ESRF	**Experiment title:** Electronic and magnetic structure of iron in bridgmanite at pressure conditions of the Earth's deep mantle	**Experiment number**: ES-773
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Report:

The spin transition in major mantle minerals was subject to many experimental and theoretical studies due to its impact on structural, physical and chemical properties of the minerals at pressure conditions of the Earth's mantle. In the case of the most abundant mantle mineral bridgmanite, the Fe spin transition is complicated by the crystal chemistry, because Fe may occupy the A and B-site of the lattice and the Fe oxidation state may vary and its mechanism is still under intense discussion.

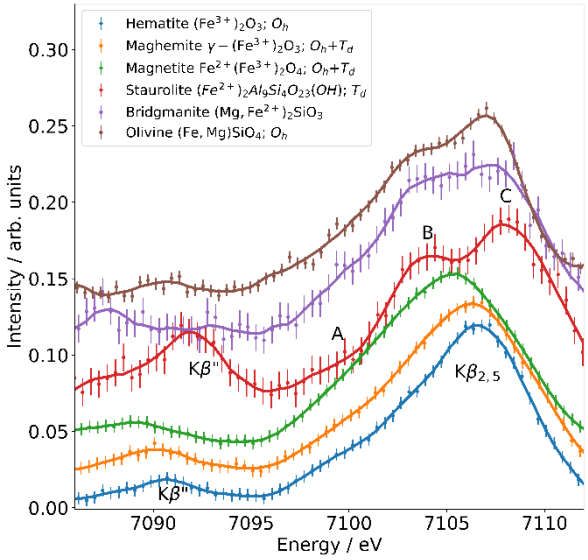

Figure 1: Shifted VtC XES spectra of iron-containing references with different oxidation-state and coordination.

The purpose of this experiment was to evaluate the capabilities of the von Hamos setup at ID09 for high pressure applications using diamond anvil cell (DAC) and to examine the magnetic high-spin (HS) to low-spin (LS) transition in bridgmanite ($Fe_{0.09}Mg_{0.91}SiO_3$) using in-situ X-ray emission spectroscopy (XES) at iron valence-to-core (VtC) and Kβ regime.

In order to characterize the von Hamos setup for application to iron-bearing materials we studied the reference systems Orthoclase (Fe(III) T_d), Acmite (Fe(III) O_h), Yoderite (Fe(III) C_{3v}), Staurolite (Fe(II) T_d), Siderite (Fe(II) O_h), Grandidierite (Fe(II) C_{3v}), Maghemite (Fe(III)), Magnetite (Fe(II+III)), and Olivine (Fe(II) O_h), a collection that covers iron in various coordination and oxidation states. These samples have been measured using a pink beam at 11 keV, a beam size of 1.5x0.5 mm^2 and a chopper setting of 6 µs resulting in about 4 10^{11} photons/s at the sample position. The von Hamos spectrometer was equipped with six Si(440) cylindrically bent analyzer crystals and the X-rays were detected using a Pilatus detector. Typical acquisition times for one spectrum were about 2-3 hours. Selected VtC spectra (Kβ regime not shown) are presented in fig. 1 as example for different local iron environments. Additionally, a series of different (synthetic and natural) iron-containing Li(Fe,Mn)PO_4 samples have been measured as references for the effect of iron content on the shape and intensity of the VtC and Kβ spectra as shown for the valence excitation regime in fig. 2. Such studies at ambient conditions can be properly conducted at ID09 but experiments on samples contained in high pressure environments are strongly limited by the necessity of using the chopper with pink beam. Moreover, occurrence of parasitic fluorescence signals excited by higher undulator harmonics can significantly obscure or contaminate the emission spectra reaching the detector by higher order reflections. Using the Si(111) monochromator suppresses these contaminations but on cost on overall intensity. Testing several settings (with monochromator, without monochromator, using different pink beam energies etc.) optimized setting for our experiment were determined as used for the measurements discussed above.

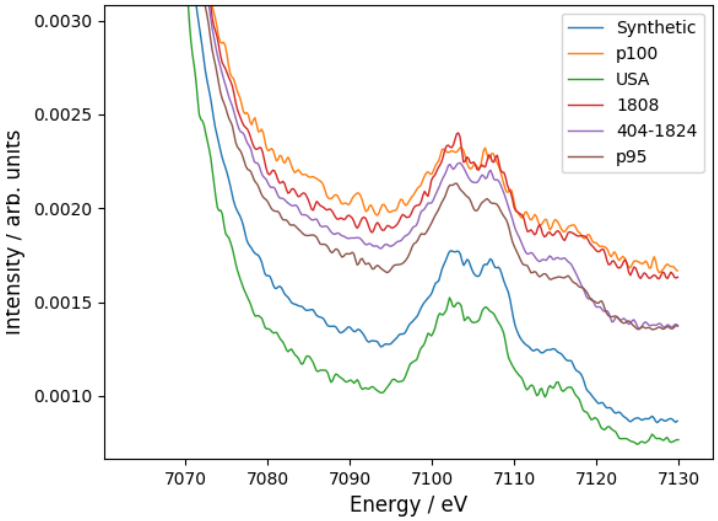

Figure 2: VtC series of lithium iron phosphates with varying iron content (e.g. high, blue). The spectra lay on the high energy tail of the $K\beta_{1,3}$ signal.

In order to test the possibility to investigate samples contained in a DAC probing the corresponding spin state by Kβ XES, we loaded a $Fe_{0.09}Mg_{0.91}SiO_3$ single crystal of 15x15x10 μm^3 in size a DAC (BX-90-RD-DAC) with a rhenium gasket and neon as pressure medium to guarantee quasi-hydrostatic conditions. The pressure was determined by the ruby fluorescence method. However, the overall intensity was not sufficient to extract a Kβ of fair quality, so that high pressure applications are feasible only if pink beam can be used without chopper.

The data of the reference samples will be further analyzed and compared to calculations of the VtC spectra pinning down the influence of iron's coordination and oxidations state on the overall shape of the measured emission lines.