

Electronic state of Fe²⁺ in (Mg,Fe)(Si,Al)O₃ perovskite and (Mg,Fe)SiO₃ majorite at pressures up to 81 GPa and temperatures up to 800 K

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Abstract Despite a large number of studies of iron spin state in silicate perovskite at high pressure and high temperature, there is still disagreement regarding the type and P – T conditions of the transition, and whether Fe²⁺ or Fe³⁺ or both iron cations are involved. Recently, our group published results of a Mössbauer spectroscopy study of the iron behaviour in (Mg,Fe)(Si,Al)O₃ perovskite at pressures up to 110 GPa (McCammon et al. 2008), where we suggested stabilization of the intermediate spin state for 8- to 12-fold coordinated ferrous iron (^{[8–12]Fe²⁺}) in silicate perovskite above 30 GPa. In order to explore the behaviour in related systems, we performed a comparative Mössbauer spectroscopic study of silicate perovskite (Fe_{0.12}Mg_{0.88}SiO₃) and majorite (with two compositions—Fe_{0.18}Mg_{0.82}SiO₃ and Fe_{0.11}Mg_{0.88}SiO₃) at pressures up to 81 GPa in the temperature range 296–800 K, which was mainly motivated by the fact that the oxygen environment of ferrous iron in majorite is quite similar to that in silicate perovskite. The ^{[8–12]Fe²⁺} component, dominating the Mössbauer spectra of majorites, shows high quadrupole splitting (QS) values, about 3.6 mm s⁻¹, in the entire studied P – T region (pressures to 58 GPa and 296–800 K). Decrease of the QS of this component with temperature at constant pressure can be described by the Huggins model with the energy splitting between low-energy e_g levels of ^{[8–12]Fe²⁺} equal to 1,500 (50) cm⁻¹ for Fe_{0.18}Mg_{0.82}SiO₃ and to 1,680 (70) cm⁻¹ for Fe_{0.11}Mg_{0.88}SiO₃. In contrast, for the silicate perovskite

dominating Mössbauer component associated with ^{[8–12]Fe²⁺} suggests the gradual change of the electronic properties. Namely, an additional spectral component with central shift close to that for high-spin ^{[8–12]Fe²⁺} and QS about 3.7 mm s⁻¹ appeared at ~35 (2) GPa, and the amount of the component increases with both pressure and temperature. The temperature dependence of QS of the component cannot be described in the framework of the Huggins model. Observed differences in the high-pressure high-temperature behaviour of ^{[8–12]Fe²⁺} in the silicate perovskite and majorite phases provide additional arguments in favour of the gradual high-spin—intermediate-spin crossover in lower mantle perovskite, previously reported by McCammon et al. (2008) and Lin et al. (2008).

Keywords Mössbauer spectroscopy · High pressure · Fe-bearing silicate perovskite · Spin transition · Garnet · Intermediate spin

Introduction

Materials with the perovskite and garnet crystal structures are very common among dense oxides containing several cations. Iron-bearing magnesium silicate perovskite and majorite (garnet-structured silicate) are abundant minerals of the Earth's transition zone and lower mantle.

(Mg,Fe)(Si,Al)O₃ perovskite has an orthorhombic structure, with Si or Al in the nearly symmetrical octahedral “B-site” (coloured green in Fig. 1a) and Mg²⁺ or Fe²⁺ in the more distorted 8- to 12-fold coordinated “A-site” (Horiuchi et al. 1987; McCammon et al. 1992). At ambient conditions A–O distances range from 2.02 to 2.43 Å with an average value of 2.21 Å. A certain amount of Fe³⁺ can also probably occupy the smaller octahedral site

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Fig. 1 Coordination polyhedron of ferrous iron (*solid blue spheres*) in the **a** silicate perovskite (Ross and Hazen 1989) and **b** majorite (Angel et al. 1989; McCammon and Ross 2003) structures. *Green octahedra* and *blue tetrahedra* represent the oxygen environment of Si, and the *purple octahedra* represent the Mg/Si site in the majorite structure

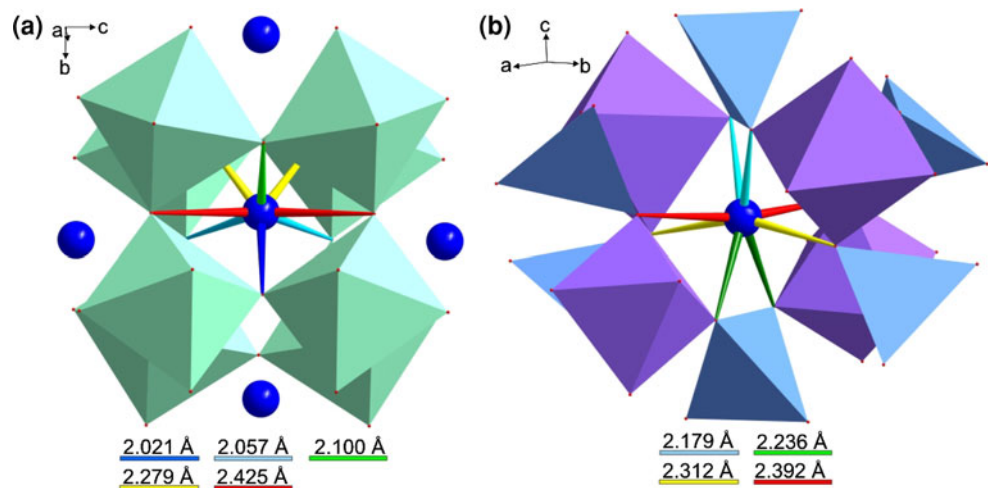
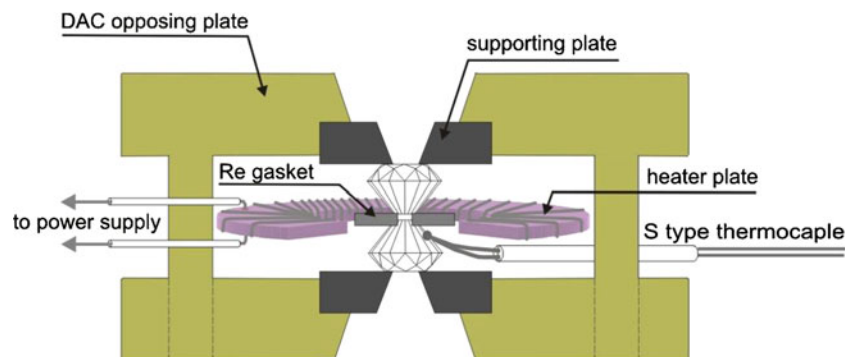


