ESRF	**Experiment title:** Fe oxidation state in dense liquid silicates probed by XAS under dynamic compression	**Experiment number**: ES-1245
Beamline: ID24	**Date of experiment**: from: 27/09/2022 to: 30/09/2022	**Date of report**: 01/03/2022
Shifts: 18	**Local contact(s)**: Angelika Rosa, João Elias Figueiredo Soares Rodrigues	*Received at ESRF:*

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Report:

The global objective of ES-1245 is to investigate dense silicate melts at the conditions of the interiors of large terrestrial planets. These melts compose the primordial, possibly persistent in some case, magma oceans formed during the accretion of the planet. Investigating such melts and obtained in situ data above 25 GPa (pressure limit for corresponding large volume press experiments) is a challenging task due to the high melting temperature of these compounds, their chemical reactivity and their incongruent melting for most compositions. For this reason the usual experimental approach consists in studying dense silicate glasses at 300 K compressed statically, assuming they are stuctural analogues of the liquid. Laser-driven dynamic compression coupled to ultrafast X-ray probes is one of the new and promising experimental routes to produce and characterize such compounds. Indeed, shock compression allows to fast (< 100 ps to reach peak PT) and uniformly a relatively large volume of sample and maintain it compressed during few nanosecond in the case of a laser-driven shock. This avoids chemical contamination of the sample with other parts of the sample assemblage and provides enough time for equilibrium to be reached at such temperatures, especially in liquid states. In this proposal, we aim at comparing the two approaches and providing complementary XAS data to on-going campaigns of shock+XRD measurements done at LCLS MEC facility.
This experimental run on BM23 corresponds to the first beamtime of ES-1245 allocation. The second one will take place in July 2023 on the ID24-ED beamline and the High Power Laser Facility.

During BM23 ES-1245 beamtime (and a previous in-house session) we performed XAS measurements of statically compressed (Mg,Fe)SiO3 glasses (Fe/Mg=0.05, 0.1 and 0.2), Mali (Andradite50-Grossular50) garnet (hoping to amorphizing it) and FeSiO alloy (relative to ID24-ED+HPLF proposal ES-1102). The samples were loading in diamond anvil cells with nanocrystalline diamonds provided to ESRF by Pr. Irifune (Ehime University, Japan). One diamond anvil per cell was perforated. This design reduces the X-ray beam absorption and background signal from the diamonds and largely improves the quality of the XAS measurements. Silicate

samples were loading as powder with a ruby sphere whose pressure-calibrated fluorescence was measured. We used the micro-XAS station of BM23 to finely control sample position/orientation relative to the beam and we also used the XRD area detector (used only for the garnet and FeSiO samples) provided on BM23 to have complementary structural measurements of our samples. XANES and EXAFS measurements were taken at Fe K-edge up to k ~ 10-12 A^{-1}.

(Mg,Fe)SiO_3 glasses. We collected XAS data in the two most Fe-enriched glasses (Fe/Mg = 0.1 and 0.2). Three different DAC were loaded (two with Fe/Mg=0.2 glass, one with Fe/Mg=0.1) and samples were compressed up to 80 GPa. The quality of the data is good and preliminary analysis shows progressive densification of the first coordination shell and no Fe oxidation state variations. The edge shape is the most affected by the compression and the reason still need to be investigated. The effect of Fe concentration was not spotted during the experiment and finer analysis must be done, although it is possible that Fe was diluted enough in both cases for not affecting much the first coordination shell.

