Effects of the Fe$^{3+}$ spin transition on the properties of aluminous perovskite—
New insights for lower-mantle seismic heterogeneities

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A B S T R A C T

We have measured the effects of the coupled substitution of Fe$^{3+}$ and Al on the density and compressibility of mantle silicate perovskite (Pv) up to 95 GPa. X-ray emission spectroscopy and synchrotron Mössbauer spectroscopy reveal a rapid increase in the population of low-spin Fe$^{3+}$ in Fe$^{3+}$, Al-bearing Pv over a narrow pressure range near 70 GPa, which is in sharp contrast with Al-free Fe$^{3+}$-bearing Pv, where Fe$^{3+}$ undergoes a gradual spin transition, and with Al-free Fe$^{2+}$-bearing Pv, where Fe$^{2+}$ does not become low spin. At low pressure, Fe$^{3+}$ and Al expand the perovskite lattice. However, near the pressure range of the abrupt increase in the low-spin population, the unit-cell volume of Fe$^{3+}$, Al-bearing Pv becomes similar to that of Mg-endmember Pv, while those of Al-free Fe$^{3+}$-bearing and Al-free Fe$^{2+}$-bearing Pv remain larger throughout the lower mantle. Consequently, Pv in Al-rich systems should have lower density in the shallow lower mantle but similar or greater density than Pv in pyrolite in the deep lower mantle, affecting the buoyancy and mechanical stability of heterogeneities. Although the Fe$^{3+}$ spin transition in Pv is unlikely to cause a seismic discontinuity at mantle temperatures, it may result in a large change in bulk sound speed at 1200–1800 km depth, such that a vertically extending structure with an elevated amount of Fe$^{3+}$ would generate slower and faster anomalies above and below the depth of the spin transition, respectively, relative to the surrounding mantle. This may have important implications for bulk sound speed anomalies observed at similar depths in seismic tomography studies.

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1. Introduction

Spin transitions in iron have been reported in the major lower-mantle minerals, magnesium silicate perovskite (Pv) and ferropericlase (Fp), at mantle pressures (Badro et al., 2003, 2004; Fei et al., 2007; Grocholski et al., 2009; Li et al., 2004; Lin et al., 2005, 2008; McCammon et al., 2008; Speciale et al., 2005; Tsuchiya et al., 2006; Unemoto et al., 2008), The spin transition in Fp, (Mg,Fe)O, has been found to induce a volume collapse to that of the magnesium endmember (i.e., MgO), resulting in a density increase at lower-mantle pressures (Fei et al., 2007; Lin et al., 2005; Speciale et al., 2005). However, Fp is expected to be a relatively minor component in the lower mantle while Pv makes up approximately 80%; thus the properties of Pv should significantly influence the bulk lower mantle. Badro et al. (2004) reported a decrease in spin moment of iron in Pv at high pressure. Recent studies proposed a high spin to intermediate spin transition in Fe$^{2+}$ at high pressure (Lin et al., 2008; McCammon et al., 2008), while other experimental (Grocholski et al., 2009) and computational (Bengtson et al., 2008; Stackhouse et al., 2007; Zhang and Oganov, 2006) studies have proposed that Fe$^{2+}$ in Pv remains high spin throughout most of the lower mantle. Regardless, Lundin et al. (2008) showed that Fe$^{2+}$ does not affect the pressure-volume relationship in Pv.

Mantle silicate perovskite is expected to contain 5–10% each of Fe and Al in the lower mantle (Kesson et al., 1998). Its crystal chemistry is complicated by the presence of two different crystallographic sites (dodecahedral, hereafter A, and octahedral, hereafter B, sites) available for cation substitution (Horiuchi et al., 1987). Iron may exist as both ferric iron and ferrous iron up to 90% each of Fe$^{3+}$ in the presence of Al, even under reducing conditions (Frost et al., 2004; McCammon, 1997). Both theoretical (Hsu et al., 2011; Stackhouse...
The complex crystal chemistry of perovskite diversifies the environments for iron and complicates the interpretation of high pressure spectroscopy results, which have been inconsistent with one another (Badro et al., 2004; Grocholski et al., 2009; Li et al., 2004; Lin et al., 2008; McCammon et al., 2008). X-ray emission spectroscopy (XES) provides a measure of integrated spin population but does not distinguish iron in different valence states. Mössbauer spectroscopy is sensitive to both the valence and spin states of iron, but the interpretation of multiple sample sites in various states is difficult. The above issues can, therefore, be best resolved by measuring the effects of different cations (Fe$^{3+}$, Fe$^{2+}$, and Al) on the properties of Pv with a combination of different spectroscopic techniques.

We have systematically studied the effects of different cations on the pressure-volume relationship of Pv, including pure magnesium endmember (Mg-Pv) (Lundin et al., 2008), with 9 and 15 mol% Fe$_{3}$SiO$_{4}$ (Fe$^{2+}$-Pv) (Lundin et al., 2008), with 9 mol% Fe$_{3}$O$_{4}$ (Fe$^{2+}$-Pv) (Catalli et al., 2010), with 10 mol% Al$_{2}$O$_{3}$ (Al-Pv), and with 10 mol% FeAlO$_{3}$ (Fe$^{3+}$ Al-Pv) (the latter two are reported here). All systems have been studied using the same pressure scale (gold) and pressure medium (argon) to allow for direct comparison between the different compositions. Therefore, these data sets provide important information on the effects of compositional variation on the density (dV/dP) and bulk sound speed (dV/du) of Pv. Here we report synchrotron Mössbauer spectroscopy (SMS), XES, and X-ray diffraction (XRD) on Fe$^{3+}$Al-Pv in the laser-heated diamond cell to 95 GPa to measure the spin state of Fe$^{3+}$ and its effect on the pressure-volume relationship in aluminous Pv. We discuss the effects of the Fe$^{3+}$ spin transition in Pv on lower mantle structure and dynamics.