Fig. 2 Schematic drawing of the DAC with an external resistive heating system



(McCammon et al. 1992, 1998; Jephcoat et al. 1999). Physical properties (elasticity, thermal and electrical conductivity, etc.) of silicate perovskite are believed to be influenced by the electronic state of iron at high pressures and temperatures (Badro et al. 2004; McCammon et al. 2008; Goncharov et al. 2008; Keppler et al. 2009).

(Mg,Fe)SiO₃ majorite has a tetragonal structure, with Mg²⁺ and Fe²⁺ cations in the dodecahedral (or distorted cubic) site and Si in the octahedral (coloured purple in Fig. 1b) and tetrahedral (coloured blue in Fig. 2b) sites; a small amount of Fe³⁺ can also occupy the octahedral site. The addition of Al to end member tetragonal MgSiO₃ majorite stabilizes cubic symmetry (Hatch and Ghose 1989). At ambient conditions, interatomic distances for the dodecahedral position range from 2.18 to 2.39 Å with an average value of 2.28 Å. Since the silicate garnet and perovskite structures have clear similarities in the environment of Fe²⁺ located in the eight-coordinated position, one might expect some similarities in the iron behaviour in these two minerals.

There have been several experimental and theoretical studies on the iron spin state in magnesium silicate perovskite at high pressures, but the results are rather controversial. Badro et al. (2004), using K_β X-ray emission spectroscopy (XES), suggested that iron in silicate

perovskite first undergoes a high-spin (HS)—intermediate-spin (IS) crossover at 70 GPa and then the transition to the low-spin (LS) state occurs at 120 GPa. Jackson et al. (2005), using nuclear forward scattering (NFS), interpreted their data to indicate a spin-pairing transition in ferric iron at 70 GPa, while ferrous iron remained HS through the entire studied region. Li et al. (2006), combining XES and NFS techniques, suggested a gradual HS–LS crossover in iron at 20–100 GPa. Recently, our group published results of Mössbauer spectroscopy studies of iron behaviour in (Mg,Fe)(Si,Al)O₃ perovskite at pressures up to 110 GPa (McCammon et al. 2008). We observed a gradual change of the electronic state of ferrous iron in silicate perovskite at 30–65 GPa, which we interpreted as HS–IS crossover. In particular, at about 30 GPa a new Mössbauer component with an unusually large value of quadrupole splitting (QS) (about 4 mm s⁻¹) was detected, and the amount of the component increases with pressure and temperature. This new component was assigned to intermediate-spin Fe²⁺ in the 8- to 12-fold coordinated site in the perovskite structure.

The QS of 4 mm s⁻¹ is nearly the highest value that has ever been reported for any iron-containing material (Bancroft et al. 1967). A similar value (3.6 mm s⁻¹) was previously observed for eightfold coordinated high-spin

ferrous iron in the garnet structure (Amthauer et al. 1976; Murad and Wagner 1987; McCammon and Ross 2003). Since Fe^{2+} in silicate perovskite has a similar oxygen environment to garnet (Fig. 1), we compared the behaviour of the “high-QS component” in $(\text{Mg,Fe})\text{SiO}_3$ perovskite with that of $(\text{Mg,Fe})\text{SiO}_3$ majorite as a function of pressure and temperature in order to understand whether the origin of the high QS value for ferrous iron in silicate perovskite is similar to that in majorite. This work complements and extends the results published by McCammon et al. (2008).

Experimental procedure

In order to evaluate the influence of the synthesis procedure on the behaviour of iron-bearing silicate perovskite at high pressure, we investigated two types of samples: the first had been pre-synthesized in a multianvil press and the second was synthesized in situ in a diamond anvil cell (DAC).

The first set of samples of $^{57}\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$ perovskite were synthesized from ^{57}Fe -enriched clinopyroxene starting material in a Re capsule using a multianvil press at 25 GPa and 1,650°C with heating duration of 20 min. Further details are given in McCammon et al. (2004) and Frost et al. (2004). The second set of $^{57}\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$ perovskite samples was synthesized from the same starting material in a DAC at a pressure of 30–35 GPa and temperature about 2,500°C, which corresponds to lower mantle conditions. Chemical compositions of silicate perovskite samples synthesized in a DAC and in the multianvil apparatus (after recovering to ambient conditions) were checked by electron microprobe, and within the uncertainties of measurements they turned out to be the same. According to X-ray diffraction data, samples contain pure silicate perovskite although in some cases traces of SiO_2 stishovite were detected.

$^{57}\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ and $^{57}\text{Fe}_{0.11}\text{Mg}_{0.88}\text{SiO}_3$ majorite samples were also synthesized from ^{57}Fe -enriched clinopyroxene starting material in a Re capsule using a multianvil press at 19 GPa and 1,900°C with heating duration of 25 min. The chemical composition of majorite samples was also checked by electron microprobe, and X-ray diffraction showed the presence of a single majorite phase. Further details are given in McCammon and Ross (2003).

