

Mössbauer modeling to interpret the spin state of iron in (Mg,Fe)SiO₃ perovskite

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[1] The properties of (Mg,Fe)SiO₃ perovskite at lower mantle conditions are still not well understood, and particular attention has recently been given to determining the Fe spin state. A major challenge in spin states studies is interpretation of Mössbauer spectra to determine the electronic structure of iron under extreme conditions. In this paper *ab initio* methods are used to predict quadrupole splitting values of high-, intermediate- and low-spin Fe²⁺ and Fe³⁺ in perovskite, as a function of pressure and composition. The calculations in (Mg_{0.75}Fe_{0.25})SiO₃ yield quadrupole splitting values in the range of 0.7–1.7 mm/s for all spin and valence states except high-spin Fe²⁺, which has two possible quadrupole splittings, 2.3 and 3.3 mm/s. The unexpected multiple quadrupole splitting values for high-spin Fe²⁺ are explained in terms of small changes in local structure and *d*-orbital occupations. The computed results are applied to interpret existing perovskite Mössbauer data for iron's spin state. **Citation:** Bengtson, A., J. Li, and D. Morgan (2009), Mössbauer modeling to interpret the spin state of iron in (Mg,Fe)SiO₃ perovskite, *Geophys. Res. Lett.*, **36**, L15301, doi:10.1029/2009GL038340.

[2] The spin state of iron (Fe) in (Mg,Fe)SiO₃ perovskite (pv) at lower mantle conditions has been the subject of a number of recent studies [Badro *et al.*, 2004; Bengtson *et al.*, 2008; Jackson *et al.*, 2005; Li *et al.*, 2006; Lin *et al.*, 2008; McCammon *et al.*, 2008; Umemoto *et al.*, 2008]. The spin state of Fe could affect lower mantle material properties such as density, elastic properties, sound velocities, and thermal conductivities [Li, 2007; Lin *et al.*, 2005], hence knowledge of the spin state is necessary for constructing accurate chemical, geodynamic, and seismological models of Earth's deep interior.

[3] All ferrous iron (Fe²⁺) and some ferric iron (Fe³⁺) in ABO₃ pv are generally assumed to adopt the pseudocubic A-site. Iron typically exists as high-spin (HS) ($2e_g\uparrow 3t_{2g}\uparrow e_g\downarrow - Fe^{2+}$, $2e_g\uparrow 3t_{2g}\uparrow - Fe^{3+}$) at ambient conditions, and pressure can induce a transition to a lower spin state such as intermediate-spin (IS) ($2e_g\uparrow 2t_{2g}\uparrow 2e_g\downarrow - Fe^{2+}$, $2e_g\uparrow 2t_{2g}\uparrow e_g\downarrow - Fe^{3+}$) or low-spin (LS) ($2e_g\uparrow t_{2g}\uparrow 2e_g\downarrow t_{2g}\downarrow - Fe^{2+}$, $2e_g\uparrow t_{2g}\uparrow 2e_g\downarrow - Fe^{3+}$). Pressure can stabilize lower-spin states by increasing crystal field energy or structural favoring of the smaller lower-spin Fe ion. Abundant evidence exists for LS Fe in

(Mg,Fe)O ferropericlasite [Badro *et al.*, 2003; Persson *et al.*, 2006, and references within], a likely component of the lower mantle [Ito and Takahashi, 1987]. The spin states of Fe in pv, however, are not as well understood as ferropericlasite.

[4] The spin state of Fe at high pressure is typically measured experimentally by X-ray Emission Spectroscopy (XES) and/or Mössbauer spectroscopy. In XES, a spin reduction in Fe manifests as an intensity drop and a position shift of the satellite peak $K\beta'$ relative to the main peak $K\beta$ [Tsutsumi *et al.*, 1976]. Measured XES data in pv show ~50% drop in satellite peak intensity and shift in its position between 1 bar and ~100 GPa [Badro *et al.*, 2004; Li *et al.*, 2004; Lin *et al.*, 2008] indicating pressure-induced crossover to IS [Li *et al.*, 2004; Lin *et al.*, 2008] or mixed-spin state [Badro *et al.*, 2004; Li *et al.*, 2004]. One study found the disappearance of the satellite peak at 120 GPa, indicative of LS Fe [Badro *et al.*, 2004].

