

## Thermal elasticity of $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ olivine and wadsleyite

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[1] We present first-principles results for elastic moduli (bulk,  $K$ , and shear,  $G$ ) and acoustic velocities (compressional,  $V_P$ , shear,  $V_S$ , and bulk  $V_\phi$ ) of olivine ( $\alpha$ ) and wadsleyite ( $\beta$ )  $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ , at high pressure ( $P$ ) and temperature ( $T$ ) with varying iron content ( $0 \leq x \leq 0.125$ ). Pressure and temperature derivatives of these properties are analyzed. We show that adding 12.5% of Fe in forsterite softens  $V_P$  and  $V_S$  by  $\sim 3$ –6%, the same effect as raising temperature by  $\sim 1000$  K in dry olivine at 13.5 GPa—the same is true in wadsleyite. This study suggests that Fe is effective in producing seismic velocity heterogeneity at upper mantle and transition zone conditions and should be another key ingredient, in addition to temperature and water content variations, in interpreting seismic heterogeneities in the transition zone. The effect of Fe on density, elastic, and velocity contrasts across the  $\alpha \rightarrow \beta$  transition is also addressed at relevant conditions. We show that simultaneous changes of composition, temperature, and pressure do not affect significantly the relative density contrasts. We also find that compressional and shear impedance contrasts result primarily from velocity discontinuities rather than density discontinuity. **Citation:** Núñez-Valdez, M., Z. Wu, Y. G. Yu, and R. M. Wentzcovitch (2013), Thermal elasticity of  $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$  olivine and wadsleyite, *Geophys. Res. Lett.*, 40, 290–294, doi:10.1002/grl.50131.

### 1. Introduction

[2] Wadsleyite ( $\beta$ -phase) is a high-pressure polymorph of olivine ( $\alpha$ -phase),  $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ . These minerals are the main constituents of the Earth's upper mantle (UM) and upper transition zone (TZ) in pyrolitic lithologies [Ringwood, 1975; Irifune and Ringwood, 1987; Putnis, 1992]. At  $\sim 13.5$  GPa, the  $\alpha \rightarrow \beta$  transformation takes place near 1700 K [Akaogi et al., 1989; Katsura and Ito, 1989; Brown and Shankland, 1981]. This transformation is associated with the 410 km seismic discontinuity in the Earth. Interpretation of seismic data of this region in terms of mineralogy and chemical composition requires detailed knowledge of bulk ( $K$ ) and shear ( $G$ ) moduli as a function of pressure ( $P$ ) and temperature ( $T$ ) of constituent minerals [Li and

Liebermann, 2007]. The dependence of seismic velocities on  $T$  and chemical composition at mantle conditions is of particular interest to interpret, for example, lateral shear-wave velocity ( $V_S$ ) variations in the TZ region [see e.g., Meier et al., 2009]. So far, the elasticity database for minerals in the TZ is still incomplete, especially for those containing Fe, Al, and Ca. In the past two decades, much experimental effort has been devoted to understanding the effect of adding iron on elasticity of minerals, and quite a few techniques have been used to measure elasticity of olivine and wadsleyite, including Brillouin spectroscopy [Zha et al., 1998], ultrasonic interferometry [Li and Liebermann, 2000; Liu et al., 2005, 2009], resonant ultrasound spectroscopy and resonant sphere techniques [Isaak, 1992; Mayama et al., 2004; Isaak et al., 2010], impulsively stimulated laser scattering [Abramson et al., 1997], etc. However, different experimental conditions and the lack of a unified uncertainty scale on available experimental data disallow an accurate extraction of the effect of iron on elasticity at conditions of the 410 km seismic discontinuity. Previous computations on elasticity of  $\alpha$ - and  $\beta$ - $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$  were limited to static calculations (0 K) [Núñez Valdez et al., 2010, 2011; Stackhouse et al., 2010], and simple extrapolations to high  $T$  do not work well because  $T$ -derivatives of  $K$  and  $G$  usually decrease in magnitude with increasing  $P$  (see section 3.1). In the past, thermal elastic properties of MgO and  $\text{MgSiO}_3$ -perovskite have been calculated by first principles using the quasi-harmonic approximation (QHA), valid up to  $\sim 2/3$  of the melting temperature [e.g., Karki et al., 1999; Wentzcovitch et al., 2004], or using molecular dynamics [e.g., Oganov et al., 2001; Li et al., 2006]. Both methods demand enormous computational efforts. For example, QHA calculations have required vibrational density of states (VDoS) for strained atomic configurations at several  $P$ 's, usually summing to about 1000 parallel jobs [Da Silva et al., 2007; Da Silveira et al., 2008]. As such, reports on high  $P$ - $T$  thermal elasticity calculations of mantle minerals have been scanty. Here we use a new semi-analytical method [Wu and Wentzcovitch, 2008, 2011] to calculate  $K$ ,  $G$  and compressional ( $V_P$ ), shear ( $V_S$ ), and bulk ( $V_\phi$ ) velocities of  $\alpha$ - $\beta$ - $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ . This approach uses only static elastic constants and phonon density of states for unstrained configurations, therefore reducing computational time, resources, and especially manpower, by 1 to 2 orders of magnitude. We distinguish the effect of Fe from that of  $T$  on elasticity and acoustic velocities, and the two effects are compared. We then address the contrasts' behavior across the  $\alpha \rightarrow \beta$   $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$  transition near conditions of the 410 km seismic discontinuity.

