

From thermodynamics to geodynamics: An overview of the geophysical thermodynamics of phase relations

Craig R. Bina



Dept. of Earth and Planetary Sciences
Northwestern University
Evanston, Illinois, U.S.A.

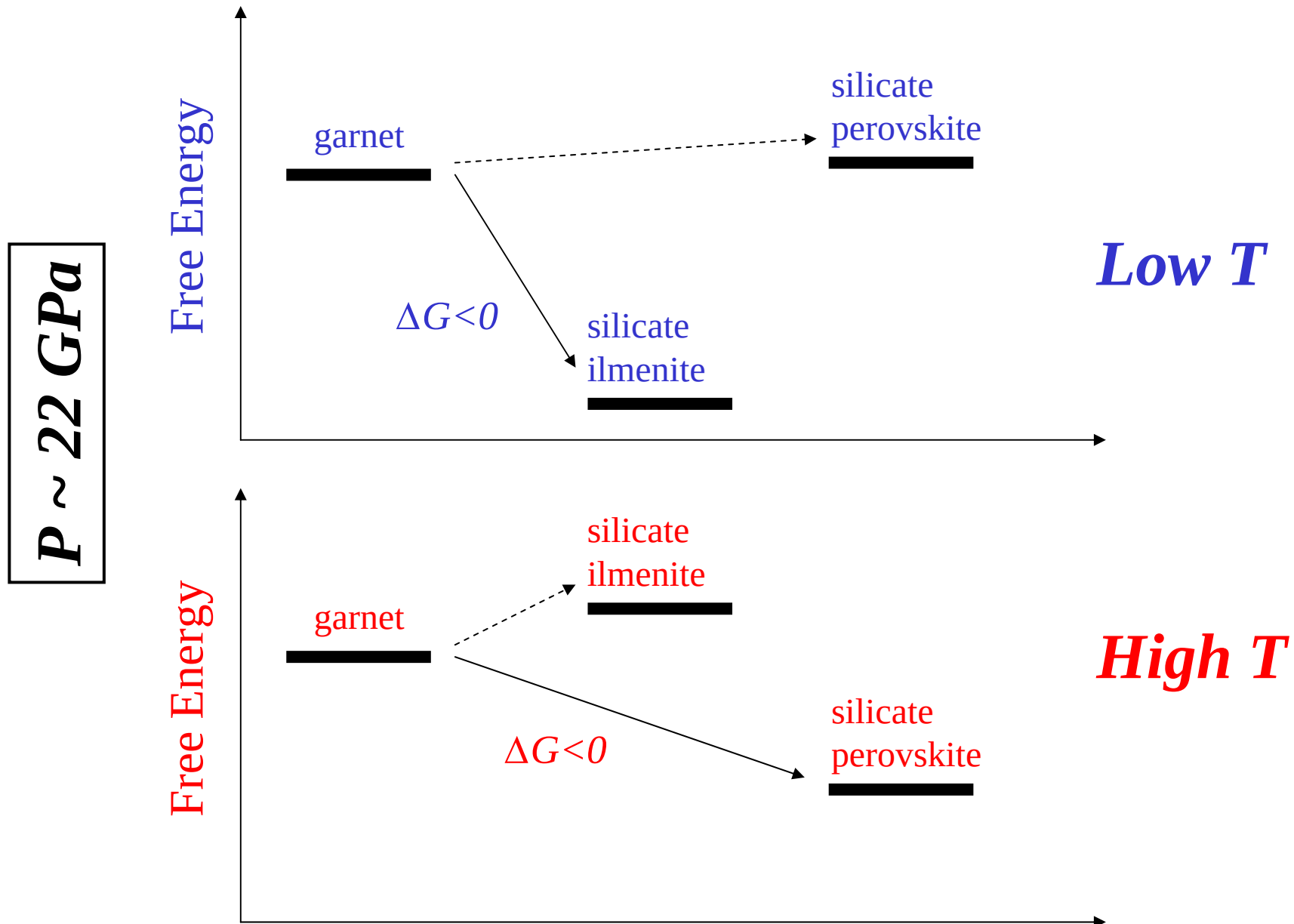


*Katedra geofyziky
Matematicko-fyzikální fakulta
Univerzita Karlova v Praze*

*přednášky na podzim 2011
5. lekce 9.11.*

Temperature-Dependent Changes in Phase Relations

Silicate ilmenite becomes stable, between garnet and silicate perovskite, at low T .



(cf. Irifune and Ringwood [1987], Irifune et al. [1996])

Temperature-Dependent Changes in Phase Relations

Silicate ilmenite becomes stable, between garnet and silicate perovskite, at low T.

Energy

$$G = H - TS$$

What does this say about entropies?

$$S_{pv} > S_{il}$$

Low T

garnet

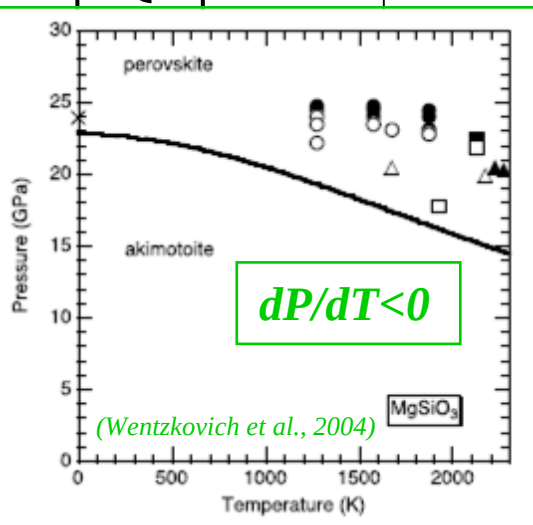
silicate perovskite

$$\Delta G < 0$$

silicate ilmenite

What does this say about Clapeyron slopes?

$$dP/dT = \Delta S / \Delta V$$



net

silicate ilmenite

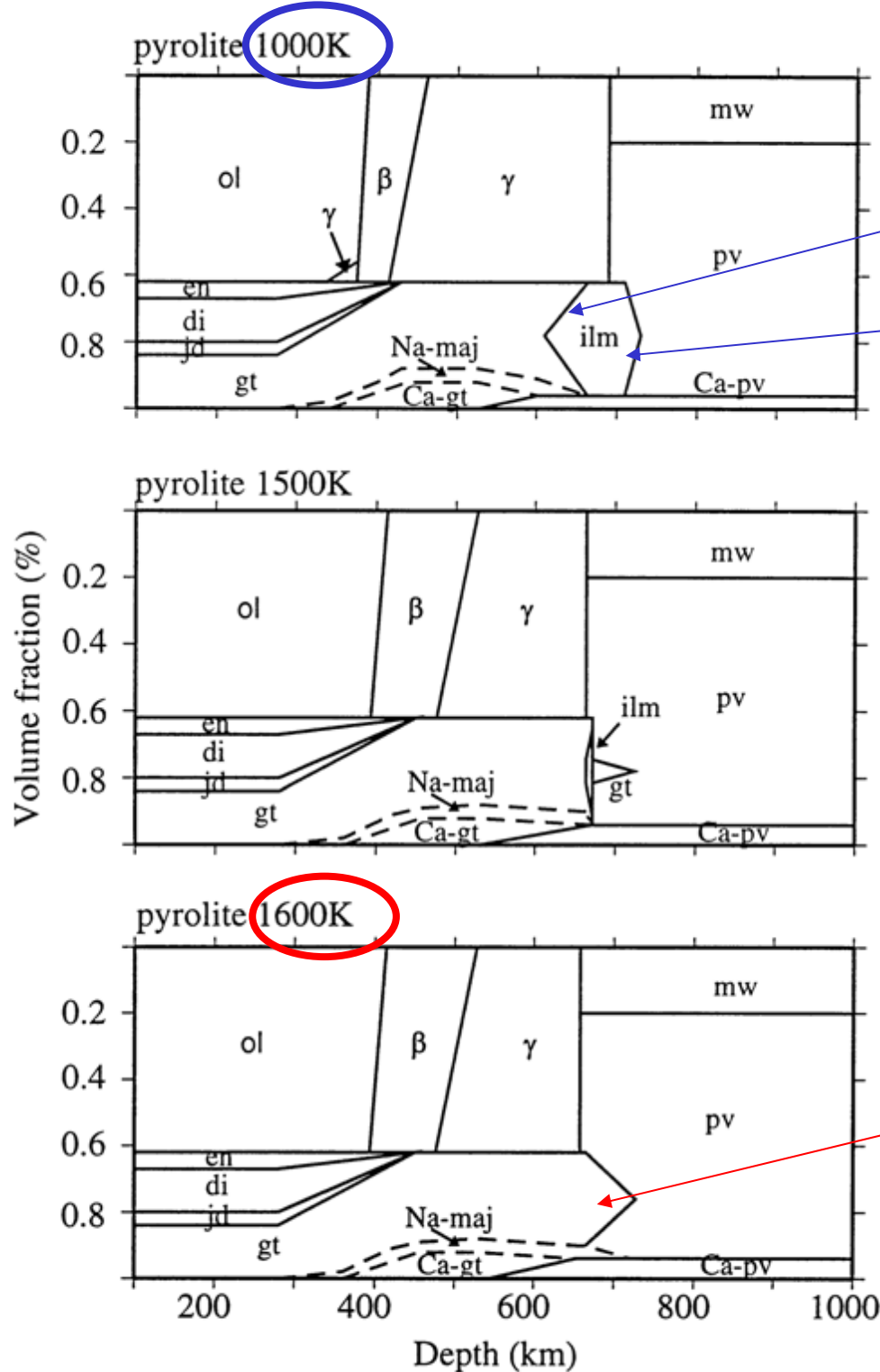
$$\Delta G < 0$$

silicate perovskite

High T

(cf. Irifune and Ringwood [1987], Irifune et al. [1996])

