

## Pressure-induced changes in the electronic structure of iron in lower mantle minerals

# Jie Li[1]

[1] Dep. of Geology  
Univ. of Illinois, Urbana Champaign

Aluminum-bearing ferromagnesian silicate perovskite (hereafter referred to as 'Al-PV') and ferropericlase (hereafter referred to as 'FP') are major components of the Earth's lower mantle. As a transition element with unfilled 3d subshell, iron may exist in various valence state and spin state under lower mantle conditions. The electronic structure of iron could influence the density, element partitioning, and transport properties of its host phases. Recent studies show that iron in FP is predominantly Fe<sup>2+</sup> in the octahedral site, which transforms from the high-spin state to the low-spin state within the pressure range of the lower mantle at ambient temperature (Badro et al. 2003; Lin et al. 2005). The change of spin state affects the density and compressibility of FP (Fei et al. 2005; Lin et al. 2005). The electronic structure of iron in Al-PV is much more complex than that in FP. Iron occurs as both Fe<sup>2+</sup> (probably in the 8-12-coordinated site) and Fe<sup>3+</sup> (possibly distributed between the 8-12-coordinated site and octahedral site). The valence state and site occupancy of iron in Al-PV depends on the aluminum content. X-ray emission spectra revealed pressure-induced spin crossover in one Al-PV sample and two Al-free PV samples at ambient temperature (Li et al. 2004; Badro et al. 2004). A synchrotron Moessbauer spectroscopy study on a different Al-free PV sample found indications for a gradual spin crossover in Fe<sup>3+</sup> (Jackson et al. 2004). In order to resolve the path of spin evolution as a function of pressure, we combined the synchrotron Moessbauer spectroscopy and x-ray emission spectroscopy methods on the same Al-PV sample. At low pressures, our Moessbauer spectra can be sufficiently fitted by a 'two-doublet' model, which assumes one ferrous Fe<sup>2+</sup>-like site and one ferric Fe<sup>3+</sup>-like site with distinct hyperfine parameters. The simplest interpretation that is consistent with both the Moessbauer and x-ray emission data is that the Fe<sup>2+</sup>-like site is high-spin Fe<sup>2+</sup>, and the Fe<sup>3+</sup>-like site is high-spin Fe<sup>3+</sup>. Under higher pressures, a 'three-doublet' model is necessary and sufficient to fit the Moessbauer spectra. This model assumes two Fe<sup>2+</sup>-like sites and one Fe<sup>3+</sup>-like site distinguished by their hyperfine parameters. Between 12 and 20 GPa, the fraction of the Fe<sup>3+</sup>-like site, Fe<sup>3+</sup>/total Fe, changes abruptly from about 50% to 75%, possibly due to a spin crossover in octahedral-coordinated Fe<sup>2+</sup>. At pressures above 20 GPa, the fraction of the Fe<sup>3+</sup>-like site remains unchanged to the highest pressure, indicating a fixed valence state of iron within this pressure range. From 20 to 100 GPa, the isomer shift between the Fe<sup>3+</sup>-like and Fe<sup>2+</sup>-like sites increases slightly, while the values and widths of the quadruple splitting of all three sites remain essentially constant. In conjunction with the previous x-ray emission results, the Moessbauer data suggest that a spin crossover in Fe<sup>2+</sup> or concurrent spin crossovers in Fe<sup>2+</sup> and Fe<sup>3+</sup> may have occurred between 20 and 100 GPa. Further understanding of the pressure-induced changes in the electronic structure of iron in Al-PV requires more accurate knowledge of the site occupancy of iron and quantitative modeling of the hyperfine parameters as a function of valence state, spin state, crystallographic site, and pressure. To explore the implications of spin crossover for the physics and chemistry of the lower mantle, it is crucial to investigate the effect of temperature.