	Experiment title:	**Experiment number:**
![ESRF logo] **ESRF**	"Spin transition in ferric and ferrous silicate magmas at high pressure"	ES-959

Beamline: ID18	**Date of experiment:** from: 27/10/2020 to: 02/11/2020	**Date of report:**
Shifts: 15	**Local contact(s):** Georgios Aprilis	*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 it has been reported that the fO_2 can change in silicate magma as a function of pressure [1] due to the differences in the free energies of Fe^{2+} and Fe^{3+} as follows:

$$FeO_{(liq)} + 1/4\ O_2 = FeO_{1.5\ (liq)}\ (1)$$
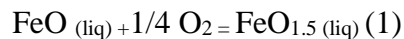
However, these experiments were limited in pressure to 24 GPa, and on compositions not relevant for the deep mantle (*i.e.* andesitic melt). During a previous beamtime we measured an iron-rich silicate $Mg_{0.7}Fe_{0.3}SiO_3$ composition with mixed Fe^{3+}/Fe_{total}, as analogue of dense magma on top of the core-mantle-boundary (CMB) (see report ES-777). We found that a possible spin crossover between high-spin Fe^{2+} and low-spin Fe^{2+} takes place in such composition at about 110 GPa. During this beamtime our aim was to investigate peridotitic compositions with pure Fe^{2+} and pure Fe^{3+} end-members to clearly elucidate if a spin transition can be expected for these two components or if it applies only to Fe^{2+} species, which would then affect the equilibrium constant of equation (1) and therefore the convention processes and the interaction of magma ocean with the first atmosphere.

Experimental procedure

On the beamline, we measured the synchrotron Mössbauer spectroscopy (SMS) signal on our enriched ^{57}Fe-glass at high pressure and room temperature (298 K) using a BX90 diamond anvil cell [2] equipped with different diamond culet's size (100 µm, 150 µm, 250 µm) depending on the pressure target. Both reduced and oxidized ^{57}Fe-enriched peridotitic glass were ground to a powder and then loaded inside a rhenium gasket without pressure-transmitting medium. The rhenium foils were pre-indented down to 40, 20 or 15 µm thick for 250 µm,150 µm and 100 µm diamond culet size respectively. A hole in the rhenium gasket of 120 µm, 60 µm or 40 µm, depending on diamond culets, was drilled using a laser drill machine that serves as a sample chamber for the powdered glass. Typically, the pressure is increased by steps of 6 - 12 GPa over the entire pressure range, up to 172 GPa. Pressure was measured using the Raman shift of the diamond culet at the centre of the compression chamber. We mounted an optical bench offline in the laser-lab of ID18 to conduct absorption measurements. A tungsten-lamp was shine through the sample and the signal intensity through the sample was

recorded from the backside by a spectrometer. We repeated these measurements up to pressure of 172 GPa. Spectra were fitted using a recent developed SYNCmoss software (Yaroslavtsev *et al.*, submitted).