### 2. Theory

[3] Adiabatic elastic constants were obtained using the relation  $C_{ijkl}^S = C_{ijkl}^T + \frac{T}{V C_V} \frac{\partial S}{\partial \epsilon_{ij}} \frac{\partial S}{\partial \epsilon_{kl}} \delta_{ij} \delta_{kl}$ , where  $C_V$  is heat

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capacity and  $V$ ,  $S$ , and  $e$  are volume, entropy, and strain, respectively.  $C_{ijkl}^T$  are isothermal elastic constants calculated as strain derivatives of the Gibbs free energy,  $C_{ijkl}^T = \left[ \frac{\partial^2 G(P,T)}{\partial e_{ij} \partial e_{kl}} \right]_{P,T}$  [Wentzcovitch et al., 2004], using the QHA [Wallace, 1972] and static elastic constants [Núñez Valdez et al., 2010, 2011]. Computations are based on density functional theory within the local density approximation (LDA) [Ceperley and Alder, 1980]. Details about structure relaxation [Wentzcovitch, 1991] calculations can be found in previous publications [Núñez Valdez et al., 2010, 2011]. VDoS were calculated using density functional perturbation theory [Baroni et al., 2001], with the quantum-ESPRESSO [Giannozzi et al., 2009]. At 10 different  $P$ 's, dynamical matrices were obtained on a  $2 \times 2 \times 2$   $\mathbf{q}$ -point mesh for one atomic configuration only. Force constants were interpolated on a  $12 \times 12 \times 12$  regular  $\mathbf{q}$ -point mesh to produce VDoS. This sampling is sufficient for accurate aggregate elastic properties [Núñez Valdez et al., 2010; Wu and Wentzcovitch, 2011]. Free energies were computed exactly on a  $T$ -grid of 10 K spacing and interpolated on a  $P$ -grid of 0.1 GPa using third order finite strain expansions at every  $T$ . All  $P$ - and  $T$ -derivatives were computed on this grid. The main difference between this study and previous thermal elastic calculations using QHA free energies [Karki et al., 1999; Wentzcovitch et al., 2004] is that here  $C_{ijkl}^T$  are expressed analytically in terms of strain and mode Grüneisen parameters. Under the assumption that the angular distribution of strain Grüneisen parameters is isotropic,  $C_{ijkl}^T$  can be calculated without performing phonon calculations for strained configurations [Wu and Wentzcovitch, 2011]. This

