Composition versus temperature induced velocity heterogeneities in a pyrolitic lower mantle

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Abstract

Interpretation of lateral velocity heterogeneities is essential for our understanding of Earth's interior. Ferropericlase's (Fp) spin crossover (FSC) fundamentally changes their interpretation in the mid lower mantle. In a typical pyrolitic aggregate, FSC induces an unusual increase in bulk sound velocity ($V_p$) with increasing temperature at mid-lower-mantle depths. This reduces the sensitivity of longitudinal velocity ($V_p$) to lateral temperature variations around 1700 km. Here we show that FSC also dramatically impacts the manifestation of two important types of compositional heterogeneities: i) variations in iron concentration in Fp, e.g., caused by changes in iron partitioning; ii) variation in molar fraction of Fp, as expected in slab subduction regions. FSC enhances the sensitivity of $V_p$ and $V_p$ to these compositional variations by several-fold at similar depths. The opposite effects of lateral variations of temperature and composition on $V_p$ is critical for distinguishing the possible physical origin of heterogeneities in tomographic P-models. Temperature and composition variations also produce opposite types of correlation between $V_p$ and shear velocity ($V_s$) heterogeneities and between $V_s$ and density ($\rho$) heterogeneities. Only lateral temperature variations can produce anti-correlation between $V_p$ and $V_s$ at mid lower mantle depths, while only these compositional variations can produce anti-correlation between $V_s$ and $\rho$ in the spin crossover region and at greater depths. Together these effects suggest that heterogeneities in $V_p$ in the mid lower mantle common to multiple seismic models could originate in simultaneous lateral temperature and compositional variations in this region.

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1. Introduction

(Mg,Fe)O ferropericlase (Fp) is the second most abundant mineral in the lower mantle. Knowledge of its thermoelastic properties is fundamental for interpretation of seismic tomography models of Earth's lower mantle. Since the discovery of high spin (HS) to low spin (LS) crossover in iron in Fp (Badro et al., 2003), extensive studies have been carried out on the effect of the spin state of iron on the elasticity of Fp (e.g. Lin et al., 2013; Muir and Brodholt, 2015; Wu et al., 2013; Yang et al., 2015). The effect of Fp’ spin crossover (FSC) on its elastic properties is unusual at least in two aspects: (1) in comparison to other phase transitions in the Earth’s mantle, this state change is remarkably broad and smooth, spanning a pressure/temperature (PT) range that covers most of the lower mantle (Kantor et al., 2006; Komabayashi et al., 2010; Lin et al., 2010, 2007; Lin and Tsuchiya, 2008; Mao et al., 2011; Speziale et al., 2005; Sturhahn et al., 2005; Tsuchiya et al., 2006; Wentzcovitch et al., 2009; Wu et al., 2009; Holmstrom and Stixrude, 2015). (2) As indicated by several mineral physics studies (Crowhurst et al., 2008; Marguardt et al., 2009; Wentzcovitch et al., 2009; Wu et al., 2013; Yang et al., 2015) Fp’s bulk modulus exhibits a dramatic softening in the spin crossover region. This softening leads to complex anomalies in Fp’s thermoelastic properties in the spin crossover region (Wu et al., 2013), most notably, a positive isobaric temperature gradient in Fp’s bulk modulus at certain PT conditions of the lower mantle, resulting in an insensitivity of $V_p$ to lateral temperature variations at depths of ~1730 km (Figs. 1a and Tables S1 and S2) for aggregates with compositions and elastic properties well constrained by the PREM model (Wu and Wentzcovitch, 2014; Wu, 2016). These anomalies produce a well-defined behavior that might be identified in...
seismic tomographic models, although the FSC might not generate an obvious signature in one-dimension velocity profiles (Wu and Wentzcovitch, 2014). Some seismic tomographic structures, e.g., the global disruption of fast P-wave velocities at ~1700 km depth (van der Hilst and Karason, 1999) and the gap displayed by slow P-wave heterogeneities beneath some hotspots (Zhao, 2007; Boschi et al., 2007) are consistent with the insensitivity of \( V_P \) to lateral temperature variations caused by FSC. It also produces anomaly in other thermodynamics properties such as thermal expansion and heat capacity in Fp (Wu et al., 2009) and plays an important role in generating the sharp boundaries and high elevations in large low shear velocity provinces (LLSVPs) (Huang et al., 2015).