Preliminary results

SMS data were collected at the end of October 2020 at ID-18. We performed SMS in-situ at high pressures in a diamond anvil cell (DAC) on two peridotitic silicate glasses, PM10-05 and PM10-02 based on the composition of KLB-1 and synthesized under different redox conditions, up to pressures of 172 GPa. As shown in *Figure 1*, Mössbauer spectra of PM10-05 show a clear change in the general shape with increasing pressure. At pressure below 26.5 GPa, the spectra are characterised by two well-defined dips, of different intensity, in the count rate. However, increasing the applied pressure the distance between the two absorption peaks increases. Indeed at 103 GPa a new clear dip appears, which becomes the second most important absorption peak at the maximum pressure condition of 172 GPa. SMS show that PM10-05 at 1 bar, contain Fe with 87% of a Fe^{2+} high spin (HS) doublet, '*d1*', and a 13% contribution from a second site, known as the '*d2*' feature, with hyperfine parameters intermediate between those of Fe^{2+} HS and Fe^{3+} HS. With increasing pressure, the contribution of *d2* increases at the expense of *d1* to become the predominant site at pressures beyond 120 GPa (*Figure 5*) , suggesting therefore that *d2* is actually Fe^{2+} in the low spin (LS) configuration, which is in agreement with its hyperfine parameters at higher pressure (*Figure 2*). Thus, PM10-05 is entirely made of ferrous iron.
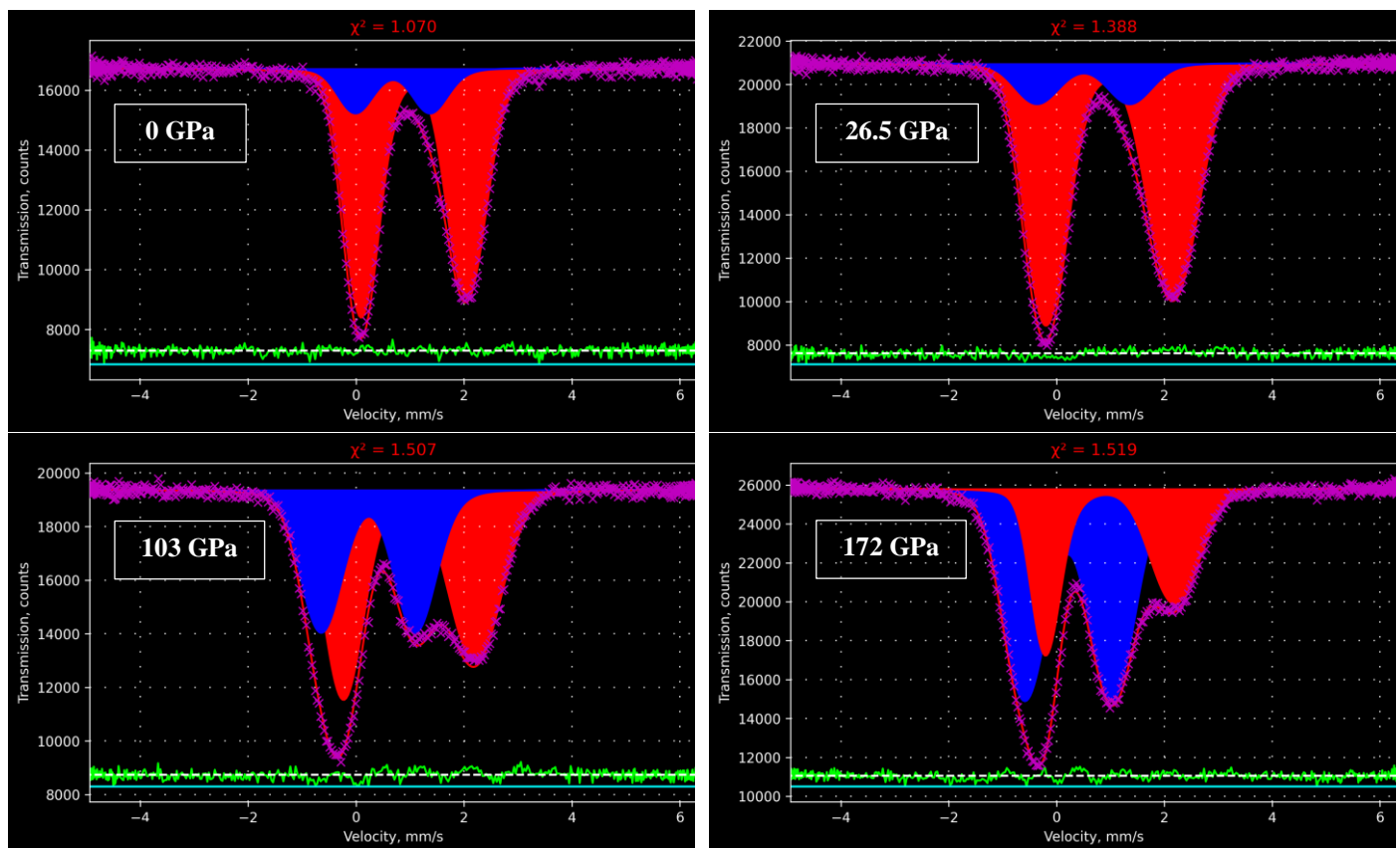

