eV. The beam spot at the sample was set to 20 x 20  $\mu\text{m}^2$  (v x h). XES spectra for about 10 pressure steps per sample were taken (fig. 1). For the preliminary analysis the integral of absolute difference (IAD) values were calculated from the K $\beta_{1,3}$ -spectra as a quantitative assessment of the observed spin state changes (fig. 2). As we observe significant changes in the shape of the K $\beta$  satellite, changes in the IAD values not necessarily indicate changes in the iron's spin state but also changes in coordination environment.

The XES Spectra of 13%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  show a peculiar change in shape of the K $\beta'$  satellite (see fig. 1). Up to 30 GPa its intensity as well as the corresponding IAD values decrease. Between 30 GPa and 49 GPa the IAD values increase accompanied by a shift of the K $\beta'$  maximum to higher emission energy which might indicate a change in coordination environment (see fig. 2 a)). For higher pressures the IAD signal decreases again, typically for changes from high spin to low spin iron. These observations are accompanied by variations in shape of the vtc

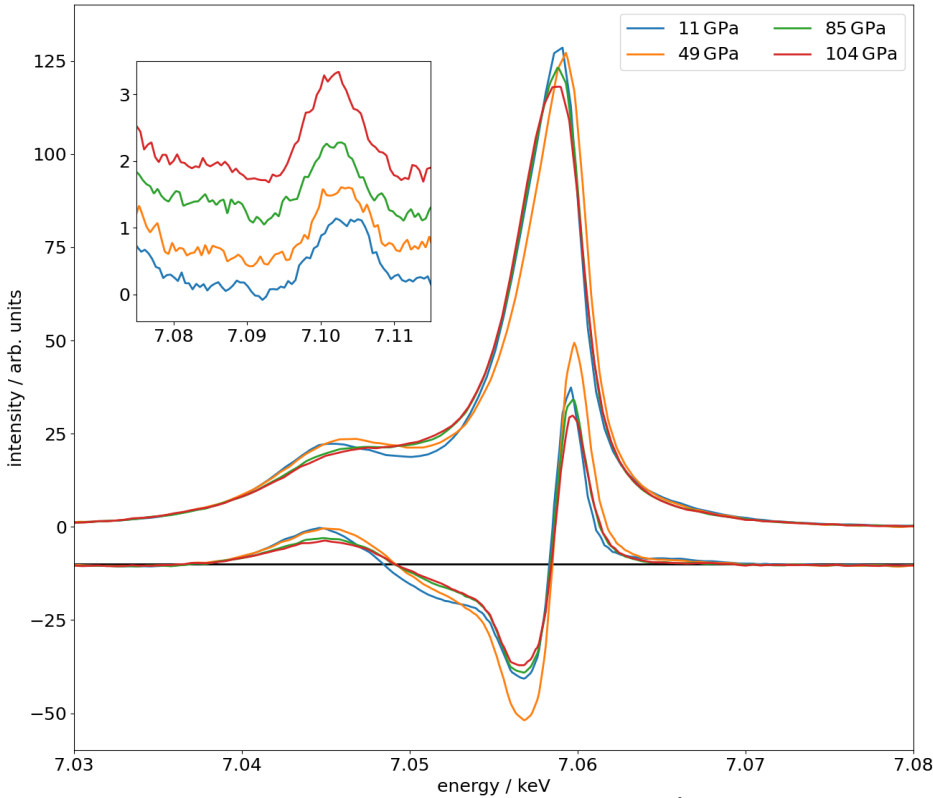


Fig. 1: Selected pressure dependent XES spectra of 13%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  haplobasaltic glass and differences to a low spin reference ( $\text{FeCO}_3$  at 80 GPa) as well a zoom into the vtc regime. The spectra for the vtc emission are set-off in intensity and the difference is shifted in y.

expected to reveal and disentangle variations in the spin state and the local environment in these glasses. This information will be complemented and constrained by experimental results on the local coordination of oxygen in the glasses.

In order to obtain such information, we measured XRS spectra at the oxygen K-edge scanning the incident energy between 10213 eV to 10253 eV in 160 steps with 160 seconds measuring time per step resulting in a total time of about 5 hours per sample and pressure point. The measurements of the 61%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  glass were performed at 33 GPa and of glass with 13%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  at 32, 65, 85 and 116 GPa. Due to time constraints, it was not possible to measure Si and Ca L-edges. The evaluation of the XRS data is pending and will help to interpret the peculiar behavior of the of the XES emission data.

In summary, we have obtained a wide range of consistent data measured *in situ* on the haplobasaltic glasses and their endmembers  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in basaltic glass in order to constrain spin state, electronic and local structure at pressures up to 120 GPa.

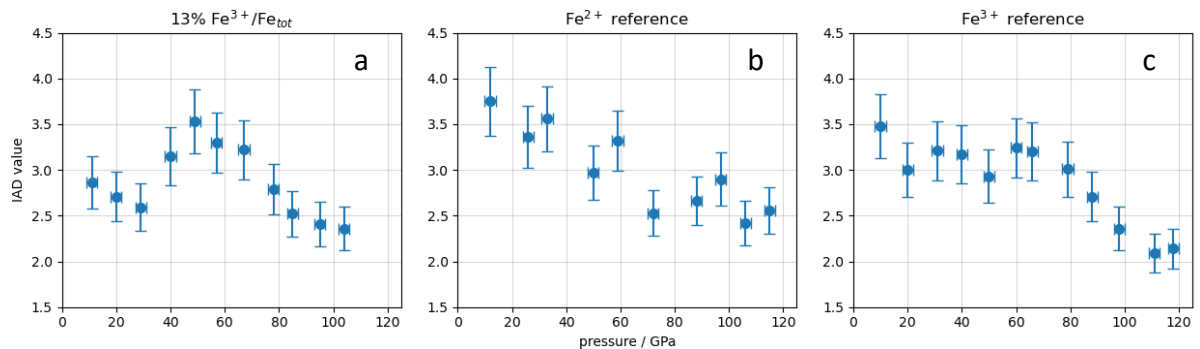


Fig. 2: Calculated IAD values in dependence of all measured pressures **a)** 13%  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratio haplobasaltic glasses, **b)**  $\text{Fe}^{2+}$  and **c)**  $\text{Fe}^{3+}$  endmembers. The reference spectra was  $\text{FeCO}_3$  at 80 GPa.

emission at 49 GPa and 104 GPa which is highly sensitive to changes in coordination environment, i.e. bond distances and symmetry.

In contrast, the  $\text{K}\beta$  emission spectra of the  $\text{Fe}^{2+}$  reference show an almost gradual change in both IAD value and shape with increasing pressure which is reflected as well in the vtc emission. Notably, the  $\text{K}\beta''$  vtc-peak becomes prominent at the highest pressure. The corresponding IAD values are presented in fig. 2b). Similarly, the  $\text{Fe}^{3+}$  reference's XES spectra change gradually, while the corresponding IAD values vary hardly up to 65 GPa where it starts to decrease significantly. For the highest pressure, the  $\text{K}\beta''$  vtc-satellite appears as observed before for  $\text{Fe}^{2+}$ , indicating a significant change in the local environment. Further detailed analysis is