# Electronic spin transition of iron in the Earth's lower mantle

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**Jung-Fu Lin · Andrea Wheat**

**Abstract** Silicate perovskite and ferropericlase are thought to be the primary constituents of the lower mantle, whereas silicate post-perovskite is more likely found in the lowermost mantle. Because these minerals contain certain amounts of iron, their properties and, consequently, those of the deep mantle, are strongly influenced by iron's spin and valence states. A high-spin to low-spin crossover in ferropericlase has been observed to occur in the middle part of the lower-mantle conditions. Recent Mössbauer results consistently show that $Fe^{2+}$ predominantly exhibits extremely high quadrupole splittings in perovskite and post-perovskite, whereas a high-spin to low-spin transition of $Fe^{3+}$ in the octahedral site occurs at high pressures. These results provide a new venue for discussion of the effects of the spin and valence states of iron on the physical and chemical properties of the lower mantle.

**Keywords** Spin transition · Lower mantle · Mössbauer spectroscopy · Diamond anvil cell

## 1 Introduction

Earth's lower mantle, the most voluminous layer of the planet, is subjected to extreme pressure-temperature ($P$-$T$) conditions of 23–136 GPa and approximately 1,600–3,500 K. The lower mantle, as described in terms of a pyrolitic compositional model, is mainly comprised of ferropericlase ($(Mg,Fe)O$; Fp; ∼33% by volume), aluminous silicate perovskite ($Al$-$(Mg,Fe)SiO_3$; ∼62% by volume; hereafter called perovskite or Pv), and ∼5% calcium silicate Pv ($CaSiO_3$, abbreviated CaPv) [1] (Figs. 1 and 2). Recent studies show that Pv transforms into silicate post-perovskite (PPv) within the D" layer, just above the core-mantle region. The implications of

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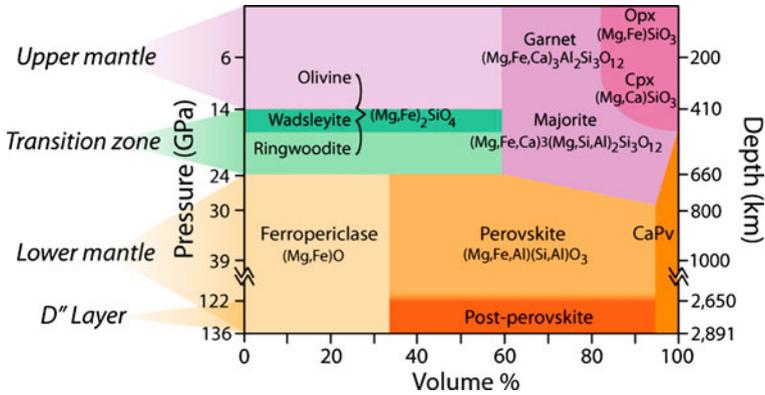
**Fig. 1** Approximate mineral distribution within Earth's interior as a function of depth, pressure and volume%. Mineral abbreviation: Opx and cpx, orthopyroxene and clinopyroxene, respectively; CaPv, calcium silicate perovskite
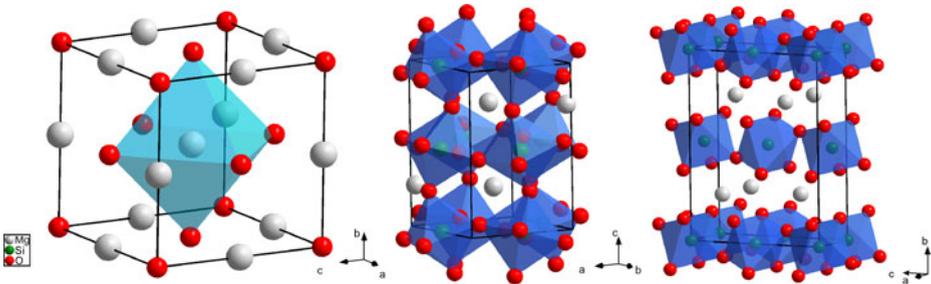


**Fig. 2** Crystal structures of lower-mantle ferropericlase (*left*), silicate perovskite (*middle*), and silicate post-perovskite (*right*). Cubic ferropericlase is in the rock salt structure ($Fm\bar{3}m$); orthorhombic perovskite is in the *Pbnm* space group; orthorhombic post-perovskite is in the *Cmcm* space group

these minerals' physical and chemical properties are needed to explain the seismic, geochemical, geodynamic, and geomagnetic observations of the lower mantle. As the most abundant $3d$ transition metal in Earth's interior, iron affects many of the chemical and physical properties of the lower-mantle minerals [1]. Amongst the majority of these, iron exists mainly as ferrous iron ($Fe^{2+}$), with approximately 20% concentrated in Fp, whereas Pv and PPv, with approximately 10% total iron, can contain very high amounts of ferric iron ($Fe^{3+}$) [1].