Figure 1: Selected Mössbauer spectra of PM10-05 at different pressures conditions and room temperature. Mössbauer data are indicated by purple crosses while the fitted curve is shown by the solid red line. The red and the blue doublets show the sites of Fe^{2+} high-spin and Fe^{2+} in the low-spin configuration, respectively. The solid green line shows the fitting residual.
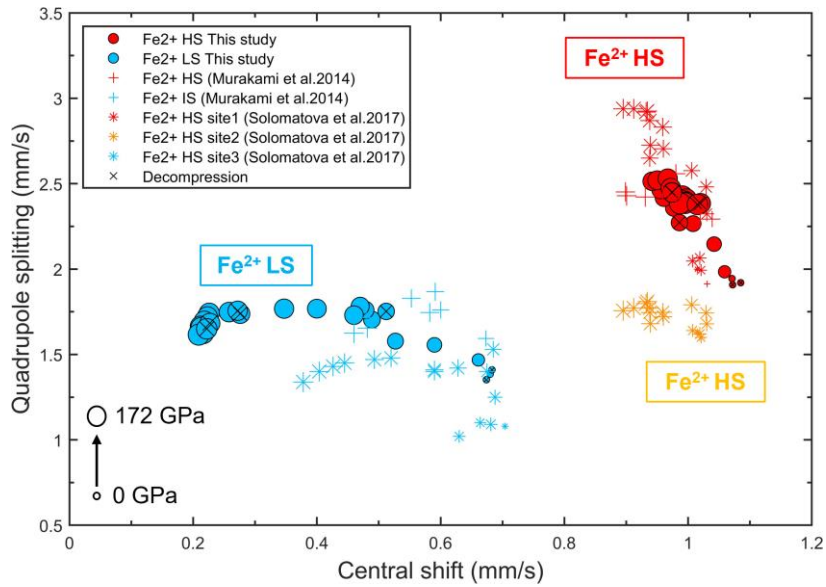
Figure 2: Hyperfine parameters of ferrous iron in PM10-05 peridotitic glass compared to results obtained by previous studies [3,4] on enstatite and basaltic glasses, respectively. The symbol size are plotted as function of pressure, in the ascending mode, as shown in the figure at the bottom left.

