



# Electronic spin state of Fe,Al-containing MgSiO<sub>3</sub> perovskite at lower mantle conditions



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## ABSTRACT

We have investigated silicate perovskite with composition Mg<sub>0.83</sub>Fe<sub>0.21</sub>Al<sub>0.06</sub>Si<sub>0.91</sub>O<sub>3</sub> relevant for the lower mantle at pressures up to 81 GPa and temperatures up to 2000 K using conventional Mössbauer spectroscopy and synchrotron Nuclear Forward Scattering (NFS) combined with double-sided laser heating in a diamond anvil cell. Room temperature Mössbauer and NFS spectra at low pressure are dominated by high-spin Fe<sup>2+</sup>, with minor amounts of Fe<sup>3+</sup> and a component assigned to a metastable position of high-spin Fe<sup>2+</sup> in the A-site predicted by computational studies. NFS data show a sharp transition (<20 GPa) from high-spin Fe<sup>2+</sup> to a new component with extremely high quadrupole splitting, similar to previous studies. Mössbauer data show the same transition, but over a broader pressure range likely due to the higher pressure gradient. The new Fe<sup>2+</sup> component is assigned to intermediate-spin Fe<sup>2+</sup>, consistent with previous X-ray emission studies. NFS data at high temperatures and high pressures comparable to those in the lower mantle are consistent with the presence of Fe<sup>2+</sup> only in the intermediate-spin state and Fe<sup>3+</sup> only in the high-spin state. Our results are therefore consistent with the occurrence of spin crossover only in Fe<sup>2+</sup> in Fe-, Al-containing perovskite within the lower mantle.

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## 1. Introduction

Magnesium silicate perovskite (Pv) is considered to be the most abundant constituent of the Earth's lower mantle with stability from a depth of 660 km to approximately 2700 km, which is several hundred kilometers above the core–mantle boundary (Liu, 1976). Pv incorporates notable amounts of iron and aluminum (5–10 mol%) into its structure (e.g., Lee et al., 2004). While the properties and behavior of pure MgSiO<sub>3</sub> Pv are mostly understood, the effects of these additional cations remain controversial.

The electronic spin state of iron in different valence states in Pv can strongly influence many properties of the Earth's interior such as thermal conductivity (Badro et al., 2004), electrical conductivity (Ohta et al., 2010; Potapkin et al., 2013), and thermodynamic properties (Frost et al., 2004; McCammon, 1997). An accurate determination of the Fe spin state in Pv is complicated by the presence of two different crystallographic sites (a large distorted 8–12-coordinated site, hereafter referred to as A, and a smaller relatively undistorted octahedral site, hereafter referred to as B). Iron occurs both as ferrous (Fe<sup>2+</sup>) and ferric (Fe<sup>3+</sup>) in Fe-, Al-containing magnesium silicate perovskite (FeAlPv), with Fe<sup>3+</sup>/ΣFe ratios up to at least 60% (Frost et al., 2004; McCammon,

1997), that strongly depend on the Al concentration (McCammon et al., 2004).

While it is well accepted that Fe<sup>2+</sup> occupies exclusively the A-site, the site occupancy of Fe<sup>3+</sup> is still under debate. Ferric iron has been observed to occupy either exclusively the A-site (McCammon et al., 2008; Potapkin et al., 2013) or both the A- and B-sites (Badro et al., 2004; Catalli et al., 2011, 2010; Hummer and Fei, 2012). Several studies have additionally predicted an exchange of Fe<sup>3+</sup> from the A-site to the B-site at high pressures (Catalli et al., 2011, 2010; Fujino et al., 2012); however the possibility of such exchange was disproved by recent single-crystal X-ray diffraction studies conducted at high pressure and high temperature (Glazyrin et al., submitted for publication; Kupenko et al., 2012).