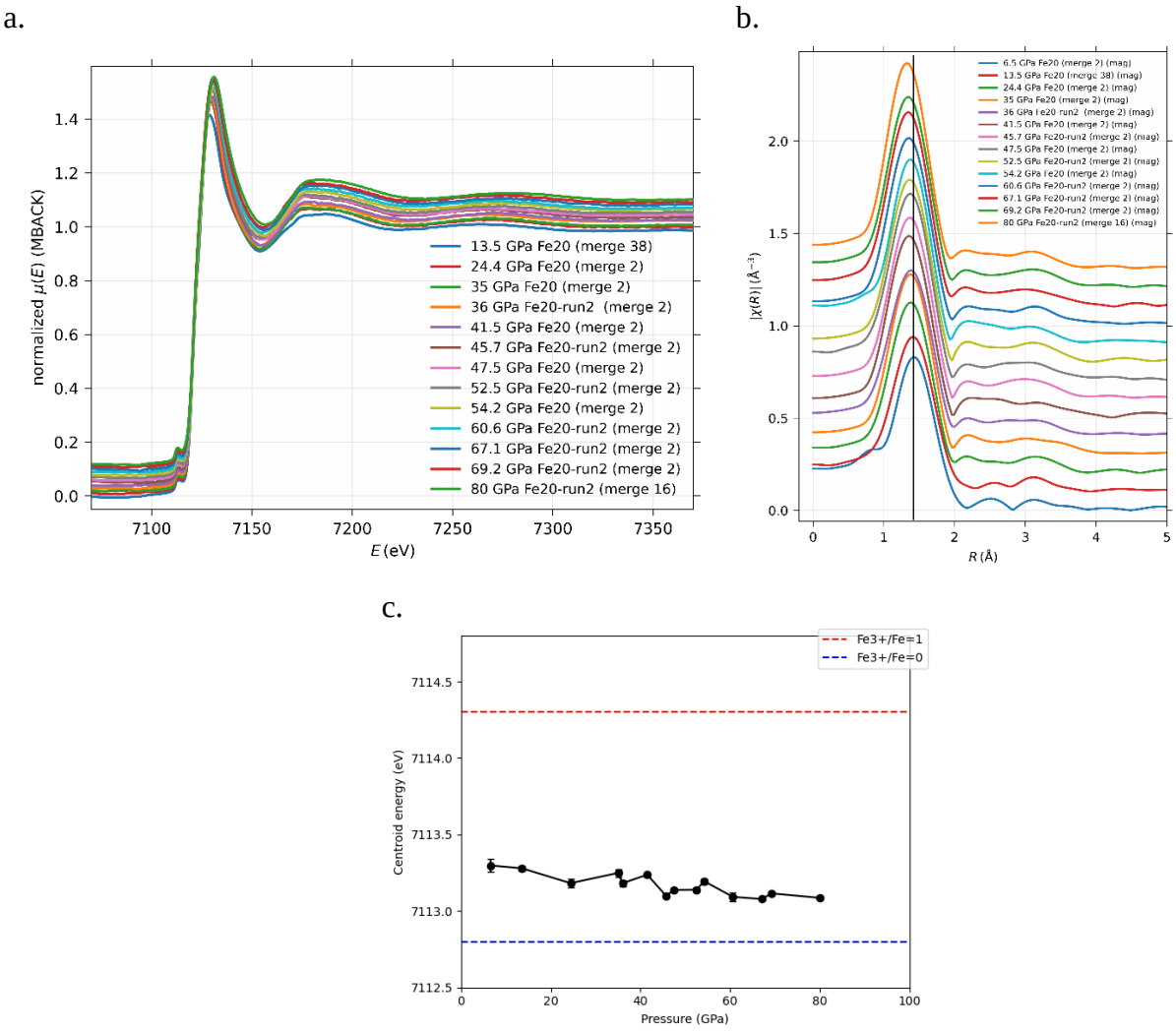

Figure 1: Preliminary results obtained on (Mg,Fe)SiO3 glasses on BM23 beamline under static compression at 300 K. a. Evolution of XAS spectra as function of pressure. b. Corresponding χ(R) modulus showing densification of the first coordination shell. The black vertical line serves as guide for the eyes to compare the spectra. c. Pre-edge centroid position shows the sample remains in the same oxidation state under pressure, close to pure Fe^{2+} according to calibrations available in the literature.

Mali garnet. Regarding the Mali garnet samples, we were able to collect XAS data up to 75 GPa. From both EXAFS and XRD we observed a densification of the garnet structure and extend existing equation of state measurements for And50-Gro50 garnet. These anisotropic P-V data at 300 K constrain the elastic compression path of garnet and comparison with recent Hugoniot measurements made at LULI2000 facility indicate a drastic compressibility change occurs in between 75 GPa and 175 GPa, possibly related to amorphization. Such insight

will be very useful for the analysis and the conduct future shock compression experiments. Although we did not observe amorphization of the sample in this pressure range, precluding the comparison between the dense glass and the future liquid data, we observed changes in the edge and pre-edge feature related to the oxidation state of Fe. Preliminary analysis suggests it could be related to a pressure-induced transition from Fe^{3+} to Fe^{2+} which would indicate a potential redistribution of Fe cations in the garnet structure above 60-70 GPa. This transition is also accompagnied by a strong edge shift at 75 GPa.