As PM10-05, also the oxidized peridotitic glass (PM10-02) shows changes in the shape of the Mössbauer spectra as a function of pressure. However, on a first sight, the Fe^{3+}-bearing PM10-02 sample seems to show an opposite trend respect to PM10-05. At room condition the Mössbauer spectrum of PM10-02 shows three dips in the count rate, however the area occupied by the less intense absorption peak decreases with increasing pressure until it almost disappears at 155 GPa (Figure 3). The decrease in the intensity of the third peak can be attributed to the decrease in the site occupancy at higher central shift, favoring iron sites with lower central shift and quadrupole splitting. The best fit of Mössbauer spectra collected on PM10-02 is achieved with two doublets at ambient conditions and then three doublets (corresponding to different three sites) over the entire high pressure range. Indeed, on the basis of the hyperfine parameters determined at 0 GPa *(Figure 4)*, the oxidized glass is not made exclusively by ferric iron but contains also a small amount of ferrous iron. In particular, PM10-02 is composed of 67(1)% Fe^{3+} and 33(1)% Fe^{2+} and this proportion is kept constant when fitting the spectra obtained at higher pressures. Indeed, the recoil free fraction has been taken into account. As shown in *Figure 5*, the ferrous iron, also in the oxidized sample, undergoes into a spin crossover from the high to the low spin configuration above 70 GPa. Hence, ferrous iron spin crossover seems strongly affected by the presence of ferric iron in the system.
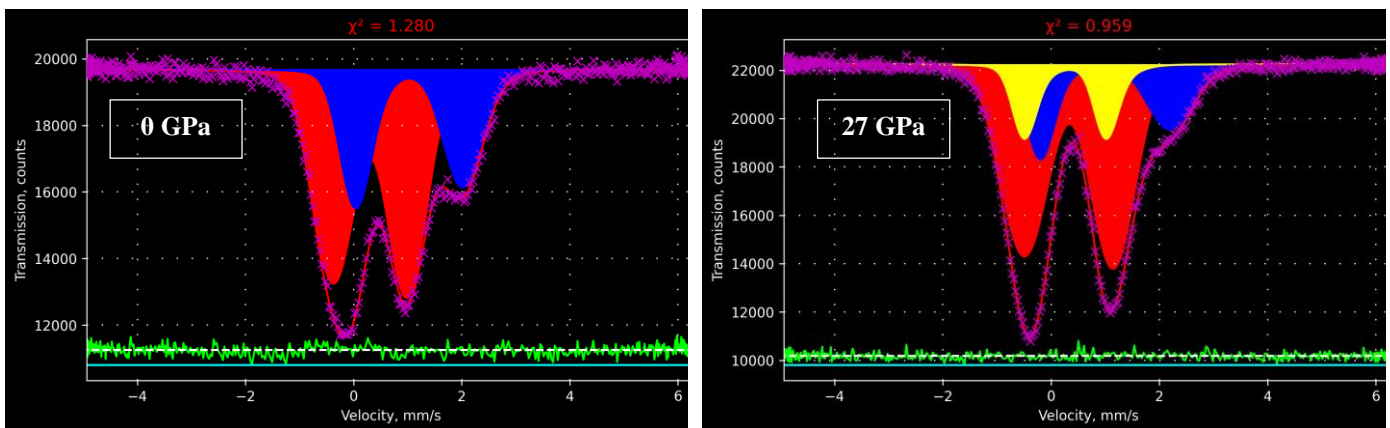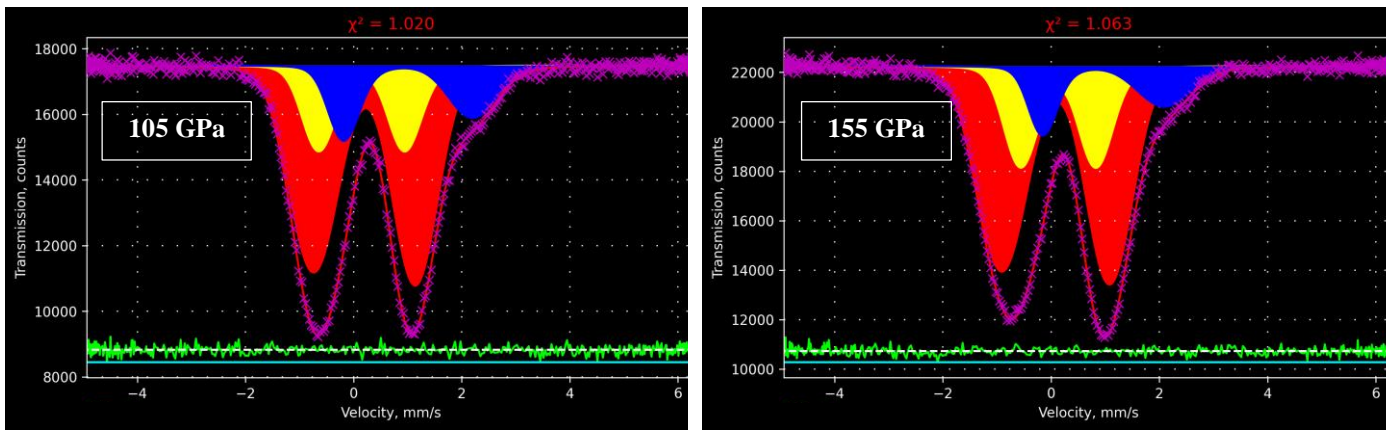
Figure 3: Selected Mössbauer spectra of PM10-02 at different pressures conditions and room temperature. Mössbauer data are indicated by purple crosses while the fitted curve is shown by the solid red line. The red and the yellow doublets show the sites of Fe^{2+} high-spin and Fe^{2+} in the low-spin configuration, respectively. Whereas, the blue doublet represent the Fe^{3+} in the high spin configuration. The solid green line shows the fitting residual.
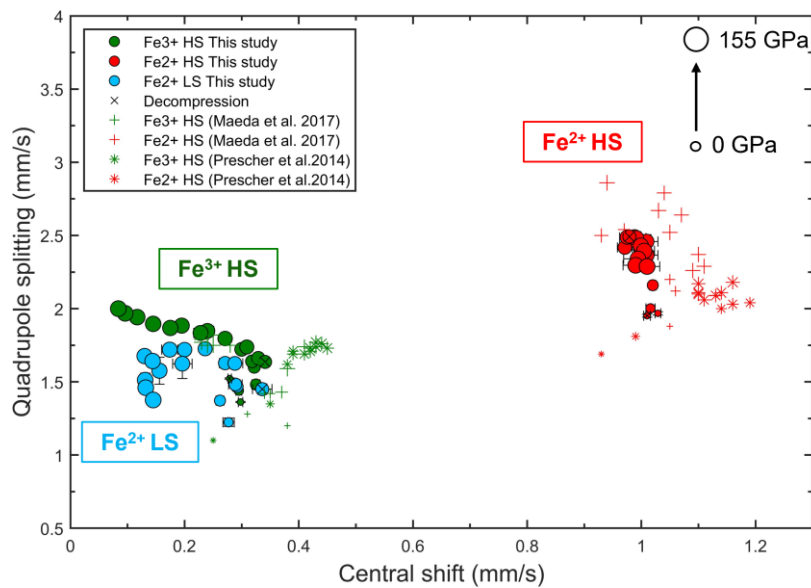