Due to its partially filled $3d$-electron orbitals, iron's electronic valence and spin states in the host phases can cause a dynamic range of physical and chemical properties of the lower mantle [1]. Previous studies have shown that Fe spin transitions and variations in Fe valence states can cause changes in density, elastic properties, electrical conductivity and radiative thermal conductivity of the lower-mantle minerals. Here, literature data on the spin and valence states of iron in Fp, Pv, and PPv at relevant *P-T* conditions have been evaluated. Focus is placed on the use of the hyperfine parameters, quadrupole splittings (QS) and chemical shifts (CS), seen in Mössbauer spectroscopic analyses including synchrotron Mössbauer
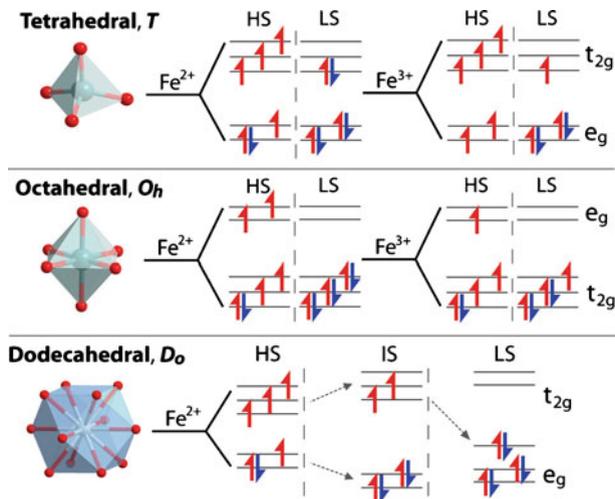
**Fig. 3** Crystal field splitting diagrams for iron in tetrahedral, octahedral, and dodecahedral sites in the lower-mantle minerals. Iron is shown as a (2+) or (3+) cation in high-spin, intermediate-spin (dodecahedral site), and low-spin electronic configurations. The crystal field splitting energy (CFSE) can be altered by pressure, temperature, and/or composition. The energy of the $e_g$ orbitals (those which are oriented towards the ligands) is heightened by increased repulsion due to shortened $e_g$ orbital-ligand distance during pressure-induced unit cell distortion, resulting in an overall larger CFSE. When the CFSE surpasses the spin-pairing energy, the spin-pairing transition of $3d$ electrons is more favorable than jumping the energy gap to achieve aligned spins. For example, the low-spin state with all six $3d$ electrons paired ($S = 0$) in $Fe^{2+}$ occurs at high pressures in the lower-mantle ferropericlase

spectroscopy (SMS), because these results act as site-specific fingerprints, assisting in the assignment of the valence and spin states of iron in the lower-mantle minerals.

## 2 Electronic spin transition of $Fe^{2+}$ in Fp

Ferropericlase has a cubic rock-salt structure and forms a solid solution between periclase (MgO) and wüstite (FeO). A high-spin (HS) to low-spin (LS) transition of $Fe^{2+}$ in the octahedral site occurs when the crystal field splitting energy exceeds the Hund's-rule exchange energy, causing the material to become low-spin and diamagnetic [1–4]. The measured values of QS, ~0.8 mm/s, and CS, ~1.2 mm/s, from Mössbauer spectra of Fp under ambient conditions are consistent with predominant high-spin $Fe^{2+}$ in the octahedral coordination (Fig. 3) [5]. The concentration of the high-spin $Fe^{3+}$ in ferropericlase, however, is typically very low (e.g., under the detection limit of the MS technique). At room temperature, the QS of the high-spin $Fe^{2+}$ increases with pressure up to ~30 GPa, plateaus until ~60 GPa, and disappears with further pressure increase [5]. The CS of the high-spin state decreases with pressure increase; a noticeable drop of the CS occurs at approximately 60 GPa. The simultaneous disappearance of the QS and the drop of the CS at approximately 60 GPa are consistent with a spin transition of iron in Fp [5]. The ratio of the high-spin to low-spin states of iron in Fp, as a function of pressure, can be derived from the

