A Spin on Lower Mantle Mineralogy

Jeffrey S. Pigott

[1]School of Earth Sciences, Ohio State University, Columbus, Ohio 43210, U.S.A.

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Abstract

Constraining the spin state of Fe in Earth's lower mantle is critical to understanding the chemistry and dynamics of Earth's interior. In this issue of *American Mineralogist*, Dorfman et al. (2015) present an experimental study of the effect of iron concentration on the spin transition in bridgmanite. Their experiments involved two different bridgmanite compositions (38% and 74% $FeSiO_3$). Based on the total spin moment determined by synchrotron-based X-ray emission spectroscopy, they show that Fe^{2+} in bridgmanite is in the high-spin state in the lower mantle but transition pressure decreases within highly-enriched iron concentrations.

Iron is the most abundant transition metal in Earth's crust and mantle and exists in either the Fe^{2+} (ferrous) or Fe^{3+} (ferric) oxidation state. At the surface of the Earth, Fe^{2+} and Fe^{3+} are in the high-spin electronic state where the partially-filled 3*d* subshell is dominated by orbitals with unpaired electrons. Fifty-five years ago, Fyfe (1960) predicted a pressure-induced high-spin to low-spin transition in Fe^{2+} when it becomes more energetically favorable for the 6 valance electrons to be paired in three of the five 3*d* orbitals leaving two orbitals unoccupied.

The theoretical prediction of an iron spin transition wasn't realized experimentally until more than 40 years later (Badro et al. 2003) when synchrotron-based X-ray emission spectroscopy (XES) revealed a spin transition in ferropericlase (Mg,Fe)O. A year later, high-pressure experiments showed a spin transition in the mineral bridgmanite (Badro et al. 2004). The perovskite-structured bridgmanite, $(Mg,Fe)SiO_3$, accounts for ~75% of the volume (e.g. Irifune et al. 2010) of the lower mantle thus making it the most abundant mineral on Earth. In ferropericlase, the spin-transition affects elasticity, density, and transport properties such as electrical and thermal conductivity (Keppler et al., 2007; Lin et al., 2007; Antonangeli et al. 2011; Chen et al. 2012). Therefore, an understanding of if and when a spin transition occurs in bridgmanite is crucial for accurate interpretations of lower mantle seismic structures. The spin transition in bridgmanite may also have significant effects on chemical properties such as iron partitioning (Fujino et al. 2014) possibly generating chemical heterogeneities in the lower mantle.

There is a consensus that iron undergoes a gradual spin transition in ferropericlase at lower-mantle pressures with a recent combined nuclear-resonant inelastic X-ray scattering and X-ray diffraction study placing the spin-crossover at ~65 GPa at 300 K (Chen et al. 2012). In ferropericlase, temperature broadens the transition region and transition pressure increases with increasing Fe content. However, the spin transition in bridgmanite is more complicated. Fe can be hosted in both the dodecahedral A-site and octahedral B-site. Iron may also be in the Fe^{2+} and Fe^{3+} valence states. This has led to a range and evolution of interpretations of spin transitions in bridgmanite. See Lin et al. (2013) and Badro et al. (2014) for excellent reviews of spin transition studies on lower mantle minerals.

In this issue, Dorfman et al. (2015) tackle the influence of Fe concentration on the Fe^{2+} spin-transition in bridgmanite. The authors performed high-pressure synchrotron-based XES experiments on samples of bridgmanite compressed in laser-heated diamond-anvil cells to pressures equivalent to the seismic D’’-layer (200 – 300 km above the core-mantle boundary).

Dorfman et al. (2015) determined the effect of iron concentration by synthesizing bridgmanite *in situ* with two Fe-rich compositions (38% and 74% $FeSiO_3$). Fe^{3+} was not detected in the starting material, based on synchrotron Mössbaurer spectroscopy, or in a run product. After synthesis the samples were purposefully not annealed to avoid possible site migration and oxidation of Fe, thereby isolating the behavior of A-site Fe^{2+}.

Dorfman et al. (2015) accurately quantify the total spin moment by disentangling the pressure and spin-state effect on the X-ray emission spectra. They accomplish this by comparing the Kβ' peak intensity to well-characterized high-spin and low-spin reference standards. The authors conclude that Fe^{2+} remains in the high-spin state throughout the lower mantle for realistic lower mantle bridgmanite Fe concentrations (i.e. ~10% $FeSiO_3$ in a pyrolite composition). However, based on an observed decrease in the total spin moment, Fe^{2+} should undergo a spin transition at lower mantle pressures (50 – 70 GPa) with increasing iron content. This becomes particularly important if regions of highly Fe-enriched bridgmanite exist in the lower mantle.

Dorfman et al. (2015) elucidate the electronic state of the lower mantle's most abundant mineral which should impact interpretations of the structure, chemistry, and dynamics of Earth's lower mantle.

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