Silicate Ilmenite Stability



gt → il

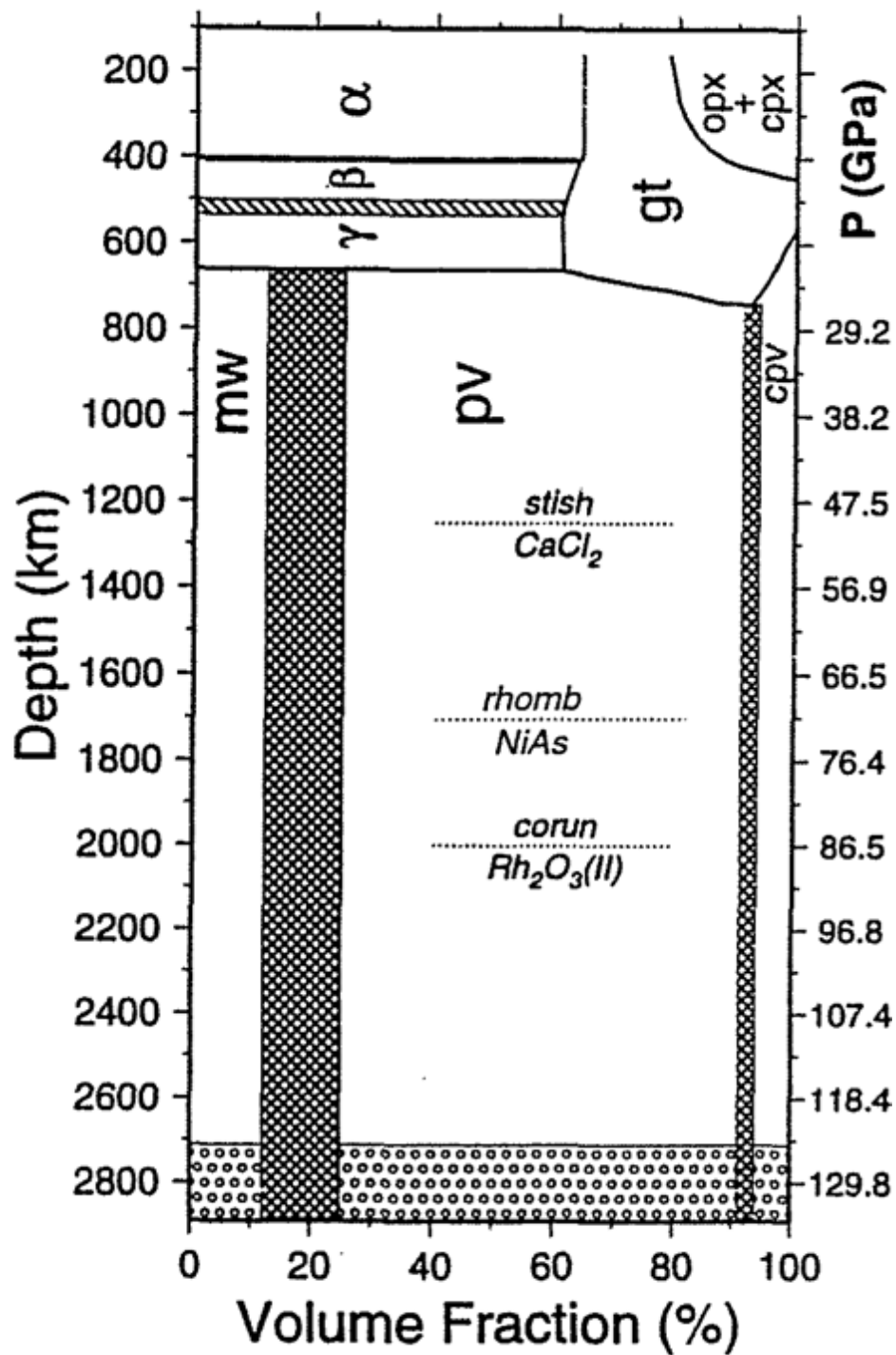
il → pv

cold

Volumic proportions of minerals and phases present in the pyrolite composition as a function of depth, along the 1000 K (top) and 1500 K (middle) and 1600 K (bottom) adiabats. Dashed lines give the proportions of ‘virtual phases’, which are part of the garnet solid solution. en: enstatite; di: diopside; jd: jadeite; Ca-gt: Ca-garnet; Na-maj: Na-majorite; other symbols are defined in Fig. 1 and Fig. 2.

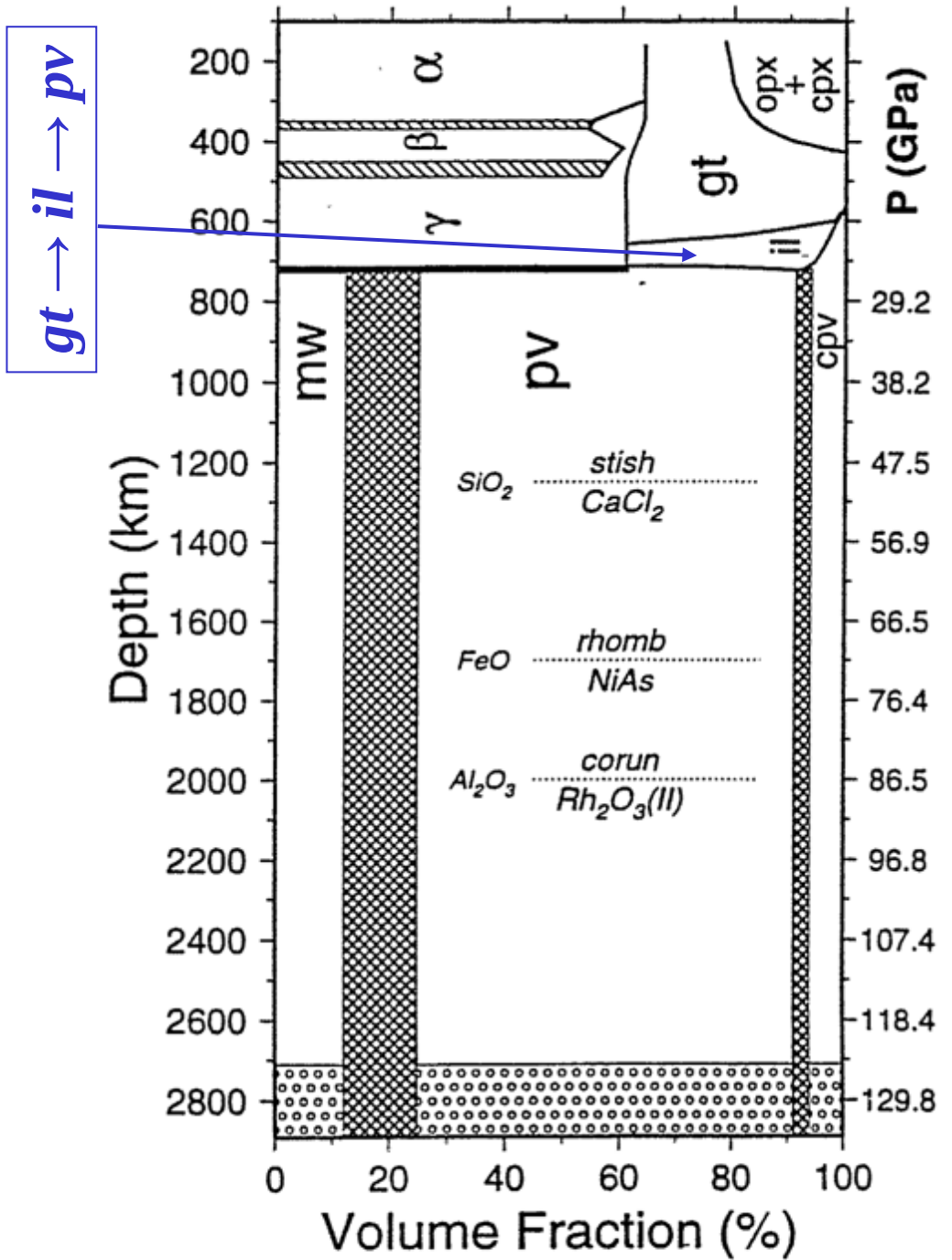
gt → pv

(Figure 3 of Vacher et al., 1998)



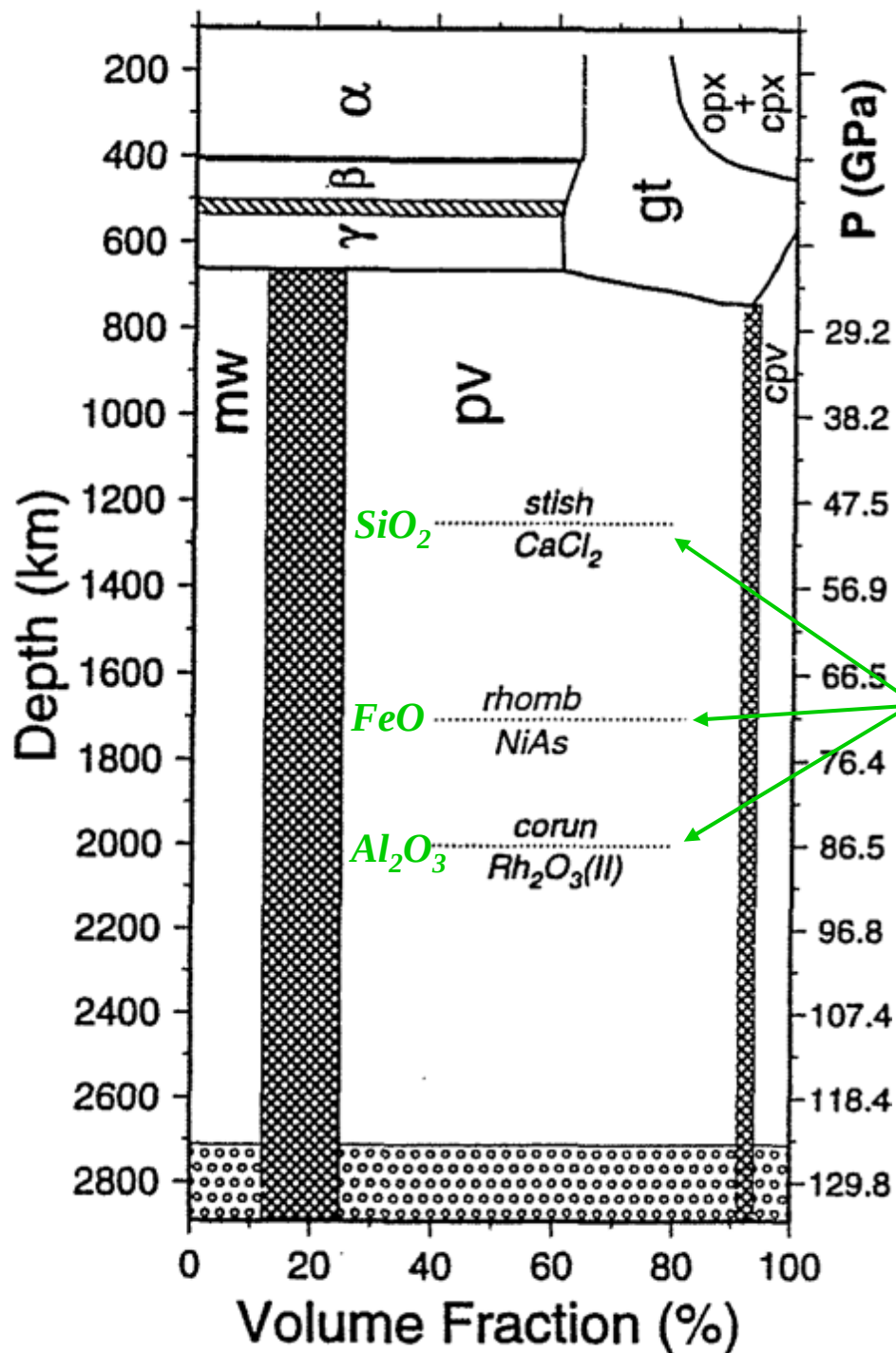
(mantle)

(from Figure 12 of Bina, 1998)



(subduction zones)