The spin state of iron in iron-containing magnesium silicate perovskite (FePv) as well as in FeAlPv is also a matter of debate. Some studies conclude that Fe<sup>3+</sup><sub>A</sub> undergoes high-spin (HS) to low-spin (LS) crossover (Jackson, 2005; Li et al., 2006), although the majority of studies do not observe spin crossover in Fe<sup>3+</sup><sub>A</sub> (Catalli et al., 2011, 2010; Fujino et al., 2012; Lin et al., 2012; McCammon et al., 2008; Potapkin et al., 2013). Meanwhile there is a general consensus that Fe<sup>3+</sup><sub>B</sub> undergoes HS to LS crossover at mantle pressures in studies where Fe<sup>3+</sup> is reported to occupy the B site (Catalli et al., 2011, 2010; Fujino et al., 2012; Lin et al., 2012). There is also general agreement that Fe<sup>2+</sup> behavior undergoes a dramatic change at mantle pressures through the appearance of a new component with extremely high quadrupole splitting in Mössbauer spectra at high pressure (reviewed by

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McCummon et al., 2013), even though there are conflicting interpretations of this change: HS to intermediate-spin (IS) crossover (Lin et al., 2008; McCummon et al., 2010, 2008; Potapkin et al., 2013), HS to LS crossover (Badro et al., 2004) or a structural modification of the local environment (Lin et al., 2012).

Numerous theoretical studies have been made that examine the spin behavior of iron in different valence states and different crystallographic sites, but with often conflicting results (Bengtson et al., 2009, 2008; Caracas et al., 2010; Hsu et al., 2011, 2010; Li, 2005; Stackhouse et al., 2007; Umemoto et al., 2010; Zhang and Oganov, 2006). However one point on which all computational models agree in the instability of IS  $\text{Fe}^{2+}$  at all lower mantle pressures, which is in conflict with experimental results that show a decrease in the unpaired spin density of iron in FePv and FeAlPv (reviewed by McCummon et al., 2013).

Despite the many investigations, a systematic study of FeAlPv with mantle composition at mantle conditions is still lacking. Moreover all predictions of FeAlPv behavior at lower mantle conditions have been inferred by extrapolation of data measured at ambient temperatures or from ab initio calculations. Here we report the first in situ Nuclear Forward Scattering (NFS) study of FeAlPv with composition  $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$  at pressure and temperature conditions of the lower mantle. The study is complemented by NFS and conventional Mössbauer spectroscopy measurements at high pressure and ambient temperature that provide high resolution data for the analysis of individual site and valence state contributions.

## 2. Experimental methods

The sample of FeAlPv was synthesized in the multianvil press from a mixture of  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $^{57}\text{Fe}_2\text{O}_3$  (90% enriched) starting materials in a rhenium capsule at 26 GPa and 1800 °C for 30 min. Before synthesis, the starting material was heated at 1273 K for 1 day in a  $\text{CO-CO}_2$  gas-mixing furnace, in which oxygen fugacity was controlled at  $\log f_{\text{O}_2} = -21$  to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . After the multianvil experiment, the recovered sample was characterized at ambient conditions using both the electron microprobe (JEOL, JXA-8200, under the operating conditions of 15 kV and 15 nA) and Mössbauer spectroscopy. Results of electron microprobe analysis showed that the chemical composition of the sample is  $\text{Mg}_{0.828(18)}\text{Fe}_{0.208(13)}\text{Al}_{0.059(2)}\text{Si}_{0.911(23)}\text{O}_3$  and Mössbauer spectroscopy showed the iron to be predominantly in the ferrous state ( $\sim 20\% \text{Fe}^{3+}/\Sigma\text{Fe}$ ).

Mössbauer spectra were recorded at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq  $^{57}\text{Co}$  high specific activity source in a 12  $\mu\text{m}$  thick Rh matrix with active dimensions of 500  $\mu\text{m} \times 500 \mu\text{m}$ . The velocity scale was calibrated relative to 25  $\mu\text{m}$  thick  $\alpha\text{-Fe}$  foil using the positions certified for (former) National Bureau of Standards, standard reference material no. 1541; line widths of 0.36 mm/s for the outer lines of  $\alpha\text{-Fe}$  were obtained at room temperature. Spectra took 3–4 days each to collect. Center shifts were calculated relative to  $\alpha\text{-Fe}$ . Spectra were fitted using a full transmission integral with a normalized Lorentzian source lineshape using the MossA software package (Prescher et al., 2012). Mössbauer spectra of the FeAlPv sample were collected up to 72 GPa at room temperature (Fig. 1). The sample was annealed preceding data collection at all pressures above 30 GPa in order to relax stress.

Nuclear Forward Scattering (NFS) data were collected on the Nuclear Resonance (ID18) beamline (Rüffer and Chumakov, 1996) of the European Synchrotron Radiation Facility during operation in 4-bunch mode, with the beam focused to 6  $\mu\text{m}$  vertical and 11  $\mu\text{m}$  horizontal dimension using Kirkpatrick–Baez mirrors. All of the spectra were collected over 10–60 min each. NFS data were fitted using the CONUSS package (Sturhahn, 2000). The center shift was determined relative to a  $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$  reference absorber. Room temperature NFS spectra were collected up to 81 GPa. Additionally at 43, 63 and 81 GPa the sample was laser-heated at 1200 K–2000 K and spectra were collected during laser heating.