Velocity heterogeneities can reveal details about mantle convection and composition variations but need to be properly interpreted. FSC fundamentally changes our interpretation of the origin of lateral heterogeneities in the mantle. In general, increasing temperature simultaneously decreases bulk (\( K \)) and shear (\( G \)) moduli and density (\( \rho \)). Thus, the anti-correlation between \( V_S(\sqrt{K/\rho}) \) and \( V_P(\sqrt{3K/\rho}) \) in the deep lower mantle (Masters et al., 2000; Simmons et al., 2010) has suggested the existence of compositional heterogeneity in this region, though lateral variations in perovskite to post-perovskite ratio can also produce anti-correlation between \( V_S \) and \( V_P \) (Wentzcovitch et al., 2006). However, anti-correlation between \( V_S \) and \( V_P \) in the mid lower mantle is not necessarily produced by chemical heterogeneity. It can be induced by lateral temperature variations in the presence of FSC in aggregates with compositions well constrained by the PREM model (Wu and Wentzcovitch, 2014).

FSC should also change dramatically the manifestation of compositional heterogeneities involving variations of Fp molar fraction or iron content in Fp, or both, since Fp's bulk modulus becomes extremely sensitive to iron concentration in the spin crossover region. How these compositional heterogeneities manifest in the presence of a spin crossover in Fp is still unclear, but it is essential to address this issue to understand the origin of mantle velocity structures. Here we investigate how these compositional heterogeneities manifest in a pyrolic mantle (Fig. 1b).

![Fig. 1](image1.png)

**Fig. 1.** Schematic representation of the nature of \( V_P \) heterogeneity in the lower mantle caused by depth independent temperature (a) and compositional (b) variations between 1000 km (top) and 2600 km (bottom). (a) Faster (slower) regions are caused by lower (higher) temperatures than those of ambient mantle. P-velocity structures are disrupted because of insensitivity of \( V_P \) to temperature variations at depths around 1750 km. (b) Faster (slower) regions are caused by less (more) \( Mg_2Fe_2O_4 \) or same amount of \( Mg_2Fe_3O_5 \) with smaller (larger) \( x \) than those in the ambient mantle. In contrast to the insensitivity of \( V_P \) to temperature variation at ~1750 km, \( V_P \) is highly sensitive to these compositional variations at similar depths.

2. First principles results

The thermoelastic properties of Fp \( (Mg_2-xFe_2)SiO_3 \) with \( x = 0 \) and \( x = 0.1875 \) used here have been previously reported (Karki et al., 2000; Wu and Wentzcovitch, 2011; Wu et al., 2013). Results for both compositions \( (x = 0 \) and \( x = 0.1875) \) agree well with available experimental data at high \( PT \) (see Karki et al., 2000; Wu and Wentzcovitch, 2011; Wu et al., 2013). Similar properties at intermediate compositions are linearly interpolated between those at \( x = 0.1875 \) and \( x = 0 \) (MgO). Such interpolation is justified by comparison of first-principles results and experimental data (Jackson et al., 2002; Wu et al., 2013), as shown in Fig. 2. Linearly interpolated results agree well with available experimental data (Jackson et al., 2006; Marquardt et al., 2009). As indicated by the last terms in Eqs. (4a) or (4b) in Wu et al. (2013), the magnitude of the anomalous depression in elasticity is determined by two factors: (1) the volume difference between high spin and low spin state, which is proportional to \( x \) and (2) the extent of the spin crossover, which is not affected by \( x \) at low concentration since the spin transition pressure is almost independent of \( x \) for \( x < 0.1875 \) (Tsuchiya et al., 2006). This suggests that the anomalous softening in elasticity caused by spin crossover is also proportional to \( x \) for \( x < 0.2 \). The linear interpolation w.r.t. composition can be used in the \( PT \) range of the spin crossover. We also use in this analysis the thermoelastic properties of Fv \( (Mg_2-xFe_3)SiO_3 \), with variable \( x \) computed by first principles (Wentzcovitch et al., 2004; Kiefer et al., 2002) and properties of cubic CaSiO\(_3\) perovskite (CaPv) fitted to a Mie–Debye–Grüneisen (MDG) model (Stixrude and Lithgow-Bertelloni, 2005). CaPv is not a major lower mantle component and despite still large uncertainties in its elastic properties this MDG model is adequate for the present purpose.