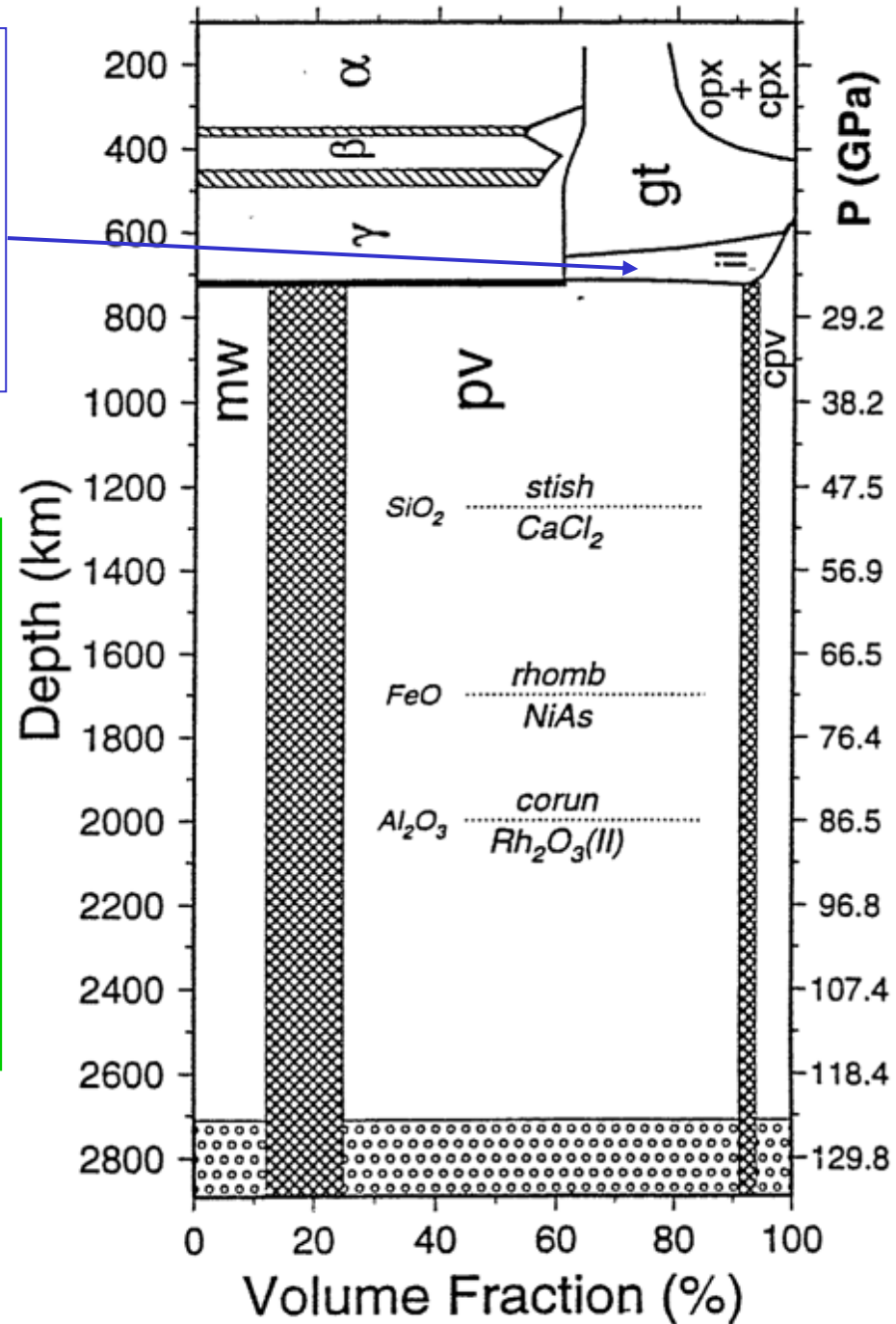
cold



(mantle)

(from Figure 12 of Bina, 1998)

Oxide transitions



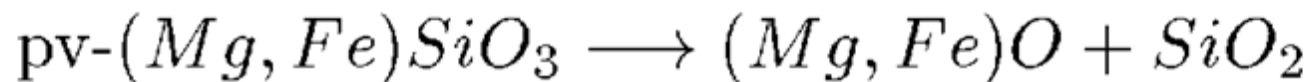
(subduction zones)

cold

PHASE DESTABILIZATION

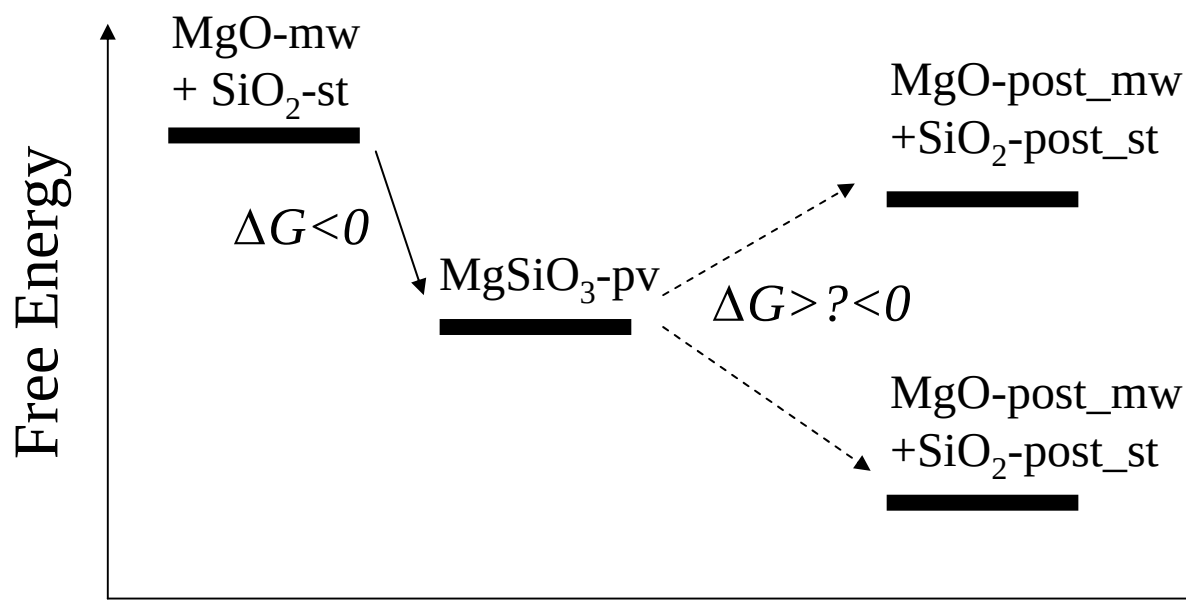
Why should we care about oxide transitions?

Disproportionation (breakdown) reaction:

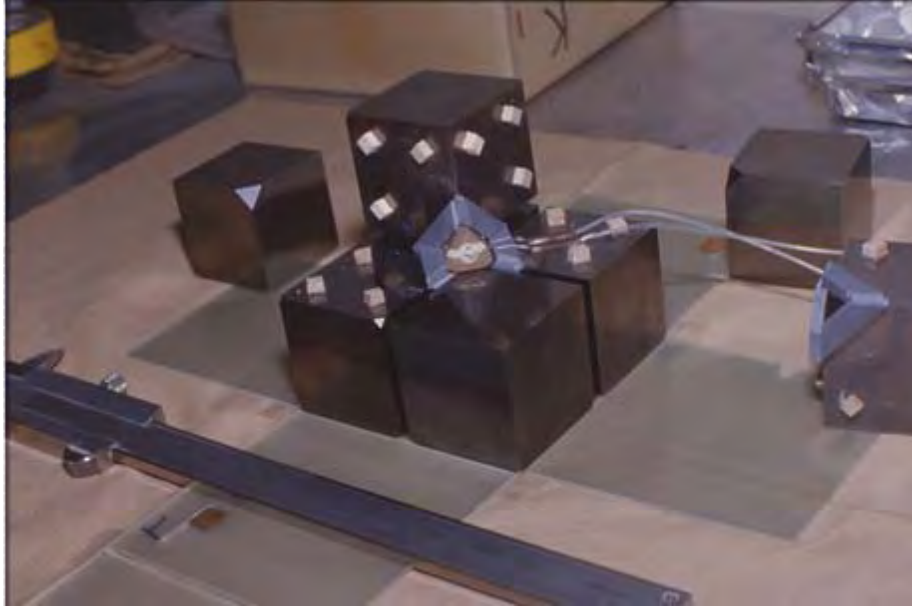


Assemblage (pv or oxides) with minimum free energy is stable.

[Note: Phase transitions in oxides can destabilize perovskite, even when free oxides are not present.]



The “post-perovskite” (pv→PPv) transition in (Mg,Fe,Al)SiO₃ may be related to the oxide cor→Rh₂O₃(II)→PPv transitions in Al₂O₃ [Tsuchiya et al., 2005; Tsuchiya and Tsuchiya, 2008]!



**Determining Phase
Stability: $f(P,T,X)$**

Extrapolating/Interpolating Phase Stability: $f(P, T, X)$

EQUATIONS GOVERNING CHEMICAL EQUILIBRIUM

Minimization of Gibbs Free Energy (Equilibrium Equations):

$$\text{Find } \{X_i^\phi, X_j^\phi, \dots, X_i^\psi, X_j^\psi, \dots\}$$

such that G is minimized at P and T

$$G(P, T, X_i^\phi, X_j^\phi, \dots) = \sum_{i, \phi} N_i^\phi \mu_i^\phi(P, T, X_i^\phi, X_j^\phi, \dots)$$

$$\text{for fixed } N_i = \sum_{\phi} N_i^\phi \quad \text{subject to } 0 \leq X_i^\phi \leq 1$$

where the chemical potentials have the form:

$$\begin{aligned} \mu_i^\phi(P, T, X_i^\phi, X_j^\phi, \dots) = & {}^o h_i^\phi(P_0, T_0) + \int_{T_0}^T {}^o c_{P_i}^\phi(P_0, \hat{T}) d\hat{T} \\ & - T \left({}^o s_i^\phi(P_0, T_0) + \int_{T_0}^T \frac{{}^o c_{P_i}^\phi(P_0, \hat{T})}{\hat{T}} d\hat{T} \right) \\ & + \int_{P_0}^P {}^o v_i^\phi(\hat{P}, T) d\hat{P} + RT \ln a_i^\phi(P, T, X_i^\phi, X_j^\phi, \dots) \end{aligned}$$

$$P(V, T) = \int \left(\frac{\partial P}{\partial V} \right)_T dV + \int \left(\frac{\partial P}{\partial T} \right)_V dT$$

$$P(V, T) = \int_{V_0}^V \left(\frac{-K_T}{\hat{V}} \right)_{T_0} d\hat{V} + \int_{T_0}^T \left(\frac{\gamma}{\hat{V}} C_V \right)_V d\hat{T} = P_{\text{cold}} + P_{\text{thermal}}$$

$$P_{\text{cold}} = 3K_{T0} f(1 + 2f)^{5/2} (1 - \xi f)$$

$$f \equiv \frac{1}{2} [(V_0 / V)^{2/3} - 1] \quad \xi \equiv -\frac{3}{4} (K_{T0}' - 4)$$

$$P_{\text{thermal}} = \frac{\gamma_D}{V} E_{\text{th}}(V, T)$$

$$E_{\text{th}}(V, T) \equiv 9nRT \left(\frac{\theta_D}{T} \right)^{-3} \cdot \int_0^{\theta_D/T} \frac{t^3}{e^t - 1} dt$$

$$\theta_D \equiv \theta_{D0} (V_0 / V)^{\gamma_0} \quad \gamma_D \equiv \gamma_{D0} (V_0 / V)^{-\alpha}$$

Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$

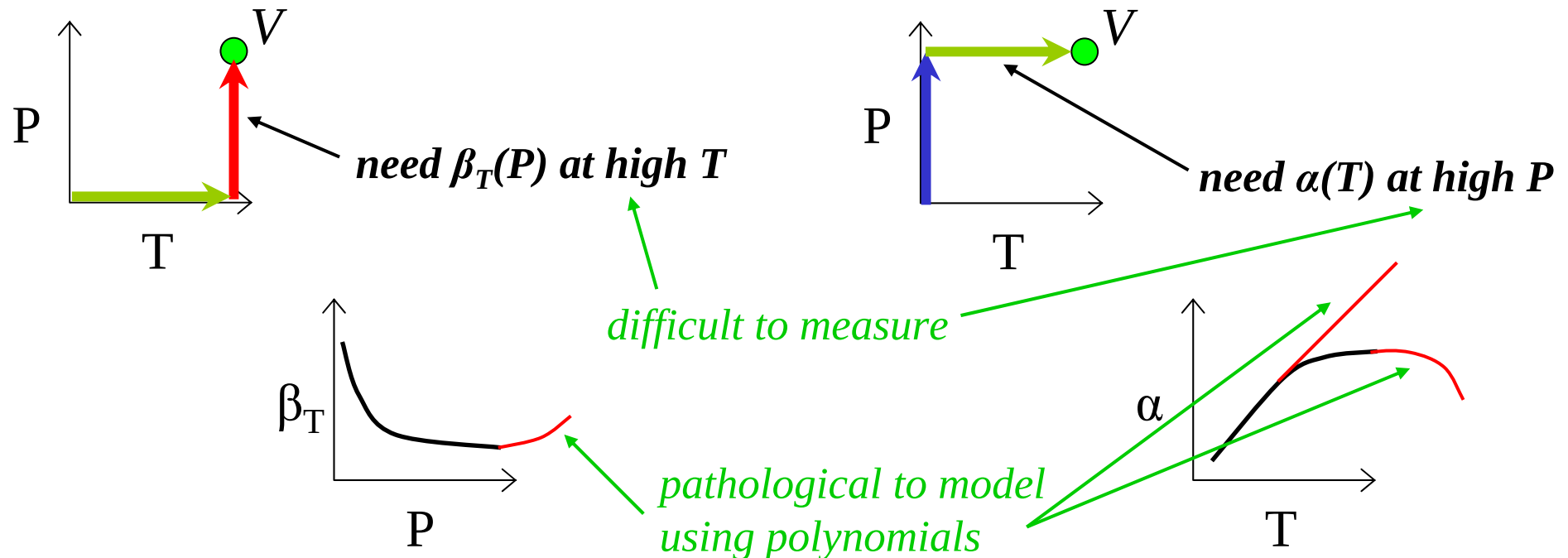
We can correct H and S to high T using $C_p(T)$.

