**CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE**

The spin state of iron in Fe$^{3+}$-bearing Mg-perovskite and its crystal chemistry at high pressure†

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**ABSTRACT**

Valence, spin states, and crystallographic sites of Fe in (Mg,Fe)SiO$_3$ perovskite were investigated using energy-domain $^{57}$Fe-synchrotron Mössbauer spectroscopy and powder X-ray diffraction up to 86 GPa. The volumes of Fe$^{3+}$-bearing perovskite in this study are slightly smaller than those of Mg end-member perovskite. Our Mössbauer data suggest that Fe$^{3+}$ prefers A sites coupled with Mg vacancies, which is consistent with previous data at ambient conditions. Fe$^{3+}$ in the A site remains in a high-spin state up to 86 GPa, and some fraction of the A site is occupied by Fe$^{2+}$ at pressures above 30 GPa. Fe$^{2+}$ in the A site is also in a high-spin state up to 86 GPa. The coupled substitution from Mg$^{2+}$ to a high-spin state of Fe$^{2+}$ and Mg$^{2+}$ vacancy would make the volume of perovskite smaller than that of Mg end-member perovskite. If the lower mantle is saturated in silica, perovskite containing high-spin Fe$^{3+}$ in A site has a higher density. Such silica oversaturated regions could sink by the density difference.

**Keywords:** Perovskite, ferric iron, spin state, Mössbauer spectroscopy, X-ray diffraction

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**INTRODUCTION**

The Earth’s lower mantle is composed mainly of iron-bearing magnesium silicate perovskite [Prv = (Mg,Fe)SiO$_3$] and magnesiowüstite (ferropericlase) [Mws = (Mg,Fe)O]. The effects of iron in these mantle materials are fundamental to understanding the deep mantle (e.g., Stixrude et al. 1992). A spin transition in the lower mantle minerals can change several important physical properties of the deep lower mantle regions, such as the thermal conductivity and partitioning behavior between Mg and Fe (Badro et al. 2003, 2004). Previous studies (e.g., McCammon 1997) revealed that a large amount of ferric iron Fe$^{3+}$, ca. ~50%, could exist in the lower mantle when aluminum is contained in Prv. Ferric iron in Prv influences the electrical conductivity and controls the thermal conductivity in the lower mantle (Xu et al. 1998; Goncharov et al. 2008; Kepller et al. 2008).

By using nuclear forward scattering of synchrotron radiation, Catali et al. (2010) reported that the population of the low-spin (LS) state of ferric iron Fe$^{3+}$ in octahedral sites (hereafter B sites) of (Mg,Fe)$^{3+}$SiO$_3$ gradually increases with pressure, and the spin transition becomes complete at 50–60 GPa. Grocholski et al. (2009) found that Fe$^{2+}$ exists in two different environments, but both are likely high spin (HS) along with Fe$^{3+}$ in B sites and possibly small amounts of LS Fe$^{2+}$ and LS Fe$^{3+}$ up to 65 GPa.

In contrast, ferric iron Fe$^{3+}$ in dodecahedral sites (hereafter A sites) remains in the HS state under conditions relevant to the lower mantle. Recently Lin et al. (2012) showed the HS to LS transition of Fe$^{3+}$ in the B sites in the range of 13–24 GPa in Al-free (Mg,Fe)SiO$_3$-Prv. Additionally, some experimental studies have proposed that Fe$^{3+}$ undergoes the HS to LS transition in Al-bearing Prv (Fujino et al. 2012; Catali et al. 2011).

Computational studies have predicted that the LS state of Fe$^{3+}$ in B sites of Prv is stable at lower mantle pressures and the HS-LS transition of Fe$^{3+}$ in A sites occurs in the range from 60 to 150 GPa (Zhang and Oganov 2006; Stockhouse et al. 2007). According to recent calculations using density functional theory and the Hubbard parameter, Fe$^{3+}$ in the B site of Prv undergoes a crossover from HS to LS state at 50–60 GPa, and Fe$^{3+}$ in the A site remains in the HS state up to 150 GPa (Hsu et al. 2012). In Prv structures, A$^{2-}$B$^{4+}$O$_6$, the incorporation of trivalent ions (M$^{3+}$) occurs by two mechanisms: A$^{2+}$ + B$^{4+}$ = M$^{3+}$ + M$^{3+}$ and B$^{4+}$ = M$^{3+}$ + 0.5O$_2^-$ (O$_2^-$, oxygen vacancy) (Knight and Bonanos 1994; Navrotsky 1999; Navrotsky et al. 2003). Fe$^{3+}$ should occupy both A and B sites in the Prv structure and these mechanisms must depend on other phases buffering Prv (McCammon 1998; Catali et al. 2010; Hsu et al. 2011). McCammon (1998) suggested that the coupled substitution could occur: 2Si$^{4+}$ + ↔ 2Fe$^{3+}$ + ↔ at lower $f_{O_2}$ using a Re capsule, whereas 4Mg$^{2+}$ + ↔ 4Si$^{4+}$ ↔ ↔ Fe$^{3+}$ + ↔ Fe$^{3+}$ at higher $f_{O_2}$ using a Fe capsule. The charge-coupled substitution mechanism makes it hard to understand the behavior of Fe$^{3+}$ in Prv. Based on NFS measurements in the time domain, Catali et al. (2010) suggested that Fe$^{3+}$ in Al-free Prv occupies both the

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† Special collection papers can be found on GSW at http://ammin.geoscienceworld.org/site/misc/specialissuestat.xhtml.

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