| ESRF | **Experiment title:** Exploration of $Fe_2O_3$ phase diagram with laser shock compression and time-resolved XAFS measurement at ESRF | **Experiment number:** HC3782 |
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| **Beamline:** ID24 | **Date of experiment:** from: 21/11/2018 to: 02/12/2018 | **Date of report:** 19/04/2019 |
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Report:

Iron–oxygen (Fe-O) binary systems are of the utmost importance for planetary evolution. However, their phase diagrams and physical properties at extreme pressure and temperatures are poorly known. As an example, recent static compression experiments have demonstrated the existence of new iron oxide stoichiometries at high pressure and temperature such as FeO2, Fe4O5, or Fe5O6. These discoveries, with the wide variety of iron oxides phases existing at high pressure, highlight the complexity of iron- oxygen phase diagram in extreme condition. In this context we propose to study the physical properties, phase transition processes and phase diagrams of Fe2O3 by the mean of laser shock compression technic.

We have measured time-resolved X-ray absorption spectroscopy of laser compressed hematite ($\alpha$-$Fe_2O_3$) at the ID24 beamline in parallel with laser compressed pure Fe samples. We used the same setup geometry of [Torchio and al., Scie. Report, 2016] (fig.1a). A 15J, 8.8 ns laser was focused down to 240$\mu$m. We used 3 different kind of target designs (fig.1b) to reach different thermodynamic conditions. The first design, used in previous experiment, consists in a CH 4$\mu$m/diamond 40$\mu$m/$Fe_2O_3$7.2 $\mu$m/diamond 40$\mu$ assembly. Hydrodynamic simulations (multi) have been performed at the laser conditions of the experiment and show that the thermodynamic conditions remain stable during 7-8ns. The pressure reached is about 30GPa. The 2 other target designs allow to reach higher pressure, roughly 70GPa, beyond the Mott phase transition of $Fe_2O_3$ (around 50GPa). The second target design is layered as following CH 60$\mu$m/$Fe_2O_3$ 5.9$\mu$m/sapphire 40$\mu$m and allows to keep thermodynamic conditions during 2-3ns. The third target design, easier to fabricate, corresponds to CH 60$\mu$m/$Fe_2O_3$ 4.0$\mu$m, and thermodynamic conditions deteriorate rapidly due to the fast expansion of the rear side of the target. Polycrystalline iron oxide samples were obtained by physical vapour deposition at IMPMC.

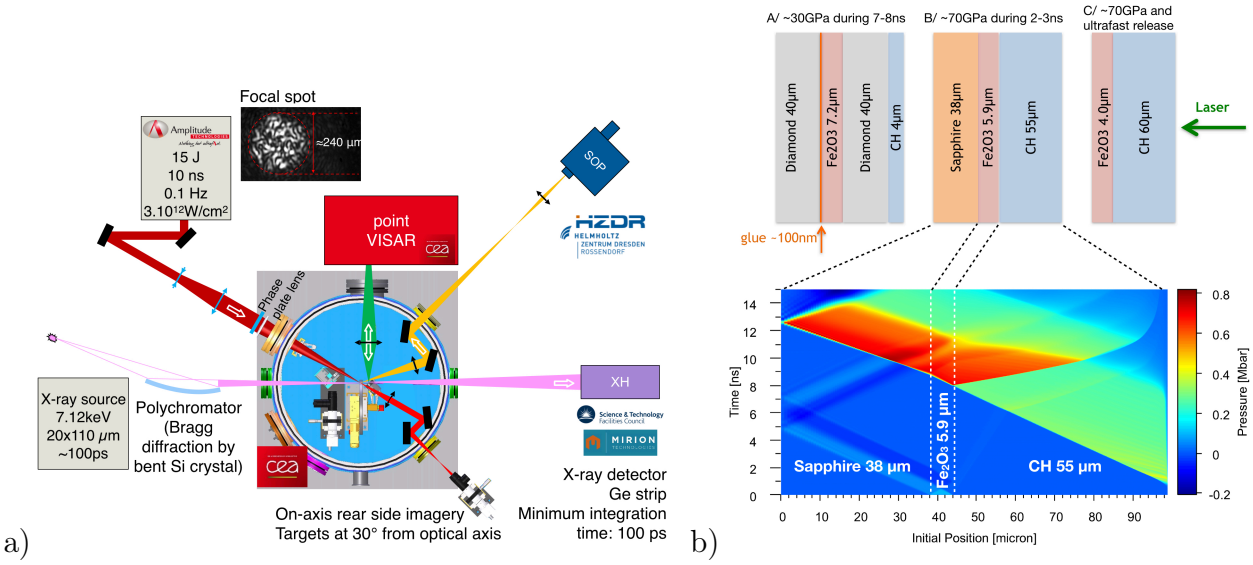


FIGURE 1 – a) Experimental setup at ID24. b) Target designs used in the experiment and MULTI hydrodynamic simulation of the shock compression for design B, with intensity of 0.95 $10^{12}$W/cm$^2$, 8.8 ns laser pulse duration and we used sesame table of hematite for EOS (7440).