2. Experimental procedure

Glass starting materials (0.90MgSiO$_{3}$ 0.05Al$_{2}$O$_{3}$ 0.05Fe$_{2}$O$_{3}$ and 0.90MgSiO$_{3}$ 0.10Al$_{2}$O$_{3}$; numbers are in mol fraction) were synthesized by the containerless laser levitation method (Tangeman et al., 2001). For the Fe$^{3+}$ Al-Pv glass, synthesis was conducted under an O$_{2}$ atmosphere in order to prevent reduction during melting. By only allowing one valence state of iron (Fe$^{3+}$), the interpretation of SMS and XES data can be considerably simplified. Electron microprobe measurements revealed that the starting material is homogenous and has a composition of (Mg$_{0.88}$Fe$_{0.13}$Al$_{0.11}$Si$_{0.88}$)O$_{3}$ ($\pm$ 0.01). The iron-bearing starting material is enriched with 95% $^{57}$Fe for SMS.

The glass starting materials were ground to a powder and mixed with 10 wt.% gold for use as an internal pressure standard (Tsuchiya, 1986) instead of mixing with gold. For XRD and SMS, the sample powder was pressed to a foil and loaded into a preindented Re gasket. Argon was cryogenically loaded into the diamond cell, acting as both an insulating and a pressure medium, with a few spacer grains of sample material separating the sample foil from the diamond. For XES, 3 mm diameter Be gaskets with an initial central thickness of 100 μm were used. A sample platelet was pre-pressed and sandwiched between 5 μm layers of dried NaCl and loaded into the gasket hole.

Symmetric-type diamond anvils cells equipped with 200 or 300 μm culet diamonds were used for measurements with a peak pressure of less than 75 GPa, while 100 or 150 μm beveled culets were used above this pressure. Measurements on Fe$^{3+}$ Al-Pv were taken from multiple sample loadings.

The perovskite phase was synthesized by double-sided laser heating at 2000 K for 30 min above 45 GPa using an Nd:YLF laser (Prakapenka et al., 2008). In addition, at each pressure the sample was scanned with the laser at 1800-2100 K for 7-15 min to synthesize the stable structure at the new pressure and to anneal deviatoric stress.

Angle-dispersive XRD was performed at the GSECARS sector of the Advanced Photon Source (APS) (Fig. 1). A monochromatic X-ray beam was focused to 5x5 μm$^2$ with energy of 40 keV for measurements on Fe$^{3+}$ Al-Pv and 10x20 μm$^2$ at 30 keV for Al-Pv. Diffraction was collected using a MarCCD detector for Fe$^{3+}$ Al-Pv and a Mar345 imaging plate for Al-Pv. Diffraction lines of argon in all diffraction patterns confirm the presence of the pressure/insulation medium. Both the hexagonal close-packed (hcp) and face-centered cubic structures are observed in some diffraction patterns (Fig. 1), likely due to the inclusion of a small amount of nitrogen during cryogenic loading of Ar, which stabilizes the hcp phase (Catalli et al., 2008; Wittlinger et al., 1997).

SMS was performed at the HPCAT and XOR-3 sectors of the APS (Fig. 2). At XOR-3, the 14.4 keV beam was focused to an area of 6x6 μm$^2$. The storage ring was operated in top-up mode with 24 bunches separated by 153 ns. Nuclear resonant scattering was measured in a time window of 15-130 ns following excitation. Data collection typically took 2-4 h (see Jackson et al., 2005; Sturhahn and Jackson, 2007; Catalli et al., 2010, for details). At beamline 16-IDD of HPCAT, the beam size was 30x40 μm$^2$ and data collection time was 8-10 h. SMS data were fit using the CONUSS package (Sturhahn, 2000) (Fig. 3).

XES was performed at the HPCAT sector of APS (Fig. 4). An 11.35 keV X-ray beam was focused down to 30x40 μm$^2$ on the sample. Emission was collected through the Be gasket. Collection time was typically 8-16 h. The spectra have been aligned relative to a reference spectrum (iron foil) according to their centers of mass.
and normalized by total area following the method of Vankó et al. (2006) (Figs. 4 and 6). The method is discussed further in Catalli et al. (2010).

Diffraction patterns of Fe\(^{3+}\) Al-Pv were measured between 0 and 95 GPa (Fig. 1, Table 1) and at 0–95 GPa on Al-Pv (Table 2). The patterns measured below 45 GPa were collected on decompression and not annealed in order to prevent back transformation to low pressure phases. Mössbauer spectra of Fe\(^{3+}\) Al-Pv were measured between 26 and 95 GPa (Fig. 2). The spectrum measured at 26 GPa was taken on decompression, and last laser-heated at 52 GPa. XES was measured between 0 and 84 GPa (Fig. 4). The emission spectra taken at 40 and 26 GPa and ambient pressure were made on decompression and last laser-heated at 50 GPa.

3. Results

3.1. Effects of Fe\(^{3+}\) and Al on the structure of perovskite

All observed diffraction lines can be explained by orthorhombic Pbnm perovskite (both Fe\(^{3+}\)Al-Pv and Al-Pv) with gold (pressure scale), argon (pressure medium), and nitrogen (captured during cryogenic loading) (Fig. 1). No diffraction lines from other phases, including SiO\(_2\), Fe\(_2\)O\(_3\), or Al\(_2\)O\(_3\), are present in the patterns, suggesting that Fe\(^{3+}\) at least predominantly remains in the perovskite structure (see Catalli et al., 2010, for more detail). The most intense line from silica (either in stishovite or the CaCl\(_2\)-type) was observed in some diffraction patterns of Al-Pv. Stishovite and CaCl\(_2\)-type silica can contain up to 5 wt.% Al\(_2\)O\(_3\) (Hirose et al., 2005). However, according to our diffraction patterns, the amount of stishovite should not exceed 5%. Therefore, the dominant amount of Al should exist in the Al-Pv phase.

