ESRF	**Experiment title:** The relation of pressure-induced spin transition and isotropic volume collapse in siderite and magnesio-siderite revealed by x-ray Raman scattering	**Experiment number**: ES-182
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Report:

The purpose of this investigation was to examine the pressure induced high-spin (HS) to low-spin (LS) transition of the end-member siderite of magnesite-siderite solid solution using in-situ X-ray Raman scattering at the iron M-edge and the iron L-edge at room temperature. Owing to the low solubility of carbon in mantle phases, these carbonates are candidates for carbon storage of the inner Earth [1,2]. Changes in the spin state of mantle minerals strongly influences the macroscopic properties as sound velocity, compressibility, and conductivity.

In the experiment ES-182 we were able to investigate the iron M-edge and iron L-edge of synthetic siderite ($FeCO_3$) single crystal in the pressure range up to 50 GPa. Lavina et al. [3,4] found the spin transition of natural siderite to occur at a pressure of 44-45 GPa by detection of a very sharp volume collapse using high-pressure x-ray diffraction and proposed the occurrence of high and low spin domains at the transition pressure. Lately, Spivak et al. [5] showed with high-pressure Raman spectroscopy that the spin transition of siderite sets in at approximately 40 GPa with a coexistence regime of high- and low-spin iron until complete transformation. Therefore, we explored the iron M- and L-edges at pressures in the transition regime to track the spin transition of a siderite single crystal.

We used the multi-analyzer spectrometer at beamline ID20 employing the Si 880 analyzer reflection at 12.9 keV to measure the XRS signal by scanning the incident energy with an overall energy resolution of about 2 eV. The iron L-edges were measured at low momentum transfer and the iron M-edges at high momentum transfer (corresponding to average

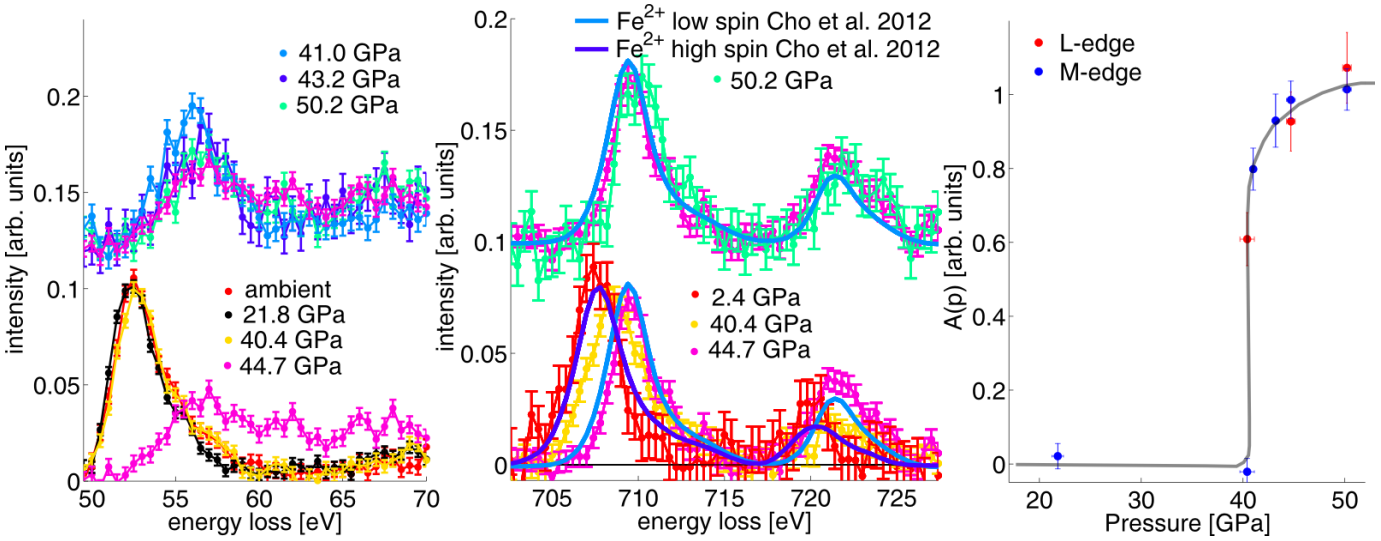

Figure 1: **Left & middle**: Results of both iron edges as a function of pressure. References for Fe2+ L-edge spectra of [Fe(tren(py)3)]2+ for the high and low spin state taken from [6] are shown as solid lines. Due to differences in resolution of the experiment, the latter were convoluted with a Gaussian (FWHM 1.7 eV). **Right:** Integral of the absolute values of the difference A(p) between the spectra taking the spectrum at ambient conditions as reference for the M-edges and the Fe2+ HS spectrum from [6] as reference for the L-edges. Values of A(p) are finally normalized to 1 in the LS state.

scattering angles of 25° and 143°). In order to expose the siderite single crystal (size about 25x35x14 µm^3) to high pressure, we used a diamond anvil cell together with a rhenium gasket and helium as a pressure medium. A ruby was loaded in the sample volume as pressure calibrant. The results of both edges as a function of pressure are presented in figure 1. Strong changes of spectral shape across the spin transition are observed. Strikingly, the changes observed at the L-edge are in line with e.g. reference spectra for low and high spin iron measured at ambient pressure conditions via soft x-ray absorption for $[Fe(tren(py)_3)]^{2+}$ [6]. This impressively exemplifies the high sensitivity of both edges to the spin state and evidences that the spin transition can be detected by M-edge spectroscopy. Analysis of the XRS spectra indicates that the spin transition is very sharp and started at approximately 41 GPa. This suggest a surprisingly large compositional effect on the spin transition as Lavina et al. used natural samples in their experiment and found the spin transition at much higher pressure.

In a next step, the experimental findings will be confronted with calculations of the XRS spectra which are currently under work. These very exciting results need to be confirmed and should be extended to a similar system, i.e. magnesite-siderite solid solution that is highly relevant for the understanding of the Earth's carbon circle, in order to investigate the compositional effect on the iron's spin transition in the solid solution which is highly debated [5,7].

[1] W.R. Panero et al., Geophys. Res. Lett. 35, L14307 (2008); **[2]** M. Isshiki et al., Nature 427, 60 (2004); **[3]** B. Lavina et al., Geophys. Res. Lett. 36, L23306 (2009); **[4]** B. Lavina et al., Phys. Rev. B 82, 064110 (2010) 427, 60 (2010); **[5]** A. Spivak et al., Phys. Chem. Minerals 41, 633 (2014); **[6]** H. Cho et al., Faraday Discuss. 157, 463 (2012); **[7]** J. Liu et al., Am. Mineral. 99, 84 (2014)