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| ESRF | **Experiment title:**<br>"Density and redox state of deep magma oceans" | **Experiment number**:<br>ES-1236 |
| **Beamline**:<br>ID16B | **Date of experiment**:<br>from: 21/09/2022 to: 26/09/2022 | **Date of report**:<br>01/03/2023 |
| **Shifts:**<br>15 | **Local contact(s)**:<br>Remi Tucoulou | *Received at ESRF:* |

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# Report:

## Scientific Background

Iron is a key element to understand the Earth's composition, formation and evolution through time. Because of its three possible valence states and abundance, iron controls the oxygen fugacity ($fO_2$) in the Earth's mantle and thus plays a major role for the speciation and partitioning of elements. Recently, Mössbauer spectroscopy was used to show that $fO_2$ can change in silicate magma as a function of pressure [1] due to differences in the relative compressibility of $Fe^{2+}$ and $Fe^{3+}$-bearing melt components, described as follows:

$$FeO_{(liq)} + 1/4\ O_2 = FeO_{1.5\ (liq)} \quad (1)$$

However, these experiments were limited in pressure up to 24 GPa, and performed on compositions (*i.e.,* andesite melt) that are not relevant for the deep mantle. The relative compressibility of oxide components in silicate melts leads to structural changes as a function of pressure (*e.g.,* [2]). At equilibrium, differences in molar volumes ($\bar{V}$) of the FeO and $FeO_{1.5}$ components with pressure ($P$) impact upon their stability, with the resultant change in Gibbs Free Energy of formation ($\Delta G^o$) described by:

$$\Delta G^o_{(1),T,P} = \Delta G^o_{(1),T,1\ bar} + \int_{1\ bar}^{P} \Delta \bar{V}_{T,P} dP, \quad (2)$$

During a previous beamtime we measured $Fe^{3+}$ and a $Fe^{2+}$ bearing-peridotitic glass up to 71 GPa. Our results show that, at low pressure, the density of peridotitic glass with 68% Fe3+ is slightly lower than that of peridotitic glass with 100% $Fe^{2+}$. However, the density of the oxidised sample increases more rapidly with pressure, such that its density is higher than that of the reduced counterpart above 10 GPa. This indicates a higher compressibility of the $Fe^{3+}$-rich glass at high pressures. During this beamtime, our aim was to perform X-ray absorption technique at ID16B on peridotitic compositions with pure $Fe^{2+}$ and 68% $Fe^{3+}$ up and on basaltic glasses containing pure-$Fe^{3+}$ and pure-$Fe^{2+}$ up to 130 GPa to estimate the change in $fO_2$ up to the core-mantle boundary. Indeed, the X-ray attenuation ($I/I_0$) through the sample, measure at ID16, permits measurement of the linear absorbance ($\mu_{HP}$), which is directly correlated to the density ($\rho$) of the material through the relationship $\rho_{HP}/\mu_{HP} = \rho_0/\mu_0$.

## Experimental procedure

On the beamline, we performed data collection on pure ferrous- (BG-08) and 100% ferric- (BG-04) basaltic glass, immersed in a methanol:ethanol mixture up to 33 GPa. we also collected data on pure-$Fe^{2+}$ (PM10-05) and 68% $Fe^{3+}$ (PM10-02) peridotitic glass, loaded as powder and without pressure medium from 0 to 130 GPa to complete our previous experiment (ES-938), hoping to have a full data set for this composition. To generate

high pressure, we used our own BX90 DACs equipped with radial openings allowing measurements through the beryllium gasket. Pressure was monitored with ruby fluorescence at low pressures (P<10 GPa), and Raman spectra for diamond were collected offline for high pressures (P >10 GPa). At each pressure step, we collected 2D absorption maps on both peridotitic and basaltic glass in two orientations: through the Be-gasket and through the diamonds *(Figure 1)* up to 118 and 33 GPa, respectively.