For the high-pressure high-temperature Mössbauer measurements in a DAC we used diamonds with 300 μm culet size. The sample was loaded in a Re gasket that was preindented to $\sim 30 \mu\text{m}$ and then drilled with a hole of 125 μm diameter. For pressure calibration and evaluation of the pressure gradient we used small ruby chips that were loaded into the cell along with the sample (no pressure medium was used). At the highest pressures (~ 81 GPa),

the uncertainty in pressure determination by ruby fluorescence was estimated to be below 4 GPa, while the pressure gradient between the centre and border of the pressure chamber did not exceed 5 GPa. After each increase or decrease of pressure with step ~ 5 GPa above 30 GPa, silicate perovskite samples were annealed at 1,700–1,900 K by laser heating.

Transmission Mössbauer spectra were recorded at temperatures of 300–800 K in the pressure range from ambient up to 81 GPa on a constant acceleration Mössbauer spectrometer with a ^{57}Co point source. The experimental procedure of high-pressure Mössbauer spectroscopic measurements is described in detail in McCammon et al. (1992) and Kantor et al. (2004).

In order to heat samples up to 800 K under pressure we used an external resistive heater mounted inside the DAC (Fig. 2). The heater consists of a ceramic plate wound with Pt wire of 0.5 mm diameter. The heater wire was isolated from other conductive parts of the cell by high-temperature ceramic glue (the layer of ceramic glue is not shown in Fig. 2). A S-type thermocouple (90%Pt10%Rh/Pt) is glued to another part of the cell as shown in Fig. 2. The temperature gradient within the pressure chamber was estimated to be a maximum of 20 K.

Results

$(\text{Mg,Fe})\text{SiO}_3$ perovskite

Pressure effect

Selected Mössbauer spectra of $(\text{Mg,Fe})\text{SiO}_3$ perovskite collected on compression at room temperature are presented in Fig. 3. We chose a fitting model that is consistent with known constraints on the hyperfine parameters [central shift (CS) and quadrupole splitting (QS)] (McCammon 1998, 2008).

At pressures up to ~ 30 GPa (Fig. 3a) the spectra were fitted to two quadrupole doublets with Lorentzian line-shape: (a) high-spin Fe^{2+} , shown in dark gray (CS is about 1 mm s^{-1} and QS is about 2.4 mm s^{-1}); and (b) Fe^{3+} , the relative amount of which varies from 8 to 12% depending on the sample (shown in black). At a pressure of about 30 GPa we observed the appearance of a third doublet (shown in blue on the Fig. 3b, c), the relative area of which increases with pressure (Figs. 3, 4c). The new doublet has CS close to that for HS Fe^{2+} and an unusually large QS, close to 4 mm s^{-1} . This component was assigned to IS Fe^{2+} by McCammon et al. 2008, but for now we will simply denote it as the high-QS component. Also during compression we observed an increase of the absorption at $\sim 0.4 \text{ mm s}^{-1}$ (doublet shaded light gray in Fig. 3b, c),

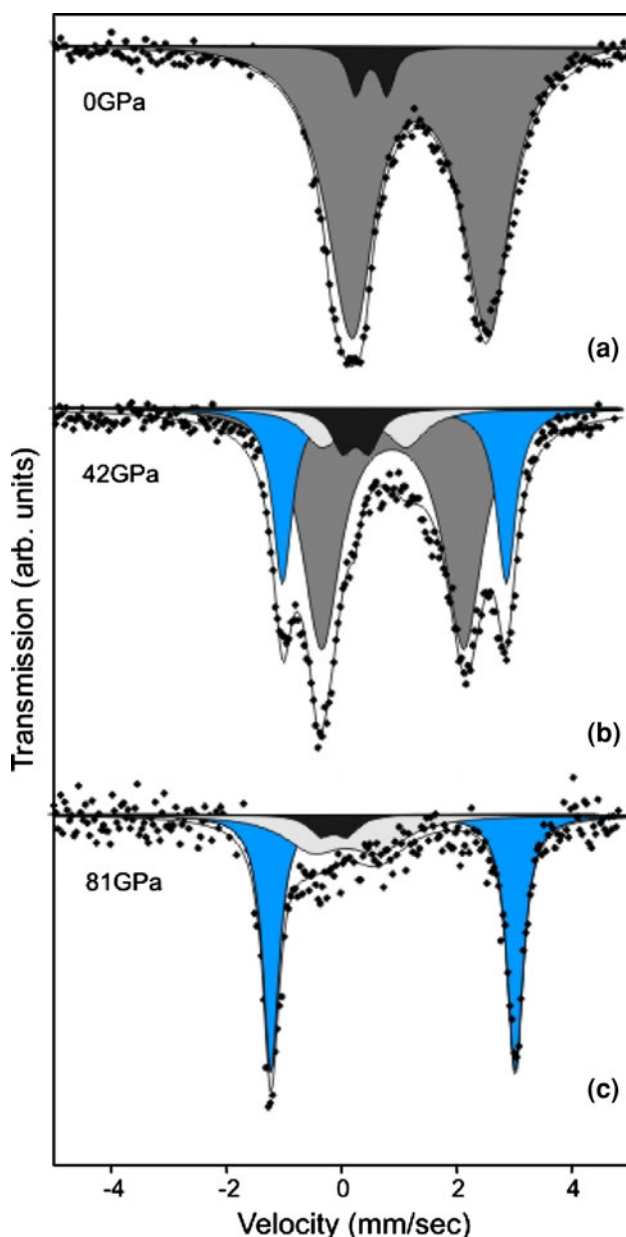


Fig. 3 Selected Mössbauer spectra of $\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$ perovskite at variable pressure collected at room temperature. The *solid circles* correspond to the experimental data. Components are shaded as follows: *dark gray* HS Fe^{2+} , *black* Fe^{3+} , *blue* high-QS component, *light gray* charge transfer component

