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: 26/07/2023 to: 02/08/2023	**Date of report**: 11/09/2023
Shifts: 18	**Local contact(s)**: Jean-Alexis Hernandez, Raffaella Torchio, Nicolas Sevelin-Radiguet	*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.

The first part of ES-1245 allocation was performed on BM23. XAS measurements of statically compressed (Mg,Fe)SiO3 glasses (Fe/Mg=0.05, 0.1 and 0.2), Mali (Andradite50-Grossular50) garnet were obtained. The results are presented in ES-1245 first experimental report and show a monotonic density increase in both samples with the exception of Mali garnet at the highest pressure conditions (80 GPa) where a potential change of oxidation state and local structure in the crystal were observed.

This second experimental report presents preliminary results that were obtained during in late July 23 on the ID24-ED beamline and the High Power Laser Facility. Both $(Mg,Fe)SiO_3$ glass (with Fe/Mg=0.2) and Mali Garnet were loaded by laser-driven shock-compression and probed by ultrafast XAS.

Laser-driven shock-compression was performed using the High-Power Laser Facility. The samples were driven with 5, 7 and 10 ns-long flat-top pulses with 60 J at 1053 nm and focused on a 450x250 μm^2 focal spot, leading to a maximum intensity of ~7 TW/cm^2 taking into account the efficiency of the focusing system. Sample free surface or sample/LiF window interface velocities were measured thanks to the two VISAR systems available on HPLF. With this setup, we reached up to ~210 GPa in Mali Garnet and ~170 GPa in $(Mg,Fe)SiO_3$ glass according to VISAR measurements and known Hugoniot of the samples and LiF.

The beamtime was initially planned over 18 shifts but due to a high-voltage electrical component failure in the probe laser, we were only able to have VISAR data during the 5 last shifts. Therefore, we shot $(Mg,Fe)SiO_3$ glass (with Fe/Mg=0.2) and Mali Garnet only during these 5 shifts as no meaningful results can be obtained without the VISAR diagnostics. This problem limited the number of shots and sampling of PT. Nevertheless, we were able to obtain reasonable results on fewer conditions. We were also able to do few test shots on Almandine garnets $(Mg,Fe)_2Al_3Si_3O_{12}$ composition (Fe with 2+ oxidation state) for next runs. It turned out that these samples have much improved XAS quality (likely due to better microscale homogeneity) and are very promising for future experiments.
Also, we positively noticed HPLF-produced shocks and probing are highly reproductible, so that it becomes possible to sum spectra (see tests on Almandine garnet). We did not follow this strategy because of the limited amount of time after repair of the probe laser but we will consider this approach in future experiments as it could drastically improve the XAS signal on samples with low concentration of absorbing atoms.
Finally, we succeeded in generating and observing reflective shock fronts in rear polystyrene windows which are used to determine the shock pressure inside the sample. This feature is still not correctly observed in other X-ray facilities coupled high-power lasers and it demonstrates the good quality of the VISAR optical system.

Hereafter we present a preliminary analysis of XAS data obtained during this beamtime, with a comparison between DAC and single-bunch shock results.