How can we correct V to high P and T ?

$V(P,T)$:

$$(1/V)(\partial V/\partial T)_P = \alpha \quad (\text{thermal expansivity})$$

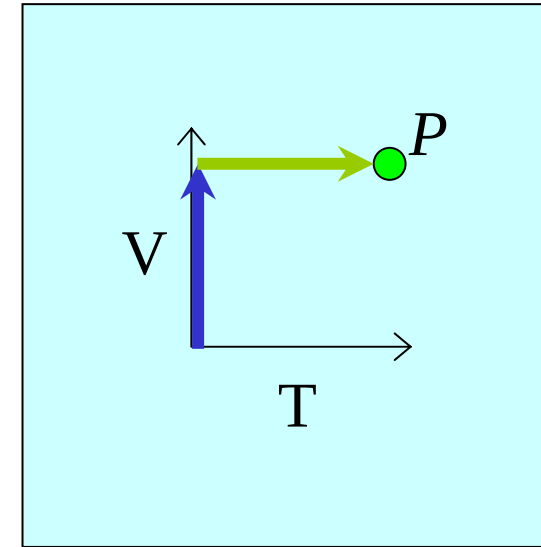
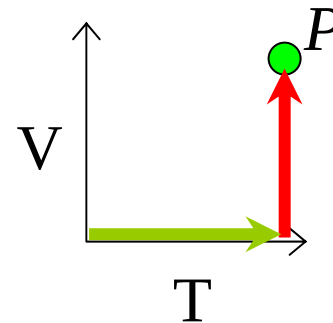
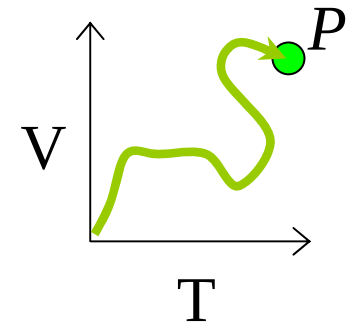
$$(-1/V)(\partial V/\partial P)_T = \beta_T \quad (\text{isothermal compressibility})$$



Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$

$$P(V, T) = \int \left(\frac{\partial P}{\partial V} \right)_T dV + \int \left(\frac{\partial P}{\partial T} \right)_V dT$$

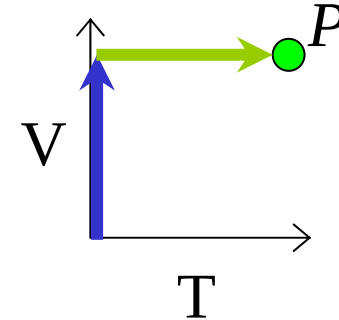
$$P(V, T) = \int_{V_0}^V \left(\frac{-K_T}{\hat{V}} \right)_{T_0} d\hat{V} + \int_{T_0}^T \left(\frac{\gamma}{V} C_V \right)_{\hat{V}} d\hat{T} = P_{\text{cold}} + P_{\text{thermal}}$$



Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$

$$P(V,T) = \int \left(\frac{\partial P}{\partial V} \right)_T dV + \int \left(\frac{\partial P}{\partial T} \right)_V dT$$

$$P(V,T) = \int_{V_0}^V \left(\frac{-K_T}{\hat{V}} \right)_{T_0} d\hat{V} + \int_{T_0}^T \left(\frac{\gamma}{V} C_V \right)_V d\hat{T} = P_{\text{cold}} + P_{\text{thermal}}$$



(isothermal bulk modulus)

$$P_{\text{cold}} = 3K_{T0} f(1 + 2f)^{5/2} (1 - \zeta f)$$

$$f \equiv \frac{1}{2} [(V_0 / V)^{2/3} - 1] \quad \zeta \equiv -\frac{3}{4} (K_{T0}' - 4)$$

Isothermal: K_{T0}, K'_{T0}

(isothermal P-derivative of bulk modulus)

$$P_{\text{thermal}} = \frac{\gamma_D}{V} E_{\text{th}}(V,T)$$

$$E_{\text{th}}(V,T) \equiv 9nRT \left(\frac{\theta_D}{T} \right)^{-3} \cdot \int_0^{\theta_D/T} \frac{t^3}{e^t - 1} dt$$

(isochoric Debye temperature)

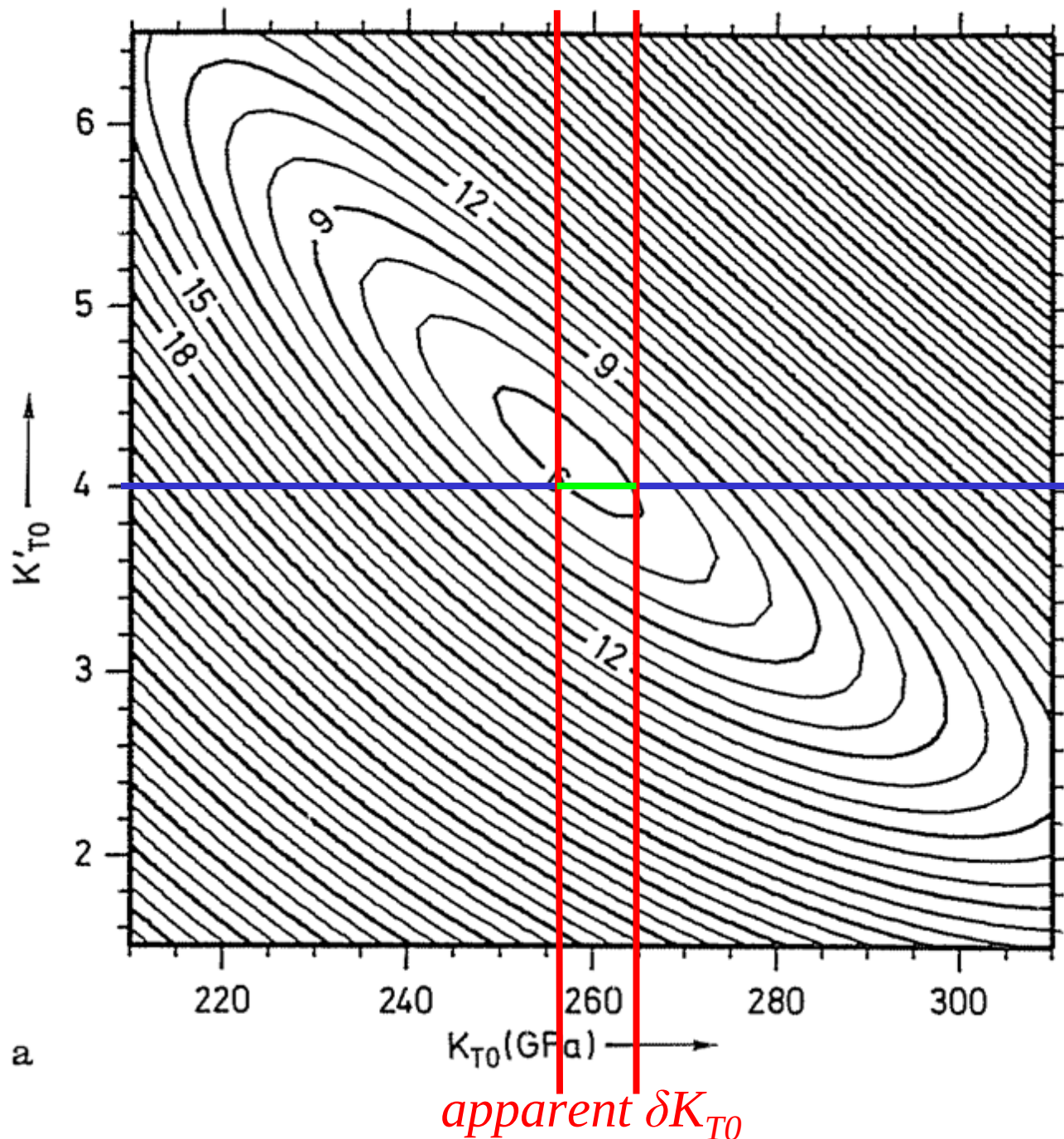
Diathermal: Θ_0, γ_0, q
(isochoric)

(isochoric Gruneisen parameter)

(q value)

$$\theta_D \equiv \theta_{D0} (V_0 / V)^{\gamma_0} \quad \gamma_D \equiv \gamma_{D0} (V_0 / V)^{-q}$$

Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$



Correlated uncertainties:

K_{T0} vs. K'_{T0}

fix $K'_{T0}=4$

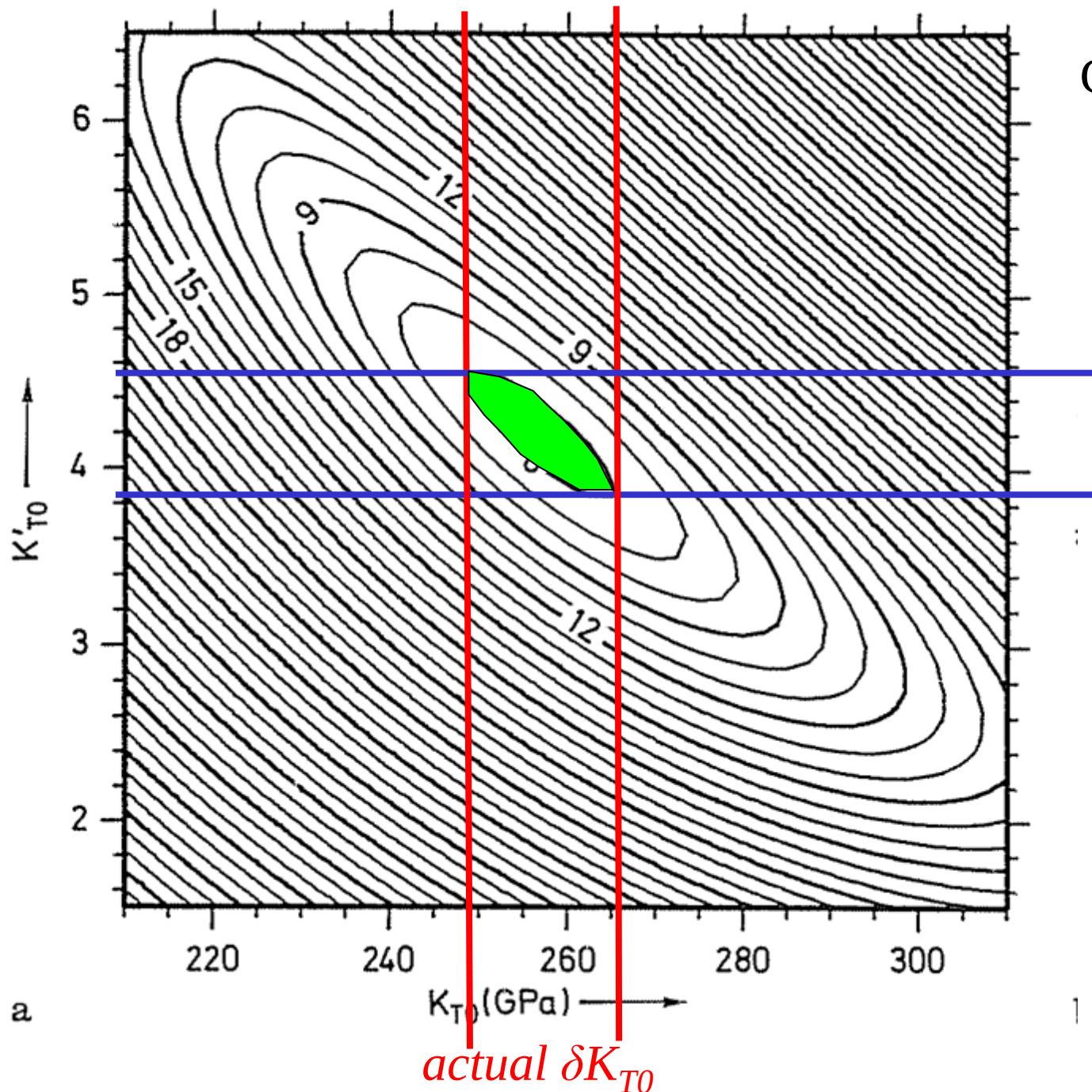
Contours of RMS misfit showing sections through five-dimensional hyper-ellipsoid about best-fit equation of state (Table 1, line 1). Four panels give complete illustration of parameter trade-offs. Contour values are of χ where the normal estimator χ^2 is given by