![Fig. 2. Synchrotron Mössbauer spectra of Fe\(^{3+}\)Al-Pv at high pressure. Data points are shown as dots, while the lines are the spectral fitting results. The Mössbauer parameters obtained from the fitting are shown in Fig. 3. Large gaps between the curve and the low-count data points at ~40 ns in low-pressure spectra are due to the logarithmic scale for the vertical axis. The misfit does not exceed 7% of the maximum counts, which is comparable for the magnitude of misfits in other spectral areas.](image)

![Fig. 3. Mössbauer parameters of Fe\(^{3+}\) in Fe\(^{3+}\)Al-Pv. Site 1: high-spin Fe\(^{3+}\), site 2: low-spin Fe\(^{3+}\), site 3: low-spin Fe\(^{3+}\) site that appears above 70 GPa. (a) Percent weightings of high (open circles) and low (closed circles) spin sites (site 2 + site 3), (b) relative center shift between sites 1 and 2 (circles) and between sites 1 and 3 (squares), (c) quadrupole splittings of high spin (open circles), low spin (closed circles), and new low spin (closed squares) sites, and (d) full widths at half maxima of quadrupole splittings (same symbols as (c)). The gray area is the pressure range where we found spectral changes in Fig. 2. Errors in parameters are outputs from CONUSS.](image)

![Fig. 4. X-ray emission spectra of Fe\(^{3+}\)Al-Pv measured at high pressure. Spectra have been aligned according to their center of mass.](image)
Trivalent cations, such as Fe$^{3+}$ and Al, enter into the perovskite structure through either oxygen vacancy substitution or charge coupled substitution (Brodholt, 2000; Navrotsky, 1999). Charge coupled substitution becomes energetically more favorable at pressures related to the lower mantle (Brodholt, 2000). We note perovskites were synthesized at pressures greater than 45 GPa in this study. Because the magnitude and high-pressure behavior of the axial ratios of Fe$^{3+}$ Al-Pv are much more similar to Al-Pv than Fe$^{3+}$ -Pv, Al is likely the more important contributor to the distortion of mantle perovskite through charge coupled substitution under these conditions.

An ideal undistorted perovskite structure has cubic symmetry, while Mg-silicate perovskite crystallizes in the distorted orthorhombic Pbnm structure, with unit cell axial ratios of $a : b : c = 1:1: \sqrt{2}$. Therefore, the axial ratios, $b/a (= 1$ in a pseudo-cubic perovskite) and $c/a (= \sqrt{2} / \sqrt{2}$ in a pseudo-cubic perovskite), are a measure of the degree of distortion in the unit cell (Fig. 5). With pressure, all perovskites presented in Fig. 5 show increasing axial ratios, suggesting increasing distortion with pressure. Fe$^{2+}$ reduces and Fe$^{3+}$ alone increases the distortion of the perovskite unit cell relative to Mg-Pv throughout the lower mantle (Catalli et al., 2010; Lundin et al., 2008). The distortion in the unit cell of Al-Pv is greater than Mg-Pv at lower pressures but approaches that of Mg-Pv at high pressure.

Fe$^{3+}$ Al-Pv is more distorted than Mg-Pv at lower pressures. However, the gap between Mg-Pv and Fe$^{3+}$ Al-Pv decreases with pressure. Because the magnitude and high-pressure behavior of the axial ratios of Fe$^{3+}$ Al-Pv are much more similar to Al-Pv than Fe$^{3+}$ -Pv, Al is likely the more important contributor to the distortion of mantle perovskite than Fe$^{3+}$ in this composition. These suggest that the degree of structural distortion in Pv is sensitive to composition (Fig. 5).

### Table 1

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### 3.2. Synchrotron Mössbauer spectroscopy

The synchrotron Mössbauer spectra of Fe$^{3+}$ Al-Pv below 70 GPa consist of one broad feature with three overlapping beats (Fig. 2). Between 70 and 83 GPa, the spectra show drastic changes to four clearly separated beats. Similar spectral changes were also observed in Al-free Fe$^{3+}$ -Pv but at a much lower pressure, 55 GPa (Catalli et al., 2010). Qualitatively, it is clear from the spectra (Fig. 2) that there is a change in the iron environments occurring between 70 and 83 GPa. The spectra taken between 26 and 70 GPa were fitted using a two iron site model, while the spectra at 83 and 95 GPa require three sites for a satisfactory fit to the data (Fig. 3).

Quadrupole splitting (QS) is a measure of the splitting of the excited nuclear state caused by an electric field gradient. The QS of iron in silicates and oxides is sensitive to both the valence and spin states of iron (Hawthorne, 1988). To a lesser degree, it is also sensitive to the coordination state of iron. In this study, we used starting materials containing all iron in Fe$^{3+}$ and the dominant valence state of iron remains $3+$ after laser heating (see below for details and also related discussions in Catalli et al. (2010)). This allows us to attribute the changes in QS to the spin state of Fe$^{3+}$.

The number of regular quantum beats in a spectrum increases with the QS of the dominant component. Therefore, the drastic change in raw spectra seen above 70 GPa (Fig. 2) indicates an increase in the QS of the dominant Fe$^{3+}$ site. Because the QS of Fe$^{3+}$ increases at a high spin to low spin transition (Bengtson et al., 2009; Hsu et al., 2006), the changes observed in the raw spectra suggest an increase in the amount of low spin Fe$^{3+}$ in Pv.