modeling of the SMS spectra with changes in the QS and CS values. Depending on experimental conditions, a narrower to broader width of the spin transition has been reported [1, 5]. Although (Mg,Fe)O has always been regarded as a fully disordered solid solution system without noticeable short-range order at ambient conditions, recent Mössbauer analyses have demonstrated broadening of the high-spin $Fe^{2+}$ quantum beats associated with significant changes in the short-range order, which deviates from the behavior of the homogeneous solid solution in Fp. These studies have indicated that the $Fe^{2+}$ ions can form localized clusters in nearest-neighboring environments under high pressures. The short-range ordering of $Fe^{2+}$ ions can cause an extension of the width of the spin crossover in (Mg,Fe)O at high pressures.

The electron shell of the high-spin $Fe^{2+}$ ions in the octahedral coordination is spherically asymmetric with $S = 2$ and $t_{2g\uparrow}^3 e_{g\uparrow}^2 t_{2g\downarrow}^1$, whereas $Fe^{2+}$ ions in the low-spin state are more spherically symmetric with $S = 0$ and $t_{2g\uparrow}^3 t_{2g\downarrow}^3$ (the arrows indicate spin up or spin down whereas the superscripted numbers represent the number of the occupied electrons). The spin crossover arises from the condition in which the thermal energy at high $P$-$T$ is sufficient to overcome the energy difference between the high-spin state and low-spin state [4]. Therefore, the local $3d$ electronic structures of the iron ions in Fp are strongly temperature dependent [4]. Most importantly, recent results show that the electronic spin-pairing transition of iron in Fp occurs over a very narrow range of pressure at room temperature but turns to a spin crossover with an extended transition pressure at the lower-mantle temperatures [4].

## 3 Spin and valence states of iron in Pv

Perovskite, with 5–10 mol% of Fe and Al, is the most abundant silicate mineral in the lower mantle, and exists at 660 km depth to several hundred kilometers above the core-mantle boundary. Iron in Pv exists in both $Fe^{2+}$ and $Fe^{3+}$ states and can occupy one of two crystallographic sites, the large dodecahedral Mg site (the A site) and the small octahedral Si site (the B site) [6–11] (Fig. 2). Current consensus on the site occupancy is that $Fe^{2+}$ mainly occupies the A site whereas $Fe^{3+}$ can occupy both the A and B sites [6–11]. Several studies have further shown that $Fe^{2+}$ may self-disproportionate into Fe metal and $Fe^{3+}$, creating $Fe^{3+}$-enriched Pv. That is, the significant amount of $Fe^{3+}$ in Pv is not a result of the oxidation state of the lower mantle, which is expected to be relatively reducing, but due to the crystal chemistry of Pv at high pressure. The $Fe^{3+}$ content in Pv is also found to vary with the amount of the $Al^{3+}$ likely through charge-coupled substitution with the $Si^{4+}$ in the octahedral site [4, 6]. The $Fe^{3+}$ content in Pv is approximately 20% without the presence of Al and 50–75% with the presence of $Al^{3+}$.

The reported spin transitions in Pv are much more complex than those in Fp, likely due to the low-symmetry oxygen ligand field and multiple site occupancies. These studies have shown that both $Fe^{2+}$ and $Fe^{3+}$ exist in the high-spin state in both of the A and B sites under ambient conditions [6–11]. Mössbauer analyses show that the high-spin $Fe^{2+}$ exhibits a QS value of ~1.6 to 2.2 mm/s and a CS of ~1 mm/s in the A site. Interpretations of the high-pressure Mössbauer analyses have been quite different, although their main results on the QS values were similar—both experimental and theoretical studies have reported extremely high QS values

of $Fe^{2+}$ (as high as ∼4.4 mm/s) at high pressures [6–11] . The relative area of the high-QS doublet (3.4–4.4 mm/s) increases with pressure at the expense of the low-QS doublet (1.6–2.2 mm/s), indicating that the transition involves $Fe^{2+}$ in the A site [7, 8]. The high-QS doublet becomes the dominant spectral feature in the high-pressure Mössbauer spectra at above approximately 30 GPa. Particularly, the new quadrupole doublet with the extremely high QS appears to have a very narrow linewidth and high CS (∼1.1 mm/s) [7]. Together with X-ray emission spectroscopic (XES) analyses for the total spin momentum of iron in Pv, the occurrence of the $Fe^{2+}$ site with the extremely high QS, very narrow linewidth, and relatively high CS has been assigned to be an intermediate-spin $Fe^{2+}$ with a total spin momentum of one ($S = 1$) in the A site [7]. That is, a high-spin to an intermediate-spin crossover occurs in Pv at around 30 GPa, and $Fe^{2+}$ remains stable in the intermediate-spin state at above 30 GPa in the lower mantle. At higher pressures, the intensity of the high QS component in the SMS spectra of PPv decreases, whereas the intensity of a new component with very low QS of less than 0.5 mm/s and a CS of ∼0 mm/s increases. This new component was assigned to the low-spin $Fe^{2+}$ occurring at 120 GPa and high temperatures.