![Fig. 2](image2.png)

**Fig. 2.** Dependence of sound velocity of \( Mg_2-xFe_2O_4 \) on \( x \) at 300 K and ambient pressure. The linear extrapolation of previous first-principles results (Wu and Wentzcovitch, 2011; Wu et al., 2013) is indicated by colored lines along with available experimental data (Jackson et al., 2006; Jacobsen et al., 2002; Marquardt et al., 2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3. Results and discussion

As previously shown (Tsuchiya et al., 2006; Wentzcovitch et al., 2009; Wu et al., 2013; Wu and Wentzcovitch, 2014), FSC consists in a broad and smooth state change in iron from HS to LS centered at ~50 GPa at room temperature. FSC’s pressure range broadens and shifts to higher pressure at higher temperatures. Fp’s bulk modulus reduces (softens) by ~250 GPa at 300 K for x = 0.1875 (Wu et al., 2013). Despite of its broadening and reduction at high temperatures, the anomaly is still considerable even at 3000 K (~100 GPa reduction) (Wu et al., 2013). In contrast, the anomalous softening is absent in shear modulus (G). Therefore, FSC produces very different effects on K_S and G in Fp or in mantle aggregates containing it. V_P in aggregates with pyrolic composition becomes insensitive to temperature at depths ~1730 km (Fig. 1a) while the sensitivity of V_S is essentially unaffected (Wu and Wentzcovitch, 2014). In an approximately pyrolic mantle, the manifestation of this property is consistent with the statistics of P-wave and S-wave velocity structures beneath more than 40 hotspots analyzed by Boschi et al. (2007), which indicated that far more continuous slow velocity structures extending all of the way from the core-mantle boundary to surface can be identified in S wave tomography models than in P wave models (Wu and Wentzcovitch, 2014).

The effect of ferrous iron without spin crossover on Fp’s and Pp’s elastic properties has been discussed extensively from both experimental (Jacobsen et al., 2002; Chantel et al., 2012) and theoretical perspectives (Kiefer et al., 2002; Shukla et al., 2015). While, \( \rho \) and \( K \) increase with increasing Fe content in Fp (x), G decreases. Because \( K \) increases relatively more slowly than \( \rho \), increase in x reduces \( V_P(\sqrt{(K + \frac{4}{3}G)/\rho}) \), \( V_S \), and \( V_P \) simultaneously (Fig. 2 and Table S3).

FSC alters dramatically these effects. \( V_P \) and \( V_P \) become extremely sensitive to Fe content in Fp (x) in the spin crossover region as shown in Figs. 3 and 4. The absolute values of \( \partial \ln V_P/\partial x(R_{P/x}) \) and \( \partial \ln V_P/\partial x(R_{P/x}) \) in Fp dramatically increase within the spin crossover region. At 2000 K, the maximum absolute value of \( R_{\Phi/x} \) at ~80 GPa (Fig. 4a and Table S4) is magnified approximately 6-fold compared to that of Fp without spin crossover (~0.2). In contrast, \( \partial \ln V_S/\partial x(R_{S/x}) \) (Fig. 4c) and \( \partial \ln \rho/\partial x(R_{P/x}) \) (Fig. 4d) increase almost monotonically with pressure from HS to LS values in the spin crossover region, since there is no softening anomaly in the shear modulus, G. (Wu et al., 2013) and the LS state is denser than the HS state. The behavior of \( R_{P/x} \) is intermediate (Fig. 4b).