At 70 GPa and below, the fitting identifies one iron site with $QS = 2.9$–3.8 mm/s and the other with $QS = 0.7$–1.3 mm/s (Fig. 3c). The lower QS value is consistent with high spin Fe$^{3+}$ (Dyar et al., 2006; Xu et al., 2001). A high QS value (∼3.0 mm/s) was found experimentally for low spin Fe$^{3+}$ in Al-free, Fe$^{3+}$ -Pv (Catalli et al., 2010) in
the B site, the interpretation of which was confirmed by computations (Hsu et al., 2011). Therefore, we assign the high QS site to low spin Fe$^{3+}$ in the B site. The site weightings reveal that ~35% of the Fe$^{3+}$ is low spin between 26 and 70 GPa in Fe$^{3+}$Al-Pv (Fig. 3a). High spin Fe$^{3+}$ can be assigned to the A site because of its greater ionic size relative to low spin Fe$^{3+}$, Al, and Si (Shannon 1976). Also, the observed low QS value is consistent with that of high spin Fe$^{3+}$ in the A site in Fe$^{3+}$-Pv (Catalli et al., 2010).

In Fig. 3b, the relative center shifts (CS) between different iron sites are presented. In addition, we measured the CS relative to a stainless steel foil at 53 GPa and 70 GPa. At 53 GPa the low QS site has a CS of 0.45 ± 0.02 mm/s and the high QS site has a CS of 0.96 ± 0.05 mm/s. At 70 GPa, the CS for the two sites are 0.48 ± 0.02 mm/s and 1.16 ± 0.05 mm/s, respectively.

The high QS value of low spin Fe$^{3+}$ is similar to that of high spin Fe$^{3+}$ (Hsu et al., 2011). However, the starting materials contain all iron in Fe$^{2+}$. Our XRD patterns show that the starting material transforms completely to Pv without evidence for SiO$_2$ or MgO (Fig. 1), ruling out the possibility of reduction of Fe$^{3+}$ to Fe$^{2+}$ during laser heating (see Catalli et al. (2010)). Previous studies showed that Al can stabilize Fe$^{3+}$ over Fe$^{2+}$ in perovskite (Frost et al., 2004; McCammon, 1997). Furthermore, our SMS interpretation of low spin Fe$^{3+}$ is consistent with our XES observation (see below).

The third site required for fitting the spectra at 83 and 95 GPa has a QS near 2.2 mm/s (Fig. 3c). For the rare-earth orthoferrite perovskites (LaFeO$_3$ and PrFeO$_3$), which have the same Pbnm perovskite structure as well as Fe$^{3+}$ in the octahedral site, Q$S$ ~2.4 mm/s was observed for low spin Fe$^{3+}$ in the B site (Xu et al., 2004). Therefore, the third iron site is also most likely low spin Fe$^{3+}$ in the B site. Combining the two low spin sites gives a total low spin fraction of 56 ± 5% at 83–95 GPa, an increase from 35% at pressures below 70 GPa (Fig. 3a).

### 3.3. X-ray emission spectroscopy

The X-ray emission spectra of high spin iron are characterized by the main K$\beta_{1,3}$ peak at 7058 eV and the K$\beta$ satellite peak at lower energy which results from the 3p core-hole 3d exchange interaction during emission (Fig. 4). The intensity of the satellite peak (K$\beta$) has been found to be proportional to the spin number of iron in the sample (Badro et al., 1999; Vankó et al., 2006). However, this requires an accurate standard for low spin Fe$^{3+}$. An orthorhombic phase of Fe$_2$O$_3$ measured at 46 GPa appears to have all iron in the low spin state (Badro et al., 2002; Shim et al., 2009). However, the structure of this phase is more likely the Rh$_2$O$_3$-II type (Shim et al., 2009; Shim and Duffy, 2002) and therefore this phase may not be a good low spin standard for Fe$^{3+}$-Al-Pv. We are aware of no other phases that would make good low spin Fe$^{3+}$ (or low spin Fe$^{2+}$) standards for Pv and, therefore, believe it is much more appropriate to present relative changes in the integrated intensity of the satellite peak with respect to that of Fe$^{3+}$-Al-Pv quenched to ambient pressure. The relative changes in the average spin measured by XES can then be compared with the SMS results.

The position of the main peak (K$\beta_{1,3}$) has also been used to detect spin transitions (Li et al., 2004; Vankó et al., 2006). Determination of the position of the more intense peak involves much less uncertainty and therefore provides a more robust measure of the spin transition. Following the method presented in Vankó et al. (2006), the position of K$\beta_{1,3}$ was obtained relative to the center of mass of the spectra (Fig. 6a, see Catalli et al. (2010) for method). These allow for robust interpretations by focusing only on first-order features in the raw X-ray emission spectra, which are not sensitive to a specific standard or fitting method.

For Fe$^{3+}$-Al-Pv, the relative position of K$\beta_{1,3}$ with respect to the center of mass of the spectrum is essentially unchanged up to 63 GPa (Fig. 4). Between 63 and 84 GPa, however, there is a large shift in the K$\beta_{1,3}$ peak (Fig. 6a). In addition, the integrated intensity of the satellite peak (K$\beta_\prime$) decreases at the same pressure range (Fig. 6b). Decreases in these quantities are related to a decrease in average spin number (Badro et al., 2003, 2004; Li et al., 2004). Therefore, our XES observations suggest an increase in the population of low spin Fe$^{3+}$ between 63 and 84 GPa. As shown in Fig. 6, this behavior is in contrast with Al-free Fe$^{3+}$-Pv where a gradual decrease in spin moment was found at pressures between 0 and 55 GPa (Catalli et al., 2010).