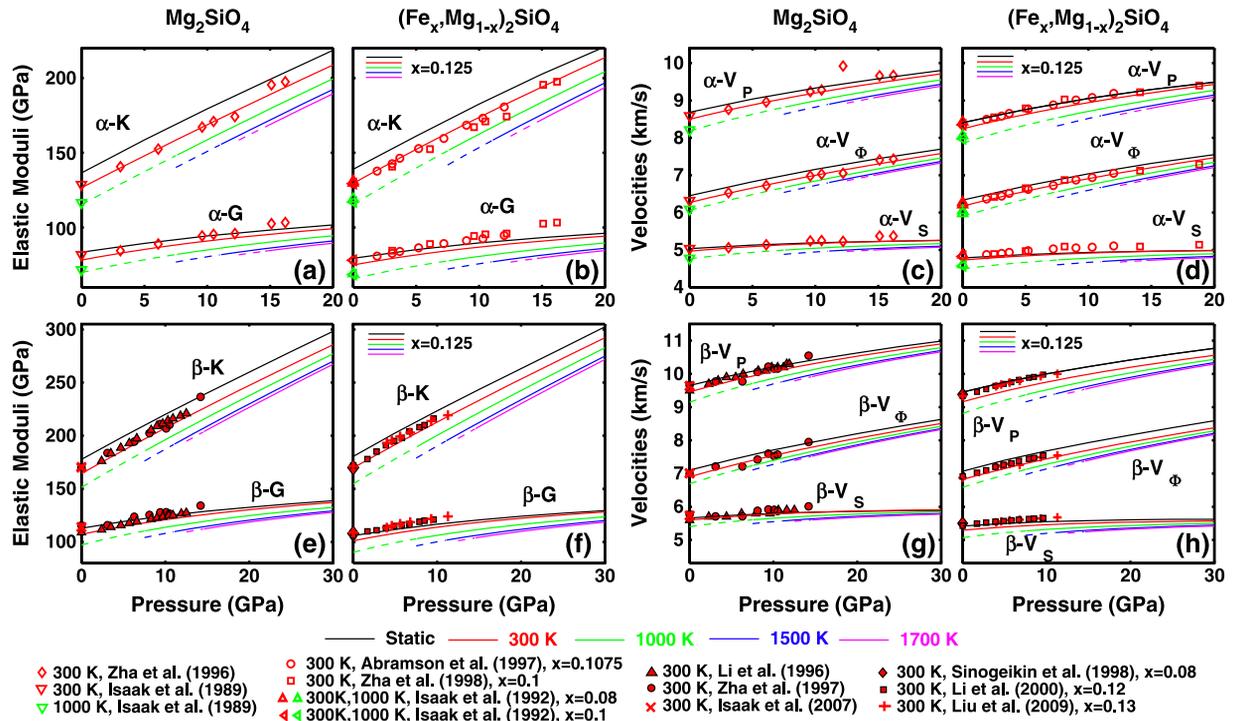
approximation is equivalent to assuming that thermal pressure is isotropic. Such assumption, although not exact, is implicit in the QHA [Carrier et al., 2007; Wentzcovitch et al., 2010] and can be quite accurate especially to address geophysical issues [Carrier et al., 2008; Wu and Wentzcovitch, 2011], such as the high- $PT$  dependence of  $\frac{d \ln V_s}{dT}$ , which cannot be readily derived from experiments.

### 3. Results and Discussion

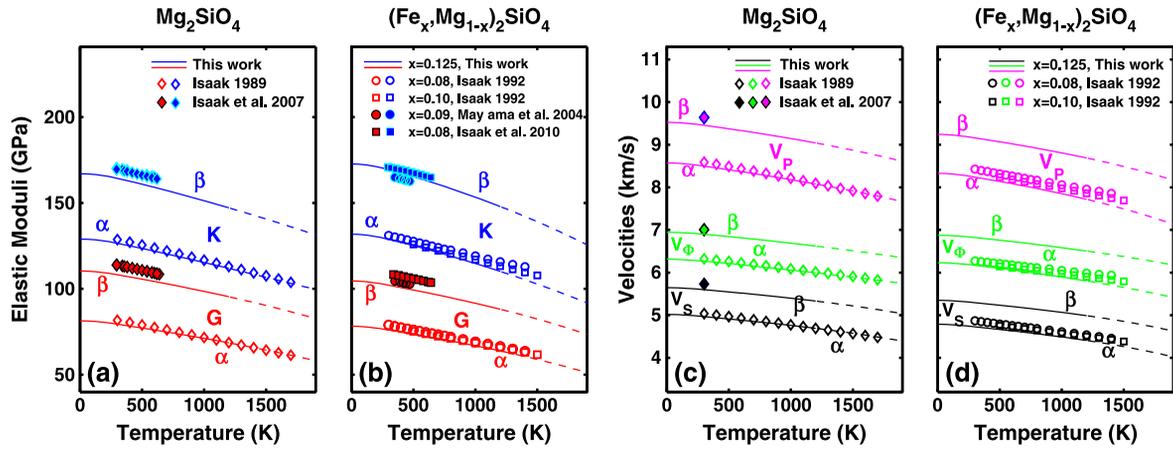
#### 3.1. Aggregate Elastic Moduli of $\alpha$ - and $\beta$ - $(\text{Mg}_{1-x}, \text{Fe}_x)_2\text{SiO}_4$