[5] Mössbauer spectroscopy measures the electronic structure of Fe through quadrupole splitting (QS), isomer shift, and magnetic hyperfine field, resulting from hyperfine interactions between electrons and nucleus. The focus of this work is on the QS, the best-constrained parameter in the existing Mössbauer spectra under high pressure. All recent Mössbauer measurements in pv find three QS values near 3.5 (QS1), 2.5 (QS2), and 1 (QS3) mm/s (Figure 1c) [Jackson *et al.*, 2005; Li *et al.*, 2006; Lin *et al.*, 2008; McCammon *et al.*, 2008], except one study [Lin *et al.*, 2008] that finds two QS values, both near 4 mm/s. The upper range of measured QS is higher than most known values for HS or LS Fe²⁺ or Fe³⁺ in oxides or sulphides (Figure 1). The exceptionally high QS values, in conjunction with the XES data, have been used to argue that Fe²⁺ in pv exists as IS under lower mantle conditions [Li *et al.*, 2004; Lin *et al.*, 2008; McCammon *et al.*, 2008].

[6] There are still some concerns about the IS identification in pv under high pressure. First, the Mössbauer literature does not show a direct connection between high QS values and IS. In fact, high QS values have been reported for HS Fe²⁺ in molecular complexes (4.55 mms/s [Evans, 1996]) and oxides (garnet, 3.71 mm/s [Geiger *et al.*, 2003]). However, the QS of IS Fe²⁺ and Fe³⁺ in molecular crystals at ambient conditions ranges from 0 to 4.13 mm/s [Riley *et al.*, 1977; Strauss *et al.*, 1985], suggesting a strong structural dependence. In addition, while typical QS values of HS and LS Fe²⁺ and Fe³⁺ are well known at ambient conditions (see Figure 1a and Dyar *et al.* [2006]), little is known about the QS of Fe at mantle conditions. Interpreting high-pressure Mössbauer data on the basis of 1-bar references is potentially unreliable. Finally, no computational evidence has been seen for stable IS Fe with respect to HS or LS Fe in lower mantle materials [Bengtson *et al.*, 2008;

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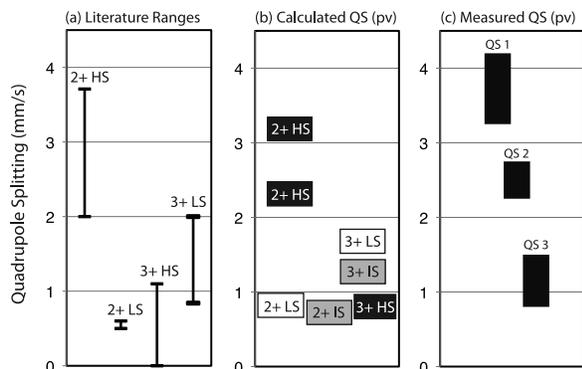


Figure 1. Experimental and computational summary of quadrupole splitting. Plots of quadrupole splitting (mm/s) (QS) values at a general pressure that best reflects the characteristic values. 2+ = Fe^{2+} , 3+ = Fe^{3+} , HS = high-spin, IS = intermediate-spin, LS = low-spin. (a) Common benchmark ranges for QS of Fe-oxide and -sulfide materials at ambient conditions as summarized in the literature for 2+ HS and 3+ HS [Bancroft *et al.*, 1967; Dyar *et al.*, 2006] (upper limit for 2+ HS is garnet [Geiger *et al.*, 2003]). 2+ LS values are pyrite and marcasite [Dyar *et al.*, 2006; King *et al.*, 1978]. 3+ LS values are Fe_2O_3 at 82 GPa & 4 K (upper limit) [Pasternak *et al.*, 1999] and 70 GPa & 300 K (lower limit) [Shim *et al.*, 2009]. The image is modeled after a figure of Li *et al.* [2006]. (b) Calculated QS values in perovskite. QS values are given at 30 GPa (see text for pressure dependence discussion) and are representative of all pressures up to 105 GPa. (c) Experimentally measured QS in perovskite at 40 GPa [Jackson *et al.*, 2005; Li *et al.*, 2006; Lin *et al.*, 2008; McCammon *et al.*, 2008]. Experiments (except Lin *et al.* [2008], see text) measure 3 QS, at 3.5 to 4 mm/s (QS1), 2.5 mm/s (QS2), and 1 mm/s (QS3). The large range given for each QS reflects the variation between different measurements. For example, QS1 is measured at 3.5 mm/s [Jackson *et al.*, 2005; Li *et al.*, 2006] and greater than 4 mm/s [Lin *et al.*, 2008; McCammon *et al.*, 2008].