As mentioned earlier, XES is much more sensitive to the spin state than the valence state (Vankó et al., 2006). This is seen in the K$\beta_{1,3}$ peak position, which is essentially insensitive to valence state within ±0.3 eV (Gamblin and Urch, 2001), but is much more sensitive to spin state. Our XES measurements clearly indicate an increase in low spin Fe$^{3+}$ at ~70 GPa and therefore we can rule out the interpretation of the new high QS site observed in SMS as being due to the creation of high spin Fe$^{2+}$.

### 3.4. Equation of state

A total of 20–32 diffraction lines were used to constrain the volume of Fe$^{3+}$-Al-Pv and 15–22 lines for Al-Pv using the UnitCell program (Holland and Redfern, 1997) (Fig. 7a). The volume of gold was measured based on 2–3 diffraction lines and used to calculate pressure (Tsukiyama, 2003). The uncertainty given is the standard deviation in pressure based on the volume of gold calculated from each individual diffraction line. In order to assess the effect of composition on the unit-cell volume of Pv, we present the volume of each composition relative to Mg-Pv (Fig. 7b).

While a dense data distribution was achieved for Fe$^{3+}$-Al-Pv, because of the lack of low pressure data on Al-Pv, except for at 1 bar, we have included the data reported by Yagi et al. (2004) on the same composition at 0–34 GPa, which is in good agreement with
A recent study on Pv with 15 mol% Fe$^{3+}$AlO$_3$ (Nishio-Hamane et al., 2008) did not find the volume collapse and change in compressibility as found here, although the study agrees with ours in that the combined substitution of Fe$^{3+}$ and Al results in an increased compressibility. The difference in the results can be attributed to the greater data scatter and the lack of coverage in pressure below 40 GPa and between 70 and 90 GPa in Nishio-Hamane et al. (2008).

Unlike Fp where a sharp decrease in volume over a narrow pressure range was observed at the spin transition (Fei et al., 2007), we found no evidence of a sharp volume change in Fe$^{3+}$Al-Pv at the spin transition in Fe$^{3+}$, within our experimental resolution. This difference is likely due to the much smaller amount of iron undergoing the spin transition (20%) in Fe$^{3+}$Al-Pv than Fp (100%). It is also notable that stress in Pv is accommodated by both tilting of the octahedra and decreasing bond distances, while in Fp it is mostly through decreasing bond distances. A negligible effect of the Fe$^{3+}$ spin transition on volume was also found in a first-principles study on Pv in a similar composition (Li et al., 2005a).

Some computational studies have proposed a smaller change in the compressibility of Pv by the spin transition of Fe$^{3+}$ (Caracas, 2010; Li et al., 2005b). However, Li et al. (2005b) only considered the spin transition of Fe$^{3+}$ in the A site. Caracas (2010) reported the elasticity of FeAlO$_3$ and AlFeO$_3$ where strong iron-iron interactions and magnetic ordering might influence the compressibility, while these are unlikely factors for our diluted system.

## 4. Implications for the crystal chemistry of perovskite

Computational studies have predicted that Fe$^{3+}$ in the B site of perovskite would be low spin at high pressure (Hsu et al., 2011; Li et al., 2005b; Stackhouse et al., 2007), and experimental studies showed that Fe$^{3+}$ undergoes a high spin to low spin change in the B site of the Pbnm perovskite phases of LaFeO$_3$ and PrFeO$_3$ at 30–50 GPa (Xu et al., 2001) and MgSiO$_3$ perovskite at 0–55 GPa (Catalli et al., 2010). Therefore, it is reasonable to assign low spin Fe$^{3+}$ to the B site.

For Pv synthesized at 25 GPa and then quenched to 1 bar for XRD measurements, Vanpeteghem et al. (2006) reported that all iron (including Fe$^{3+}$) remains in the A site while all Al exists in the B site. If we assume that Fe$^{3+}$ and Al enter Pv through charge coupled substitution, our data indicate that low spin Fe$^{3+}$ can enter the B site and move an equal amount of Al into the A site at high pressure. The assumption of charge coupled substitution for our samples is reasonable because a first-principle study found that charge coupled substitution is energetically more favorable at high pressure (Brodholt, 2000) and our samples were synthesized at sufficiently high pressures, above 45 GPa.

Our data indicates that the population of low spin Fe$^{3+}$ abruptly increases in Fe$^{3+}$Al-Pv at 70 GPa. If all low spin Fe$^{3+}$, including the new iron site, enters the B site, the abrupt increase in low spin Fe$^{3+}$ above 70 GPa would result in an abrupt increase in the amount of Al in the A site, i.e., site mixing of Fe and Al between the A and B sites in perovskite:

$$A(Mg,HSFe^{1+})B(Al,Si)O_2\rightarrow A(Mg,HSFe^{1+}_1,Al)^B(Fe^{3+}_2,Al,Si)O_2,$$

where superscripts “A” and “B” represent the A and B sites of perovskite, respectively, and superscripts “HS” and “LS” indicate high spin and low spin, respectively.

A computational study has shown that the energy difference between configurations with Fe$^{3+}$ $^{3+}$ in the A site $+$ Al in the B site” and “Al in the A site $+$ Fe$^{3+}$ in the B site” in perovskite becomes negligibly small at 92 GPa (Li et al., 2005b), supporting our interpretation of site mixing. In this case, the two different QS values for low spin Fe$^{3+}$ in the B site may result from the coexistence of different local

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**Fig. 7.** (a) Unit-cell volumes of Fe$^{3+}$Al-Pv (red circles) and Al-Pv (green circles from this study and squares from Yagi et al. (2004)). The red line is the fit to the third order Birch–Murnaghan equation for Fe$^{3+}$Al-Pv for data below 70 GPa and the green line is the EOS fit for Al-Pv. The equation of state of Mg-Pv (Lundin et al., 2008) (black line) is shown for comparison. (b) Volume difference from Mg-endmember perovskite (red: Fe$^{3+}$Al-Pv green: Al-Pv, blue: Fe$^{3+}$Pv (Lundin et al., 2008), purple: Fe$^{3+}$-Pv (Catalli et al., 2010)). The horizontal line represents the volume of Mg-Pv (Lundin et al., 2008). The gray areas show the pressure range where changes in the SMS and XES spectral features were detected.

