



# Oxidation state of the lower mantle: *In situ* observations of the iron electronic configuration in bridgmanite at extreme conditions



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## ABSTRACT

We have investigated the electronic configuration of iron in Fe-, Al-containing magnesium silicate perovskite, i.e., bridgmanite, the main component of the lower mantle, at conditions of the deep Earth's interior using the energy domain Synchrotron Mössbauer Source technique. We show that the high ferric iron content observed previously in quenched samples is preserved at high temperatures and high pressures. Our data are consistent with high-spin to intermediate-spin (HS-IS) crossover in Fe<sup>2+</sup> at high pressures and ambient temperature. We see no evidence of spin crossover in Fe<sup>3+</sup> occupying the A-position of bridgmanite. On laser heating at pressures above ~40 GPa we observe a new doublet with relative area below 5% which is assigned to Fe<sup>3+</sup> in the octahedral (B-site) position in bridgmanite. We conclude that at lower mantle conditions Fe<sup>3+</sup> remains predominantly in the HS state, while Fe<sup>2+</sup> occurs solely in the IS state.

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## 1. Introduction

MgSiO<sub>3</sub> perovskite that contains Fe and Al, i.e., bridgmanite (hereafter FeAl-Brg), is considered to be the most abundant phase in the Earth and to constitute roughly 75% of the lower mantle (e.g., Irifune et al., 2010; Ringwood, 1982). Iron can occur in both ferrous (Fe<sup>2+</sup>) and ferric (Fe<sup>3+</sup>) forms in FeAl-Brg. In contrast to phases in the upper mantle, the amount of ferric iron in FeAl-Brg is expected to be high (Frost et al., 2004; McCammon, 1997; McCammon et al., 2004), but until now all estimations of Fe<sup>3+</sup>/ΣFe in the lower mantle have been based on measurements at room temperature from quenched samples.

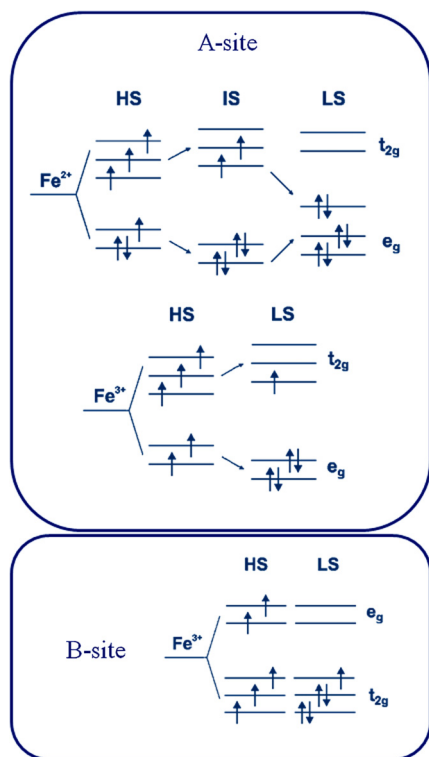
The spin state of iron in FeAl-Brg in different valence states may affect the thermodynamic properties, electrical and thermal conductivities, and other properties of the Earth's interior (e.g., Frost et al., 2004; Goncharov et al., 2008; Potapkin et al., 2013). Many studies have been performed to determine the spin state of Fe in FeAl-Brg, but the conclusions reached are not uniform. Interpretation of spectra is complicated by the presence of two sites in

the orthorhombic (CdFeO<sub>3</sub>-type) perovskite structure of FeAl-Brg: a large distorted 8- to 12-coordinated site, hereafter referred to as "A", and a smaller relatively undistorted octahedral site, hereafter referred to as "B". Ferrous iron occupies the A-site exclusively and was reported to exhibit a spin crossover from the high-spin (HS) to the intermediate-spin (IS) state (Fig. 1) (Kuppenko et al., 2014; Lin et al., 2008; McCammon et al., 2008; Potapkin et al., 2013). However, all computational studies have found the HS configuration of Fe<sup>2+</sup> to be the most stable (e.g., Hsu et al., 2012; Zhang and Oganov, 2006) and attribute the experimentally observed pressure-induced changes in hyperfine parameters of ferrous iron to small changes in its local environment (Hsu et al., 2012). Ferric iron was reported to occupy either exclusively the A-site and to be in the HS state (Kuppenko et al., 2014; McCammon et al., 2008; Potapkin et al., 2013) or to occupy both A- and B-sites with Fe<sup>3+</sup><sub>A</sub> remaining in the HS state at lower mantle conditions and Fe<sup>3+</sup><sub>B</sub> exhibiting HS to low-spin (LS) crossover (Fig. 1) at pressures around 50 GPa (Catalli et al., 2011). Several studies have additionally proposed that high pressures and high temperatures may promote the site exchange of Fe<sup>3+</sup> and Al<sup>3+</sup> by the reaction (HS Fe<sup>3+</sup><sub>A</sub>) + Al<sup>3+</sup><sub>B</sub> → (LS Fe<sup>3+</sup><sub>B</sub>) + Al<sup>3+</sup><sub>A</sub> (Catalli et al., 2011; Fujino et al., 2012).