Figure 4: Hyperfine parameters of Fe^{2+} and Fe^{3+} in PM10-02 peridotitic glass. The symbol size are plotted as function of pressure, in the ascending mode as shown in the figure at the top right.
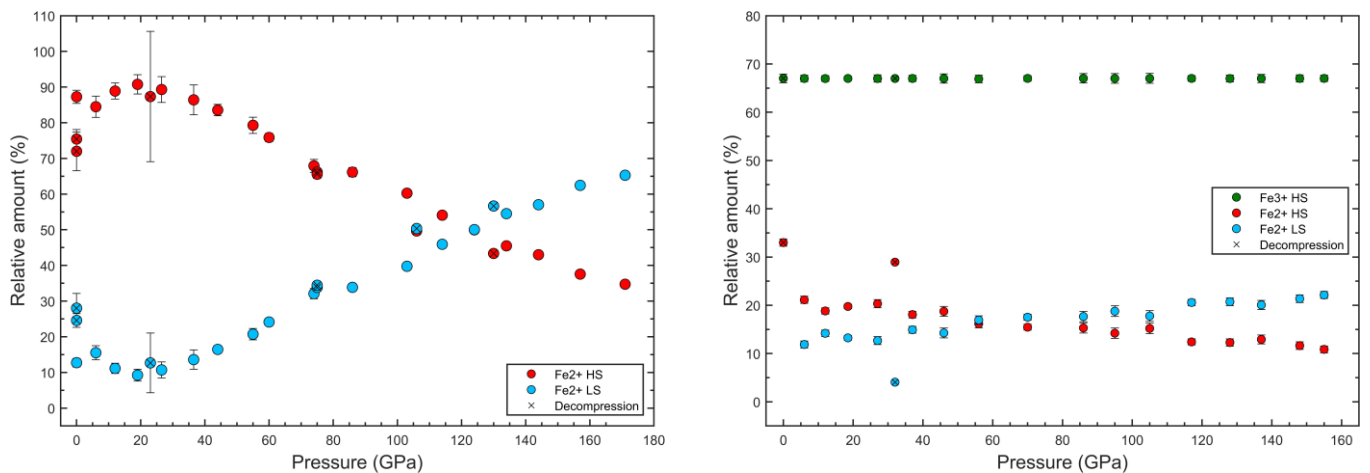

Figure 5: Relative amount of ferrous iron in the high spin (red dots) and in the low spin (light-blue dots) configuration in PM10-05 (left) and in PM10-02 (right)

References: [1] Armstrong *et al.,* (2019) *Science*, 365, 903–906; [2] Kantor *et.al.,* (2012) Rev. Sci. Instrum., 83(12), 125102; [3] Murakami *et al.,* (2014) *Nat. Commun.*, 5(1), 5428; [4] Solomatova *et.al.,*(2017) *J. Geophys. Res.*, 122(8), 6306–6322.