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First principles thermoelasticity of $MgSiO_3$-perovskite: consequences for the inferred properties of the lower mantle

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Abstract. Some key thermoelastic properties of $MgSiO_3$-perovskite (**pv**) have been determined at lower mantle (LM) pressures and temperatures using the quasi-harmonic approximation in conjunction with first principles phonon dispersions. The adiabatic bulk moduli (K_S) of **pv** and of an assemblage of 80 vol% **pv** and 20 vol% MgO were obtained along the thermodynamically inferred adiabat and compared with the seismic counterpart given by the preliminary reference Earth model (K_{PREM}). The discrepancy between calculated K_S's and K_{PREM} in the deep LM suggests a super-adiabatic gradient, or subtle changes of composition, or phase, or all beginning at about 1200 km. The Anderson Grüneisen parameter, $\delta_S = (\partial \ln K_S/\partial \ln \rho)_P$, was predicted to decrease rapidly with depth (from 2.7 to 1.2 across the LM) supporting the thermal origin for the lateral heterogeneities throughout most of the LM.

1. Introduction

A detailed knowledge of the thermoelastic properties of $MgSiO_3$-perovskite (**pv**) is essential for interpreting seismic observations of the lower mantle (LM) [e.g., *Dziewonski and Anderson,* 1981; *Robertson and Woodhouse,* 1996]. Literature values for key parameters still exhibit significant discrepancies [*Knittle et al.*, 1986; *Mao et al.*, 1991; *Wang et al.*, 1994; *Funamori et al.*, 1996; *Fiquet et al.*, 2000]. This has prevented clarification of fundamental questions related to 1) the isochemical versus chemically stratified mantle models, 2) the temperature profile of the deep interior, and 3) the interpretation of the observed 3D seismic structure. First-principles calculations have emerged lately as a powerful tool for investigation of thermoelasticity of minerals at geophysically relevant conditions [e.g., *Wentzcovitch et al.,* 1993; *Karki et al.,* 1999]. Here, we adopted a lattice dynamical approach to determine some thermoelastic properties of **pv**, in particular, the thermal expansivity and the bulk modulus within the pressure-temperature (P-T) range of the LM. Some consequences for the inferred properties of this region are then investigated.

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2. Calculation and Result

Our approach exploited the volume dependence of the vibrational frequencies to determine the thermal contribution to the free energy within the quasi-harmonic approximation (QHA) from which all thermodynamic quantities were derived. The required phonon dispersions were obtained using density functional perturbation theory [*Baroni et al.*, 1987] within the local density and pseudopotential approximations. Details of phonon calculations and results can be found in *Karki et al.* [2000].

The QHA has widely been used to study the thermal properties of minerals at typical mantle conditions [*Isaak et al.,* 1992; *Anderson and Masuda,* 1994; *Chopelas,* 1996; *Gillet et al.*, 2000; *Karki et al.*, 1999]. In the absence of sufficient experimental data for comparison, the calculated behavior of thermal expansivity, $\alpha(T,P)$, is in itself an important criterion to judge the validity of the QHA. Particularly at low pressures, it tends to overestimate α at high T's when anharmonic effects are important. This usually occurs somewhere between the Debye and melting temperatures (as also shown by the second inflection point in α, see Fig. 1a), when the solid melts from the same phase. In the case of **pv**, the melting temperature is about 3000 K at 23 GPa and increases to 4500 K at 55 GPa [*Boehler*, 1996] so that we can anticipate the QHA to be valid over the entire P-T regime of the LM.

Table 1 shows that our calculated thermoelastic parameters for **pv** fall within the ranges of reported experimental values. The volume (V) at ambient conditions is 1% larger than the experimental volume and the bulk modulus (K_T = 247 GPa) is underestimated with respect to the experimental value (256 GPa with $K'_T = 3.9$) derived from information contained in several data sets [*Mao et al.*, 1991; *Wang et al.*, 1994; *Funamori et al.*, 1996; *Fiquet et al.*, 2000]. Our V and K_T calculated at $\approx$ 2 GPa and 300 K agree nearly perfectly with the experimental data at ambient conditions thus giving an estimate of the uncertainty in our calculations.

