Names and affiliations of applicants (* indicates experimentalists):

Petitgirard Sylvain[a,*], Sossi Paolo [a,*] and Girani Alice [a,*]

a)Laboratory ETH Zuerich Institute of Geochemistry and Petrology Clausiusstrasse 25 CH - 8092 ZUERICH

Report:

Scientific Background

Iron plays a key role in understanding the Earth's composition, formation and evolution through time. Because of its three possible valence states (Fe^{2+}, Fe^{3+} and Fe^0) and its abundance, iron controls the oxygen fugacity (fO_2) in the Earth's mantle but also strongly influences the density of silicate melts because of its mildly incompatible behavior that results in its enrichment in liquids relative to solids. During the early Earth's formation, wholesale melting of its mantle could have occurred due to large planetary impacts such as the Moon-forming impact [1,2] and melt may have accumulated at the core-mantle boundary, facilitating the formation of a basal magma ocean [3]. The presence of a magma ocean may have facilitated the formation of the different terrestrial reservoirs; core, mantle and crust, as well as the segregation of elements depending on their speciation and chemical affinity. Recently, Mössbauer spectroscopy was used to show that fO_2 can change in silicate magma as a function of pressure [4] due to differences in the relative compressibility of Fe^{2+} and Fe^{3+}-bearing melt components, described as follows:

$$FeO_{(liq)} + 1/4\ O_2 = FeO_{1.5\ (liq)}\ (1)$$
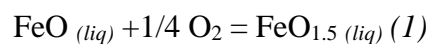
However, these experiments were limited in pressure up to 24 GPa, and performed on compositions (*i.e.,* andesite melt) that are not relevant for the deep mantle. The relative compressibility of oxide components in silicate melts leads to structural changes as a function of pressure (*e.g.,* [5]). At 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 (ΔGo) described by:

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

Therefore, during this beamtime our aim was to investigate peridotitic compositions with pure Fe^{2+} and 68% Fe^{3+} to estimate the change in fO_2 with depth by the determination of the absorption and therefore the absorbance in order to calculate the density changes between different redox state of melts at high pressure.

Experimental procedure

On the beamline, we performed data collection on pure ferrous- (PM10-05) and 68% ferric- (PM10-02) peridotitic glass, as confirmed by synchrotron Mössbauer spectroscopy at ID18, immersed in a methanol:ethanol mixture, at high pressure. 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 in two orientations: through the Be-gasket and through the diamonds up to 71 GPa.

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 two peridotitic glasses: PM10-05 and PM10-02, based on the composition of KLB-1 and synthesized under different redox conditions. During the experiments we collected 2D-maps in two orientations: i) through the diamonds to obtain the path length (x) of the X-rays through the sample and ii) through the Beryllium gasket in order to measure the X-ray attenuation of the glass under pressure (*Fig. 1*).
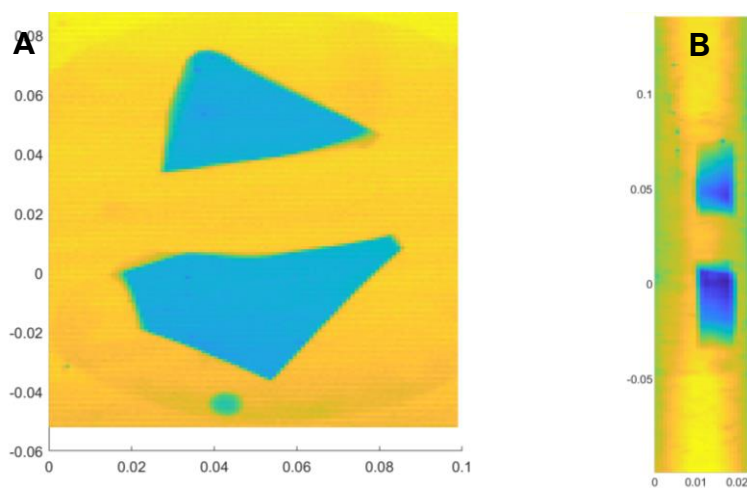

