ESRF	**Experiment title:** Electronic transitions in the deep mantle: Nuclear forward scattering of (Mg,Fe)SiO3 post-perovskite at high P,T	**Experiment number**: HE-2750
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Shifts: 15	**Local contact(s)**: Dr. Aleksandr CHUMAKOV	*Received at ESRF:*

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Report:

Our previous experiment at ESRF (HE2157) involving nuclear forward scattering (NFS) measurements in an externally heated diamond anvil cell (DAC) identified a new electronic state of Fe^{2+} in the Earth's most abundant phase, (Mg,Fe)(Si,Al)O_3 perovskite, which is predicted to dominate the lower mantle and hence influence its thermal and electronic properties (McCammon et al., 2008). The new electronic state is an intermediate-spin configuration, where four of the six 3*d* electrons are spin paired. The purpose of experiment HE-2750 was to extend NFS measurements to higher pressures in order to study the spin state of Fe^{2+} in the post-perovskite phase of (Mg,Fe)(Si,Al)O_3, which is believed to occur at the base of the lower mantle and hence influence mantle dynamics.

During experiment HE-2750 we loaded our starting material, $Fe_{0.18}Mg_{0.82}O_3$ majorite, into an externally heated DAC. NFS spectra showed high frequency quantum beats associated with the high quadrupole splitting (QS) of the dominant Fe^{2+} site (Fig. 1). After transformation to the perovskite structure and compression to 115 GPa, the NFS spectrum was dominated by intermediate-spin Fe^{2+}, which has an even larger QS than high-spin Fe^{2+} in majorite (McCammon et al., 2008). We then compressed the sample to higher pressures and used laser heating to reach the post-perovskite stability field; however X-ray diffraction showed the sample still to consist only of well crystallised perovskite phase, which was not entirely unexpected due to the slow kinetics of the structural phase transformation. NFS spectra at the highest pressure reached, 170 GPa, showed the presence of a second contribution with significantly lower quadrupole splitting, which grew in intensity when we increased the temperature within the perovskite stability field at 120 GPa (Fig. 1). We interpret the component with low quadrupole splitting to be low-spin Fe^{2+}, in which all six 3*d* electrons are spin paired. Altogether we collected fifteen NFS spectra at different pressures and temperatures, and our results indicate that (Mg,Fe)SiO_3 perovskite containing low-spin Fe^{2+} may be stable at the base of the lower mantle, competing thermodynamically and kinetically with the post-perovskite phase.

During experiment HE-2750 we also conducted nuclear inelastic scattering (NIS) measurements of the same sample at high pressure, both in the majorite and in the perovskite phases. We collected room temperature NIS data of majorite at 0 and 33 GPa, and of perovskite at eight pressures between 0 and 115 GPa. The NIS data (shown in Fig. 2 for perovskite) allowed the determination of the iron density of states, which we then used to extract the mean velocity of sound using the Debye model. Results show that the sound velocities for majorite (Fig. 3a) are in good agreement with Brillouin spectroscopy data of $MgSiO_3$ (Sinogeikin and Bass, 2002; open circle) and ultrasonic measurements of natural majorite (Irifune et al., 2008; grey circles), while sound velocities derived for perovskite (Fig. 3b) are drastically lower than those measured using Brillouin spectroscopy for $Mg(Si,Al)O_3$ perovskite (Jackson et al., 2005; open circles) and $MgSiO_3$ perovskite (Murakami et al., 2007; grey circles). The lower sound velocities for perovskite cannot be explained by compositional effects, and indicate that vibrations of the iron sub-lattice are different from those of the bulk structure at low frequencies, in contrast to majorite and most all other silicate and oxide minerals. Our results for perovskite are similar to those reported for post-perovskite (Mao et al., 2006), and challenge the assumption that NIS data can be used to extract sound velocities for such phases. Instead, the NIS data may provide insight into why such an unusual electron structure (intermediate spin) is stable, and why *ab initio* methods have so far failed to reproduce the experimental data (Stackhouse, 2008).

References:

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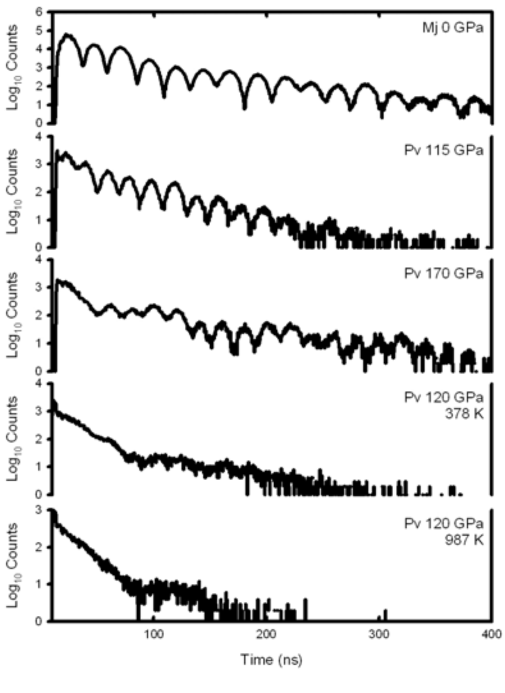

Fig. 1. NFS data for majorite (Mj) and perovskite (Pv) phases at the indicated pressures and temperatures (300 K if no temperature is given)

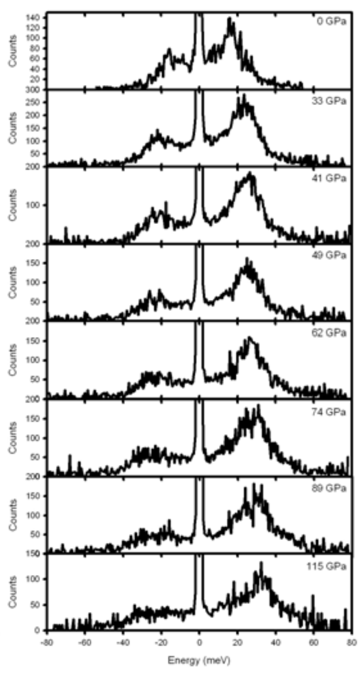

Fig. 2. NIS data for perovskite at 300 K and the indicated pressures

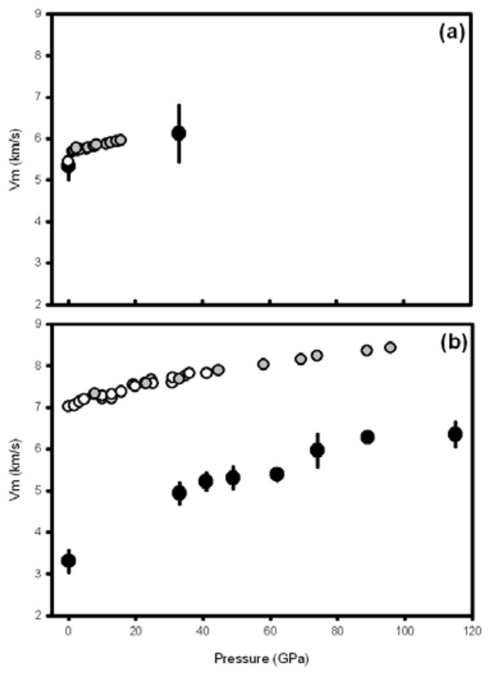

Fig. 3. Mean sound velocity for (a) majorite and (b) perovskite phases (solid circles). Open and grey circles indicate existing data derived using other methods (see text)