| ESRF | **Experiment title:** P-T Nuclear Forward Scattering study from chemical decomposition of γ-spinel to the related post-perovskite transformation | **Experiment number**: HE-2157 |
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| **Beamline**: ID18 | **Date of experiment**: from: 11.10.06 to: 17.10.06; 06.02.07 to: 11.02.07 | **Date of report**: 01.03.07 |
| **Shifts:** 18 + 9 | **Local contact(s)**: Dr. Ulrich PONKRATZ | *Received at ESRF:* |


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**Report:**

Iron is not only the most abundant element in the Earth, but it is also the only major element with multiple electronic configurations (valence and spin state). The gain or loss of an electron or a change in the distribution of electrons between orbital states can profoundly influence both physical and chemical properties of the mantle and hence its dynamic processes [1]. Mössbauer spectroscopy is a powerful method for studying the electronic structure of iron compounds because of its high resolution and sensitivity to the valence and spin state of iron as well as the structural properties of the coordinating environment. A complementary method to Mössbauer spectroscopy is nuclear forward scattering (NFS) which is not only sensitive to the same hyperfine interactions, but can provide additional and/or unique information about the iron environment. The focus of the experiment was to collect NFS data relevant for the major iron-containing phases of the lower mantle in order to elucidate the electronic structure of iron and its influence on physical and chemical properties of the mantle.

The first part of the experiment was carried out over 18 shifts on ID18 in October 2006 during operation in 4 bunch mode, where the beam was focussed to ca. 4 μm × 20 μm using a Kirkpatrick-Baez mirror. We prepared a diamond anvil cell (DAC) containing $(Mg_{0.9}{}^{57}Fe_{0.1})_2SiO_4$ olivine at 40 GPa and transformed two regions ca. 30 μm × 60 μm each to $(Mg,Fe)SiO_3$ perovskite + (Mg,Fe)O at two different laser power intensities, with the goal of studying the effect of temperature on the nature of iron produced by chemical decomposition. We mounted an image plate behind the DAC and performed what we believe to be the first simultaneous collection of NFS and X-ray diffraction (XRD) data. We adjusted the position of the DAC to record three different regions of the sample: (1) laser heated at high temperature; (2) laser heated at low temperature; and (3) not laser heated (i.e., unreacted olivine), and repeated all measurements at three different pressures. Results showed measurable differences in the NFS and XRD data collected in the regions heated to different temperatures (Fig. 1), which likely reflect variations in Fe/Mg partitioning between the two phases and/or differences in $Fe^{3+}$ concentration. Spectral fitting of NFS data using MOTIF and refinement of XRD data using FIT2D is underway. During the same beam time we also collected NFS data of $Mg_{0.8}{}^{57}Fe_{0.2}O$ in the DAC at five pressures from 44 to 85 GPa to study spin crossover. Results showed an enhanced stability of low-spin $Fe^{2+}$ with increasing pressure, but with a significant amount of high-spin $Fe^{2+}$ still present at 85 GPa (Fig. 2) contrary to literature results from X-ray emission spectroscopy (XES) [2], but in agreement with our own results from Mössbauer spectroscopy and a re-analysis of existing XES data [3]. We also collected NFS data of $Mg_{0.88}{}^{57}Fe_{0.12}SiO_3$ perovskite in the DAC at fourteen pressures from 7 to 110 GPa during both compression and decompression. Results showed the presence of a component with high

quadrupole splitting whose stability increased with pressure, with a significant proportion of high-spin $Fe^{2+}$ present at 110 GPa (Fig. 3). These results challenge existing XES data [4], and coupled with our detailed high-resolution X-ray diffraction studies conducted at ESRF (ID27) and APS (IDD-13), suggest some type of transition as a function of pressure. The success of the measurements and their potential significance for the lower mantle led us to request a continuation of the experiment in order to collect NFS data at higher temperatures.

The second part of the experiment was carried out over 9 shifts on ID18 in February 2007 during operation in 16 bunch mode with a beam size of ca. 20 µm × 150 µm. The DAC, which was loaded with $Mg_{0.88}{}^{57}Fe_{0.12}SiO_3$ perovskite, incorporated a resistive platinum external heater to achieve temperatures near 800°C, and a MAR CCD camera was mounted on the beam line to enable collection of XRD data at the same P,T conditions as the NFS spectra. Pressure was measured *in situ* using a PRL system. We collected data at 17 different P,T conditions in order to track the changes in iron environment (Fig. 4), and from a qualitative evaluation of NFS spectra we identified at least two different points at which a "phase" boundary was crossed. Quantitative analysis of the NFS and XRD data is underway in order to interpret the nature of the transition and assess the implications for the Earth's lower mantle.

**References:**


[1] C.A. McCammon, *Science* **308**, 807-808 (2005).
[2] J. Lin *et al.*, *Nature* **436**, 377-380 (2005).
[3] I.Y. Kantor, L.S. Dubrovinsky, C.A. McCammon, *Physical Review B* **73**, DOI: 10.1103/PhysRevB.73.100101 (2006).
[4] J. Badro *et al.*, *Science* **305**, 383-386 (2004).