Figure 1: A) Map through the diamonds from which the sample´s dimensions are determined. B) Absorption map through the beryllium gasket

The correlation between the X-ray attenuation and the path length of the sample obtained from both maps provides the absorbance (μ_{HP}) of the sample. As shown in *Fig.2*, μ_{HP} increases from low pressure to high pressure in both Fe^{2+} and 68% Fe^{3+} peridotitic glass. However, the slope is different in the two samples. Indeed, even if both samples show a similar absorbance at low pressure, increasing pressure the two curves start to diverge significantly one each other. Different value of absorbance (μ_{HP}) led to a different density's evolution between Fe^{2+} and Fe^{3+} (*Fig.2 B*). Indeed, our results show that, at low pressure, the density of peridotitic glass with 68% Fe^{3+} 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, as also inferred from iron force constants [6]. Hence, the fO_2 (relative to IW) of a peridotitic liquid with constant Fe^{3+}/Fe^{2+} is expected to decrease with pressure in magma oceans, in accord with previous studies [4, 7].
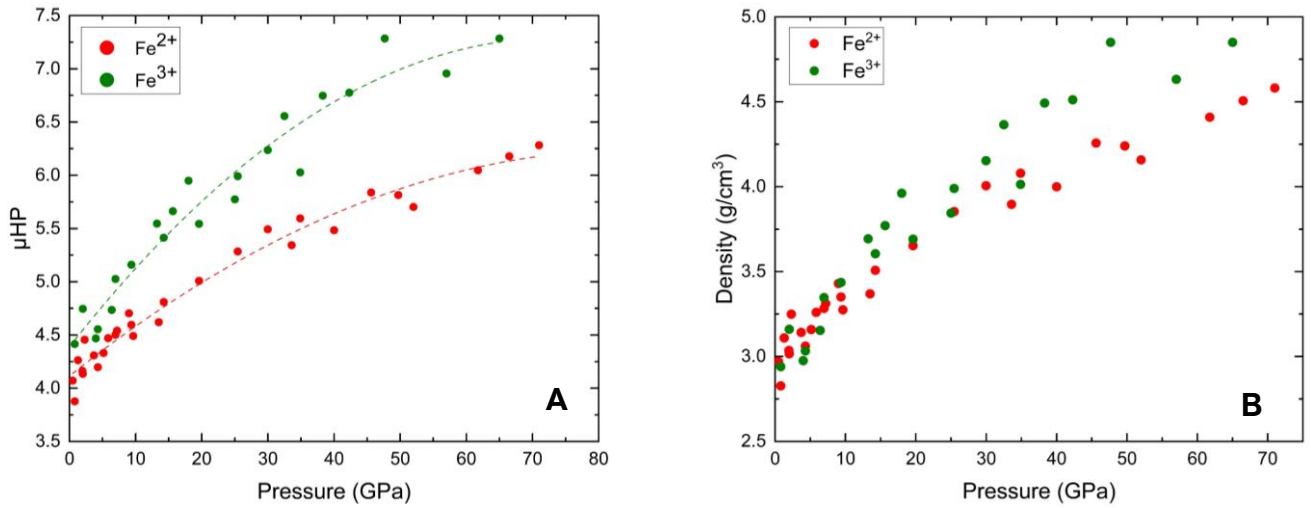
Fig 2. A) Absorbance (μ_{HP}) evolution of pure-ferrous- (Fe^{2+}) and 68% ferric (Fe^{3+})- peridotitic glass. Two dashed lines are shown to guide the reader. B) Pressure-induced density change of both ^{57}Fe peridotitic glasses. The density of the oxidised sample increases more rapidly with pressure compared to the reduced counterpart.

References:
[1] Jacobsen et al., (2014) Nature, 508, 84-87 [2] Canup et al., (2001) Nature, 412, 708-712 [3] Labrosse et al., (2007) Nature, 450, 866-869 [4] Armstrong et al., (2019) Science, 365, 903–906 [5] Kress & Carmichael (1991) CMP, 108, 82-92 [6] Ni et al. (2021), GRL, 49, e2022GL098451, [7] Deng et al. (2020), Nature Comms. 11, 2007.