The majority of previous reports describing the spin state behavior in FeAl-Brg at lower mantle conditions are based on

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**Fig. 1.** Crystal field splitting diagrams for iron on different crystallographic sites of bridgmanite. HS: high-spin; IS: intermediate-spin; LS: low-spin. Modified after Lin and Wheat (2011).

analysis of temperature-quenched samples (Catalli et al., 2011; Fujino et al., 2012; Li et al., 2004; Potapkin et al., 2013). An indication of the temperature effect to stabilize IS Fe<sup>2+</sup> relative to HS Fe<sup>2+</sup> was provided by McCammon et al. (2008); however, in their study the temperature was limited to only 1000 K. More recent results based on Nuclear Forward Scattering (NFS) (Kuppenko et al., 2014) extended temperatures to lower mantle conditions. However, NFS is not well suited to materials with a large number of components arising from multiple sites, valence states and spin states (which is the case for FeAl-Brg), which leads to spectral complexity and non-uniqueness of fitting models. Energy-domain Mössbauer spectroscopy (MS) is better suited for the analysis of iron distribution between individual structural sites in FeAl-Brg, and its oxidation and electronic states (McCammon et al., 2008; Potapkin et al., 2013). However, studies of lower mantle phases at the relevant high pressure and temperature conditions are not possible using conventional MS with a radioactive source due to the challenge of focusing gamma rays in the laboratory. The recently developed Synchrotron Mössbauer Source (SMS) allows measurements of high quality and well resolved energy-domain spectra on timescales of only a few hours, combining the advantages of synchrotron radiation and the MS technique (Potapkin et al., 2012).

In this paper we present a high-pressure high-temperature study of FeAl-Brg using the SMS technique to elucidate the electronic configuration of iron *in situ* at lower mantle conditions in order to constrain the properties of the most abundant phase in the most voluminous shell within the Earth.

## 2. Methods

The FeAl-Brg sample used in the present study was from the same synthesis run used by Potapkin et al. (2013) (sample no. 3), Kuppenko et al. (2014), and Sinmyo et al. (2014). It was synthesized in the multianvil press from a mixture of MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>,

<sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> (90% enriched) starting materials in a rhenium capsule at 26 GPa and 1800 °C for 30 min. Before synthesis, the starting materials were heated at 973 K for 1 day in a H<sub>2</sub>-CO<sub>2</sub> gas-mixing furnace, in which oxygen fugacity was controlled at log *f*O<sub>2</sub> = −21 to reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>. After the multianvil experiment, the recovered sample was characterized at ambient conditions using the electron microprobe (JEOL, JXA-8200, under the operating conditions 15 kV and 15 nA). Electron microprobe analysis on the sample used for the present study showed the chemical composition to be Mg<sub>0.832(21)</sub>Fe<sub>0.209(22)</sub>Al<sub>0.060(2)</sub>Si<sub>0.916(24)</sub>O<sub>3</sub>, which is the same within measurement uncertainty to those of the samples used by Potapkin et al. (2013) and Kuppenko et al. (2014). However the Fe<sup>3+</sup>/ΣFe ratio measured for the present FeAl-Brg sample using Mössbauer spectroscopy (35 ± 5%) is intermediate between the values measured for the samples of Potapkin et al. (2013) (50 ± 5%) and Kuppenko et al. (2014) (20 ± 3%). This difference may be due to temperature gradients that cause variations of the sample environment in the multianvil assembly: it was already demonstrated in previous work that the sample region in the center of the assembly is hotter than the sample at the edges, which can cause variations in oxygen fugacity and hence in the charge balance mechanism for Fe<sup>3+</sup>. We note that the variation of Fe<sup>3+</sup>/ΣFe ratio between 20 and 50% for the present sample falls within the 90% confidence limits of the trend between Fe<sup>3+</sup>/ΣFe ratio and Al composition of bridgmanite reported by McCammon et al. (2004).

For high-pressure generation cylindrical-type BX-90 diamond anvil cells (DAC) (Kantor et al., 2012) were used that were mounted with 250 μm culet diamonds. A 200 μm thick Re gasket was pre-indented to about 30 μm thick and a 125 μm diameter hole was drilled in the center. A thin layer (about 5 to 7 μm thick) of polycrystalline FeAl-Brg with composition as given above was loaded in the gasket at room pressure and temperature and afterwards Ne was loaded at 1.2 kbar (Kurnosov et al., 2008) as a pressure medium and thermal insulator. The pressure was determined by the ruby fluorescence method.

High temperature measurements were performed using a modified version of the portable double-sided laser-heating system (Dubrovinsky et al., 2010, 2009; Kuppenko et al., 2012). Two infrared fiber lasers were focused to ~40 μm full width at half maximum (FWHM). The system implements π-shapers (Prakapenka et al., 2008) that convert an initial Gaussian-shaped beam to one with a flat top distribution. The surface temperature was measured by the standard spectroradiometry method (Shen et al., 2010) using an Acton SP2300 spectrometer (Princeton Instruments) with a PIXIS400 CCD detector.

SMS spectra were recorded at the Nuclear Resonance Beamline (Rüffer and Chumakov, 1996) ID18 of the European Synchrotron Radiation Facility using the (111) Bragg reflection of a <sup>57</sup>FeBO<sub>3</sub> single crystal mounted on a Wissel velocity transducer driven with a sinusoidal wave form (Potapkin et al., 2012). The X-ray beam was focused to 20 μm vertical and 10 μm horizontal dimensions using Kirkpatrick–Baez mirrors. The linewidth of the SMS and the absolute position of the center shift (CS) was controlled before and after each measurement using a K<sub>2</sub>Mg<sup>57</sup>Fe(CN)<sub>6</sub> reference single line absorber. The velocity scale was calibrated using 25 μm thick natural α-Fe foil. Each spectrum took ~1–2 h to collect. The spectra were fitted using a full transmission integral with a normalized Lorentzian-squared source lineshape using the MossA software package (Prescher et al., 2012). Room temperature spectra were collected from 12 to 77 GPa. After 39 GPa the sample was laser heated at ~2000 K (measured by the spectroradiometry method) at each pressure step to relax stress and spectra were collected before, during, and after heating.

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