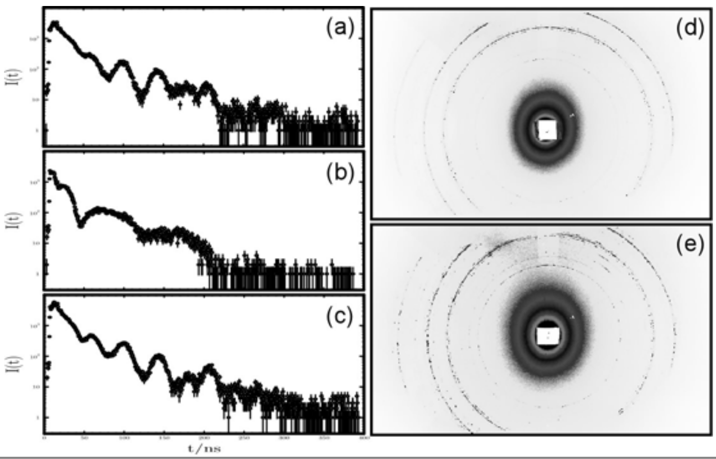


Fig. 1. NFS data collected at 74 GPa of different regions in the same DAC with starting material $(Mg_{0.9}Fe_{0.1})_2SiO_4$ olivine: (a) heated at high laser power (=high temperature) to form (Mg,Fe)$SiO_3$ perovskite + (Mg,Fe)O; (b) unreacted $(Mg_{0.9}Fe_{0.1})_2SiO_4$ olivine; (c) heated at low laser power (=low temperature) to form (Mg,Fe)$SiO_3$ perovskite + (Mg,Fe)O. XRD data were collected simultaneously with NFS data using an image plate: (d) region heated at high temperature (=spectrum a); (e) region heated at low temperature (=spectrum c). The differences in data between the regions heated to different temperatures likely reflect variations in Fe/Mg partitioning between (Mg,Fe)$SiO_3$ perovskite and (Mg,Fe)O and/or differences in $Fe^{3+}$ concentration.

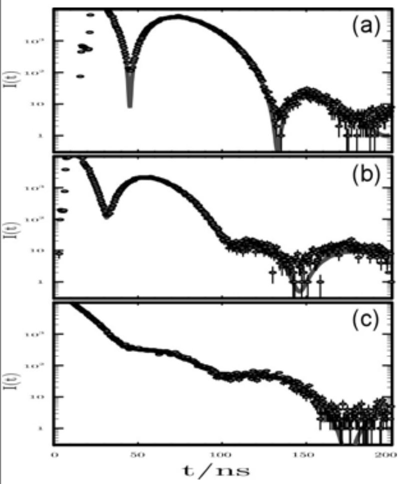


Fig. 2. NFS data of $Mg_{0.8}Fe_{0.2}O$ in a DAC at (a) 44 GPa; (b) 73 GPa; (c) 85 GPa. The reduction in beat intensity is due to the increasing stability of low-spin $Fe^{2+}$.

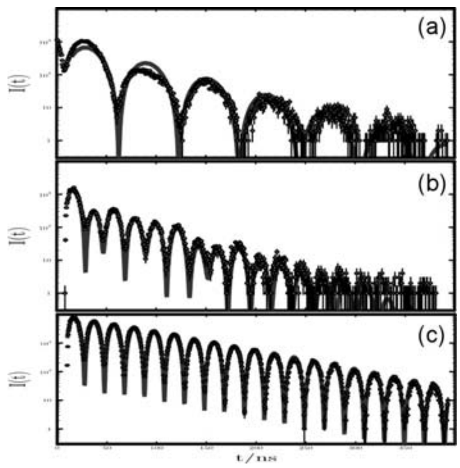


Fig. 3. NFS data of $Mg_{0.88}Fe_{0.12}O_3$ perovskite in a DAC at (a) 7 GPa; (b) 44 GPa; (c) 110 GPa. The high frequency of quantum beats at 110 GPa arises from high-spin $Fe^{2+}$.

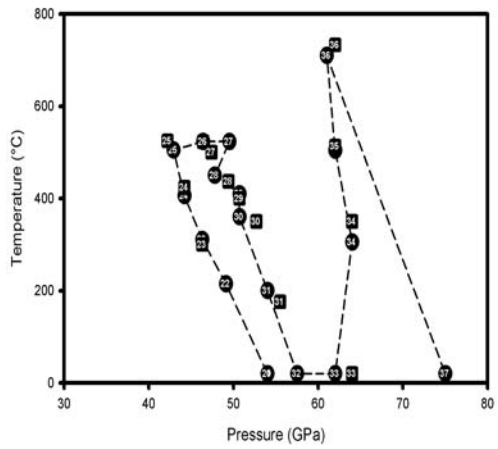


Fig. 4. Pressure-temperature path of DAC experiments on $Mg_{0.88}Fe_{0.12}O_3$ perovskite along which NFS and XRD data were collected, allowing the slope of the transition to be determined. Numbers indicate the sequence of data collection.