[4] Our calculated averaged elastic moduli,  $K$  and  $G$ , shown as solid lines in Figure 1 (QHA valid region), agree very well with experimental data for both iron-free (Figures 1a and 1e) and iron-bearing ( $x=0.125$ , Figures 1b and 1f)  $\alpha$ - and  $\beta$ -phases [Zha et al., 1996; Isaak et al., 1989; Li et al., 1996; Zha et al., 1997; Isaak et al., 2007; Abramson et al., 1997; Zha et al., 1998; Isaak, 1992; Sinogeikin et al., 1998; Li and Liebermann, 2000; Liu et al., 2009]. For  $x=0$ , we find  $K'_\alpha \approx 4.3$  and  $G'_\beta \approx 1.6$  at ambient conditions [On-line, 2012], which are consistent with experimental values, 4.4 and 1.3, respectively [Li et al., 1996]. Similarly calculated,  $K'_\beta \approx 4.5$  and  $G'_\beta \approx 1.6$  agree well with measurements of 4.2 and 1.5, respectively, by Li et al. [1996]. At ambient conditions,  $K'_{\alpha, x=0.125} \approx 4.7$ ,  $K'_\beta, x=0.125} \approx 4.5$ , and  $G'_{(\alpha, \beta), x=0.125} \approx 1.5$ . Besides,  $K'_{x=0.125} \gg G'_{x=0.125}$  for both phases in the entire pressure interval considered [On-line, 2012]. These results suggest only minor effects of iron on the pressure derivatives of these elastic moduli.

[5] Figure 2 shows the temperature dependence of aggregate properties of  $\alpha$ - and  $\beta$ -phases at 0 GPa. Within the valid



**Figure 1.** Pressure and temperature dependence of elastic moduli  $K$  and  $G$  (calculated as Voigt-Reuss-Hill averages [Watt, 1979]) and velocities  $V_P$ ,  $V_S$ , and  $V_\phi$  for (a, c, e, g) Fe-free olivine-wadsleyite and (b, d, f, h) Fe-bearing olivine-wadsleyite. First-principles calculations within LDA (lines) are compared to available experimental data (symbols). Low-pressure-high temperature trends (dash lines) are outside the validity of the QHA.



**Figure 2.** Temperature dependence of  $K$ ,  $G$ ,  $V_P$ ,  $V_S$ , and  $V_\phi$  for (a, c) Mg end-members olivine-wadsleyite and (b, d) Fe-bearing olivine-wadsleyite. First-principles calculations within LDA (lines) are compared to available experimental data (symbols) at  $P=0$  GPa.

QHA regime (solid lines), the predictive power of our calculations is outstanding for the iron-free and iron-bearing  $\alpha$ -phases (Figures 2a, 2b, 2c, and 2d), even though iron concentrations in experiments differ somewhat from  $x=0.125$  [Isaak et al., 1989; Isaak, 1992]. For  $\alpha$ - and  $\beta$ -phases,  $\frac{d(K,G)}{dT} < 0$  with  $|\frac{dK}{dT}| > |\frac{dG}{dT}|$  in the entire 300–1200 K temperature interval, irrespective of  $x$  [On-line, 2012].

[6] We also find that iron addition increases the bulk modulus, [ $K_\alpha \approx (126.54 + 24x)$  GPa and  $K_\beta \approx (164.37 + 42.2x)$  GPa], and decreases the shear modulus, [ $G_\alpha \approx (78.17 - 26.2x)$  GPa and  $G_\beta \approx (107.11 - 47.6x)$  GPa] for  $0 \leq x \leq 0.125$  at ambient conditions [On-line, 2012]. These trends agree with experimental data for  $K_\alpha$  and  $G_{\alpha,\beta}$  (Figures 1a, 1b, 1e, and 1f, and 2a and 2b). But for  $K_\beta$ , the experimental determination is still unclear. Some studies suggest that  $K_\beta$  does not increase significantly with  $x$  [Li et al., 1996; Zha et al., 1997; Isaak et al., 2007; Sinogeikin et al., 1998; Li and Liebermann, 2000; Liu et al., 2009] or maybe could even decrease [Mayama et al., 2004; Isaak et al., 2010] (Figure 2b). In contrast, calculations show clearly the dependence of  $K_\beta$  on  $x$  without ambiguity.