which was assigned to Fe^{2+} – Fe^{3+} charge transfer, the intensity of which increases with pressure and temperature (Fei et al. 1994; McCammon 1998, 2008). Due to the significant overlap between Fe^{3+} and charge transfer components, analysis of the behaviour of Fe^{3+} is ambiguous, especially at high pressures and temperatures, where the relative area of the charge transfer component is comparable to or even exceeds that for Fe^{3+} (Fig. 3b, c). This behaviour makes it almost impossible to track pressure and temperature effects on the electronic properties of

ferric iron in silicate perovskite with the given composition ($\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$). Therefore, in the present work we concentrated mainly on the behaviour of Fe^{2+} cations. The hyperfine parameters and relative areas of all spectral components (except for Fe^{3+}) are presented in Fig. 4. The CS of HS Fe^{2+} and high-QS components decreases with pressure, while QS slightly increases (Fig. 4a, b). There are no noticeable differences between the spectra of samples synthesized in a multianvil press and in a DAC, except for a small difference in Fe^{3+} content (silicate perovskite synthesized in a multianvil press contains 2–4% more Fe^{3+} than the sample synthesized in a DAC), but there is no observable influence on the hyperfine parameters of spectral components.

Temperature effect

Increase of temperature decreases the signal/noise ratio (Fig. 5b) due to the fact that the recoil-free fraction is inversely proportion to the temperature (Mössbauer and Wiedemann 1960), which introduces additional uncertainty to the fitting procedure. Nevertheless, we were able to resolve the hyperfine parameters of Mössbauer spectral components. In addition to the usual temperature-induced decrease of QS and CS values for all components and intensification of charge transfer between ferrous and ferric iron (doublet shaded light gray in Fig. 5), we also detected a gradual increase of the amount of the high-QS component with temperature (Fig. 6). For example, at 55 GPa the relative area of the component increases from 41 (1)% at room temperature to 69 (2)% at 800 K (Fig. 5). We will discuss the temperature effect on the high-QS component in more detail in the following.

(Mg,Fe) SiO_3 majorite

Pressure effect

The pressure evolution of Mössbauer spectra collected from $^{57}\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ majorite at room temperature is shown in Fig. 7. The main component (about 80% relative to the total amount of iron) represents HS Fe^{2+} in eightfold coordinated polyhedra ($^{181}\text{Fe}^{2+}$) (doublet shaded blue), the quadrupole doublet shaded dark gray corresponds to HS Fe^{2+} in the octahedral site, and the black doublet represents ferric iron in an octahedral site, the amount of which varies from 8 to 12% depending on the sample (McCammon and Ross 2003). At ambient pressure the $^{181}\text{Fe}^{2+}$ component has CS around 1.2 mm s⁻¹ and a large value of QS 3.6 mm s⁻¹ (which is comparable to the hyperfine parameters of the high-QS component in silicate perovskite, which will be discussed in the following section). The CS of all three doublets slowly decreases with pressure while QS increases

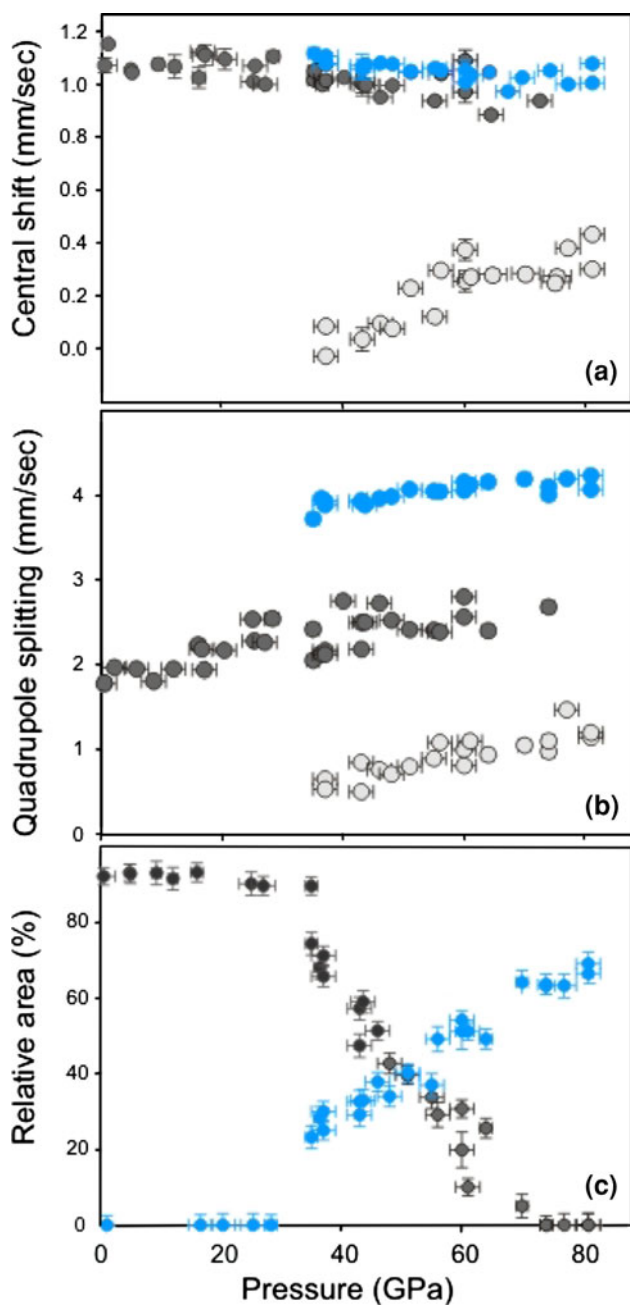


Fig. 4 Central shift (a), quadrupole splitting (b) and relative area (c) as a function of pressure for $\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$ perovskite HS Fe^{2+} (dark gray circles), high-QS component (blue circles) and the charge transfer component (light gray circles). For clarity the relative area of the charge transfer component is not shown

(Fig. 8a, b). However, the relative amounts of all components remain the same within uncertainty through the entire studied pressure region (up to 52 GPa) (Fig. 8c).