$$\frac{1}{N} \sum_{i=1}^N \frac{1}{2} (\Delta P_i / \sigma_i)^2 \text{ for } \Delta P_i = P_i^{\text{expt}}(V_i, T_i) - P_i^{\text{calc}}(V_i, T_i)$$

with σ_i arbitrarily fixed at 0.1 GPa.

(Figure 2a of Bina, 1996)

Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$



Correlated uncertainties:

K_{T0} vs. K'_{T0}

actual $\delta K'_{T0}$

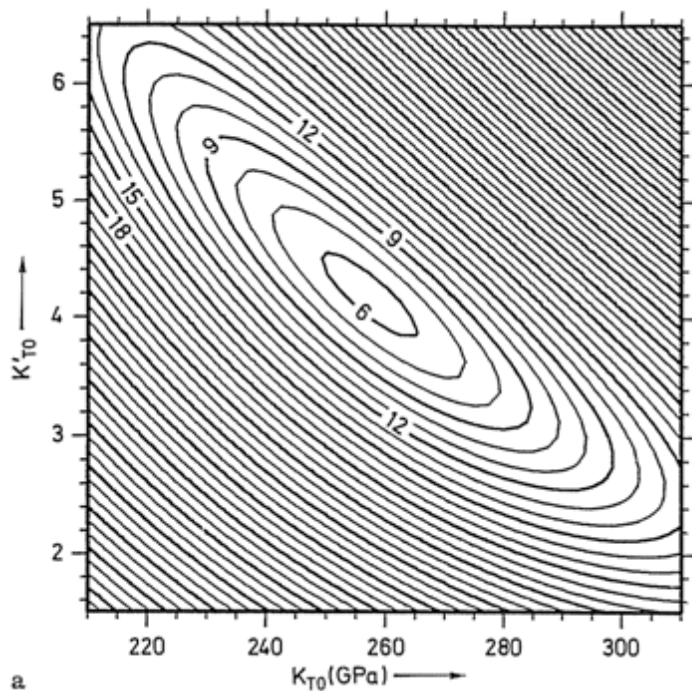
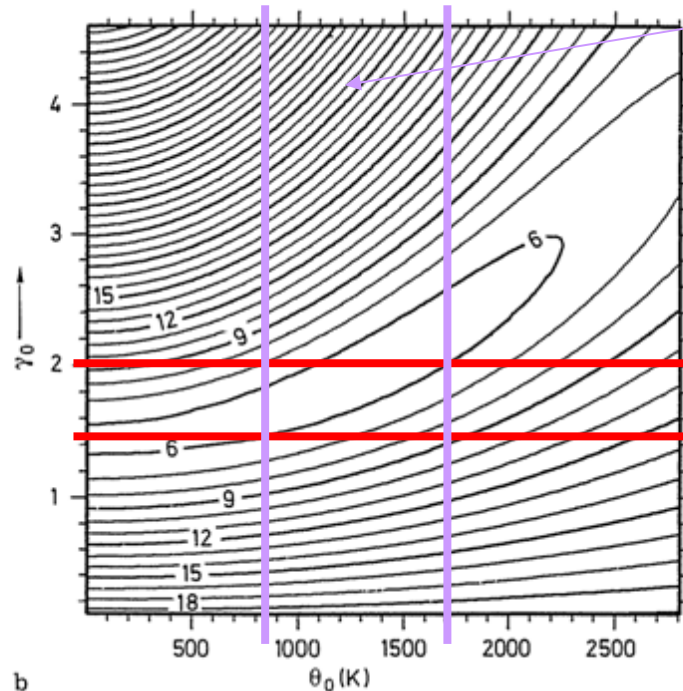
Contours of RMS misfit showing sections through five-dimensional hyper-ellipsoid about best-fit equation of state (Table 1, line 1). Four panels give complete illustration of parameter trade-offs. Contour values are of χ where the normal estimator χ^2 is given by

$$\frac{1}{N} \sum_{i=1}^N \frac{1}{2} (\Delta P_i / \sigma_i)^2 \text{ for } \Delta P_i = P_i^{\text{exp}}(V_i, T_i) - P_i^{\text{calc}}(V_i, T_i)$$

with σ_i arbitrarily fixed at 0.1 GPa.

(Figure 2a of Bina, 1996)

Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$



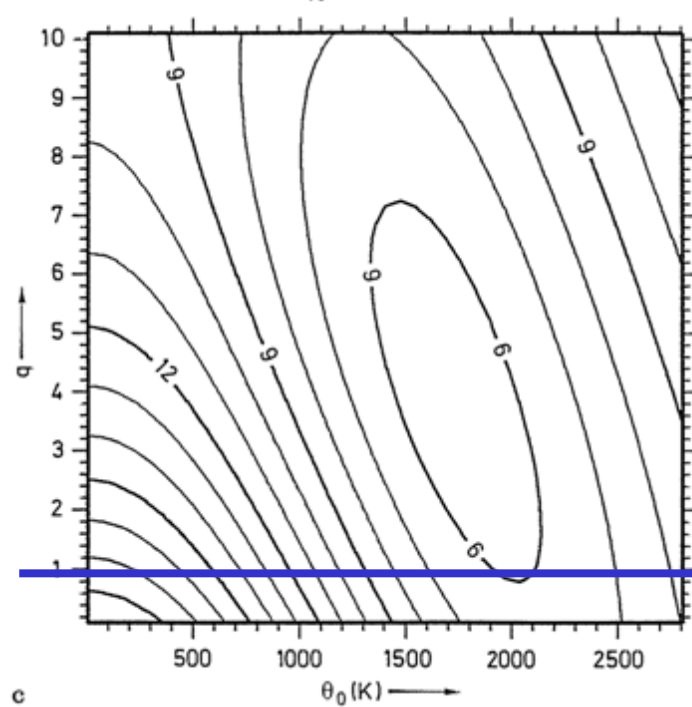
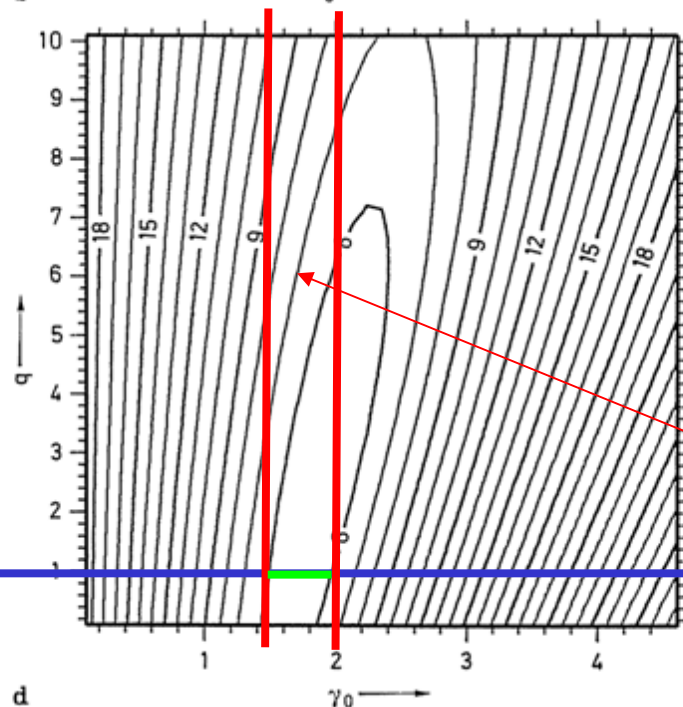
Correlated uncertainties:

K_{T0} vs. K'_{T0}

Θ_0 vs. γ_0

γ_0 vs. q

Θ_0 vs. q



Contours of RMS misfit showing sections through five-dimensional hyper-ellipsoid about best-fit equation of state (Table 1, line 1). Four panels give complete illustration of parameter trade-offs. Contour values are of χ where the normal estimator χ^2 is given by

$$\frac{1}{N} \sum_{i=1}^N \frac{1}{2} (\Delta P_i / \sigma_i)^2 \text{ for } \Delta P_i = P_i^{\text{expt}}(V_i, T_i) - P_i^{\text{calc}}(V_i, T_i)$$