Li *et al.*, 2005; Stackhouse *et al.*, 2007; Umemoto *et al.*, 2008; Zhang and Oganov, 2006]. In order to help identify the spin state of Fe in pv under high pressure and, more broadly, understand the electronic structure of lower-mantle Fe, *ab initio* methods are used in this study to predict QS values for HS, IS, and LS Fe^{2+} and Fe^{3+} in pv as a function of pressure and composition.

[7] Two density functional theory (DFT) codes are used here: Vienna Ab Initio Simulation Package (VASP) for structural relaxations [Kresse and Hafner, 1993; Kresse and Furthmuller, 1996] and WIEN2k for QS calculations [Blaha *et al.*, 1999]. Due to the challenges of performing complex relaxations in WIEN2k, all structural relaxations are performed using VASP with the projector-augmented wave method [Blochl, 1994; Kresse and Joubert, 1999], Generalized Gradient Approximation exchange-correlation with the Perdew-Burke-Ernzerhof parameterization (GGA-PBE) [Perdew *et al.*, 1996], a cutoff of 441 eV, and $3 \times 3 \times 2$ Monkhorst-Pack *k*-point mesh for sampling the Brillouin zone of the 20-atom primitive *Pbnm* MgSiO_3 pv cell. Variable Fe^{2+} concentrations are created by substitution on

the A site for Mg, Fe^{3+} is created by substitution for Mg on the A site coupled with an Al substitution for Si on the B site (Fe-Al distance of 2.809 Å). The relaxed VASP structures come from the work of Bengtson *et al.* [2008]. WIEN2k is used to calculate the electric field gradients (EFG) from which the QS splitting is determined [Fanciulli *et al.*, 1997] (currently VASP cannot calculate EFG). WIEN2k calculations are performed using GGA-PBE method with an energy separation between the core and valence state of -8 Rydbergs with a *k*-point mesh of $4 \times 4 \times 3$ for the 20-atom MgSiO_3 unit cell. All runs are done with point symmetry. Moments are treated equivalently between VASP and WIEN2k runs. HS and IS are run as spin-polarized with ferromagnetic ordering and the spin magnitude is allowed to relax in HS and is fixed to 2 (3) μ_B in IS Fe^{2+} (Fe^{3+}). LS Fe^{2+} is run as non-spin polarized and LS Fe^{3+} is run as ferromagnetic spin-polarized with a moment of 1 μ_B .

[8] To assess accuracy the calculated QS splitting values are compared to experimental results for Fe in different spin states and magnetic orderings (Figure 2). For hematite, marcasite and pyrite our results agree well with similar calculations [Dufek *et al.*, 1995]. The calculated QS match experimental results to within 0.1 mm/s for all systems except forsterite and LiFePO_4 (both have the olivine structure), where the predicted values are lower by 0.3–0.7 mm/s, suggesting the calculations may under-predict larger QS values. The effect of temperature is not included in the calculations, but the good agreement in Figure 2 suggests that the *ab initio* predictions reliably reproduce experiments at 300 K. At higher temperatures QS values can deviate significantly from the zero-temperature *ab initio* data [Lin *et al.*, 2009].

