ESRF	**Experiment title:** Compositional effect in the pressure-induced spin crossover transition of magnesio-siderite solid solution revealed by x-ray Raman scattering	**Experiment number**: ES-357
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Report:

The aim of this study was to examine the pressure driven magnetic high-spin (HS) to low-spin (LS) transition in magnesio-siderite solid solution using in-situ X-ray Raman scattering at the iron $M_{2/3}$-edge at room temperature with focus on the impact of the material's composition on the transition pressure, the width of the transition and the transition range. Owing to the low solubility of carbon in mantle phases, magnesio-siderite solid solution is a candidate for carbon storage of the inner Earth [1,2]. The spin state in mantle minerals strongly influences its macroscopic properties as conductivity, sound velocity and compressibility. Therefore, it is important to study pressure induced spin state changes at conditions which are present in the interior of the Earth to better understand the dynamic behavior of such a complex system.

A $[(Mg_{0.6}Fe_{0.4})CO_3]$ single crystal of 20x25x10 μm^3 in size was loaded into a diamond anvil cell (DAC) with a gas driven membrane provided by the ESRF with rhenium gasket and helium as pressure medium to guarantee quasi-hydrostatic conditions. The pressure was determined by the ruby fluorescence method. Spectral changes in the spin-transition range of the magnesio-siderite single crystal would allow us to characterize the spin state in very detail, complementary to other techniques such as x-ray absorption, x-ray emission and Mössbauer spectroscopy.

In the experiment ES-357 we were able to measure the iron $M_{2/3}$-edge of magnesio-siderite single crystal by means of x-ray Raman scattering (XRS) to study the pressure induced high-spin to low-spin transition of iron. Compared to previous studys on the $M_{2/3}$-edge (ES-182, [3]) of siderite single crystal, the background subtraction is more complicated. This can be

explained by the fact that in addition to the scattered signal from the diamond the $L_{2/3}$-edge of magnesium also contributes to the background. The background subtraction procedure and the extracted iron $M_{2/3}$-edges are shown in Figure 1. Due to the imaging properties of XRS, one is able to separate the scattered photons coming from the sample

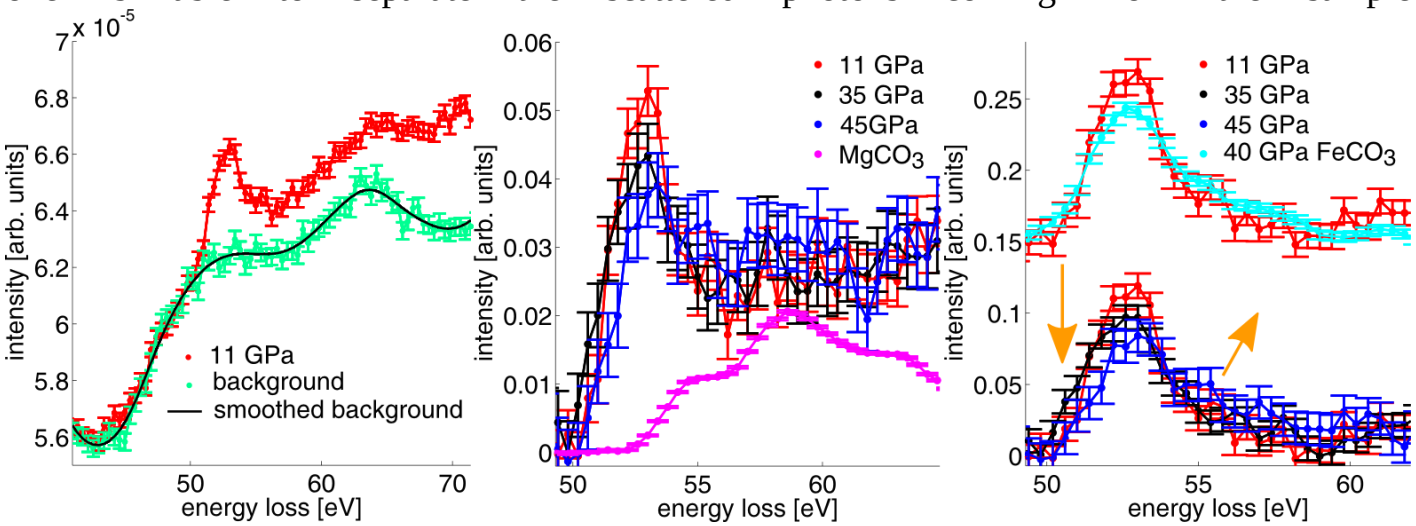

Figure 1: **Left:** Raw spectrum of the 11 GPa measurement of $Mg_{0.6}Fe_{0.4}CO_3$ and the corresponding background signal coming from the sample environment. **Middle:** Background corrected spectra of the magnesio-siderite solid solution and the Mg L-edge of $MgCO_3$. **Right:** Fe M-edges after subtracting the Mg L-edge spectrum. The changes as indicated by the arrows points towards an onset of the spin transition. The results so far suggest that increasing amount of magnesite shifts the transition to larger pressures.

environment from the sample signal. In order to subtract the Mg L-edge, we measured MgCO3 powder at ambient conditions. Due to pressure stability problems during the 45 GPa (non-hydrostatic conditions, large pressure gradient) measurement, we were not able to reach stable pressures in which the iron atom is in LS state although first indications for a spin state change (see arrows in Fig. 1) appear in the spectra. This trend suggests a strong compositional effect because the spectral changes of the end-member siderite iron M- and L-edges show a sharp magnetic transition already starting at 41 GPa [3]. Furthermore, problems with the diamonds within the DAC occurred so that we were not able to reach higher pressure. These problems have been solved for future experiments. However, a comparison of the 11 GPa spectrum shape with measurements of FeCO3 shows that we can control the complex background and are able to measure the iron M2/3-edge of geophysical relevant samples like magnesio-siderite solution. Moreover we identified an alignment and data acquisition scheme to conduct such experiments at samples with significant lower Fe content compared to siderite.

In a next step, we need to continue these measurements and to extend the pressure range up to 60 GPa to clearly identify the spin state change. The experimental findings will be confronted with calculations of the XRS spectra which are currently under work. Nyrow et al. [4] have shown, that it is possible to determine the crystal field splitting by comparing atomic multiplet calculations with the experimental data. With these findings we can verify whether there is a compositional effect on the transition pressure, the width of the transition and the transition range.

[1] W.R. Panero et al., Geophys. Res. Lett. 35, L14307 (2008); **[2]** M. Isshiki et al., Nature 427, 60 (2004); [3] C. Weis et al., Report to ES-182; [4] A. Nyrow et al., Appl. Phys. Lett. 104, 262408 (2014);