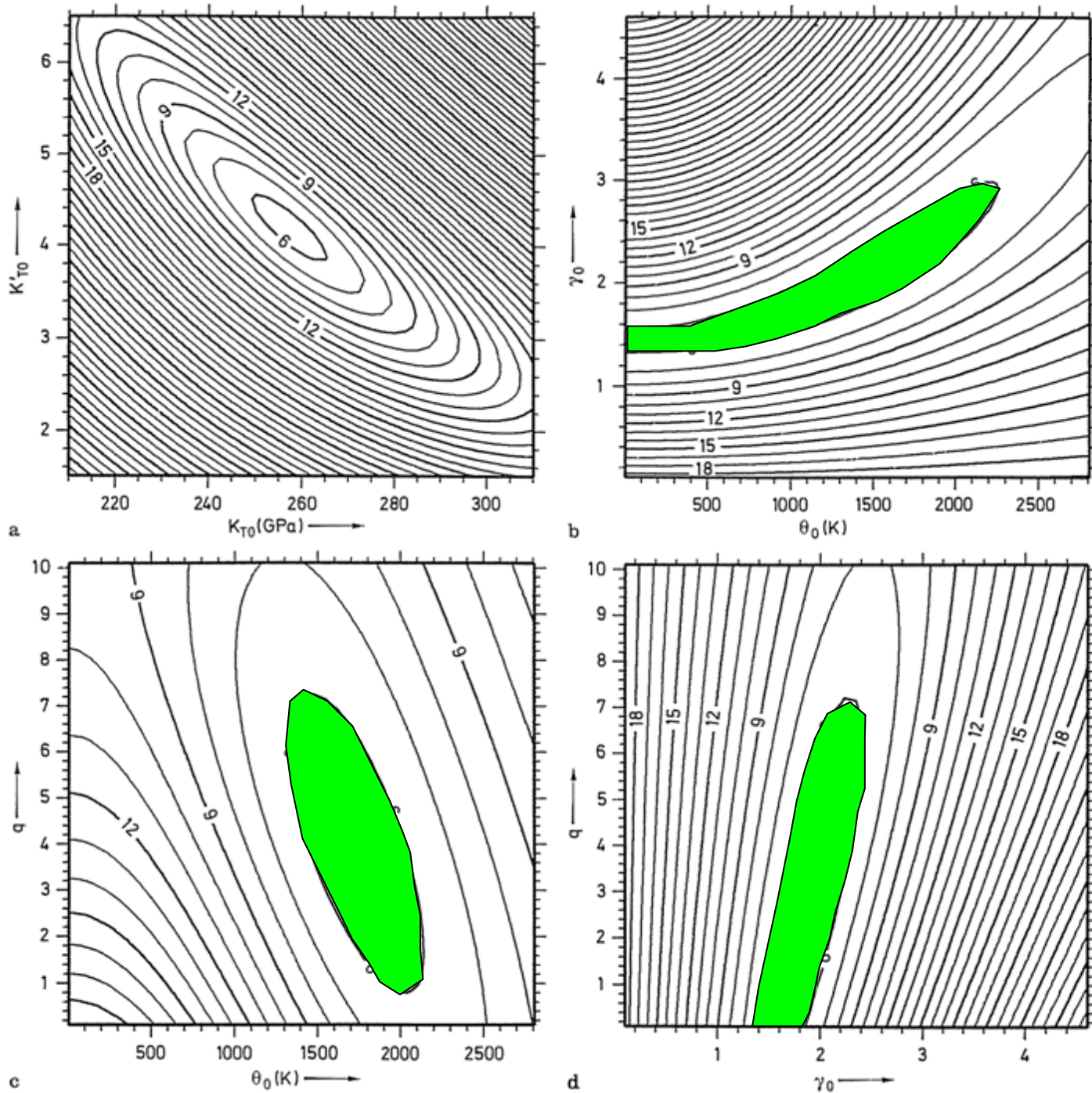
with σ_i arbitrarily fixed at 0.1 GPa.

apparent $\delta\gamma_0$

fix $q=1$

(Figure 2 of Bina, 1996)

Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$



Correlated uncertainties:

K_{T0} vs. K'_{T0}

Θ_0 vs. γ_0

γ_0 vs. q

Θ_0 vs. q

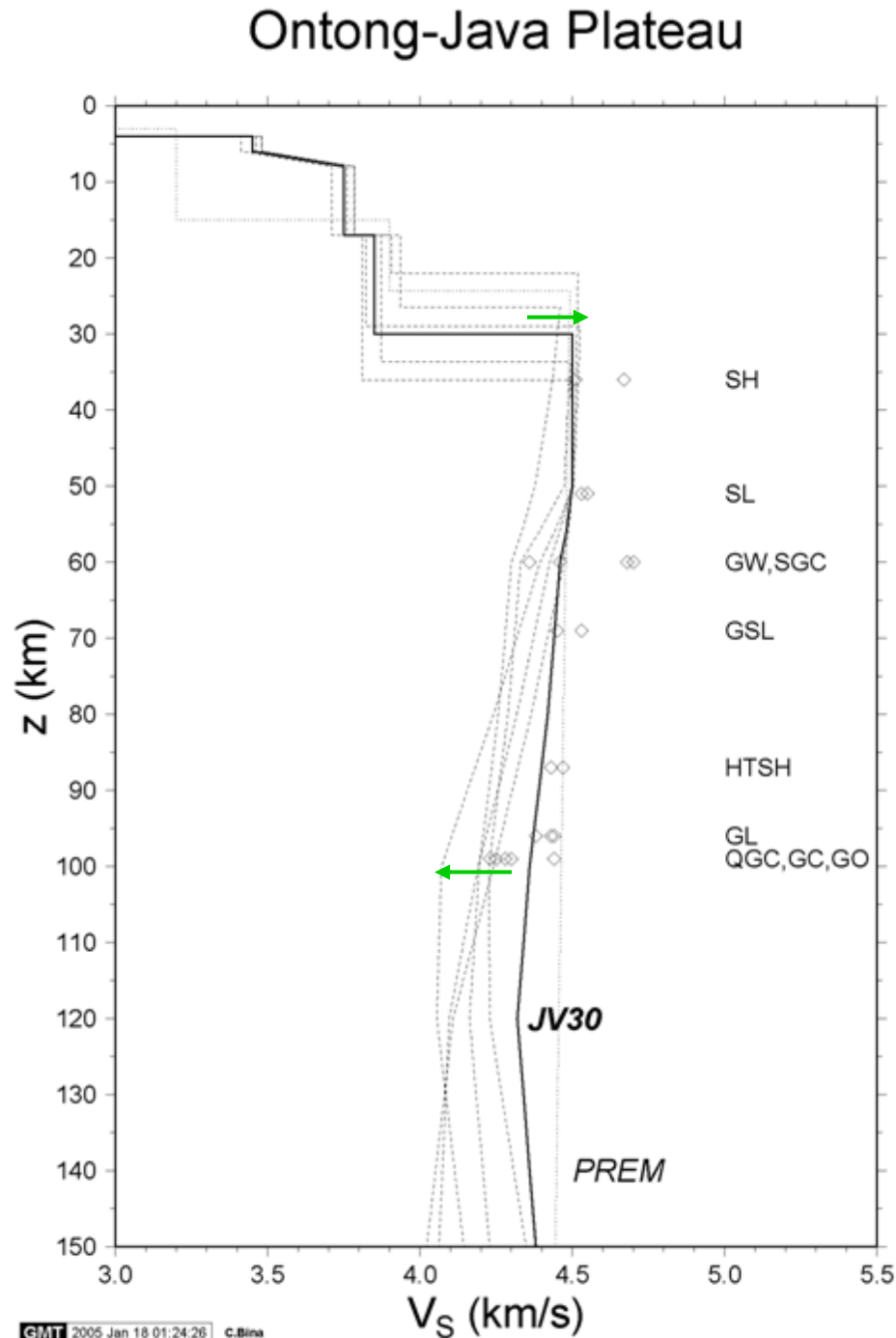
Contours of RMS misfit showing sections through five-dimensional hyper-ellipsoid about best-fit equation of state (Table 1, line 1). Four panels give complete illustration of parameter trade-offs. Contour values are of χ where the normal estimator χ^2 is given by

$$\frac{1}{N} \sum_{i=1}^N \frac{1}{2} (\Delta P_i / \sigma_i)^2 \text{ for } \Delta P_i = P_i^{\text{exp}}(V_i, T_i) - P_i^{\text{calc}}(V_i, T_i)$$

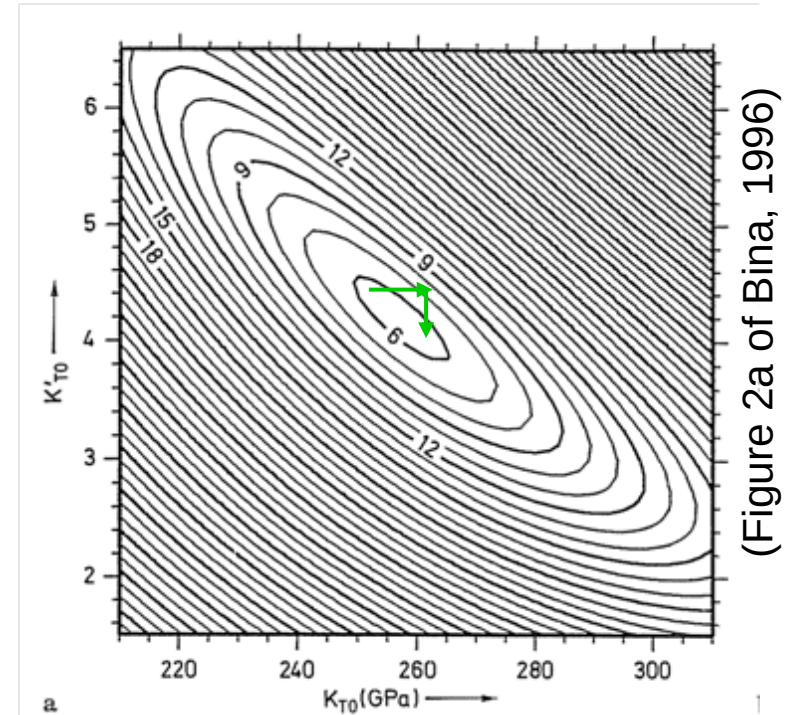
with σ_i arbitrarily fixed at 0.1 GPa.

(Figure 2 of Bina, 1996)

Thermoelastic Equations of State: $V(P,T)$ or $P(V,T)$



(Figure from Bina et al., 2005)



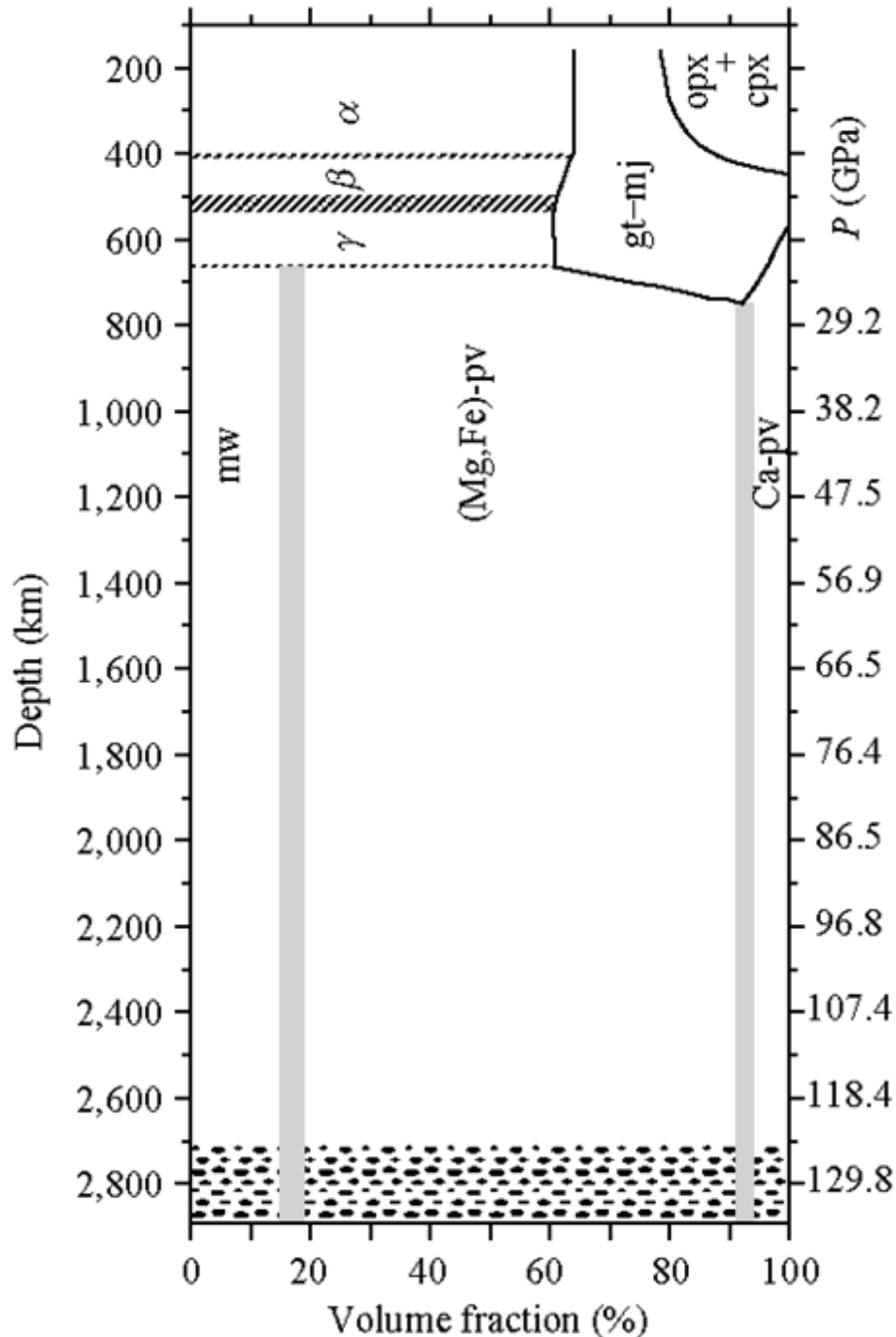
(Figure 2a of Bina, 1996)

Correlated uncertainties in EoS are similar to those in seismology; a change in one parameter requires a change in another. For example:

K_{T0} vs. K'_{T0}
 $V_S(30 \text{ km})$ vs. $V_S(100 \text{ km})$

These are not just simple error bars.