Temperature effect

Mössbauer spectroscopic measurements were performed at variable temperature for two majorite samples with different

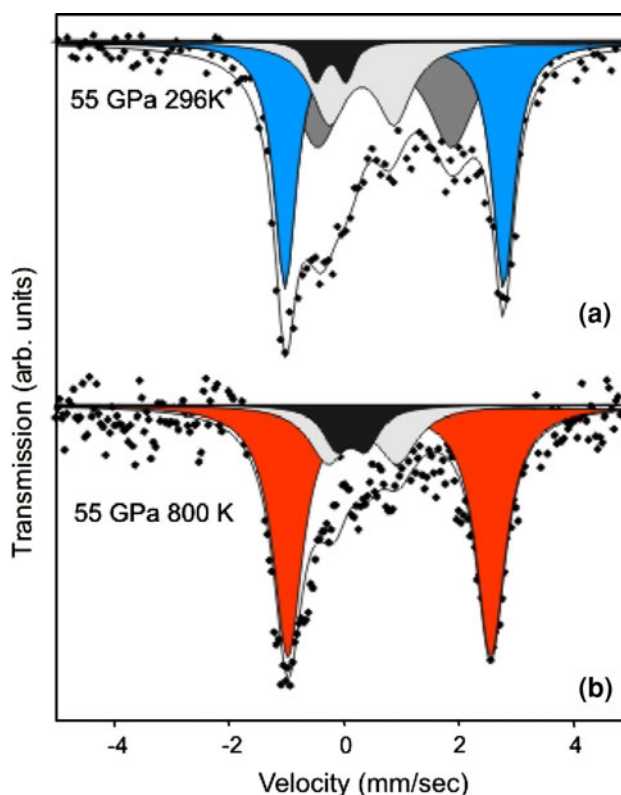


Fig. 5 Mössbauer spectra of $\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$ perovskite at 55 GPa collected at room temperature (a) and at 800 K (b). Solid circles correspond to the experimental data. Components are shaded as follows: dark gray HS Fe^{2+} , black Fe^{3+} , light gray charge transfer component, blue high-QS component at room temperature, red high-QS component at 800 K

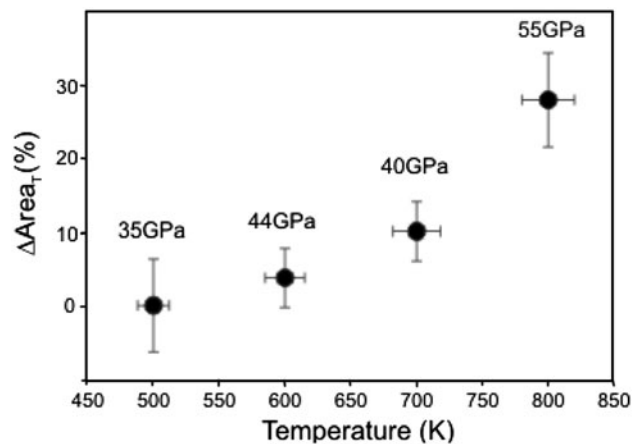


Fig. 6 Change in the relative area of the high-QS component of $\text{Fe}_{0.12}\text{Mg}_{0.88}\text{SiO}_3$ perovskite with temperature relative to room temperature data collected at the same pressure

compositions: $^{57}\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ and $^{57}\text{Fe}_{0.11}\text{Mg}_{0.89}\text{SiO}_3$. The temperature dependence of hyperfine parameters obtained for both samples at 20 GPa is presented in Fig. 8d–f. An increase of temperature up to 670 K does not introduce any significant changes to the Mössbauer absorption spectra

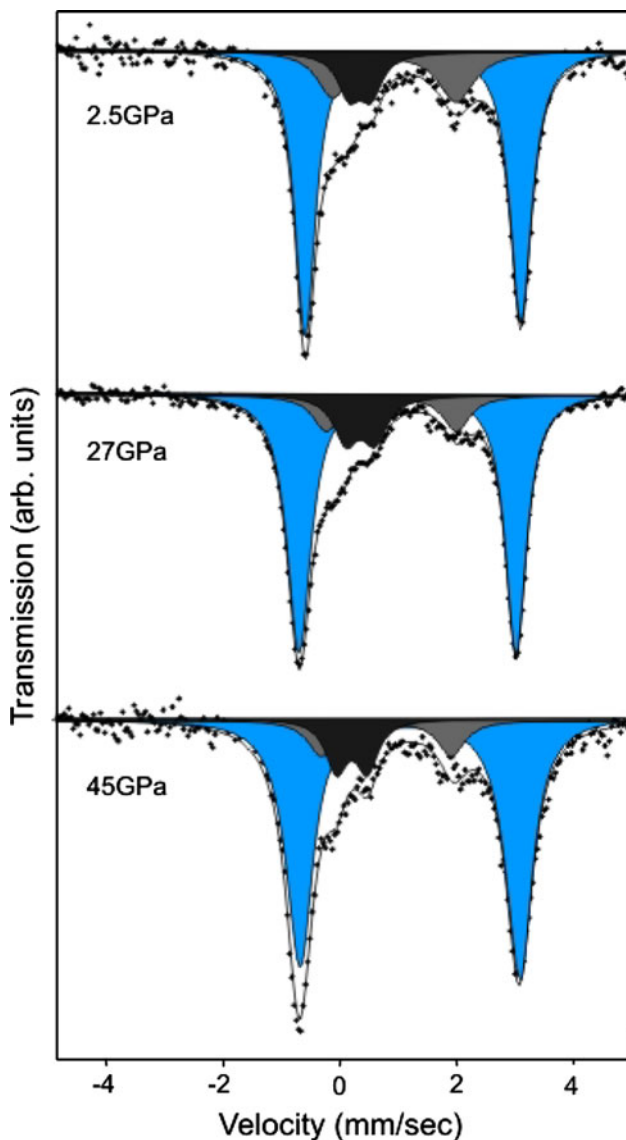


Fig. 7 Selected Mössbauer spectra of $\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ majorite at variable pressure collected at room temperature. *Solid circles* correspond to the experimental data. Components are shaded as follows: *blue* HS $^{81}\text{Fe}^{2+}$, *dark gray* HS $^{61}\text{Fe}^{2+}$, *black* Fe^{3+}

except for the usual decrease in the values of hyperfine parameters with temperature; the relative areas of individual components remain the same (Figs. 8d–f, 10).