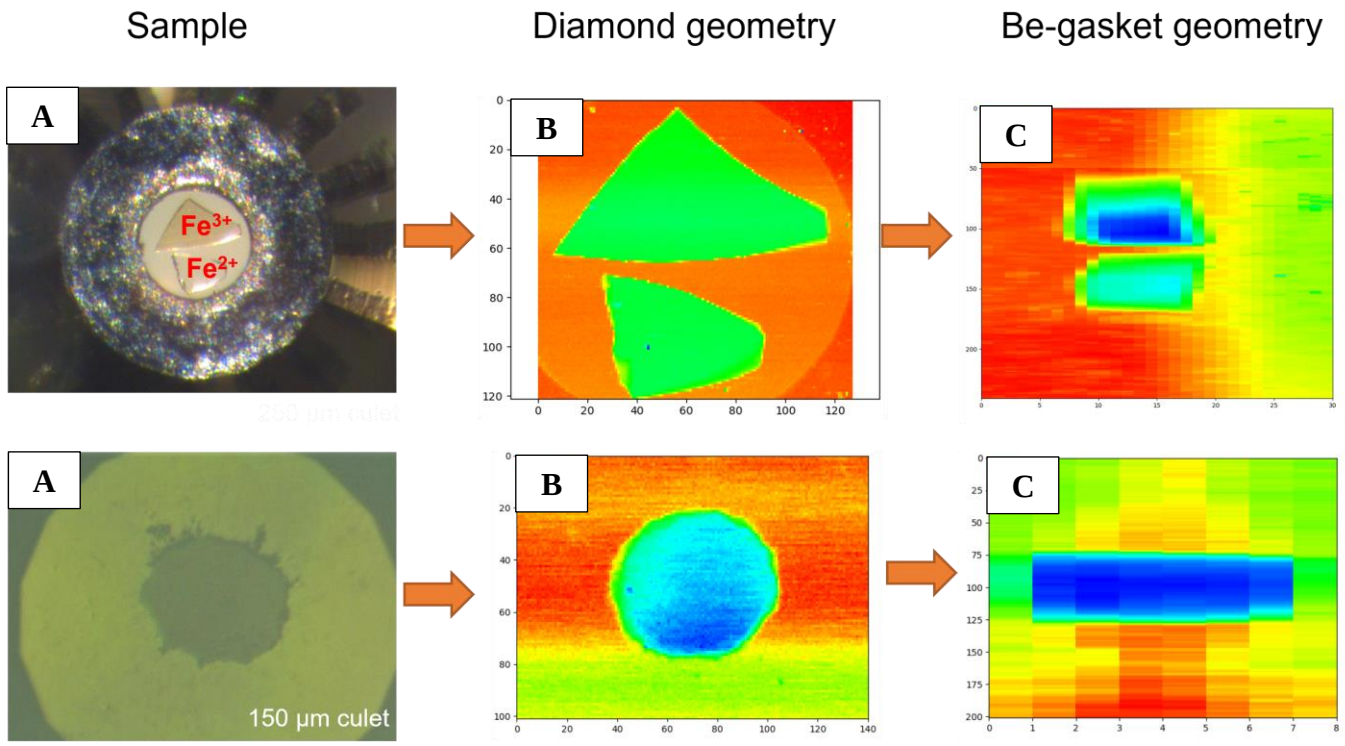


**Figure 1**: First row, two samples loaded together in the same DAC with methanol:ethanol mixture as pressure medium, observed by optical microscope and through X-Ray attenuation (B,C). Second row, one sample loaded as powder, without any pressure transmitted medium in a DAC, observed by optical microscope (A) and through X-Ray attenuation (B,C).