Fig. 1a displays the good agreement between calculated and directly measured thermal expansivities near ambient conditions [*Wang et al.*, 1994; *Ross and Hazen*, 1989; *Parise et al.*, 1990]. Above 400 K the reported trends for α differ for Fe-bearing [*Knittle et al.*, 1986; *Mao et al.*, 1991] and Fe-free [*Wang et al.*, 1994; *Fiquet et al.*, 2000; *Chopelas*, 1996; *Gillet et al.*, 2000] phases. Comparison with experiments on Fe-free **pv** above 400 K and P = 0 GPa is not straightforward either. The available experimental α's were derived either by extrapolating to 0 GPa the V-T data obtained at high pressures [*Wang et al.*, 1994; *Fiquet et al.*, 2000] or by using spectroscopic data on relatively few vibrational modes [*Chopelas*, 1996; *Gillet et al.*, 2000]. In contrast, comparisons are clearer in the thermodynamically stable regime. First,

our α displays good linear behavior. It also compares favorably with the direct results from recent finite temperature molecular dynamics simulations which account for anharmonic effects [*Oganov et al.*, 2000]. Last, the current results agree quite well also with those determined experimentally at 25 GPa [*Funamori et al.*, 1996] and with higher pressure data within the experimental uncertainties [*Fiquet et al.*, 2000] (Fig. 1a). Our results for the temperature derivative of the isothermal bulk modulus ($|(\partial K_T/\partial T)_P|$) at zero pressure is substantially lower than the value adopted for Fe-bearing **pv** [*Mao et al.*, 1991] but is close to the Fe-free-**pv** value [*Wang et al.*, 1994; *Fiquet et al.*, 2000] (Fig. 1b). With increasing pressure we predict both α and $|(\partial K_T/\partial T)_P|$ to decrease rapidly and the temperature effect on these quantities to be suppressed to a great extent.

3. Discussion

Below we discussed the implication of these results for: a) the temperature-depth ($T(z)$) profile and b) the possible thermal origin for lateral heterogeneities in the LM.

3.1. K_S and Temperature Profile

The predominantly convective nature of heat transport in the mantle has lead to the widely accepted view that the geotherm in this region should follow an isentrope [*Brown and Shankland*, 1981]. We investigated this hypothesis in two ways: a) comparing directly the calculated $K_S(z)$ of plausible compositional models along an the inferred isentrope with the bulk modulus profile in the LM, $K_{PREM}(z)$; b) extracting the temperature profiles required to match $K_S(z)$ for these models with $K_{PREM}(z)$. The two models considered are: 1) a chemically homogeneous pyrolitic mantle with 80 vol% **pv** and 20 vol% magnesiowüstite ((Mg,Fe)O) in the LM and 2) a stratified mantle with a chondritic LM consisting of 100 vol% **pv** [*Stixrude et al.*, 1992; *Wang et al.*, 1994; *Zhao and Anderson*, 1994]. Although a rigorous comparison would take into account the effects of Fe on the bulk moduli of **pv** and (Mg,Fe)O, these can probably be ignored as evidenced by experimental studies [*Mao et al.*, 1991; *Fei*, 1999]. Also, the presence of Al and Ca should not affect our conclusions (discussed later).

The isentropes ($T_S(z)$) for **pv** and MgO (Fig. 2's inset) were obtained by anchoring them to 1900 K at 670 km (23 GPa) which is reasonably well constrained based on dissociation of ringwoodite into **pv** and MgO [*Ito and Katsura,*, 1989]. The derived **pv**-isentrope (thick black line in the inset) is essentially identical to the LM adiabat proposed earlier by *Brown and Shankland* [1981]. Comparison between the calculated K_S for **pv** or pyrolite along the isentrope (thick and thin black lines in Fig. 2) with $K_{PREM}(z)$ shows that with increasing pressure their slopes deviate systematically from K_{PREM}'s for depths greater than 1,200 km.

We tentatively extracted the temperature profile ($T(z)$) required to match $K_S(z)$ with $K_{PREM}(z)$ for both compo-