Discussion

(Fe,Mg)SiO₃ majorite

Let us now consider in detail the high pressure and temperature behaviour of $^{81}\text{Fe}^{2+}$ in majorite, and then compare it with the high-QS component in silicate perovskite.

In general, the value of QS is determined by two factors: (a) lattice contribution, which is proportional to the electrical field gradient (EFG) produced by the charge distribution surrounding the absorbing nucleus (which is normally negligible and does not vary significantly with pressure and temperature) and (b) valence contribution, which is proportional to the EFG produced by the electrons distributed over the valence energy levels associated with the absorbing nucleus; therefore, the valence contribution to the QS value is temperature and pressure dependent (Ingalls 1964).

In the case of $^{81}\text{Fe}^{2+}$ in majorite, the valence contribution to the EFG is determined by the Boltzmann distribution of six 3d-electrons over the five 3d levels, which are split into two levels with lower energy, e_g , and three levels of higher energy, t_{2g} , that are separated by the crystal field splitting energy, Δ_C , as illustrated in Fig. 9a (Burns 1993).

The lower energy levels correspond to the d_{z^2} and $d_{x^2-y^2}$ electronic orbitals and the high-energy levels correspond to the d_{xy} , d_{yz} , d_{xz} orbitals. If the d_{z^2} and $d_{x^2-y^2}$ orbitals are equally populated, the magnitude of their contributions to the EFG would be the same, but opposite in sign. Consequently, their total contribution to the EFG would be zero. The same is true in the case of the three t_{2g} orbitals.

According to the Boltzmann distribution the population of the i -th level is given by $n_i = n_0 \times \exp\left(-\frac{\Delta_i}{kT}\right)$, where Δ_i is the energy of the i -th level and n_0 is a normalization constant. The values of Δ_i and therefore the population of energy levels depend on the relation between crystal field splitting (Δ_C) and spin-pairing energy (SPE) as well as on temperature. The relative magnitudes of Δ_C and SPE determine which spin configuration is stable.

In the case of high-spin $^{81}\text{Fe}^{2+}$ in majorite ($\text{SPE} \gg \Delta_C$), five 3d electrons occupy each of the five energy levels and the last (sixth) electron pairs with the one occupying the lowest energy level (Fig. 9b). For this configuration only e_g orbitals contribute to the EFG, because the t_{2g} orbitals are equally populated and compensate each other. Consequently, the value of QS in this case is mainly determined by the energy difference between e_g levels $-\Delta_1$ (Fig. 9a). Note that the larger the value of Δ_C and the lower the temperature, the higher the QS will be. The value of Δ_1 in this particular case (HS $^{81}\text{Fe}^{2+}$ in majorite) can be estimated through the temperature dependence of quadrupole splitting, as was shown by Huggins (1975). Based on the Ingalls model (1964), Huggins (1975) derived the following simple expression for the variation of quadrupole splitting, QS, with temperature, T , for the case of ferrous iron in garnet:

$$\text{QS}(T) = (\text{QS}(0) + F_{\text{lat}}) \left(\frac{1 - e^{-\Delta_1/kT}}{1 + e^{-\Delta_1/kT}} \right) - F_{\text{lat}}, \quad (1)$$

