Decomposition of siderite and formation of tetracarbonates at conditions of the lower mantle

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Keywords: X-ray Raman spectroscopy, X-ray emission spectroscopy, Carbonates

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Iron-bearing carbonates are candidates for carbon storage in the deep Earth. Some of these carbonates, like siderite and magnesiosiderite, exhibit a complex chemistry at pressures above 80 GPa and temperatures above 1500 K resulting in the formation of tetracarbonates featuring tetrahedraly coordinated CO_4-groups instead of the typical triangular-planar CO_3-coordination of the parent materials. The understanding of the electronic properties, chemistry, and formation conditions of these tetracarbonates at high pressure and high temperature are in focus of recent research. Their stability field possibly reaches into the Earth's lower mantle [1, 2, 3].

We present a setup to establish the conditions in the lower mantle (up to 100 GPa, 3000 K) that can be apply for in situ studies of the carbonates' electronic and local atomic structure. The required pressure is accomplished by diamond anvil cells [4], in which the sample is heated double-sided by a Nd:YAG-laser. So far we used this setup to heat and pressurize $FeCO_3$ samples at core-mantle boundary conditions in order to synthesize samples for ex-situ studies. Alternatively, we exploited a different laser-heating scheme utilizing a CO_2-Laser. The temperature-quenched but still pressurized samples are characterized using x-ray diffraction and optical Raman spectroscopy. Subsequently, the electronic structure of the synthesized compounds is analyzed via combined x-ray absorption spectroscopy at the Fe K-edge (oxidation state, coordination) and x-ray emission spectroscopy (spin state, coordination). The measurements of changes in the shape of the Fe K_β emission is a fast and reliable way to obtain information about the spin state of iron (see Figure 1), while the valence-to-core emission provides information about the coordination chemistry around the iron. By using an energy dispersive von Hamos type spectrometer in combination with a Pilatus area detector, both spectra can be measured simultaneously [5]. These experiments will be complemented by parallel x-ray absorption measurements exploiting spatial mapping of the samples.

We present first results of these experiments and discuss the capabilities of this setup for in-situ x-ray spectroscopic studies.

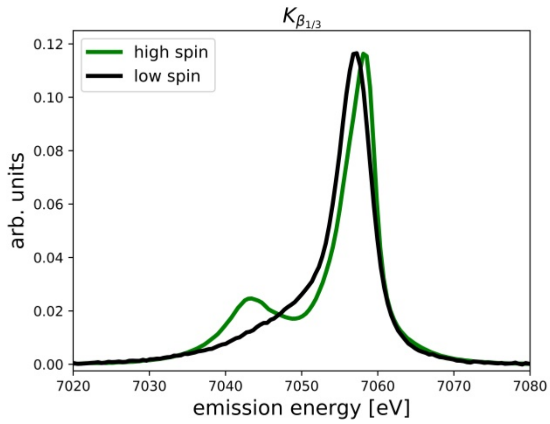

Figure 1: K_β emission spectra of high-spin and low-spin iron.

Acknowledgments: We thank PETRA III (beamlines P01 and P06) and Soleil (GALAXIES) for providing synchrotron radiation. We also thank S. Chariton, C. McCammon and L. Dubrovinsky for the synthesis of $FeCO_3$ single crystals at Bayerisches Geoinstitut. This work was supported by the DFG via STE 1079/4-1 (FOR2125, CarboPaT) and STE 1079/4-2. The FXE-group of XFEL is kindly acknowledged for providing a set of analyzer crystals for use with the von Hamos spectrometer.

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