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our results. Al expands the volume of Pv at low pressures (Fig. 7). However, due to the higher compressibility of Al-Pv, its volume becomes essentially identical to Mg-Pv by ~50 GPa (Fig. 7). Fitting the combined Al-Pv dataset to the Birch–Murnaghan equation of state (EOS), we find that the incorporation of 10 mol% Al$_2$O$_3$ results in a ~7% decrease in bulk modulus relative to Mg-Pv (Lundin et al., 2008), yielding $K_0 = 244 \pm 3$ GPa when $K'_0$ is fixed to 4 (where $K_0$ is the bulk modulus at 1 bar and $K'_0$ is its pressure derivative).

Fe$^{3+}$Al-Pv has a larger volume than Mg-Pv, Al-Pv, and Fe$^{3+}$-Pv but smaller volume than Fe$^{3+}$Al-Pv at pressures lower than 55 GPa (Fig. 7b). This is consistent with the Al-Pv and Fe$^{3+}$-Pv data, where Al and Fe$^{3+}$ individually increase the unit cell volume of Pv. Fe$^{3+}$ and Al together (Fe$^{3+}$Al-Pv) increase the compressibility of Pv below 70 GPa ($K_0$ of 262 ± 8 GPa with $K'_0 = 3.0 \pm 0.3$ for fixed $V_0 = 164.807$ Å$^3$, where $V_0$ is volume at 1 bar), consistent with cases where either Al or Fe$^{3+}$ alone exist in Pv (Al-Pv and Fe$^{3+}$-Pv).

Above 70 GPa, the unit cell volume of Fe$^{3+}$Al-Pv becomes essentially the same as that of Mg-Pv, necessitating a change in compressibility (Fig. 7). We consider the region above 70 GPa to be a different regime, and fit it with a separate EOS. Because $V_0$ is unknown for this pressure range, it was allowed to vary in the EOS fitting. This yielded $K_0 = 269 \pm 13$ GPa with $V_0 = 162 \pm 1$ Å$^3$ for a fixed $K'_0$ of 4. The EOS of the higher pressure range was constrained by only 6 data points over a pressure range of 28 GPa without constraint from a known $V_0$ and is, thus, less reliable. However, $K_0$ and $V_0$ match well with Mg-Pv (Lundin et al., 2008) within the uncertainty. It is notable that the pressure where the volume of Fe$^{3+}$Al-Pv merges into that of Mg-Pv coincides with the pressure range where changes in SMS and XES were detected.
clusterings in perovskite, which maybe energetically similar with each other (Bengtson et al., 2009; Hsu et al., 2010; Stackhouse et al., 2007). We also do not rule out the possibility of a lower-symmetry structure for Fe\(^{3+}\)-Al-Pv which has two symmetrically distinct B sites with long-range order. While our diffraction patterns of Fe\(^{3+}\) Al-Pv are consistent with the \textit{Pbnm} perovskite structure, the resolution of the powder diffraction technique may not detect subtle distortions in the crystal structure. Alternatively, the new site could be assigned to low spin Fe\(^{2+}\) in the A site, while the B site remains predominantly occupied by Al. However, this would require a mixture of high spin and low spin Fe\(^{3+}\) in the A site, that remains stable with no further increase in low spin component over a span of at least 15 GPa.

The former hypothesis may also provide some explanations why the spin transition is gradual in Al-free Fe\(^{3+}\)-Pv and sharp in Fe\(^{3+}\) Al-Pv. While no inter-site diffusion is necessary for the Fe\(^{3+}\) spin transition in Al-free Fe\(^{2+}\)-Pv, because Fe\(^{2+}\) exists in the B site from low pressures, inter-site diffusion may be critical for the Fe\(^{3+}\) spin transition in Al-bearing Pv because Al may be dominant in the B site at low pressure and the B site is more favorable for the spin transition of Fe\(^{3+}\) (Hsu et al., 2011). This might also explain why the Fe\(^{3+}\) spin transition does not reach 100% in Fe\(^{3+}\) Al-Pv; it would require diffusion of all Al from the B to the A site, which could be energetically costly for the system.

In Al-free Fe\(^{3+}\)-Pv, Catalli et al. (2010) found a gradual high spin to low spin transition in Fe\(^{3+}\) in the B site (Fig. 6) that increases the compressibility of Pv at low pressure. However, in this study, we found that the population of low spin Fe\(^{3+}\) does not change up to 70 GPa when Al is present in the system and, therefore, the higher compressibility of Fe\(^{3+}\) Al-Pv at 0–70 GPa (Fig. 7) should be the result of some other factor. Because Al increases the compressibility of Pv as shown in Al-Pv (Fig. 7), Al is the more likely source of the higher compressibility of Fe\(^{3+}\) Al-Pv at low pressure.

At ambient pressure, high spin Fe\(^{3+}\) is approximately 21% larger than Al, whereas low spin Fe\(^{3+}\) is comparable in size to Al (Shannon, 1976). Therefore, in the highly compressed lattice of Al-bearing Pv near 70 GPa (Fig. 7), where the unit cell volume of Pv approaches to that of Mg endmember, the smaller-sized low spin Fe\(^{3+}\) would be energetically more favorable than high spin Fe\(^{3+}\). This means that Fe plays an important role in the spin behavior of Fe\(^{3+}\) in mantle silicate perovskite.