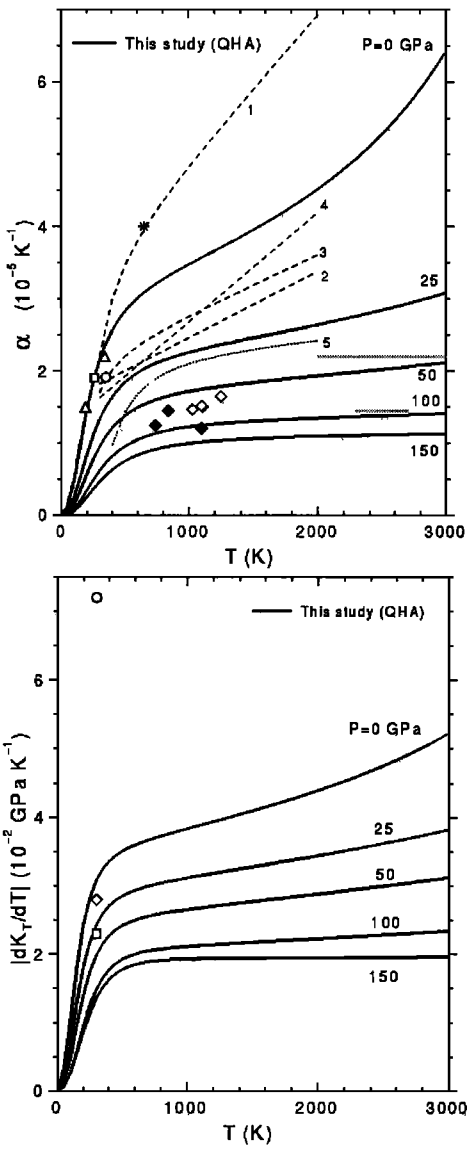

Figure 1. a) Calculated temperature dependence of the coefficient of thermal expansion (α) along several isobars. Grey lines are the results from molecular dynamics at 38 and 88 GPa [*Oganov et al.*, 2001]. Experimental results for Fe-bearing **pv** at zero pressure are denoted by star [*Knittle et al.*, 1986] and the dashed curve 1 [*Mao et al.*, 1991]. Those for pure **pv** are denoted by circle[*Wang et al.*, 1994], triangle [*Ross and Hazen*, 1989] and square [*Parise et al.*, 1990]. The dashed curves 2, 3 and 4 are the results inferred indirectly from experiments ([*Wang et al.*, 1994], [*Chopelas*, 1996] and [*Fiquet et al.*, 2000]). The high pressure data are denoted by the dotted curve 5 at 25 GPa [*Funamori et al.*, 1996]), by open diamonds in the 47 to 52 GPa range and by solid diamonds in the 88 to 94 GPa range [*Fiquet et al.*, 2000]. b) Calculated $|(\partial K/\partial T)_P|$ along the same isobars. Symbols are the zero pressure experimental data; circle [*Mao et al.*, 1991], square [*Wang et al.*, 1994], and diamond [*Funamori et al.*, 1996].

Table 1. Comparison of Calculated Thermoelastic Parameters of $MgSiO_3$ **pv** with Experimental Data

	Calc (300 K)	Calc (static)	Expt (300 K)
V (Å^3)	164.1	162.0	162.3[1], 162.5[2]
K_T (GPa)	247	259	253[1], 261[2]
$\frac{\partial K_T}{\partial P}$	3.97	4.01	3.9[1], 4[2]
$\frac{\partial^2 K_T}{\partial P^2}$ (GPa^{-1})	-0.016	-0.015	
$\frac{\partial K_T}{\partial T}$ (GPa K^{-1})	-0.031		-0.017[1], -0.023[3], -0.072[2]
$\frac{\partial^2 K_T}{\partial P \partial T}$ (10^{-4}K^{-1})	3.2		
α (10^{-5} K^{-1})	2.15		1.8[3], 2.2[2]
γ	1.61		1.4[1], 1.96[4]

[1] *Fiquet et al.* [2000]; [2] *Mao et al.* [1991]; [3] *Wang et al.* [1994]; [4] *Stixrude et al.* [1992]

sitions (Fig. 2's inset). These are lower bound estimates. Correction due to the intrinsic uncertainties in the calculated K_S (shown by grey stripes in Fig 2.) would shift $T(z)$ upwards for a pure **pv** model by 400 to 600 K across the LM. The possibility of super-adiabatic gradients approaching the core-mantle boundary [*Stacey*, 1992] or throughout the lower half LM [*da Silva et al.*, 2000] has previously been suggested. Similar deviations of extrapolated K_S of **pv** to LM conditions has often been hinted in other works as well [*Stixrude et al.*, 1992]. In particular, the semi-empirical analysis by *da Silva et al.*[2000] led to a similar conclusion. Here we confirmed based on fully first principles results that this feature is robust beyond numerical uncertainties and therefore must be meaningful.