Inverting seismological profiles for lower mantle bulk composition



An application of thermoelastic equations of state

minimize $f(X)$: $(\rho^{EoS} - \rho^{seism})^2$

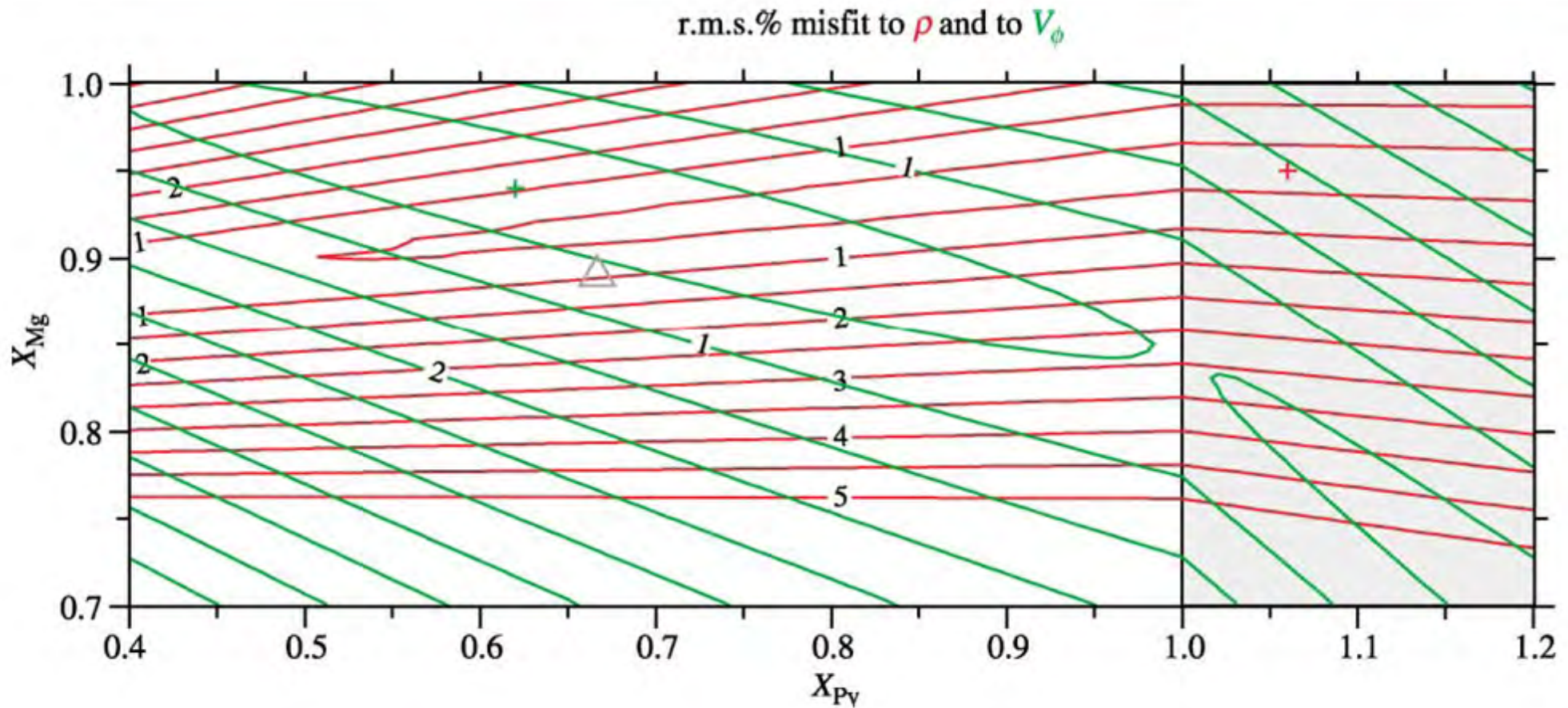
minimize $f(X)$: $(V_{\phi}^{EoS} - V_{\phi}^{seism})^2$

Depth-varying phase proportions in a pyrolite model mantle after the manner of Ringwood (1989), Ita and Stixrude (1992), and Bina (1998b). Phases are: (α) olivine, (β) wadsleyite, (γ) ringwoodite, (opx) orthopyroxene, (cpx) clinopyroxene, (gt-mj) garnet-majorite, (mw) magnesiowüstite, ((Mg,Fe)-pv) ferromagnesian silicate perovskite, and (Ca-pv) calcium silicate perovskite. Patterned region at base denotes likely heterogeneity near core-mantle boundary.

(Figure 1 of Bina, 2003)

(C.Bina, 9/2011)

Inverting seismological profiles for lower mantle bulk composition

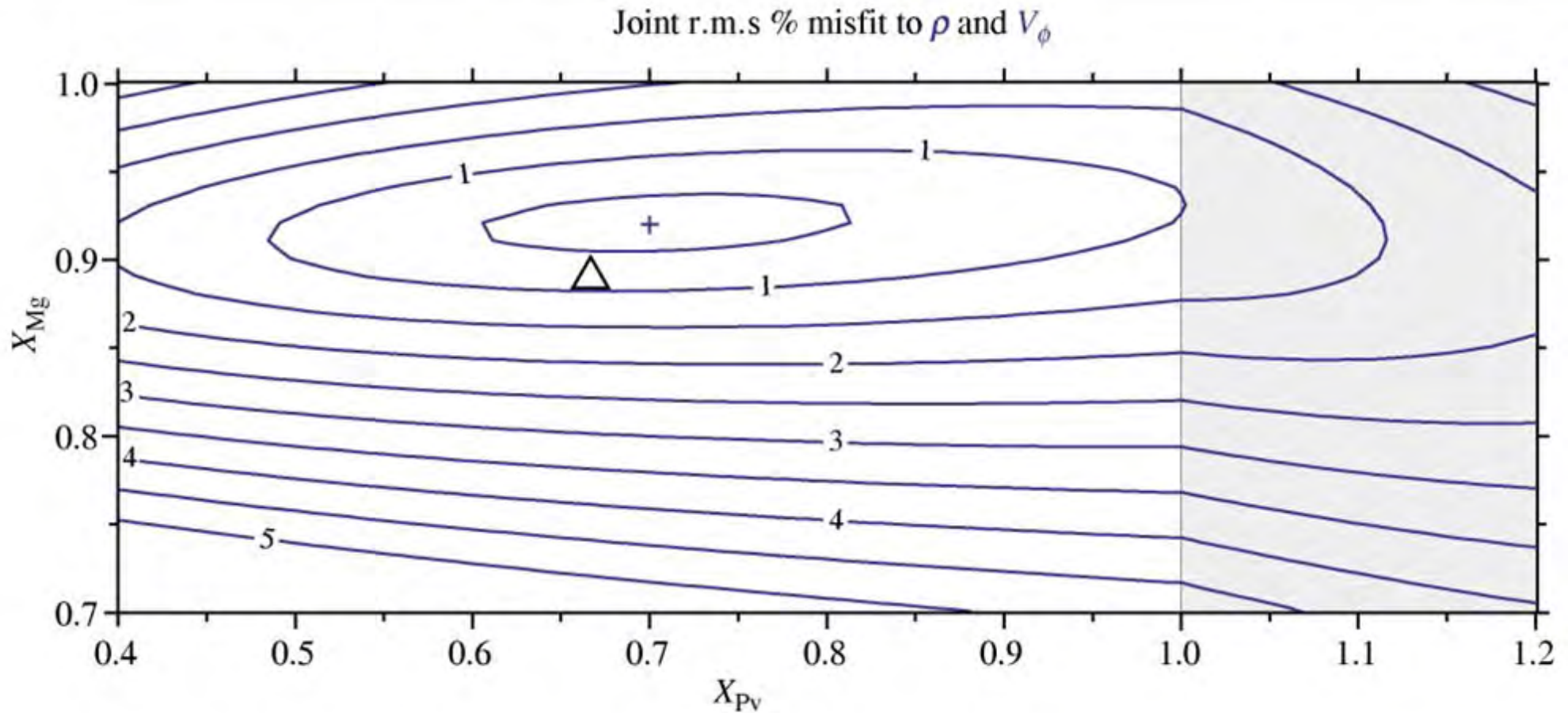


Contours of r.m.s. misfit (%) to seismological reference model *ak135* of density (red) and bulk sound velocity (green) for candidate lower-mantle compositions, parameterized in terms of Mg/(Mg+Fe) ($=X_{Mg}$) and Si/(Mg+Fe) ($=X_{Pv}$), over the entirety of the lower mantle. Shaded region at $X_{Pv} > 1$ indicates free silica. Triangle denotes pyrolite. Plus signs denote minima of r.m.s. misfit. Root of lower-mantle adiabat is 2,000 K at 660 km depth.

(Figure 5 of Bina, 2003)

(C.Bina, 9/2011)