However, it has been realized that the occurrence of the intermediate-spin state is very rare in geological materials and that high QS in iron does not necessarily imply the occurrence of the intermediate-spin state. For example, iron in almandine garnet is in the high-spin state with a QS of ∼3.5 mm/s under ambient conditions. Theoretical calculations have been performed to interpret the spin states and the extremely high QS values of $Fe^{2+}$ in Pv. Although not always in agreement with each other, these calculations show that the intermediate-spin state is not stable over all lower-mantle pressures, irrespective of the exchange-correlation functions used in the calculations [9]. The high-spin $Fe^{2+}$ with QS of 2.3–2.5 mm/s is more stable at relatively low pressures, while the high-spin $Fe^{2+}$ with QS of 3.3–3.6 mm/s is more favorable at higher pressure [9]. Based on these calculations, the extremely high QS site is a result of the iron atomic-site change, in which Fe ions move away from the central positions in the A site, rather than a spin-pairing transition.

For $Fe^{3+}$ in Pv, it has been shown both experimentally and theoretically that $Fe^{3+}$ enters into both A and B sites, suggesting a charge-coupled substitution mechanism [8, 10]. High-spin $Fe^{3+}$ is known to exhibit very low QS compared to $Fe^{2+}$ because all five $3d$ electrons are unpaired and form relatively spherical orbitals. Theoretical calculations further suggest that the $Fe^{3+}$ in the A site has an even lower QS value than the B site $Fe^{3+}$ [10]. Combined SMS and XES results for $Fe^{3+}$-containing Pv suggest that the low-spin population in the B site gradually increases to 100% with pressure up to 50–60 GPa, whereas $Fe^{3+}$ in the A site remains high-spin to at least 136 GPa, consistent with recent theoretical calculations [8, 10]. SMS analyses further suggest that A site $Fe^{3+}$ remains in the high-spin state in Al-bearing Pv, in which $Fe^{3+}$ is expected to predominantly exist in the A site [8]. Therefore, these results indicate that the $Fe^{3+}$ in the octahedral B site undergoes a high-spin to low-spin transition in Pv.

The QS of the $Fe^{2+}$ in the A site and the $Fe^{3+}$ in the B site exhibit exactly the opposite trends across the high-spin to the low-spin transition, and can be understood through their orbital occupancies. The low-spin $Fe^{2+}$ in the A site located near the center of the site forms a $3d$ charge density with a cubic-like shape that barely contributes to the effective electric field gradient, leading to a very small QS [8, 10]. The high-spin $Fe^{3+}$ also has a small QS (a small effective electric field gradient) in the

A and B sites because of an almost spherically-shaped electron charge distribution [8, 10]. However, the $3d$ orbitals of the low-spin $Fe^{3+}$ contribute more significantly to the effective electric field gradients and lead to a larger QS.

## 4 Spin and valence states of iron in PPv

Post-perovskite is expected to be the most abundant phase in the Earth's core-mantle boundary region. Deciphering the spin and valence states of iron in PPv at relevant *P-T* conditions provides new insight into the properties of the region, including seismic discontinuities, rheology and plasticity, dynamic evolution and formation of superplumes, thermal gradients, core-mantle heat flux, and chemistry [11]. The PPv phase is found to be stable in the $CaIrO_3$-type structure (*Cmcm*). However, a number of kinked structures, formed by sliding the {010} planes of the Pv structure with variation in the stacking sequence of $SiO_6$ octahedral layers, have also been reported. Thus far, the presence of the kinked PPv phase has been found to increase the amount of $Fe^{3+}$ in the sample. Experimental SMS results show $Fe^{2+}$ likely exists in the bipolar-prismatic site and exhibits extremely high QS of 3.8–4.5 mm/s and relatively high CS in PPv [11]. Complementary high *P-T* XES studies, which are sensitive to the total spin momentum of iron, suggest that iron predominantly exists in the intermediate-spin $Fe^{2+}$ state with $S = 1$ in the $CaIrO_3$-typed PPv at relevant *P-T* conditions of the lowermost mantle [11]. Since the intermediate-spin $Fe^{2+}$ in PPv is found to be stable at 25 mol% and 40 mol% Fe, it is conceivable that the intermediate-spin $Fe^{2+}$ is stable over a wide range of Fe content in PPv relevant to the D" region, where Fe-enrichment may be expected [11]. Similar to the discussion for $Fe^{2+}$ in Pv, however, theoretical calculations suggest that $Fe^{2+}$ in PPv is in the high-spin state at all mantle pressures, although theoretical QS values of the $Fe^{2+}$ and $Fe^{3+}$ remain to be computed.