Based on these profiles one might be tempted to favor the pyrolitic model with respect to the chondritic one. The argument against the latter is the associated high $T(z)$'s which are close or above the current estimate of the mantle solidus [*Boehler*, 1996] (see Fig.2's inset). However, the uncertainties in the absolute value of these profiles are, in reality, greater than shown by the error bars. The bulk modulus of Al-bearing **pv** ($\approx$ 5 mol% Al) is considerably smaller ($\approx$ 234 GPa) than that of pure **pv** [*Zhang and Weidner*, 1999] so $T(z)$ could shift downwards by as much as 300 K. Unless T has a significantly distinct effect on the Al-bearing phase or on $CaSiO_3$ ($\approx$ 6 vol%), the super-adiabatic nature of the inferred profile should not change. Such a profile would imply a small thermal boundary layer in the shallow LM, which is generally expected in a stratified mantle model. Accounting for the eventual presence of pyrope in the shallow LM would lower these profiles in that region and increase even further their super-adiabatic nature. Simultaneous comparisons of the shear modulus and density with PREM must be made for these scenarios to achieve a more consistent and complete description of the LM. Nevertheless, here we provided robust evidence that, irrespective of composition, a homogeneous and adiabatic LM model seems incompatible with PREM.

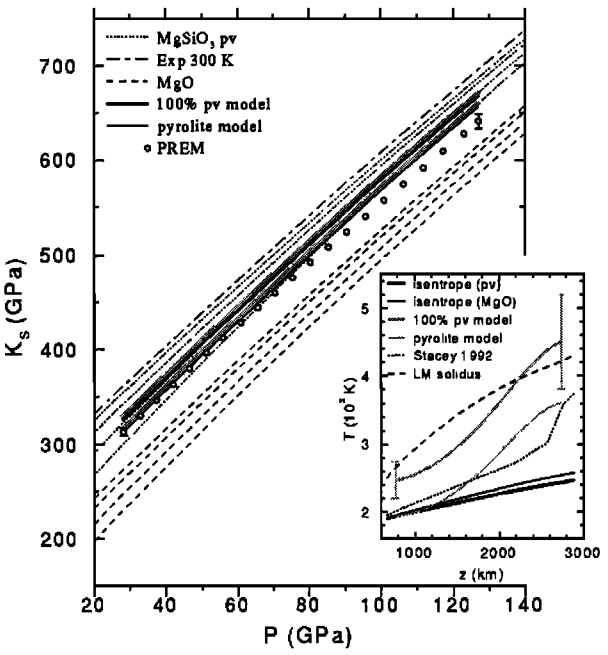

Figure 2. Pressure variations of the calculated adiabatic bulk modulus (K_S) of $MgSiO_3$ **pv** (dotted lines) and MgO (dashed lines) [*Karki et al.*, 1999] along 300, 1000, 2000 and 3000 K isotherms (from top to bottom). Thick solid line represents K_S of a 100 V% **pv** LM along the calculated **pv**-isentrope (thick black line in the inset) with the uncertainty shown by grey stripe. Thin solid line is K_S for pyrolite composition (80 V% **pv** and 20 V% MgO) with the uncertainty shown by grey stripe. Symbols are the seismic data (K_{PREM}) [*Dziewonski and Anderson*, 1981] with typical error bars shown at extreme points. Dash-dotted line is the experimental result for **pv** at 300 K. The inset shows the calculated isentropes for **pv** (thick black line) and for MgO (thin black line); and temperature-depth profiles inferred for **pv** (thick grey line) and pyrolite (thin grey line) LM compositions by comparing K_S with K_{PREM}. An earlier super-adiabatic geotherm is shown by a dashed line [*Stacey*, 1992], while the adiabatic geotherm of *Brown and Shankland* [1981] is indistinguishable from our **pv** isentrope (thick black line).

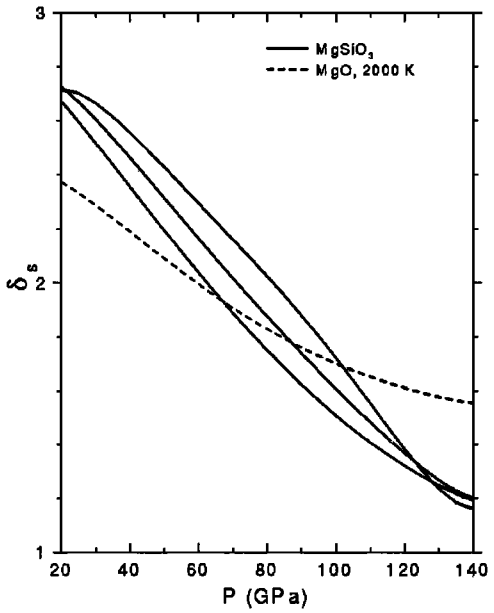

Figure 3. Pressure variation of the Anderson-Grüneisen parameter (δ_S) of $MgSiO_3$ **pv** along 1000, 2000 and 3000 K isotherms (solid lines from bottom to top) and MgO at 2000 K (dashed line) [*Karki et al.*, 1999].

