ESRF	**Experiment title:** Spin transition in Fe-rich silicate glass at high pressure using Synchrotron Mössbauer source at ID18	**Experiment number**: HC-4029
Beamline: ID18	**Date of experiment**: from: 18/10/2018 to: 23/10/2018	**Date of report**: 27/02/2020
Shifts: 15	**Local contact(s)**: Valerio Cerantola	*Received at ESRF:*

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Report:

Silicate magmas play a fundamental role in controlling the chemical and heat exchanges across the mantle during Earth's history as well as the evolution of the atmospheric composition through mantle degassing, thus Earth's habitability over time. While at low pressure, their composition, density and valence state related to the oxygen fugacity are quite well known, at pressure of the deep lower mantle such physical parameters remain elusive. The electronic structure of iron in silicate melts is of great importance because it can control several parameters that can impact the dynamic and chemistry of the deep Earth. Indeed, the ratio of Fe^{3+}/Fe_{Tot} can impose the oxygen fugacity in silicate melts thus the partitioning of elements between solid and liquid. However, a change in spin states can complicate this vision as it may stabilise some component with pressure thus affecting the oxygen fugacity of silicate melts.

To bring a clearer picture of the spin state evolution with pressure in glasses and melts, we measured in situ synchrotron Mossbauer spectroscopic data on two compositions relevant for the deep earth interior with mixed oxygen fugacity for the starting material with Fe3+-rich composition and measured the SMS data up to 174 GPa. We provide an evaluation of the hyperfine parameters as a function of pressure and follow the evolution of the different spin components up to CMB pressure and beyond.

Experimental procedure:

Glasses were synthetized using an aerodynamical system coupled with a CO2 laser heating at the CEMThi (Orleans, France). Samples were prepared from high purity regent oxide mixtures and iron oxide enriched in ^{57}Fe was used in order to enhance the Mossbauer signal in the small confinement of the diamond anvil cell (DAC). We prepared two compositions: i) $Mg_{0.7}Fe_{0.3}SiO_3$ as a potential simplified composition for deep mantle magma and ii) a basaltic

glass with a mid-ocean ridge basalt (MORB) composition. High-pressure conditions were generated using BX90 type DAC. The glasses were finely ground into a powder and compacted into the sample chambers in the rehnium gasket. Pressure was recorded offline using the optical Raman system on beamline ID15-B by measuring the shift of the diamond stretching line as a function of pressure.
The Synchrotron Mossbauer Spectroscopy (SMS) was performed at the Nuclear Resonance beamline (ID18). The X-ray beam was focused down to 12 x 7 micrometre using a pair of mirrors in a Kirkpatrick-Baez (KB) geometry. All spectra were treated using the MossA software package to obtain the hyperfine parameters as well as proportions of the different iron components. At ambient conditions the two glasses synthetized with 5% oxygen display a ratio of Fe3+/Fe2+ equal to 35% and 40 % for MgFeSiO3 and basalt respectively. At high pressure, we constrain the Fe^{3+}/Fe_{Tot} ratios as constant by fixing the amount of Fe^{3+} and leave all other parameters free.

Preliminary results:
Here we report the results on one run from ambient to 174 GPa on $Mg_{0.7}Fe_{0.3}SiO_3$ (Fe^{3+}/Fe_{Total} ≈ 40%). As the pressure increase, we noticed a new component appearing at about 50 GPa and become predominant beyond megabar. We have attributed this new component to a change of Fe^{2+} high-spin (HS) to the low-spin (LS)

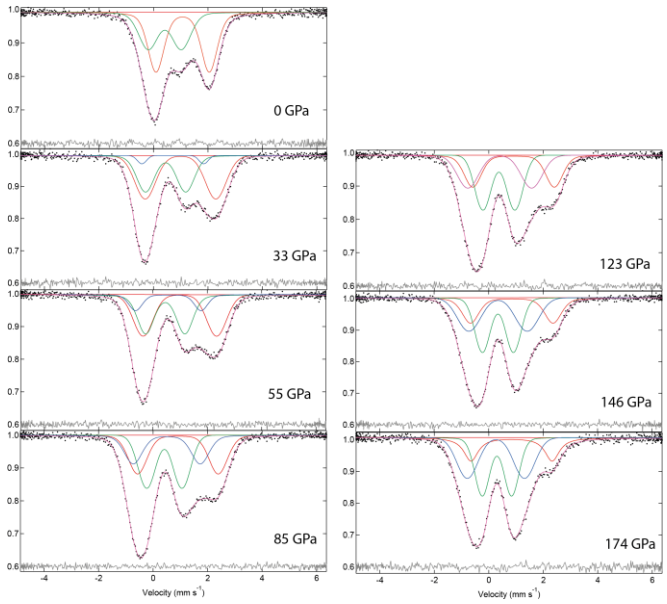

Figure 1. Examples of Mossbauer spectra collected on the MgFeSiO3 glass up to 174. At low pressure the spectra can be easily fitted with two components while beyond 30 GPa a third component is increasing and necessitate a different fitting procedure with a third component.

We fitted the spectra using two components at low pressure and added a third component after 30 GPa, the evolution of the theee components as a fucntion of pressure are reported in Figure 2. We observed a reducction of the Fe2+HS at the expense of the Fe2+LS with pressure and a crossover between the two components at about 110 GPa.

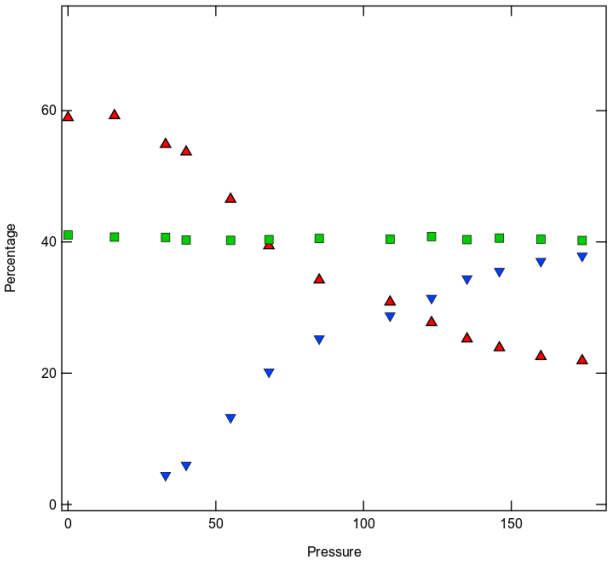

Figure 2. Fe components evolution with pressure. In green the Fe^{3+} component was fixed to 40%. In red the Fe^{2+} HS and blue the Fe^{2+} LS. Using our fiiting procedure, we found out a reducction of the Fe^{2+} HS at the expense of the Fe^{2+} LS.