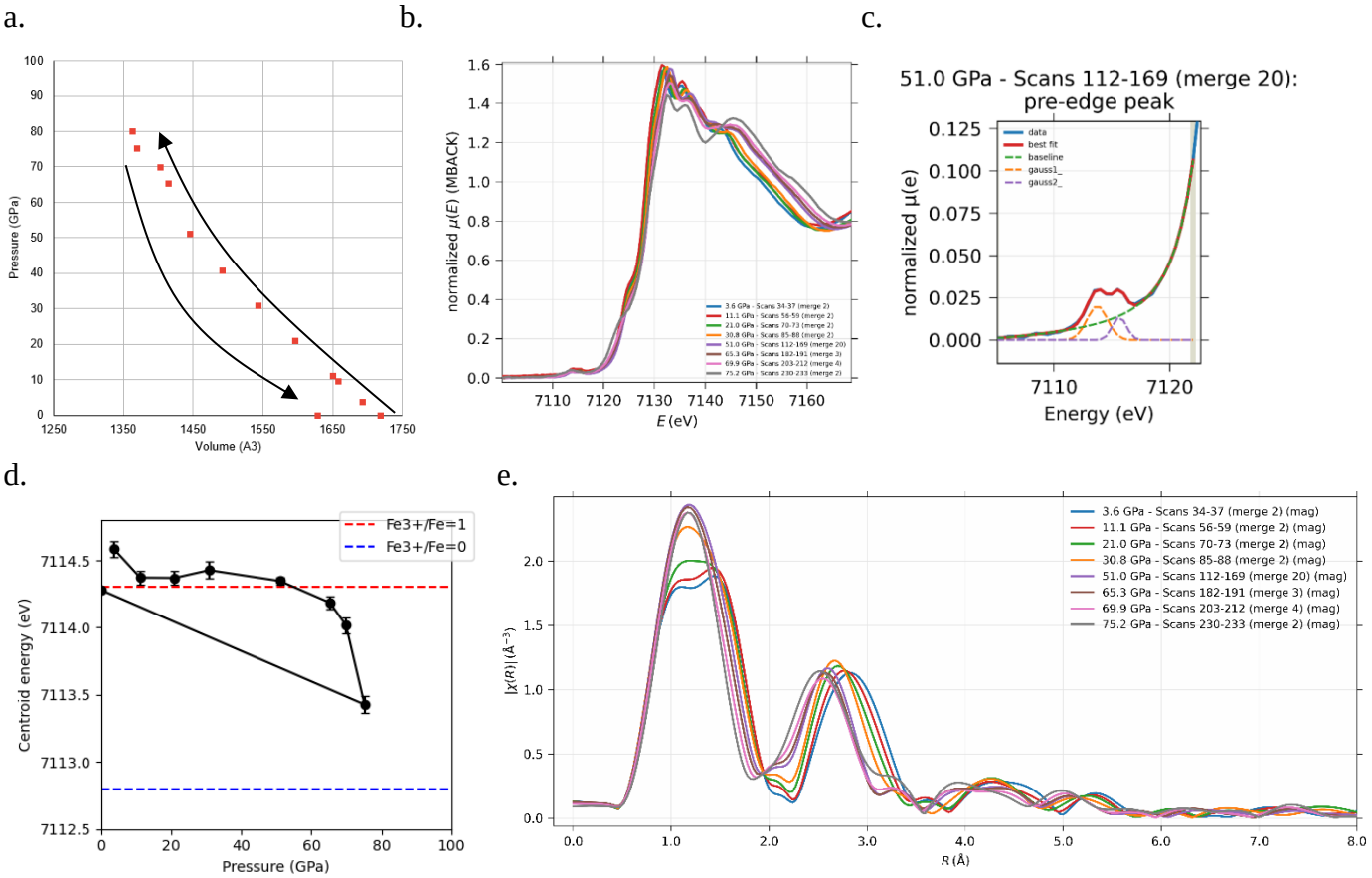

Figure 2: Preliminary results obtained on And50-Gro50 garnet on BM23 beamline (ES1245) under static compression at 300 K. a. P-V equation of state data. Arrows indicate the compression path followed during the experiment. b. XANES part of the normalized XAS data. c. Example of pre-edge feature at 51 GPa, fitted using a two-component model. d. Pressure dependence of the pre-edge centroid. The dotted lines show the expected values for pure Fe^{3+} silicates (red) and for pure Fe^{2+} silicates (blue). e. χ(R) modulus as function of pressure, showing the shortening of atom distances around Fe atoms.

FeSiO alloys. Iron mixed with 11wt% Si and 16wt% O was loaded in a diamond anvil cell together with a KCl flakes that served as pressure transmitting medium and pressure calibrant for XRD. This type of sample was shot on ID24-ED+HPLF during beamtime ES1102 (PI: G. Morard). The sample was compressed up to 73 GPa and revealed a behaviour and XAS signal extremely similar to the one expected for pure Fe or Fe with < 4 wt% Si, to such an extent it helped us understand the sample shots during ES1102 did not have the expected composition. This triggered further characterization and helped a lot the analysis of ES1102 (internship of Gabriele Garofalo).

As a conclusion, we obtained interesting results during this first experiment on BM23. In addition of the strong support these results will provide to future ID24-ED+HPLF experiments, they also represent high-quality and likely publishable results by themselves. The comparison with the upcoming second part of ES1245 will determine the strategy to approach.