3.2. δ_S and Lateral Heterogeneities

Lateral velocity heterogeneities expressed by

$$\nu = \left(\frac{\partial \ln V_S}{\partial \ln V_P}\right)_P, \tag{1}$$

can be caused by variations in temperature, composition, phase or all. The seismic value of this ratio rises from 1.7 at the top to ~3 towards the bottom of the LM (D'' layer) [*Robertson and Woodhouse*, 1996]. To the extent that these heterogeneities are of thermal origin, the observed 3D structure can be used to infer temperature inhomogeneities and be related to mantle flow. In this case, one can write [*Isaak et al.*, 1992]

$$\nu = \frac{1 + (4/3)(G/K_S)}{(\delta_S - 1)/(\Gamma - 1) + (4/3)(G/K_S)} \tag{2}$$

where δ_S is the "Anderson-Grüneisen" parameter

$$\delta_S = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P \tag{3}$$

indicating the isobaric variation of $K_S(T)$ with density ($\rho(T)$), and Γ is the equivalent parameter for the shear modulus ($G(T)$).

Eq. 2 indicates that ν increases with decreasing δ_S and with increasing Γ, more strongly so for smaller values of G/K_S. When $\delta_S = 1$, $\nu = 2.5\pm0.1$ irrespective of Γ, for $G/K_S = 0.5\pm0.05$ across the LM [*Dziewonski and Anderson*, 1981]. Our calculated δ_S decreases with increasing pressure remaining nearly independent of temperature (Fig. 3). Γ for **pv** is only known to be 6.5 near ambient conditions [*Sinelnikov et al.*, 1998] which yields $\nu \sim 1.4$ with $\delta_S = 3.2$ and $G/K_S = 0.68$ at ambient conditions. At LM temperatures anelastic effects on G should further increase Γ [*Karato*, 1993] and contribute to a more rapid increase of ν with depth. Therefore, for the predicted variation of δ_S in **pv** across the LM, i.e. $\sim$2.7 to $\sim$1.2, ν is expected to increase rapidly with depth suggesting that thermal contributions to lateral heterogeneities can be substantial. This is consistent with the behavior of ν previously predicted for MgO [*Agnon and Bukowinski*, 1990; *Isaak et al.*, 1992; *Karki et al.*, 1999].

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References

Agnon, A., and M. S. T Bukowinski, δ_S at high presure and $dlnV_S/dlnV_P$ in the lower mantle, *Geophys. Res. Lett.*, 17, 1149-1152, 1990.

Anderson, O. L., and K. Masuda, A thermoelastic method for computing thermal expansivity, α, vs. T along isobars for silicate perovskite, *Phys. Earth Planet. Int., 85*, 227-236, 1994.

Baroni, S., P. Giannozzi, and A. Testa, Green's-function approach to linear response in solid, *Phys. Rev. Lett., 58*, 1861-1864, 1987.

Boehler, R. Melting of mantle and core materials at very high pressures, *Phil. Trans. R. Soc. London, A354*, 1265-1278, 1996.

Brown, J. M., and T.J. Shankland, Thermodynamical parameters in the Earth as determined from seismic profiles, *Geophys. J. R. Astr. Soc., 66*, 579-596, 1981.

Chopelas, A., Thermal expansivity of lower mantle phases MgO and $MgSiO_3$ perovskite at high pressure, derived from spectroscopy, *Phys. Earth Planet. Inter., 98*, 3-16, 1996.

da Silva, C. R. S., R. M. Wentzcovitch, A. Patel, G. D. Price, and S. I. Karato. The composition and geotherm of the lower mantle: constraints from the elasticity of silicate perovskite, *Phys. Earth Planet. Inter., 118*, 103-109, 2000.

Dziewonski, A. M., and D. L. Anderson, Preliminary reference Earth model, *Phys. Earth Planet. Inter., 25*, 297-356, 1981.

Fei, Y., Effects of temperature and composition on the bulk modulus of (Mg,Fe)O, *Am. Mineral., 84*, 272-276, 1999.

Fiquet, G., A. Dewaele, D. Andrault, M. Kunz, and T. Bihan, Thermoelastic properties and crystal structure of $MgSiO_3$ perovskite at lower mantle pressure and temperature conditions, *Geophys. Res. Lett., 27*, 21-24, 2000.