Because increasing Fe content in Fp (x) reduces all of Fp’s velocities, variation in x leads to a positive correlation between all wave velocities at lower mantle conditions (Fig. 5 and top–right part of Table 1). The same is true for bridgmanite containing ferrous iron (Shukla et al., 2015). Without spin crossover in iron, Fp’s \( V_S \) is more sensitive to x than \( V_P \) or \( V_P \). Therefore, by varying x, \( \partial \ln V_P/\partial \ln V_S(R_{P/S}) \) and \( \partial \ln V_P/\partial \ln V_S(R_{P/S}) \) are always positive but significantly smaller than 1 (Fig. 5a, 5b). FSC completely changes these effects. \( V_P \) becomes far more sensitive to x than \( V_S \) because of the dramatic softening effect on K. \( R_{P/S} \) and \( R_{P/S} \) can be far larger than 1 in the spin crossover region (Fig. 5a, 5b).

In general, increasing temperature decreases all acoustic velocities, i.e., isobaric temperature variation does not generate anti-correlation between sound velocities, unless there is a phase change involved, such as the post-perovskite transition (Wentzcovitch et al., 2006). Therefore, anti-correlation between \( V_P \) and \( V_S \)

![Fig. 3. Velocities and density of Mg_{1-x}Fe_xO with x = 0 (dashed line) and x = 0.1875 (solid line) at 2000 K.](image)
has been regarded as a signature of compositional heterogeneity in Earth’s mantle. As shown in our previous work (Wu and Wentzovitch, 2014), this is not necessarily true in the presence of FSC. This spin crossover can produce positive and negative isobaric temperature gradients for \( V_\varphi \) and \( V_S \), respectively, and anti-correlation between \( V_\varphi \) and \( V_S \) at mid lower mantle depths in a pyrolitic aggregate, even in the absence of any compositional heterogeneity (Wu and Wentzovitch, 2014) (see the bottom–left part of Table 1). It is important to clarify whether compositional heterogeneities can cause anti-correlation between sound velocities. It should be clear that isothermal variation in ferrous iron content in both Fp and Pv (Shukla et al., 2015) is not able to cause anti-correlation between sound velocities (Fig. 4, Table 1).

In general, in the absence of FSC, increasing Fe content in Fp (\( x \)) reduces velocities and increases density simultaneously, and variation in \( x \) causes positive correlation between sound velocities and anti-correlation between velocities and density, \( \rho \), (e.g., Wu et al., 2013; Shukla et al., 2015). This is still true for Fp undergoing spin crossover. However, the absolute values of \( R_{\varphi/S} \), \( R_{P/S} \), and \( \partial \ln \varphi/\partial \ln \rho \) are far larger than expected (Fig. 5) because \( V_\varphi \) and \( V_P \) are particularly sensitive to \( x \) in the crossover region. In contrast to variation in \( x \), without FSC isobaric temperature variation generally leads to positive correlation between sound velocity and \( \rho \). This is no longer true for Fp or in a pyrolitic aggregate in some \( PT \) range of the lower mantle, where \( dV_\rho/dT \rho \) can be positive because of FSC (Wu and Wentzovitch, 2014; Wu, 2016). Because shear modulus does not show anomalous softening throughout FSC, temperature variation alone results in positive correlation between \( V_S \) and \( \rho \). Therefore, anti-correlation between \( V_S \) and \( \rho(R_S/\rho) \) should result from some form of compositional heterogeneity.

Besides variation of Fe content in Fp and/or Pv, another likely compositional heterogeneity in the lower mantle is the variation of the Mg/Si ratio or weight fraction of Fp and Pv. The aggregate we discuss in this paper has the following composition

\[
7\text{ wt}\% \text{CaSiO}_3 + X\text{ wt}\% \text{Mg}_0.905\text{Fe}0.091\text{SiO}_3 \\
+ (93 - X)\text{ wt}\% \text{Mg}_{0.8125}\text{Fe}_{0.1875}\text{O}.
\]  

(1)