X-ray absorption spectrum have been acquired for each target design and with varying delays between the laser pump and the X-ray probe. Fig 2a shows a delay scan for the target design B and for similar laser intensities (3.0 $10^{12}$ W/cm2). When comparing with hydrodynamic simulations, we can relate the changes in the XANES features with the thermodynamic history of the sample. Before laser compression, the XANES spectrum shows the typical ambient Fe2O3 XANES spectral features. During compression, the first XANES oscillation shifts to higher energies and shift back to lower energies during the shock release. This behaviour is similar to the observations obtained with static compression (Laser Heated Diamond Anvil Cell, LH-DAC) at equivalent pressures as seen in

fig2b.

In addition, we can observe successives energy shifts of the edge during laser shock compression, first towards higher energy at early times and back to lower energy during release. X-ray absorption spectrum on target design C show also shift of the edge of 1-2 eV, but at low energy, as we see on Fig1c. Further analysis are needed and comparison with DFT simulations will allow understanding such changes that might be related to changes of the oxidation state and spin transition during shock compression.

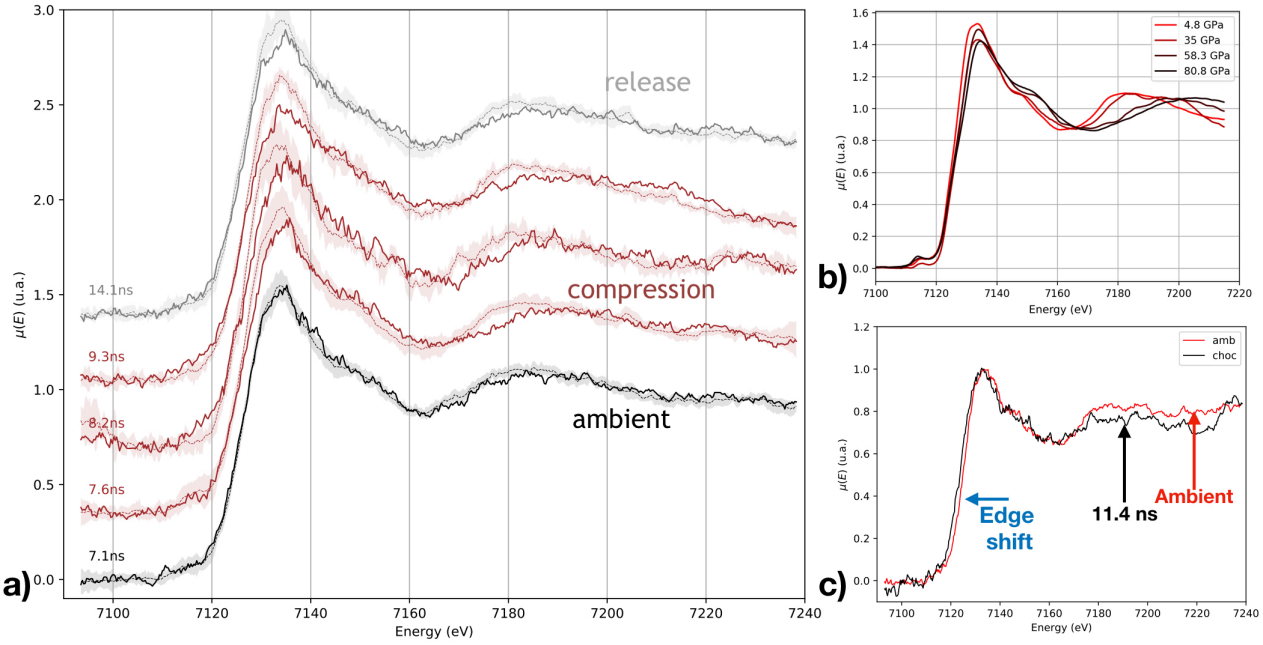


FIGURE 2 – a) X-rays absorption spectra obtained for target design B for different delays showing the evolution of XANES during the shock. Continuous lines are shocked spectra and dotted lines corresponding to the average of ambient spectrum before shock. b) X-rays absorption spectra of $Fe_2O_3$ compressed with diamond anvil cell, done at ID24 in November 2017 [Boulard and al., Am. Geo. Union, 2019]. c) X-rays absorption spectrum for target design C and a delay of 11.4 ns.

To continue the analysis we will extract exact thermodynamic conditions for each target design. For that purpose, we will compare different approaches : we will estimate the pressure in the sample by comparing the XANES spectrum obtained from pure iron target with previous laser compressed iron data from [Torchio and al., Scie. Report, 2016] ; we will compare quantitatively the shift of the XANES oscillation of $Fe_2O_3$ samples with static measurements [Boulard and al., Am. Geo. Union, 2019] ; we will constrain hydrodynamic simulations with VISAR data performed on Al/CH targets ; we will finally use the laser shock arrival time estimated from the XANES delay scans.

In the near future more advanced analysis will be done comparing our experimental data with spectra obtained with ab initio calculations, such as FEFF and Quantum Espresso.

Future experiments at the ID24 beamline will benefit from a higher energy of the drive laser and from additional optical diagnostics (VISAR and SOP) to extract more precisely thermodynamic conditions. We would also plan to vary the spectrometer settings in order to measure higher resolution XANES around the edge, as well as wider spectral range settings to measure single-shot EXAFS. It will allow following fine pre-edge features of Fe2O3 and refine structural properties (EXAFS fit) at several hundreds of GPa, and above, by using the foreseen higher intensity laser. Those measurements will be improved also with higher x-ray flux (within the EBS upgrade) and higher signal to noise ratio (with an improved version of the detector). Finally we will extend this project to FeO and Fe3O4 iron oxides.