Funamori, N., T. Yagi, W. Utsumi, T. Kondo, and T. Uchida, Thermoelastic properties of $MgSiO_3$ perovskite determined by in situ X-ray observations up to 30 GPa and 2000 K, *J. Geophys. Res, 101*, 8257-8269, 1996.

Gillet, P., I. Daniel, F. Guyot, J. Matas, and J. C., Chervin, A thermodynamic model for MgSiO3-perovskite derived from pressure, temperature and volume dependence of the Raman mode frequencies, *Phys. Earth Planet. Int., 117*, 361-384, 2000.

Isaak, D. G., O. L. Anderson, and R. E. Cohen, The relationship between shear and compressional velocities at high pressures: Reconciliation of seismic tomography and mineral physics, *Geophys. Res. Lett., 19*, 741-744, 1992.

Ito, E., and T. Katsura, A temperature profile of the mantle tranzition zone, *Geophys. Res. Lett., 16*, 425-428, 1989.

Karato, S.-i., Importance of anelasticity in the interpretation of seismic tomography, *Geophys. Res. Lett., 20*, 1623-1627 (1993).

Karki, B. B., R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, First-principles determination of elastic anisotropy and wave velocities of MgO at lower mantle conditions. *Science, 286*, 1705-1707, 1999.

Karki, B. B., R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, Ab initio lattice dynamics of $MgSiO_3$ perovskite at high pressure *Phys. Rev. B, 62*, 14750-14756, 2000.

Knittle, E., R. Jeanloz, and G. L. Smith, Thermal expansion of silicate perovskite and stratification of the earth's mantle, *Nature, 319*, 214-216, 1986.

Mao, H. K., R. J. Hemley, Y. Fei, J. F. Shu, L. C. Chen, A. P. Jephcoat, Y. Wu, and W. A. Bassett, Effect of pressure, temperature, and composition on lattice parameters and density of (Fe,Mg)SiO_3-perovskites to 30 GPa, *J. Geophys. Res., 96*, 8069-1079, 1991.

Oganov, A. R., J. P. Brodholt, and G. D. Price, Ab initio elasticity and thermal equation of state of MgSiO3 perovskite, *Earth and Planet. Sci. Lett., 184*, 555-560, 2001.

Parise, J. B., Y. Wang, A. Yeganeh-Haeri, D. E. Cox, and Y. Fei, Crystal structure and thermal expansion of (Mg,Fe)SiO_3 perovskite, *Geophys. Res. Lett., 17*, 2089-2092, 1990.

Robertson, G. S., and J. H. Woodhouse, Ratio of relative S to P velocity heterogeneity in the lower mantle, *J. Geophys. Res., 101*, 20041-20052, 1996.

Ross, N. L., and R. M. Hazen, Single crystal X ray diffraction study of $MgSiO_3$ perovskite from 77 to 400 K, *Phys. Chem. Mineral., 17*, 228-237, 1989.

Sinelnikov, Y. D., G. Chen, D. R. Neuville, M. T. Vaughan, and R. C. Liebermann, Ultrasonic shear wave velocities of $MgSiO_3$ perovskite at 8 GPa and 800 K and lower mantle composition, *Science, 281*, 677-679, 1998.

Stacey, F. D. *Physics of the Earth*, 459, 3rd ed., Brookfield Press, Queensland, 1992.

Stixrude, L., R. J. Hemley, Y. Fei, Y., and H.-K. Mao, Thermoelasticity of silicate perovskite and magnesiowüstite and the stratification of the Earth's mantle, *Science, 257*, 1099-1101, 1992.

Wang, Y., D. J. Weidner, R. C. Liebermann, and Y. S. Zhao, P-V-T equation of state of (Mg,Fe)SiO_3 perovskite. Constraints on composition of the lower mantle, *Phys. Earth Planet. Inter., 83*, 13-40, 1994.

Wentzcovitch, R. M., J. L. Martins, and G. D. Price, *Ab initio* Molecular dynamics with variable cell shape: application to $MgSiO_3$-perovskite, *Phys. Rev. Lett., 70*, 635-638, 1993.

Zhang, J., and D. J. Weidner, Thermal equation of state of aluminium-enriched silicate perovskite, *Science, 284*, 782-782, 1999.

Zhao, Y. S., and D. L. Anderson, Mineral physics constraints on the chemical composition of the Earth's lower mantle, *Phys. Earth Planet. Inter., 85*, 273-292, 1994.

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