5. Implications for the lower mantle

We have built a large dataset for understanding the effects of different cations on the compressional behavior of mantle silicate perovskite (Catalli et al., 2010; Lundin et al., 2008) by using a consistent experimental setup, including pressure scale, pressure medium, and stress annealing (Table 3). This allows for direct comparison among the different compositions without contamination from the use of different pressure scales or samples under different stress conditions, and therefore allows us to reliably extract compositional effects on density, bulk modulus, and bulk sound speed (Fig. 8).

The density of Fe\(^{3+}\)-Al-Pv was calculated using the unit cell volume data measured from XRD and the composition measured by electron microprobe of the starting material. For a more reasonable comparison, the iron content of each of the other compositions (Fe\(^{3+}\)-Pv and Fe\(^{2+}\)-Pv) was scaled to be equal to that of Fe\(^{3+}\)-Al-Pv (Fig. 8a,b). For Fe\(^{2+}\)-Pv, we performed a linear interpolation of volume at ambient pressure based on iron content between 15 mol% Fe\(^{2+}\)-Pv and pure Mg-Pv (Lundin et al., 2008). The compressibility of Pv was found to be essentially insensitive to Fe\(^{2+}\) content, so \(K_0\) was set to 259 GPa for \(K_0 = 4\) (Lundin et al., 2008). Because Fe\(^{3+}\)-Pv has a more complicated pressure-volume behavior, volume and bulk modulus were scaled to 6.5 mol% Fe\(^{2+}\)O\(_3\) by a linear interpolation between 8.5 mol% Fe\(^{2+}\)O\(_3\)-bearing Pv (Catalli et al., 2010) and Mg-Pv (Lundin et al., 2008) at each individual pressure. All of the perovskite data presented were measured at 300 K. The expected effect of temperature on the density measured in MgSiO\(_3\) (Fiquet et al., 2000) is shown by an arrow in Fig. 8a,b, and assumes that cation substitution up to 13% does not change the thermal properties of Pv.

At pressures lower than 55 GPa, Fe\(^{3+}\) Fe\(^{3+}\)-Al-Pv is the most dense composition, while Fe\(^{3+}\)-Pv and Fe\(^{3+}\)-Al-Pv are less dense (1% at 1 bar) (Fig. 8a). The larger unit cell volumes of Fe\(^{3+}\)-Pv and Fe\(^{3+}\)-Al-Pv are perhaps due to lattice expansion by Fe\(^{3+}\) and Al in the B site, because of their larger ionic sizes relative to Si. Near 60 GPa, Fe\(^{3+}\)-Al-Pv becomes roughly the same density as Fe\(^{3+}\)-Pv (Fig. 8a). This is due to the fact that while Fe\(^{2+}\)-Pv has essentially the same bulk modulus as Mg-Pv, Fe\(^{3+}\)-Al-Pv is more compressible, resulting in a much faster increase in density with pressure than either Fe\(^{2+}\)-Pv or Mg-Pv. Fe\(^{3+}\)-Al-Pv and Fe\(^{3+}\)-Pv have similar densities up to ~55 GPa. At 55 GPa, the completion of the spin transition in Fe\(^{3+}\)-Pv results in the stiffening of the structure, which translates to a lower rate of increase in the density of the composition. However, the volume collapse in Fe\(^{3+}\)-Al-Pv allows the density of this composition to rapidly increase with pressure.

We calculated the bulk moduli of perovskites with different compositions using the EOS fitting results (Table 3 and Fig. 8b). The bulk modulus of Fe\(^{2+}\)-Pv remains essentially the same as that of Mg-Pv (Lundin et al., 2008), while Al decreases the bulk modulus by 3%–4% throughout the lower mantle. In Fe\(^{3+}\)-Pv and Fe\(^{3+}\)-Al-Pv, we found changes in bulk modulus at 55 and 70 GPa, respectively. Because we rely on the first-derivative of the EOS for the calculation of bulk modulus, our data are not of sufficiently high-resolution to distinguish between a continuous or discontinuous increase in the bulk modulus (Catalli et al., 2010).

The rate of increase in bulk modulus is distinct in Fe\(^{3+}\)-Al-Pv compared with all other compositions. This is because we fit all of the other compositions using the second-order Birch–Murnaghan (B-M) equation (\(K_0 = 4\) fixed), while the EOS fit for Fe\(^{3+}\)-Al-Pv is made with the third-order B-M equation. When the third-order equation was used we did not find significant changes in \(K_0\) from 4 for all the compositions except for Fe\(^{3+}\)-Al-Pv. Statistically, the fitting quality for Fe\(^{3+}\)-Al-Pv data improves significantly from the second-order to third-order B-M equation, while it is not the case for the Fe\(^{3+}\)-free compositions. This indicates that the lower rate of increase in bulk modulus in Fe\(^{3+}\)-Al-Pv is at least qualitatively robust. Due to the large uncertainty in the EOS fitting for high pressure segments of Fe\(^{2+}\)-Pv (\(P \geq 55\) GPa) and Fe\(^{3+}\)-Al-Pv (\(P \geq 70\) GPa), the difference in the bulk modulus between Fe\(^{2+}\)-Pv and Fe\(^{3+}\)-Al-Pv may be
statistically less significant at these pressure ranges. Yet, it is qualitatively clear from the slope change in Fig. 7 that an increase in bulk modulus is required to explain our data.