The aggregate with \( X = 78 \) has composition very close to pyroilite. We only show results for 20 < \( P < 110 \) GPa, where \( \rho \) should be stable (Murakami et al., 2004; Tsuchiya et al., 2004). Based on iron partitioning between Pv and Fp (e.g., Sinmyo and Hirose, 2013), Fe content (\( x \)) in Pv may be less than 9 mol\%, while in Fp it may be larger than 18.75 mol\% in Earth’s mantle. Since increasing \( x \) reduces all sound velocities for both Fp and Pv, and Pv has larger velocities than Fp, \( \partial \ln V_P/\partial X(R_P/X) \) and \( \partial \ln V_S/\partial X(R_S/X) \) are always positive, as shown in Fig. 6. Therefore, \( R_{P/S} \) is also positive for variations in weight fractions of Fp, i.e., Mg/Si ratio. However, FSC increases \( R_{\varphi/X} \) and \( R_{P/X} \) significantly because of its large effect in reducing \( V_P \) and \( \varphi \) in Fp (see Figs. 6a–6b and Fig. 1b). Throughout the FSC, Fp’s density in the LS state surpasses that of Pv, i.e., Pv’s density is intermediate between those of Fp\textsuperscript{HS} and Fp\textsuperscript{LS} (\( \rho_{\text{Fp}\textsuperscript{HS}} < \rho_{\text{Fp}} < \rho_{\text{Fp}\textsuperscript{LS}} \)). Therefore, \( \partial \ln \rho/\partial X(R_{P/X}) \) and hence correlations between velocities and density change from positive to negative throughout the spin crossover in Fp (see Figs. 6d, 7c, 7d, and Table S5).

Thermally and compositionally induced pairwise correlations between velocities and density changes are summarized in Table 1. As indicated there and in Figs. 5a and 7a, both compositional variations considered here are unable to cause anti-correlation between \( V_\varphi \) and \( V_S \). Therefore, the anti-correlation between \( V_\varphi \) and \( V_S \) in the mid lower mantle suggested by some seismic models

### Table 1

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\( a \) The variation of iron content (\( x \)) in Fp or Pv causes the anti-correlation in the whole lower mantle while the variation in Fp with (\( X \)) causes the anti correlations at the depth \( > 1600 \) km.

\( b \) Positive correlation changes to anti-correlation at mid lower mantle because of FSC.

Fig. 5. (a) \( \partial \ln V_\varphi/\partial \ln V_S \), (b) \( \partial \ln V_P/\partial \ln \varphi \), (c) \( \partial \ln V_\varphi/\partial \ln \rho \), and (d) \( \partial \ln V_S/\partial \ln \rho \) for Mg\textsubscript{0.8125}Fe\textsubscript{0.1875}O at \( x = 0.1875 \) caused by variation in the iron concentration, \( x \).
Fig. 6. Dependence on variation in X (Mg/Si ratio) of (a) $V_\phi$, (b) $V_P$, (c) $V_S$, and (d) $\rho$ in a pyrolitic aggregate with 7 wt% CaSiO$_3$, $X$ wt% Mg$_{0.909}$Fe$_{0.091}$SiO$_3$ and $(93 - X)$ wt% Mg$_{0.8125}$Fe$_{0.1875}$O, for $X = 78$.

Fig. 7. (a) $\partial \ln V_\phi / \partial \ln V_S$, (b) $\partial \ln V_P / \partial \ln V_S$, (c) $\partial \ln \rho / \partial \ln V_S$, and (d) $\partial \ln \rho / \partial \ln V_\phi$ of the pyrolitic aggregate with 7 wt% CaSiO$_3$, $X$ wt% Mg$_{0.909}$Fe$_{0.091}$SiO$_3$, and $(93 - X)$ wt% Mg$_{0.8125}$Fe$_{0.1875}$O with $X = 78$ caused by variation in $X$.