SMS results on $Fe^{3+}$-rich PPv show that $Fe^{3+}$ exists in two different sites, one site with a high QS of ∼2 mm/s and another with a low QS of 0.3 mm/s, similar to the $Fe^{3+}$ in Pv [12]. The low QS site is assigned to be the high-spin $Fe^{3+}$ in the bipolar-prismatic site, whereas the high QS site with QS of ∼2 mm/s is assigned as the low-spin $Fe^{3+}$ in the octahedral site [12]. Based on the hyperfine parameters associated with the site assignments, the $Fe^{3+}$ in the octahedral site undergoes a high-spin to low-spin transition at high pressures, causing the QS to increase from the high-spin state to the low-spin state [12]. In this mixed spin-state scenario, $Fe^{3+}$ enters the site through charge-coupled substitution, as also suggested by theoretical calculations. Because the ionic radius of the low-spin $Fe^{3+}$ is smaller than that of the high-spin $Fe^{3+}$, the low-spin $Fe^{3+}$ is more stable in the smaller octahedral site of PPv.

The notable difference between the Mössbauer parameters of the Pv and PPv phases is that the QS of the low-spin $Fe^{3+}$ site is much smaller in PPv. The smaller QS of the low-spin site in PPv can be explained by a less distorted octahedral site, since distortion from a cubic environment around the iron nucleus results in an increased QS value. Since PPv is the high-pressure polymorph of Pv, the QS of $Fe^{2+}$ in PPv could be similar or related to that of $Fe^{2+}$ in Pv as both phases exhibit extremely high QS values of around 4 mm/s. The calculated QS of $Fe^{2+}$ in Pv is 3.3–3.6 mm/s at lower mantle pressures, consistent with the QS values for $Fe^{2+}$ from SMS analyses in PPv [7–12].

## 5 Conclusions

The disappearance of the QS and drop in the CS of the octahedrally-coordinated $Fe^{2+}$ in ferropericlase indicates the high-spin to low-spin transition at high pressures. The spin transition of iron in ferropericlase turns into a wide spin crossover at lower-mantle temperatures. Iron exists in the $Fe^{2+}$ and $Fe^{3+}$ states in both perovskite and post-perovskite. Both $Fe^{2+}$ and $Fe^{3+}$ exist in the high-spin state in perovskite under ambient conditions. Most recent studies have observed extremely high QS values of the $Fe^{2+}$, as high as ~4.4 mm/s, in perovskite under high pressures. The relative area of the high-QS doublet increases with pressure at the expense of the low-QS doublet, and has been assigned as an intermediate-spin $Fe^{2+}$ in the A site, occurring at approximately 30 GPa. However, recent theoretical calculations support the notion that the extremely QS site is a result of the atomic-site change rather than a high-spin to intermediate-spin transition. At higher pressures, a new doublet component was assigned to the low-spin $Fe^{2+}$ occurring at 120 GPa and high temperatures. Recent studies on $Fe^{3+}$-containing perovskite suggest that $Fe^{3+}$ in the octahedral B site undergoes a spin-pairing transition in perovskite, whereas $Fe^{3+}$ in the A site remains high-spin to at least 136 GPa.

Fe$^{2+}$ likely exists in the bipolar-prismatic site with an extremely high QS of 3.8–4.5 mm/s in post-perovskite, which has been assigned to the intermediate-spin $Fe^{2+}$ state with $S = 1$. However, theoretical calculations have found the intermediate-spin state unstable at lower-mantle pressures. $Fe^{3+}$ exists in two different sites, the high-spin $Fe^{3+}$ in the bipolar-prismatic site and the low-spin $Fe^{3+}$ in the octahedral site. These site assignments indicate that the $Fe^{3+}$ in the octahedral site undergoes a high-spin to low-spin transition at high pressures through charge-coupled substitution.

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