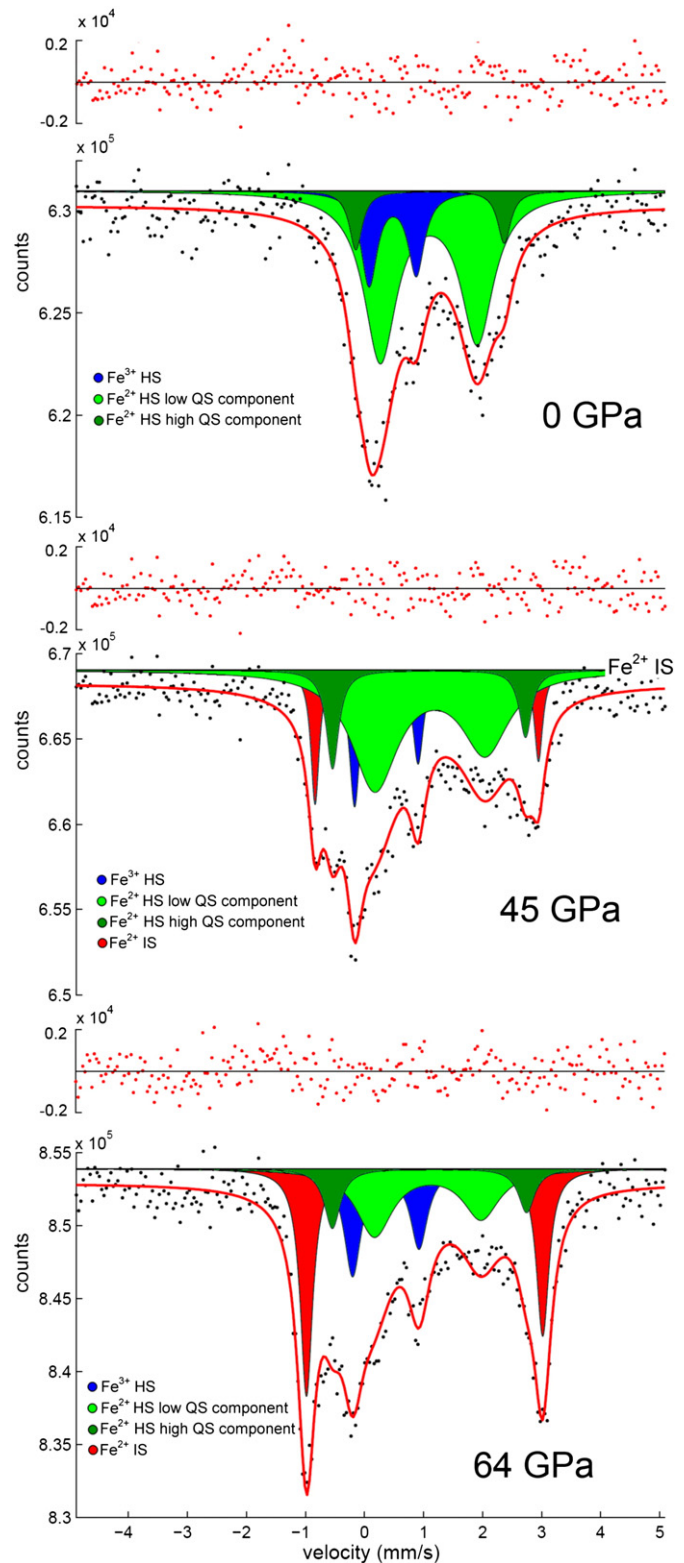


Fig. 1. Selected high-pressure conventional Mössbauer spectra of  $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$  perovskite at room temperature. The solid lines show the theoretical fit and the residual is indicated above each spectrum.

High-pressure measurements were carried out using cylindrical-type diamond anvil cells (Kantor et al., 2012). Samples of FeAlPv were loaded together with a few ruby balls used as a pressure marker. The diamond anvils used had 250  $\mu\text{m}$  culets. A 200  $\mu\text{m}$  thick Re gasket was pre-indented to be about 30  $\mu\text{m}$  thick and a 125  $\mu\text{m}$  hole was drilled

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