Using the density and bulk modulus, we calculated the effect of composition on the bulk sound speed of Pv \( \left( \frac{d\ln V}{dX} \right) \) (Fig. 8c), which is important in the interpretation of seismic tomography of the lower mantle (e.g., Trampert et al., 2004). As shown in Fig. 8c, for \( Fe^{2+} \) and \( Al \), \( d\ln V_{\phi} \) remains nearly constant throughout the lower mantle. However, \( d\ln V_{\phi} \) is much more negative for \( Fe^{3+} \)-bearing systems at shallow lower mantle pressures. However, after the spin transition of \( Fe^{3+} \), \( d\ln V_{\phi} \) becomes either indistinguishable from that of \( Fe^{2+} \) if \( Al \) exists in the system (\( Fe^{3+}Al-Pv \)) or even positive if \( Al \) is absent (\( Fe^{3+}-Pv \)). The uncertainty in \( d\ln V_{\phi} \) is larger for \( Fe^{3+} \) after its spin transition than those for other compositions and those for \( Fe^{3+} \) before the spin transition, mainly due to the unknown \( V_0 \), for the high-pressure segments of the \( P-V \) datasets of \( Fe^{3+}-Pv \) and \( Fe^{3+}Al-Pv \). However, it is clear from Fig. 7 that the \( Fe^{3+} \) and \( Fe^{3+}Al \) cases require large increases in bulk modulus (and therefore \( d\ln V_{\phi} \)) across the spin transition.

The property changes associated with the \( Fe^{3+} \) spin transition may have important implications for the stability of chemical heterogeneities and the interpretation of seismic tomography of the lower mantle. For demonstration, in Fig. 9 we assumed a structure in the lower mantle with an elevated \( Fe^{3+}/\Sigma Fe \) while the total iron content remains constant. We assume a structure extending across the depth of the \( Fe^{3+} \) spin transition with no temperature difference between the surrounding mantle and the structure.
Sturhahn et al. (2005) proposed that high temperature in the mantle would broaden the pressure interval over which spin transitions occur in the mantle. Therefore, in the lower mantle, the spin transition in Fe$^{3+}$ is unlikely to result in a seismic velocity discontinuity. Instead, it would be a broad boundary as indicated by the two dashed lines in Fig. 9.

As shown in Fig. 8a, due to lattice expansion by the incorporation of Fe$^{3+}$, the Fe$^{3+}$-rich structure in Fig. 9 would have a lower density than the surrounding mantle before the spin transition. However, due to the high compressibility, particularly for Fe$^{3+}$Al-Pv, the density of an Fe$^{3+}$-rich vertical structure with a sufficient amount of Al may become comparable or even slightly greater than that of the surrounding mantle (Fig. 9). Therefore, an Fe$^{3+}$-rich structure may be positively and negatively buoyant before and after the spin transition, respectively, which would decrease the mechanical integrity of the structure in the mid-mantle.

As demonstrated in Fig. 9c, based on our results, Fe$^{3+}$-rich structures would have distinctively low bulk sound speeds in the shallow lower mantle before the spin transition of Fe$^{3+}$. However, the Fe$^{3+}$ spin transition would make the bulk sound speed of the structure similar to (Fe$^{3+}$Al-Pv) or slightly higher (Fe$^{3+}$-Pv) than that of the surrounding mantle. The change in $\Delta n/V_{sl}$ by the spin transition may have important implications for the interpretation of bulk sound speed tomography of the lower mantle. For example, an Fe$^{3+}$-rich structure would be imaged as a negative anomaly at shallower depths, while it would be imaged as a positive anomaly at deeper depths (Fig. 9c).

Trampert et al. (2004) showed that the distribution of bulk sound speed anomalies in the lower mantle changes between 1200 and 2000 km depth. This depth range is similar to the depth expected for the spin transition of Fe$^{3+}$ in Pv. If indeed the spin transition contributes to the seismic change, chemical layering in the middle to lowermost regions of the lower mantle may not be required to explain the seismic changes and the spin transition might be an interesting candidate for the origin of the seismic observation. It is notable that Pv in basalt (15 mol% Al$_2$O$_3$ and likely 10 mol% Fe$_2$O$_3$) contains more Al and therefore likely more Fe$^{3+}$ than Pv in pyrolite (5 mol% Al$_2$O$_3$ and likely 3 mol% Fe$_2$O$_3$) (Hirose et al., 2005), considering the observation that Al elevates the concentration of Fe$^{3+}$ in Pv to Fe$^{3+}//Fe$ = 0.6 (McCammon, 1997). Therefore, our calculation (6.5 mol% Fe$_2$O$_3$) would be more applicable for basaltic systems.

For further implications for the lower mantle, it is important to investigate the thermal effects. In Fp, it has been found that the high spin to low spin transition occurs over a much wider pressure range at high temperature (Fei et al., 2007; Lin et al., 2007; Sturhahn et al., 2005). Because Al-Fe$^{3+}$ mixing between two different sites is likely involved in the high spin to low spin transition in Fp, the mixing entropy can influence the broadness of the spin transition together with temperature. Also, temperature may increase the depth at which the high spin to low spin transition occurs (Sturhahn et al., 2005). It is also important to understand the effects of the Fe$^{3+}$ spin transition on shear-wave speed in Pv.

6. Conclusions

Our synchrotron X-ray spectroscopy measurements reveal that the presence of aluminum increases the pressure of the high spin to low spin transition in ferric iron and decreases the pressure interval over which the transition occurs. Furthermore, the unit cell volume of ferric aluminum perovskite merges to that of magnesium end-member perovskite at 70 GPa, while the unit cell volume of aluminum-free ferric perovskite remains greater than that of magnesium end-member throughout the lower mantle, resulting in distinct density profiles for mantle silicate perovskites depending on aluminum content. Our study reveals that the spin transition in ferric iron is strongly influenced by aluminum and increases the bulk modulus of perovskite. The bulk sound speed calculated from our measured density and bulk modulus shows that the spin transition in ferric iron would generate different seismic velocity anomalies in Fe$^{3+}$-rich structures extending across the spin transition depth.

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