Masters et al., 2000; Simmons et al., 2010 provides a strong argument in favor of FSC plus a thermal origin of this phenomenon (Wu and Wentzcovitch, 2014). Some seismic models (Antolik et al., 2003; Ishii and Tromp, 1999; Resovsky and Trampert, 2003) also suggest that $\rho$ and $V_S$ are anti-correlated ($R_{S/P} < 0$) in the lower mantle. This anti-correlation in an aggregate with Fp undergoing spin crossover cannot have a purely thermal origin. This type of anti-correlation should be related to some form of compositional heterogeneity. The variation of the fraction of Fp and Pv considered here, produces positive $R_{S/P}$ and $R_{P/P}$ above the spin transition region. However, these parameters become negative throughout and beyond the spin crossover in Fp (see Fig. 7c, 7d). Together with negative $R_{S/P}$ and $R_{P/P}$ in the whole mantle produced by the variation of iron content in Pv or Fp, the anti-correlation between velocities and density should become more noticeable at the bottom of the lower mantle in the presence of FSC (see Fig. 7d), which is in consistence with the seismic observation (Resovsky and Trampert, 2003). Therefore, this analysis supports the notion that the deep lower mantle is both thermally and compositionally heterogeneous.

As discussed by Wu and Wentzcovitch (2014), thermally induced $R_{S/P}$ is sensitive to the amount of Fp in the mantle aggregate in the depth range where spin crossover occurs (Fig. 8a). Some aspects of the predicted behavior of this parameter are consistent with seismic observations of $R_{S/P}$ on slab and non-slab regions (Fig. 8b) (Saltzer et al., 2001): i) above 1200 km depth, where there is no significant signature of FSC, $R_{S/P}$ is not sensitive to the composition of the aggregate because mantle minerals have
similar thermally induced $R_{S/P}$ values (Karato and Karki, 2001); ii) at depths where the spin crossover manifests, thermally induced $R_{S/P}$ is sensitive to composition and the maximum value of $R_{S/P}$ increases quickly with Fe content in Fp ($x$) or with Mg/Si ratio ($X$) in the aggregate. This is because FSC results in insensitivity of $V_P$ to temperature variation (Fig. 1a) (Wu and Wentzcovitch, 2014). Thus, Saltzer et al. (2001) data suggests that non-slab regions may contain more Fp than slab regions, which is reasonable since eclogitic material in slab areas has no Fp, though slab compositions are not expected to be uniform. However, there are several other points in Saltzer et al. (2001) data that can hardly be reconciled with purely thermally induced heterogeneities in a homogeneous mantle, particularly the depth for maximum $R_{S/P}$. Predictions calculate this maximum at shallower depths (~1700 km) but than observed (~2100 km) (Wu and Wentzcovitch, 2014). Besides, thermally induced $R_{S/P}$ of various aggregates intersect at the depth ~2000 km (Fig. 8a). This happens because FSC enhances the temperature sensitivity of $V_P$ in some PT range while reduces it in a different PT range (Wu and Wentzcovitch, 2014). Seismic observations by Saltzer et al. (2001) do not show this type of effect when contrasting $R_{S/P}$ from slab and non-slab regions, presumably with different Mg/Si ratio. Therefore, this analysis supports the notion that both slab and non-slab regions have thermal and compositional heterogeneities.

$V_P$ in aggregates responds in unusual ways to both lateral temperature (Fig. 1a) and composition variations (Fig. 1b) in the spin crossover region, therefore inclusion of compositional variations should not change the fact that $R_{S/P}$ of slab and of non-slab regions diverge at depths greater than ~1200 km. In contrast to the FSC induced insensitivity of $V_P$ to temperature in the mid lower mantle (Wu and Wentzcovitch, 2014), FSC significantly enhances the sensitivity of $V_P$ to compositional variations considered here, i.e., Fe content in Fp ($x$) and Mg/Si ratio ($X$) (Figs. 1b, 4 and 6) and reduces significantly $R_{S/P}$ (or increase $R_{P/S}$) (see Figs. 5 and 7). In short, thermal and compositional effects on $R_{S/P}$ compete against each other in the spin crossover region (Fig. 8a). If compositional effects dominate, there could be a shallow minimum in $R_{S/P}$, rather than a maximum, in the mid lower mantle.