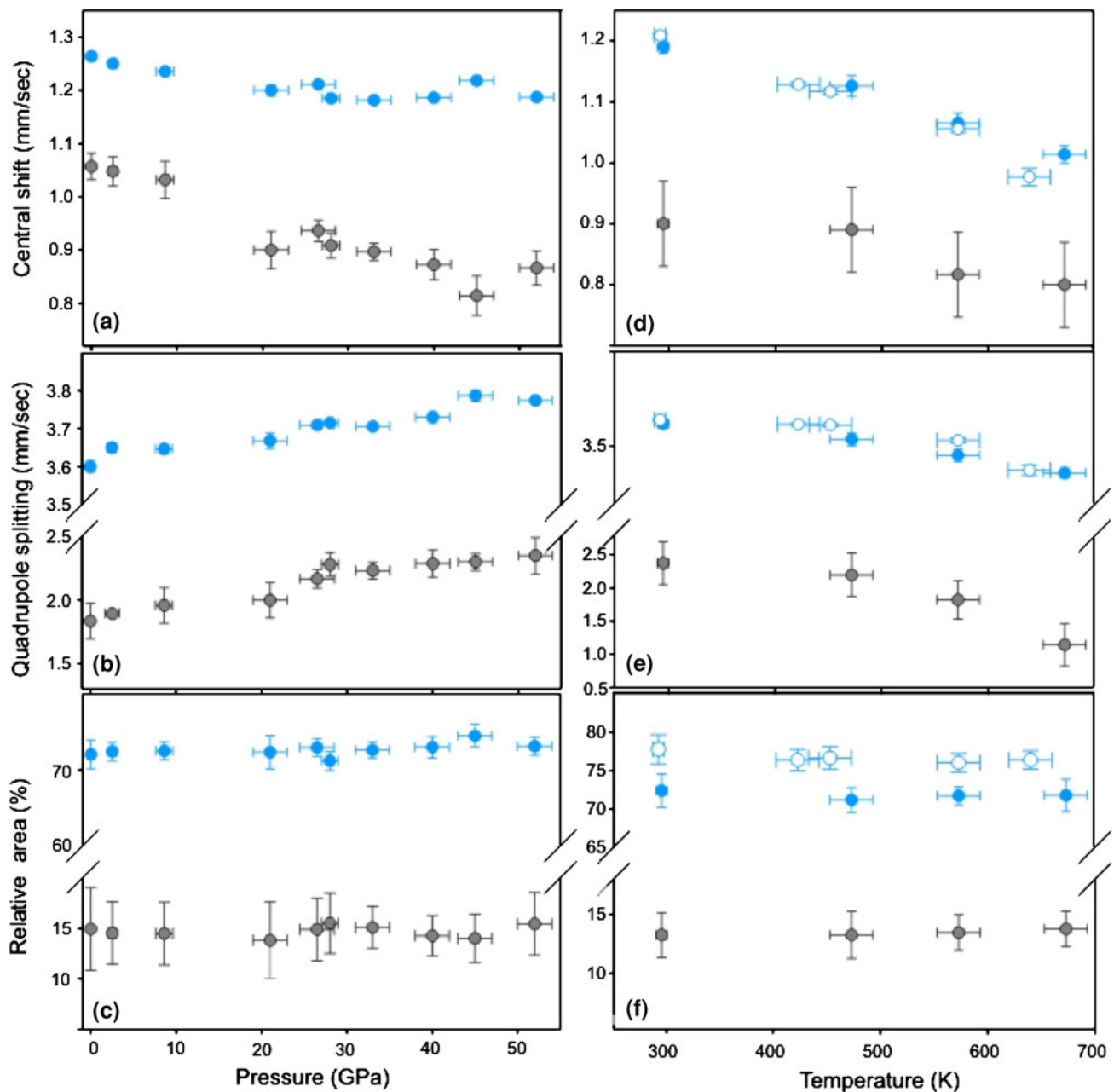


Fig. 8 Central shift, quadrupole splitting and relative area as a function of pressure (a, b, c) and temperature (d, e, f) for $\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ majorite $^{181}\text{Fe}^{2+}$ (blue circles), $^{66}\text{Fe}^{2+}$ (light gray circles) and for $^{181}\text{Fe}^{2+}$ in $\text{Fe}_{0.11}\text{Mg}_{0.89}\text{SiO}_3$ majorite (open blue circles)

where $\text{QS}(0)$ is the quadrupole splitting (in mm s^{-1}) at 0 K, Δ_1 is the separation of e_g levels (Fig. 9a), k is Boltzmann's constant and F_{lat} is the lattice contribution (in mm s^{-1}) to the QS.

Applying this formula to our variable temperature data for majorite (Fig. 10) and assuming $F_{\text{lat}} = 0$ (Huggins 1975), we obtained the result that at 20 GPa, Δ_1 is 1,500 (50) and 1,680 (70) cm^{-1} for ferrous iron in $^{57}\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ and $^{57}\text{Fe}_{0.11}\text{Mg}_{0.89}\text{SiO}_3$ majorites, respectively [for comparison, an ambient pressure value of Δ_1 in garnets was estimated to be $1,100 \pm 50 \text{ cm}^{-1}$ (Huggins 1975; Burns 1993)]. With

these values of Δ_1 we were able to obtain a good fit of our data to Eq. 1, which is shown by the dashed lines in Fig. 10.

Consequently, in the case of majorite we can account for the high value of the QS (about 3.6–3.7 mm s^{-1}) as a consequence of the large splitting between the lower energy levels e_g .

(Fe,Mg)SiO₃ perovskite

As a first approximation the energy diagram for $^{18-12}\text{Fe}^{2+}$ in silicate perovskite is similar to that for $^{181}\text{Fe}^{2+}$ in

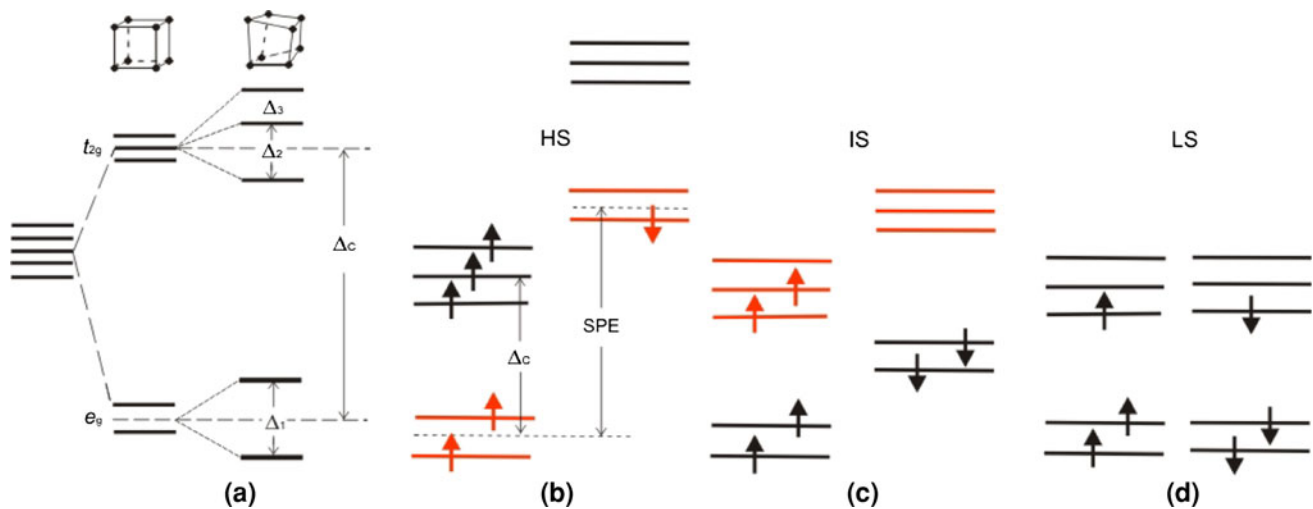


Fig. 9 Splitting of Fe^{2+} energy levels (a) and possible spin state configurations (b, c, d) in a distorted cubic field (modified after Burns 1993). The energy levels that predominantly contribute to the EFG for a certain spin configuration are highlighted in red