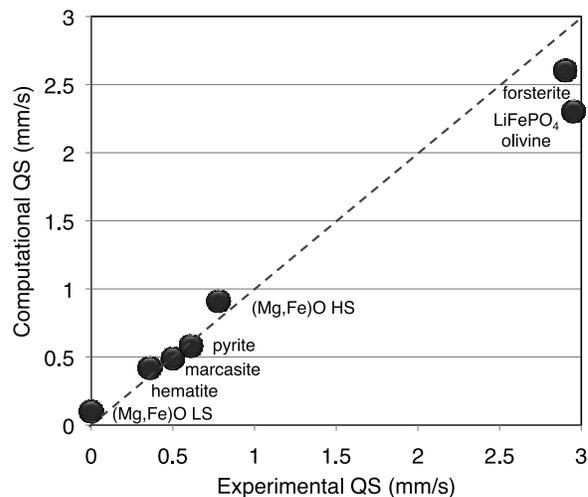


Figure 2. Comparison of calculated quadrupole splitting with experimental measurements. All calculations are HS Fe and ferromagnetic unless otherwise stated. Structures include Fe_2O_3 hematite (HS antiferromagnetic), FeS_2 marcasite (non-magnetic), FeS_2 pyrite (LS) [Dufek *et al.*, 1995], $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{O}$ magnesiowüstite (HS and LS) [Lin *et al.*, 2006], LiFePO_4 olivine [Yamada *et al.*, 2001] and $(\text{Mg}_{88}\text{Fe}_{12})_2\text{SiO}_4$ forsterite [Dyar *et al.*, 2006]. The dashed line represents perfect agreement between calculations and experimental measurements.

Table 1. Quadrupole Splitting of Fe in $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$ Perovskite at 30 GPa

Spin State	Quadrupole Splitting (mm/s)	
	Fe^{2+}	Fe^{3+}
High	3.2 (state 1), 2.3 (state 2)	0.8
Intermediate	0.7	1.2
Low	0.8	1.7

[9] The calculated QS for Fe in $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$ pv are summarized in Table 1 and Figure 1b. For Fe^{2+} in the A site, HS has a much larger QS (3.2 mm/s) than IS (0.7 mm/s) and LS (0.8 mm/s). The QS for HS Fe^{3+} in the A site is 0.8 mm/s, lower than IS Fe^{3+} (1.2 mm/s) and LS (1.7 mm/s). The QS for LS Fe^{3+} on the B site (Fe substituted for Si coupled with Al substituted for Mg) is 1.6 mm/s. Neither HS nor IS Fe^{2+} on the B site is stable, consistent with previous calculations [Cohen *et al.*, 1997], and results on those spin states have not been calculated.

[10] An unexpected result of this study is the prediction of two HS Fe^{2+} states with distinct energies, lattice parameters, Fe-O bond lengths, QS, and *d*-orbital occupancies. Only two states are found and they were reproduced in multiple calculations and at all Fe concentrations. Furthermore, at no time was more than one Fe state seen for any valence or spin state besides HS Fe^{2+} . To further assure that the correct locally stable states were identified, small random perturbations were added to each atomic position before relaxing the cells to their lowest energy (following Bengtson *et al.* [2008]). Five separate tests, each consisting of different random perturbations, were performed on the 100% Fe end member starting from *Pbnm* symmetry. All five tests robustly found two distinct states, with the QS of each state reproduced within ± 0.2 mm/s. However, no systematic search for stable or metastable Fe^{2+} states was performed.

[11] The following data describes the two Fe^{2+} states for $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$, but similar characteristics occur at other compositions. State 2 has three bonds shifted farther apart than state 1, by up to 0.4 Å (Figure 3). At 1 bar, state 2 is more stable than state 1 by about 8 meV/Fe. Under pressure, the energy difference between the states diminishes, becoming indistinguishable near 60 GPa. For all pressures below 60 GPa, state 2 has lower QS (by about 0.9 mm/s), different *d*-orbital occupancies, and changed lattice parameters (approximately +0.5%, -0.5%, +0.2% for *a*, *b*, and *c*, respectively) compared to state 1. Significant changes in QS resulting from *d*-orbital occupation and small local distortions are consistent with previous studies [Evans, 1996; Evans *et al.*, 2005].

[12] Except for the Fe^{2+} HS state 2 discussed above, little pressure dependence was found for QS between pressures of 0 to 105 GPa. The maximum change in QS was a 0.4 mm/s decrease with pressure for LS. The changes with pressure were less than 0.1 mm/s for HS and IS. QS of Fe^{2+} was found approximately to decrease linearly or remain constant with Fe content for all spin states (HS state 1: 3.2 mm/s (25% Fe) to 2.3 mm/s (100% Fe); HS state 2: 2.3 mm/s (25% Fe) to 1.7 mm/s (100% Fe); LS: 0.8 mm/s (25% Fe) to 0.6 mm/s (100% Fe); IS: 0.7 (25% Fe) to 0.7 (100% Fe)). The linear decrease of QS with Fe concentration is consis-

tent with trends in other oxide materials [Bancroft *et al.*, 1967].