The temperature sensitivity of $V_P$ at ~1700 km depth is less than half of that at ~2100 km depth for aggregates well constrained by PREM (Wu and Wentzcovitch, 2014; Wu, 2016). Therefore, lateral variation in $V_P$ at ~1700 km depth should be significantly smaller than that at ~2100 km depth in a chemically homogeneous mantle, assuming lateral temperature variations are not several fold different at ~1700 km and ~2000 km. Therefore, $V_P$ variations of similar magnitudes at these mid lower mantle depths observed in different seismic models (Houser et al., 2008; Ishii and Tromp, 2001; Karason and van der Hilst, 2001; Masters et al., 2000; Montelli et al., 2006; Su and Dziewonski, 1997) suggest that both lateral (and possibly radial) composition and temperature variations may coexist in this region. Compositional variations can also significantly change the depth of the $R_{S/P}$ maximum and change the thermally induced $R_{S/P}$ depth profiles in slab and non-slab regions. The distinct behavior of thermally and compositionally induced variations in $R_{S/P}$ shown in Fig. 8 is critical for distinguishing the source of velocity variations in the mid lower mantle. Within this simple but most important range and type of composition variations, it is possible to infer the thermal and compositional contributions to velocity heterogeneities in the mid lower mantle by matching calculated and seismologically observed $R_{S/P}$.

4. Summary and conclusions

The iron spin crossover in Fp softens anomalously its bulk modulus throughout the broad pressure range of the crossover. Since this softening is proportional to Fe content in Fp ($x$) at low $x$ (Wentzcovitch et al., 2009; Wu et al., 2013), or to the amount of Fp in the aggregate, i.e., Mg/Si ratio ($X$), the spin crossover changes dramatically the manifestation of these chemical heterogeneities in the mantle in several respects (Fig. 1b):

1. The sensitivity of $V_\phi$ to variations of $x$ in Fp and variations of Mg/Si ratio in the aggregate, increases by several fold in the spin crossover range, surpassing the sensitivity of $V_S$. This behavior contrasts to the effect of these compositional heterogeneities in the absence of FSC. $R_{\phi/S}$ can be $\sim$2 under variations of $x$ in Fp and $\sim$3 under variations of Mg/Si ratio in the aggregate.

2. All sound velocities decrease with increasing $x$ in Fp or in Pv. The spin crossover does not change this. Furthermore, all velocities in Fp are smaller than those of Pv and all aggregate velocities decrease with increasing Mg/Si ratio. Therefore, velocity variations are always positively correlated for the two primary compositional variations inspected here.

3. Velocities and density variations anti-correlate for variations of $x$ in Fp and Pv because density always increases with $x$, while velocities decrease. However, Pv (Mg$_{0.92}$Fe$_{0.08}$SiO$_3$) is denser than HS Fp (Mg$_{0.80}$Fe$_{0.20}$SiO$_3$) but less dense than LS Fp. Therefore, variation in Fp content in the aggregate, i.e., changing Mg/Si ratio, produces a change in the nature of velocities and density correlations, $R_{V/P}$, from positive, when Fp is in the HS state, to negative when Fp is in the LS state.

4. The spin crossover of iron in Fp can cause $\partial ln V_\phi/\partial T > 0$ in a pyrolitic lower mantle and leads to anti-correlation between $V_\phi$ and $V_S$, i.e., $R_{\phi/S} < 0$, in the mid lower mantle (Wu and Wentzcovitch, 2014). The two primary compositional variations investigated here are unable to generate anti-correlation between velocities at mid lower mantle. Therefore, the anti-correlation between $V_\phi$ and $V_S$ reported by some seismic studies (Masters et al., 2000; Simmons et al., 2010), might be considered a strong evidence of lateral temperature variations in a lower mantle that experiences spin crossover in iron in Fp.

5. Thermal and spin crossover effects in Fp cannot produce the anti-correlation between $\rho$ and $V_S$ reported in the deep lower mantle by some seismic studies (Ishii and Tromp, 1999; Antolik et al., 2003; Masters et al., 2000; Resovsky and Trampert, 2003), which suggests significant compositional and/or mineralogical heterogeneities in this region. The post-perovskite transition (Murakami et al., 2004; Tsuchiya et al., 2004; Oganov and Ono, 2004) is an example of the latter.
Acknowledgements

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.10.009.

References