**Preliminary results**

X-ray absorption data were collected using a sub-micron beam size at 9 keV. We performed experiments at high pressure in diamond anvil cells (DACs) on peridotitic glasses and basaltic glasses up to 118 GPa and 33 GPa, respectively. However, between the two experimental runs, the beamline electronic has been changed and the gain for the diodes have been modified compared to our first visit. This caused a saturation of the diode (*Figure 2*) for the background measurements of the high pressure (HP) samples, such that data collected above 40 GPa *(Figure 3)* are unusable and therefore losing about a couple of days of measurements. As can be seen in *Figure 3* part of the information of the sample is lost and smeared with the background. The diode only starts to count after a certain threshold and part of the sample is below that threshold and the background only shows one value that makes it impossible to fit and subtract from the sample data.

Furthermore, the gain range of the "It" diode is not the same for the high pressure sample and the standards, thus the later are not possible to use to extract the density of the sample. Therefore, to conclude our density work (*e.g.* ES-938) we have to measure again both $Fe^{2+}$ and $Fe^{3+}$ peridotitic glass up at high pressure.

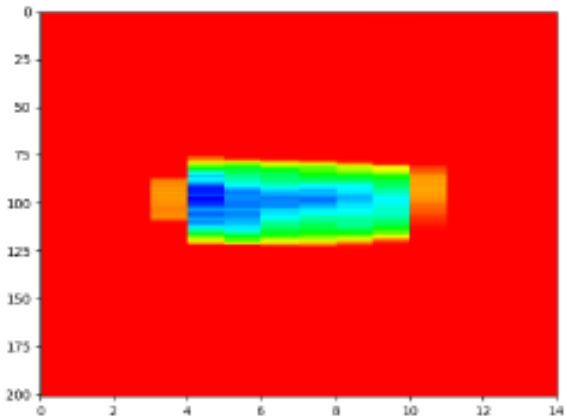

**Figure 2:** Example of a saturation of the diode with loss of background information

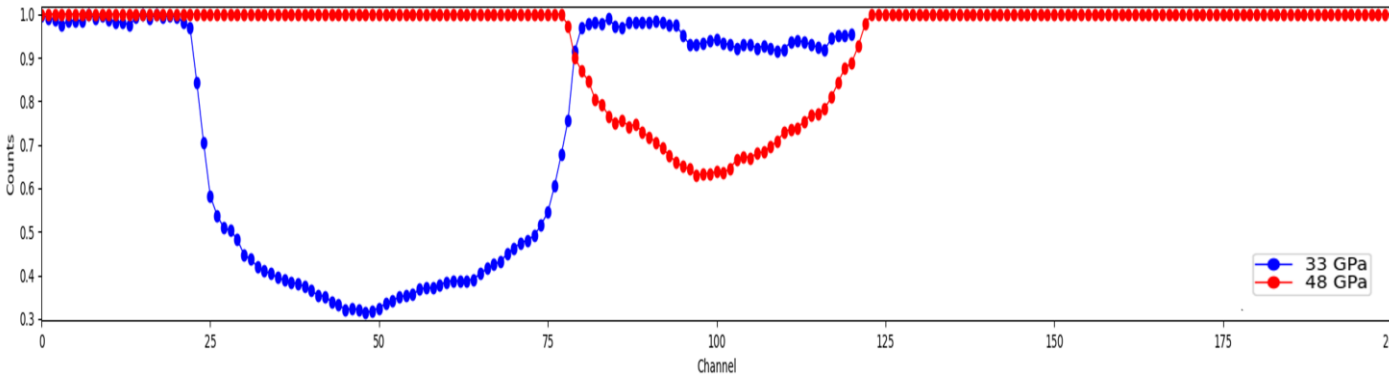


**Figure 3:** Red line show the data collected on PM10-02 at 48 GPa, which is an example of a saturation of the diode resulting in loss of background information and its impossibility to compared the X-ray attenuation ($I/I_0$) with the same sample at different pressure (e.g. the blue line). Indeed, the $I/I_0$ should increase with pressure.

**References:**

[1] Armstrong et al., (2019) Science, 365, 903–906 [2] Kress & Carmichael (1991) CMP, 108, 82-92