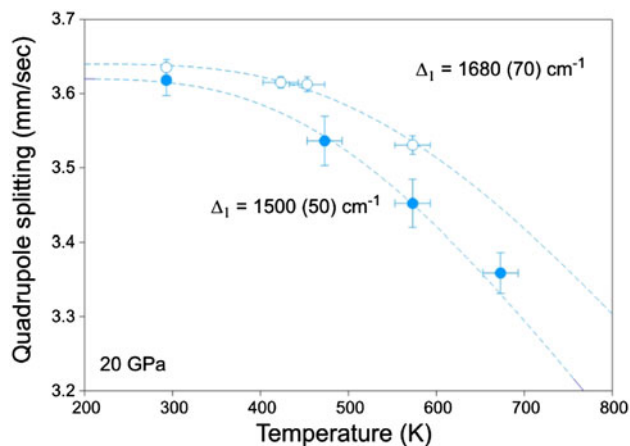


Fig. 10 Variation of QS with temperature at 20 GPa for $^{57}\text{Fe}_{0.18}\text{Mg}_{0.82}\text{SiO}_3$ majorite (solid circles) and $^{57}\text{Fe}_{0.11}\text{Mg}_{0.89}\text{SiO}_3$ majorite (open circles). The dashed lines represent the fit of the experimental data with Eq. 1

majorite (Fig. 9a); hence we can interpret the origin of the high QS-component in the Mössbauer spectrum of silicate perovskite (blue doublet in Fig. 2b, c) in the framework of the same theoretical model that was used for majorite. If we consider the pressure and temperature dependence of CS and QS of the high-QS and $^{57}\text{Fe}^{2+}$ components, they have the same trend without any abrupt changes (compare Figs. 4a, b, 8a, b, d, e). However, the relative areas of the two components behave very differently at high pressure and temperature: in the case of majorite, the amount of $^{57}\text{Fe}^{2+}$ almost does not change with pressure and temperature within the range of uncertainty (Fig. 8c, f), while in the case of silicate perovskite we clearly observe an increase of the relative area of the high-QS component with pressure and temperature (Figs. 4c, 6). Therefore, we

suggest that the origin of the high-QS component in silicate perovskite is different from that of majorite.

In order to understand the origin of the high-QS component, we come back to the energy diagram for ferrous iron in a distorted cubic site (Fig. 9a) to explore possible spin configurations. As already mentioned, the stability of a particular spin configuration is determined by the relation between crystal field splitting (Δ_C) and SPE. If SPE exceeds Δ_C the HS state is stable (Fig. 9b), and only e_g orbitals contribute to the EFG and therefore to the QS value. With increasing pressure, Δ_C increases while SPE remains the same (Sherman 1988), and when at a certain point Δ_C becomes higher than SPE, the intermediate-spin state (IS) becomes energy favourable: the two lower levels are completely populated by four 3d-electrons, and the other two valence electrons occupy two of the three upper levels (Fig. 9c). Hence, in this case the EFG (and consequently the value of QS) is determined by the population of t_{2g} orbitals. Finally, with the further increase of Δ_C and if $\Delta_2 \neq 0$ the low-spin state (LS) becomes energy favourable: all valence electrons are spin-paired and the EFG is equal to zero and does not contribute to the QS value (Fig. 9d).

According to Keppler et al. (1994), in the case of $^{57}\text{Fe}^{2+}$ in silicate perovskite the energy difference between t_{2g} levels is much higher than between e_g levels, implying a higher QS value for IS $^{57}\text{Fe}^{2+}$ compared with that for HS $^{57}\text{Fe}^{2+}$. The last statement as well as the reported decrease of the spin number of Fe^{2+} in silicate perovskite with pressure revealed by XES studies (Li et al. 2006; Badro et al. 2004) guides us to the same conclusion previously suggested by McCammon et al. (2008): the high-QS component, which appears above 30 GPa in the Mössbauer spectra of silicate perovskite (Figs. 3, 4), can be assigned to IS $^{57}\text{Fe}^{2+}$.

Conclusions

Using conventional Mössbauer spectroscopy we performed a systematic study of the ferrous iron electronic state in magnesium-bearing silicate perovskite and majorite at pressures up to 81 GPa in the temperature range 300–800 K. The high data quality allowed us to calculate the energy splitting between e_g levels of $^{57}\text{Fe}^{2+}$ in majorite at 20 GPa and describe the effect of temperature on QS of this component in the framework of the Huggins (1975) model. Based on comparison between the high-pressure high-temperature behaviour of $^{57}\text{Fe}^{2+}$ in silicate perovskite and $^{57}\text{Fe}^{2+}$ in majorite, we conclude that the origin of the component with high QS in these two phases is different.

Using a simplified energy diagram for $^{57}\text{Fe}^{2+}$ in silicate perovskite, we confirmed that the continuous changes of electronic properties of Fe^{2+} in the pressure range 30–65 GPa can be interpreted as HS–IS crossover (consistent with McCammon et al. 2008). The gradual nature of this transition is not expected to cause any abrupt changes in elasticity, thermal or electrical conductivity, or element partitioning in the Earth's lower mantle. However, physical and chemical properties of iron-bearing silicate perovskite could be affected by HS–IS crossover, and any extrapolations of the properties of Fe-free silicate perovskite to geophysically and geochemically relevant materials at conditions of the Earth's lower mantle should be made with caution.

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