$(Mg,Fe)SiO_3$ glasses

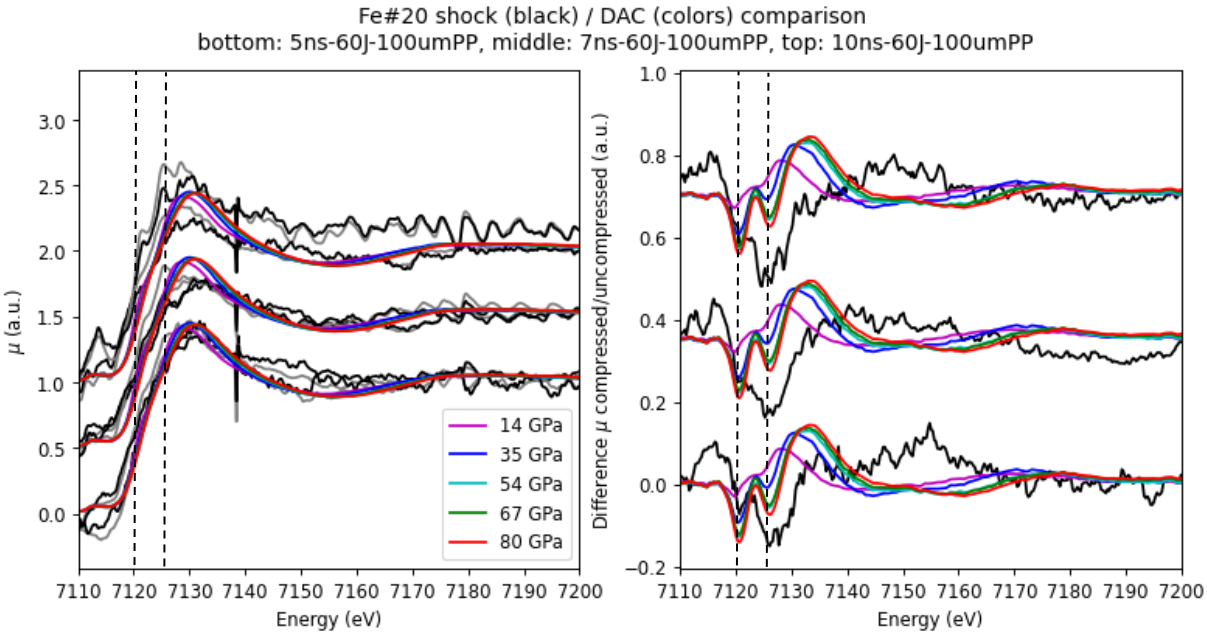

Figure 1: Left: XAS spectra obtained on shocked $(Mg,Fe)SiO_3$ glasses on ID24-ED+HPLF beamline (gray: unshocked sample; black: shocked). The top spectra were collected at a pressure of ~170 GPa along $(Mg,Fe)SiO_3$ glass Hugoniot, well above the liquidus. The middle and bottom spectra were collected at lower

pressure yet to be determined (estimated around 100 GPa for the bottom spectrum). DAC data at 300 K from BM23 are visible ontop of each shock data and are colored according to the legend.
Right: Difference between ambient and compressed XAS spectra. It shows similarities between DAC and shock compressed samples, with in particular to dips at 7120 and 7126 eV which are enhanced by increasing pressure/density. The remaining discrepancy between DAC and shock data is interesting and reproductible, and is likely due to the effect of temperature and will be investigated in depth.

Mali garnet.

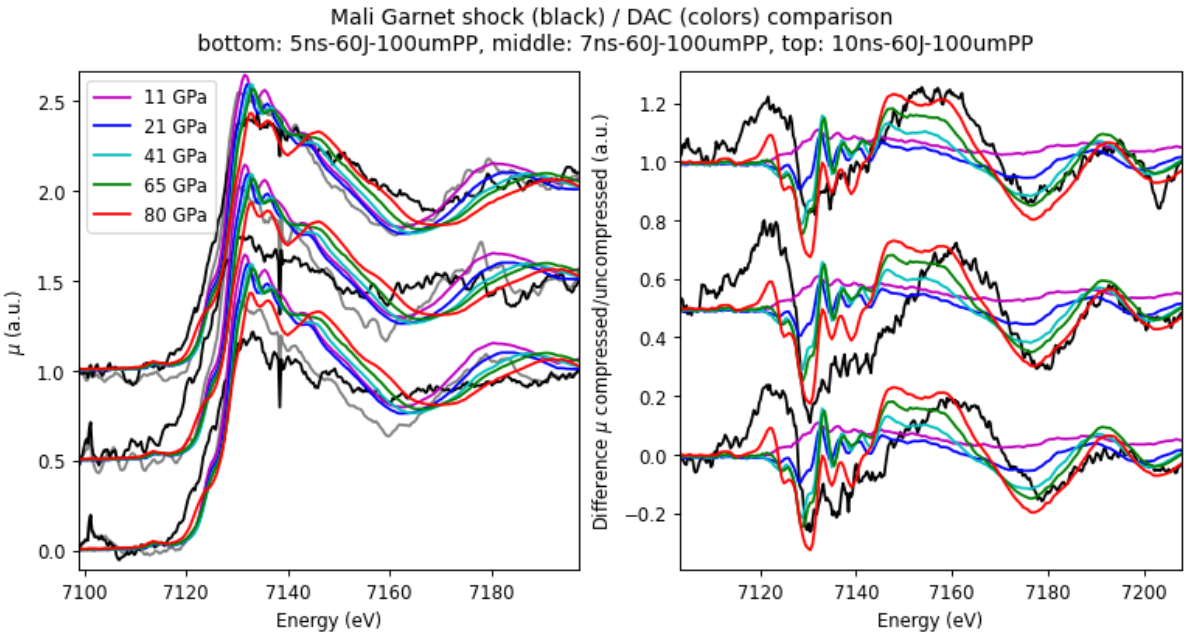

Figure 2: Similar analysis and DAC/shock comparison for the Mali Garnet. Highest shock pressure is around 210 GPa (top) and lowest shock pressure is 135 GPa (bottom).