### 3.2. Effects of Iron and Temperature on Acoustic Velocities

[7] In the geophysics literature, the topography and seismic velocity anomalies at 410 km depth have been attributed mainly to lateral temperature variations [Gu et al., 1998; Houser and Williams, 2010]. More recently, it has been recognized that the presence of water in variable amounts in the TZ [Jacobsen, 2006] can also affect topography and velocities in this region. Therefore, the interpretation of the origin of lateral variations in TZ [Meier et al., 2009] depends crucially on the extent of the information available on various effects on velocities and on their accuracy. According to Karato [2011], the influence of water on seismic wave velocities is small compared with the effect of temperature, composition, and mineralogy changes at real mantle conditions [see e.g., Irifune et al., 2008; Weidner and Wang, 2000]. The discussion on the effects of water velocity variations in TZ is still ongoing and will not be addressed in this paper. Here we only compare the effects of variations in iron

concentration,  $x$ , and temperature on velocities at 13.5 GPa and 1700 K.

[8] Figures 1 and 2 show how acoustic velocities [ $V_P = \sqrt{(K + \frac{4}{3}G)/\rho}$ ,  $V_S = \sqrt{G/\rho}$ , and  $V_\phi = \sqrt{(K/\rho)}$ ] of  $\alpha$ - and  $\beta$ -phases are affected by the ratio  $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.125$ . At ambient conditions,  $V_P$  decreases by  $\sim 3\%$  and  $V_S$  by  $\sim 5\%$ . On the other hand, at 300 K and 0 GPa, a perturbation of 100 K results in a  $\sim 0.5$ – $0.6\%$  reduction in velocities (quite consistent with the  $\sim 0.7\%$  reduction reported by Karato [2011]). At  $\sim 410$  km depth, this perturbation is reduced to  $\sim 0.3$ – $0.4\%$  only. This can also be seen from the variation of  $\frac{dV_S}{dT}$  with pressure. For instance,  $\frac{dV_{S,\alpha}}{dT} \Big|_{x=0(x=0.125)} = -5 \times 10^{-5} \text{ K}^{-1} (-6 \times 10^{-5} \text{ K}^{-1})$  at ambient conditions but  $-4 \times 10^{-5} \text{ K}^{-1} (-5 \times 10^{-5} \text{ K}^{-1})$  at  $\sim 410$  km depth conditions. Similar values can be found for wadsleyite [On-line, 2012]. Thus, the effect of lateral temperature variations on velocities decreases with pressure, while the effect of variation in  $x$  increases. For example, at  $\sim 410$  km depth, the effect of a  $\sim 100$  K perturbation on velocities is comparable to an increase in  $x$  by  $\sim 1\%$  only. Therefore, mineralogy, such as variations in iron concentration in different phase assemblages, should be an important source of lateral velocity heterogeneities in the UM and TZ.

### 3.3. Effect of Iron Heterogeneity on Discontinuities across the $\alpha \rightarrow \beta$ Transition

[9] Accurate data on elasticity of  $\alpha$ - and  $\beta$ -( $\text{Mg}_{1-x}, \text{Fe}_x$ ) $_2\text{SiO}_4$  at UM and TZ conditions are critical for investigating the role of the  $\alpha \rightarrow \beta$  transformation on the 410 km seismic discontinuity. Predicted contrasts,  $\Delta$ , for a property  $M$  with iron content  $x$  across the  $\alpha \rightarrow \beta$  transformation,  $\Delta M = 2(M_{x,\beta} - M_{x,\alpha}) / (M_{x,\alpha} + M_{x,\beta}) \times 100$ , show important differences in elastic moduli and velocities between these two phases near 410 km depth conditions (Table 1). The reconstructive  $\alpha \rightarrow \beta$  transition, which involves the pairing of isolated  $\text{SiO}_4$  units in  $\alpha$  to form  $\text{Si}_2\text{O}_7$  dimers in  $\beta$ , substantially strengthens  $K$  and  $G$  (Figures 1a, 1b, 1e, and 1f). For example, at 1700 K and 13.5 GPa,  $\Delta K_{x=0} = 20.1\%$  and  $\Delta G_{x=0} = 28.1\%$  (Table 1). In the presence of iron ( $x=0.125$ ), these contrasts decrease. As a result, velocity contrasts  $\Delta V_P$  and  $\Delta V_S$  decrease (by 5.5% and 7.0%, respectively). Thus, the effect