[13] The ranges of calculated QS for $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$ (under all pressures up to 105 GPa) (Figure 1b) are within or near the known range of values for HS and LS Fe^{2+} and Fe^{3+} in Fe-oxide and Fe-sulphide materials (Figure 1a). Moreover, the calculations are generally consistent with observed QS values in pv (Figure 1c), although a value as high as 4 mm/s observed in some studies [Lin *et al.*, 2008; McCammon *et al.*, 2008] is not seen in the calculations. This discrepancy may result from an enhancement of the measured values (e.g., due to anisotropy [Grodzicki *et al.*, 2001]) or from an under-prediction of high QS values in the *ab initio* calculations (see Figure 2).

[14] The relative energy difference between the states decreases with pressure, suggesting the occupancy of state 1 will increase with pressure, consistent with experimental data showing an increase in the fraction of iron with QS1 at the expense of QS2 [Jackson *et al.*, 2005; McCammon *et al.*, 2008]. Calculated results are for zero-temperature. Increasing temperature could excite Fe from state 2 into the slightly less stable state 1, hence increasing the fraction of iron with QS1, as observed by McCammon *et al.* [2008]. Across the transition from QS2 to QS1, measurements show *a*, *b* become more compressible while *c* becomes less compressible [McCammon *et al.*, 2008]. The reason for different *a*, *b* and *c* changes between the calculations and experiments is not clear, and may be due to the calculations sampling only limited Fe orderings or stable Fe states.

[15] Typical interpretations of experimental Mössbauer data (Figure 1c) assume that QS1 = IS or HS Fe^{2+} , QS2 = HS Fe^{2+} , QS3 = Fe^{3+} any spin or LS Fe^{2+} [Jackson *et al.*, 2005; Li *et al.*, 2006; Lin *et al.*, 2008; McCammon *et al.*, 2008]. Our calculated QS values (Figure 1b) suggest that both QS1 and QS2 are HS Fe^{2+} , with different local distortions, while QS3 is Fe^{3+} in any spin state or LS or IS Fe^{2+} . However, this interpretation cannot explain simultaneous XES and Mössbauer measurements on pv, indicating a pressure-induced spin reduction [Li *et al.*, 2004; Lin *et al.*, 2008]. It is possible that changes in XES spectra observed for high pressure pv originate from other sources than reduced magnetic moment, although such changes have been used to identify spin crossover in a number of other systems [e.g., Badro *et al.*, 2003; Rueff *et al.*, 1999]. Alternatively, the calculations may have missed a stable

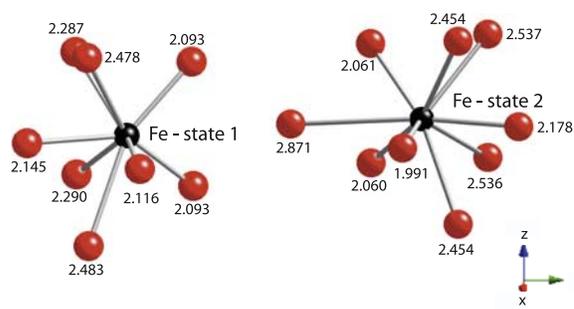


Figure 3. Fe-O distances (Å) around high-spin A-site Fe in state 1 (QS = 3.2 mm/s) and state 2 (QS = 2.3 mm/s) in $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$ perovskite at zero pressure. State 2 is 8 meV/Fe more stable than state 1 at zero pressure.

local distortion for IS, which could stabilize IS and enhance its QS to a much higher value.

[16] In summary, calculations were performed for quadrupole splitting (QS) of known benchmark Fe-bearing materials at ambient conditions and of Fe in pv as a function of spin state, valence, pressure, and iron content. The calculations reproduce the benchmark values within 0.7 mm/s. The calculated QS values for high-spin and low-spin Fe²⁺ and Fe³⁺ in 25% Fe perovskite agree well with ranges in other Fe-bearing materials, and with experimental data on perovskite. No computational evidence is found that intermediate-spin leads to high QS, rather the QS of intermediate-spin Fe is near 1 mm/s for Fe²⁺ and Fe³⁺, including pressure and composition effects. Two nearly degenerate states for Fe²⁺ were identified with different *d*-orbital occupations, local bond lengths and associated lattice parameters, and QS values. Although further details must be clarified, our results suggest the experimentally observed high QS values in perovskite may reflect small structural and orbital changes rather than a change of spin state.

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