Tests on Almandine garnet.

a. b.

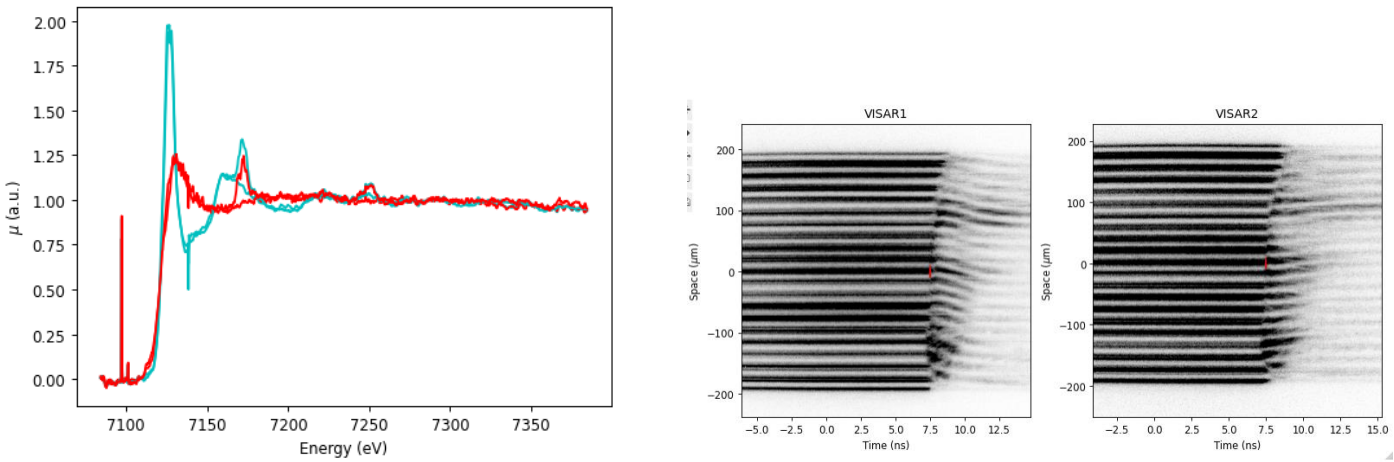

Figure 3: a. XAS data for two shots on Almandine garnets (cyan: unshocked, red: shocked. In the two shots conditions were the same, except the presence of a LiF window in one target in order to have a good pressure determination (207 GPa). However the Bragg spots from the LiF window create the peaks visible in one of the two spectra. The XAS quality is much better than in glass and Mali Garnet, so that it is unambiguous the shocked sample underwent melting/amorphization. b. VISAR images corresponding to the target with a LiF window

attached at the rear of the sample. The breakout of the shock from the sample into the LiF window occurs at 7.4 ns and the fringeshift is proportional to the velocity of the sample/LiF interface. Pressure is then determined by impedance mismatching between LiF and the sample. The red bar indicate the space-time region probed by XAS, i.e. right at breakout from the sample here, meaning 100% of the sample was shocked.

The low XAS quality of Mali Garnet and glass compare to Almandine garnet is likely due to microscale heterogeneities inside these samples and also on lower Fe concentration. However, qualitative comparison with DAC data is excepted to be achievable. In particular, temperature effects are still visible (edge broadening and EXAFS oscillation dampening) and visible trends will be further investigated with DFT-MD+FEFF simulations. The excellent quality of shocked almandine garnet XAS data will allow more quantitative analysis and refinement of the first coordination shell. Summing several shots could even allow to resolve pre-edge feature in more details.

As a conclusion, the results obtained on ID24-ED+HPLF will provide a nice comparison between shock and DAC on two different silicate systems relevant for geoscience. They prove that study of dense silicate liquids with shock+XAS is possible and it may become a common approach in the future. We learnt the sample quality is crucial for having good XAS quality due to the dispersive geometry of ID24-ED, although acquiring data over multiple shocks could be a simple way to improve the XAS quality. Finally, in depth analysis of the results should provide the first experimental insights of the local structure of dense Fe-bearing silicate liquids over 100 GPa.