**Table 1.** Predicted Contrasts in % Across the  $\alpha \rightarrow \beta$  Transition at 13.5 GPa

$T$ (K)	1500		1700	
$x$	0.0	0.125	0.0	0.125
$\Delta\rho$	5.4	5.2	5.4	5.3
$\Delta K$	20.0	19.6	20.1	19.7
$\Delta G$	28.0	26.3	28.1	26.4
$\Delta V_P$	9.0	8.5	9.1	8.6
$\Delta V_S$	11.4	10.6	11.4	10.6
$\Delta V_\Phi$	7.3	7.2	7.4	7.3
$\Delta(\rho V_P)$	14.4	14.2	14.5	14.3
$\Delta(\rho V_S)$	16.7	16.6	16.8	16.7

of a change of 12.5% in iron concentration on contrasts is much larger than the effect of a 200 K in temperature variation at fixed composition (Table 1). We can also see that, at ambient conditions(\*) and 1700 K and 13.5 GPa(†), lateral temperature variations cause heterogeneity ratios ( $R_{A/B} = \frac{\delta \ln V_A}{\delta \ln V_B}$ ) of  $R_{S/P,x=0(x=0.125)}^\alpha \sim [1.28(1.05)]^*$  versus  $[1.20(1.39)]^\dagger$ ,  $R_{\Phi/S,x=0(x=0.125)}^\alpha \sim [0.79(0.77)]^*$  versus  $[0.72(0.69)]^\dagger$ ,  $R_{S/P,x=0(x=0.125)}^\beta \sim [1.27(1.04)]^*$  versus  $[1.18(1.81)]^\dagger$ , and  $R_{\Phi/S,x=0(x=0.125)}^\beta \sim [0.81(0.78)]^*$  versus  $[0.75(0.48)]^\dagger$ . For comparison, at 0 K between 0 and 13.5 GPa,  $R_{S/P}^\alpha \sim 1.54 - 1.67$ ,  $R_{\Phi/S}^\alpha \sim 0.37 - 0.34$ ,  $R_{S/P}^\beta \sim 1.99 - 2.16$ , and  $R_{\Phi/S}^\beta \sim 0.1 - 0.09$  due to iron heterogeneity [Núñez Valdez et al., 2010, 2011]. All these results show that iron heterogeneity is more effective than lateral temperature variations in producing observed velocity heterogeneity ratios in  $\alpha$ - and  $\beta$ - phases separately and across the  $\alpha \rightarrow \beta$  transition. Obviously, these results should be affected by the presence of coexisting phases. If the interaction between the olivine system and coexisting phases (i.e., garnet, pyroxenes, and  $\text{CaSiO}_3$ ) is negligible, this conclusion should still hold, although these ratios could change somewhat.

[10] We also find that velocity contrasts across the transition are essentially unaffected by pressure, i.e., along the topography of the “410 discontinuity” should not affect velocity contrasts. This is consistent with inferences from experiments at 300 K in iron-free samples [Li et al., 1996; Zha et al., 1997]. Also,  $\Delta\rho$  and  $\Delta K$  are not significantly affected by iron (Table 1). Therefore, the mantle aggregate at 410 km depth will have  $\Delta\rho$  reduced (buffered) from the current value of  $\sim 5.3\%$  (at 1700 K and 13.5 GPa) for pure olivine to  $\sim 3\%$  in an aggregate with 60 vol % of olivine, as in pyrolite (a simple derivation can be found in [Yu et al., 2008]). This is consistent with the 0.2–4% density increase at 410 km depth from the seismic study by Shearer and Flanagan [1999]. Compared to the Mg end-members, overall the presence of iron decreases only slightly contrasts in properties across the transition. We also conclude that velocities contribute more than density to  $P$ - and  $S$ -impedance contrasts (see Table 1).

#### 4. Conclusions

[11] We presented extensive first-principles results for aggregate elastic properties and sound velocities of  $\alpha$ - and  $\beta$ - $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ , with variable  $x$  at relevant mantle conditions. A novel semi-analytical method used here [Wu and Wentzcovitch, 2011] expedited the thermal elasticity

calculation by approximately 2 orders of magnitude compared to QHA-based calculations [e.g., Wentzcovitch et al., 2004]. We showed the difference between physical properties at ambient conditions and conditions expected near the 410 km seismic discontinuity. In overall, we showed the importance of using accurate thermal elasticity data obtained at local conditions and compositions prevailing in the mantle in the interpretation of seismic data. We concluded that variation in iron concentration might impact more significantly than temperature variation on velocity heterogeneity ratios, including discontinuity ratios at  $\sim 410$  km depth. Other chemical and phase heterogeneities, such as variations in amounts of aluminum and calcium-bearing minerals, should presumably have similar effects. Finally, calculated contrasts in properties across the 410 km discontinuity indicate that compressional and shear impedance contrasts are caused primarily by velocity discontinuities rather than density discontinuity.

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