Inverting seismological profiles for lower mantle bulk composition

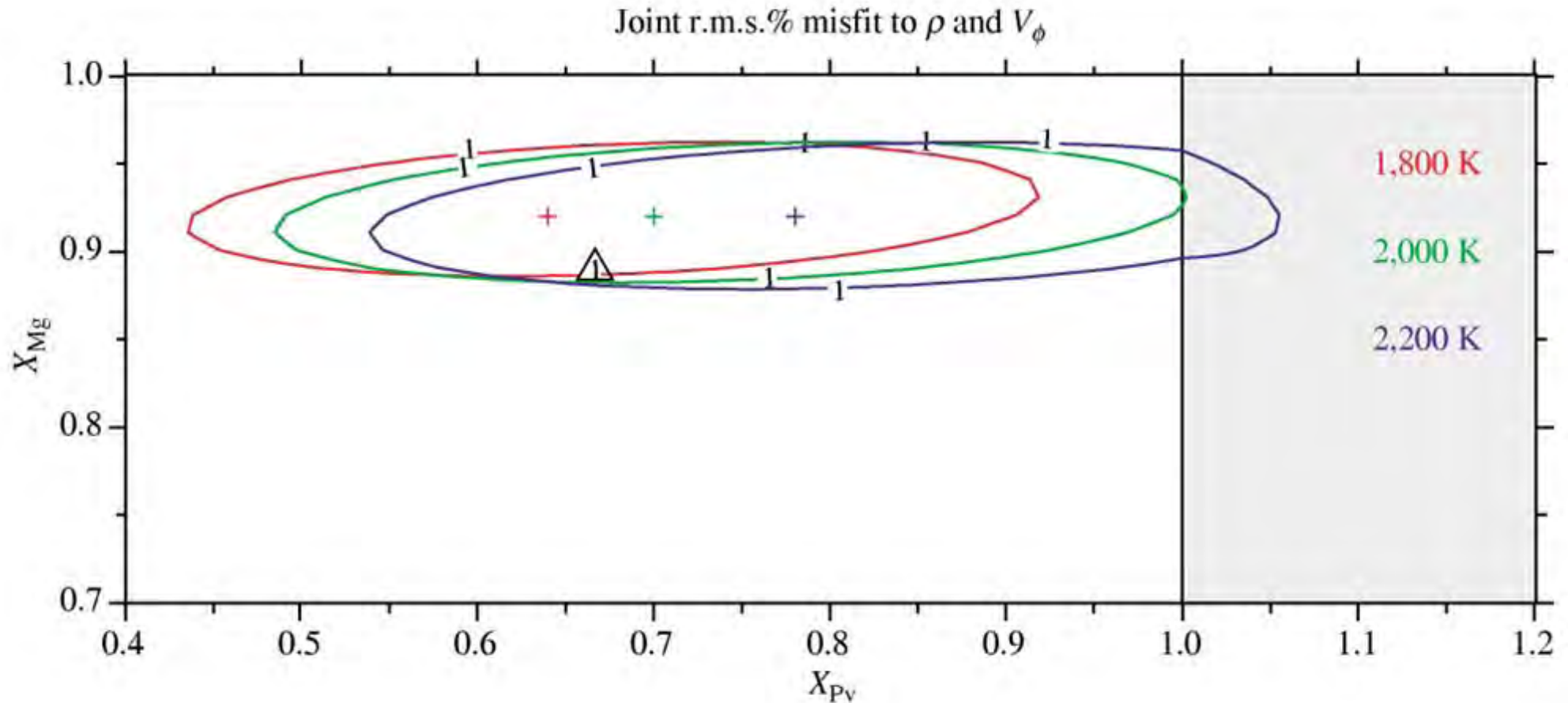


Contours of joint (blue) r.m.s. misfit (%) to seismological reference model *ak135* of density and bulk sound velocity for candidate lower-mantle compositions, parameterized in terms of Mg/(Mg+Fe) ($=X_{Mg}$) and Si/(Mg+Fe) ($=X_{Pv}$), over the entirety of the lower mantle. Shaded region at $X_{Pv} > 1$ indicates free silica. Triangle denotes pyrolite. Plus sign denotes minimum of r.m.s. misfit. Root of lower-mantle adiabat is 2,000 K at 660 km depth.

(Figure 6 of Bina, 2003)

(C.Bina, 9/2011)

Inverting seismological profiles for lower mantle bulk composition



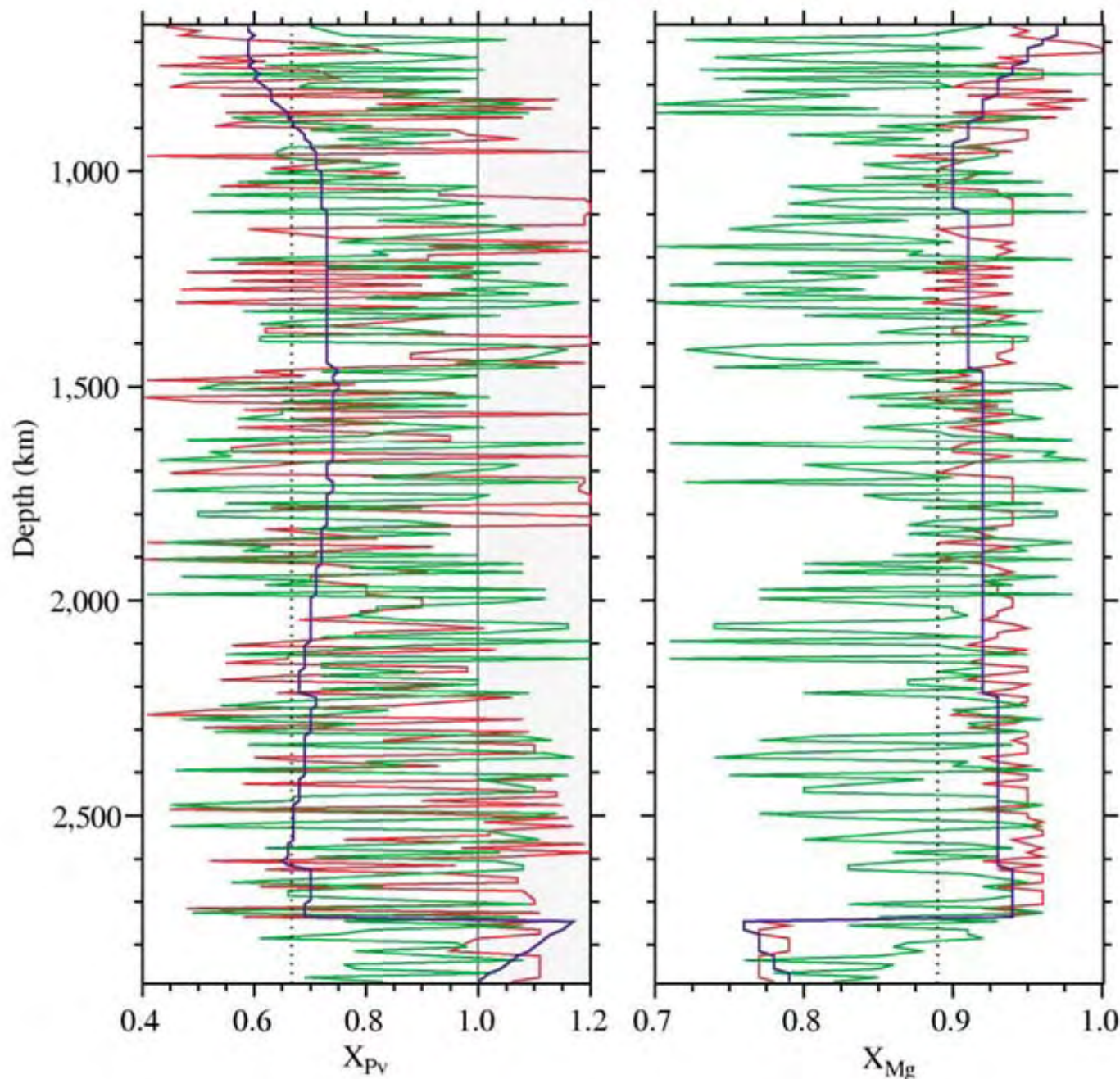
Contours of joint r.m.s. misfit (1%) to seismological reference model *ak135* of density and bulk sound velocity for candidate lower-mantle compositions, parameterized in terms of Mg/(Mg+Fe) ($=X_{Mg}$) and Si/(Mg+Fe) ($=X_{Pv}$), over the entirety of the lower mantle. Shaded region at $X_{Pv} > 1$ indicates free silica. Triangle denotes pyrolite. Plus sign denotes minimum of r.m.s. misfit. Roots of lower-mantle adiabats are 1,800 K (red), 2,000 K (green), and 2,200 K (blue) at 660 km depth.

(Figure 7 of Bina, 2003)

(C.Bina, 9/2011)

Inverting seismological profiles for lower mantle bulk composition

Depthwise fits to ρ , V_ϕ , and ρ and V_ϕ

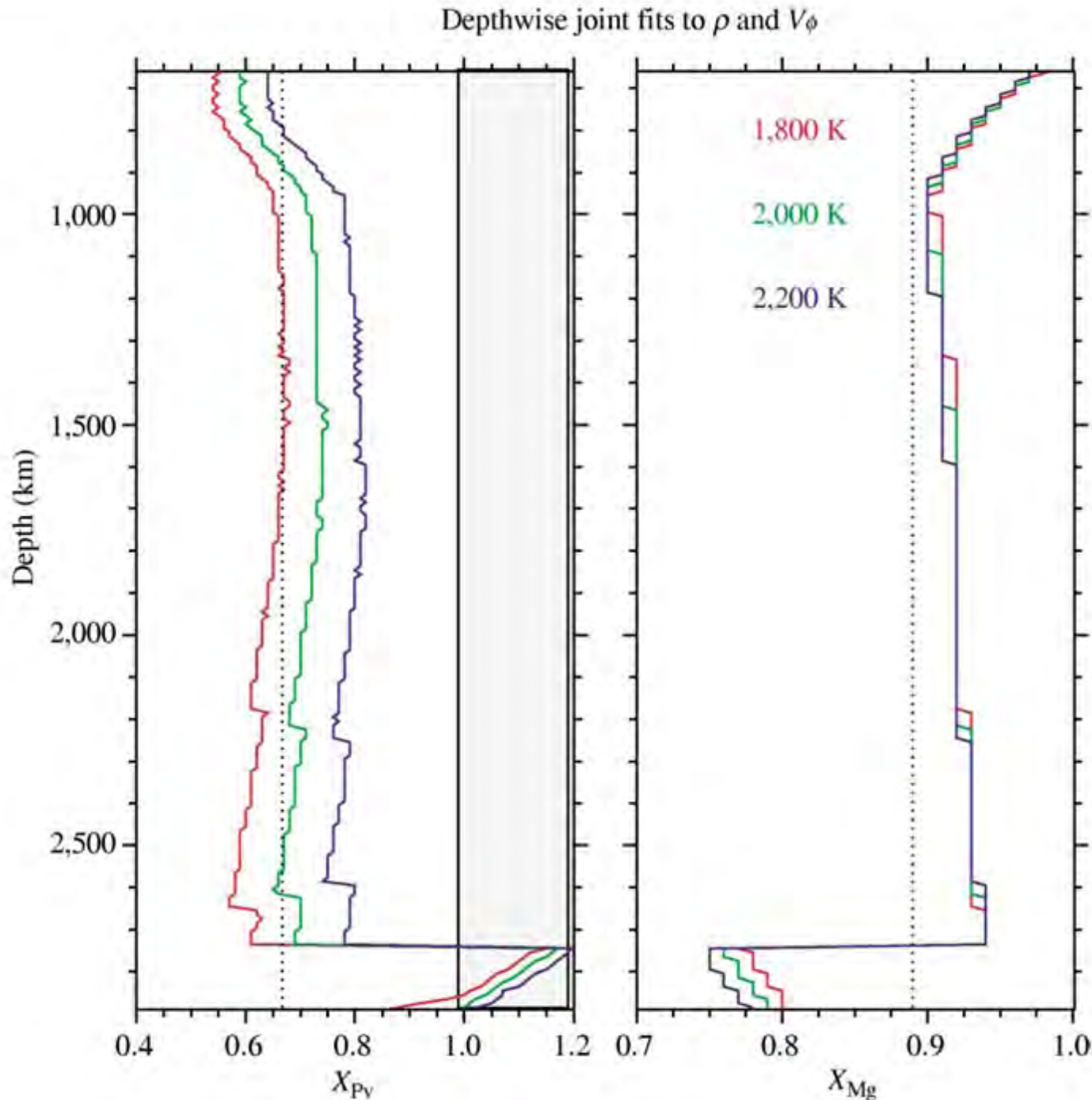


Depthwise best-fit compositions to seismological reference model *ak135* for density alone (red), bulk sound velocity alone (green), and both density and bulk sound velocity jointly (blue), with compositions parameterized in terms of Mg/(Mg+Fe) ($=X_{Mg}$) and Si/(Mg+Fe) ($=X_{Pv}$), in 10 km depth slices through the lower mantle. Shaded region at $X_{Pv} > 1$ indicates free silica. Dotted lines (at $X_{Pv} = 0.67$ and $X_{Mg} = 0.89$) denote pyrolite. Root of lower mantle adiabat is 2,000 K at 660 km depth.

(Figure 8 of Bina, 2003)

(C.Bina, 9/2011)

Inverting seismological profiles for lower mantle bulk composition



Depthwise best-fit compositions to seismological reference model *ak135* for both density and bulk sound velocity jointly, with compositions parameterized in terms of $\text{Mg}/(\text{Mg}+\text{Fe}) (=X_{Mg})$ and $\text{Si}/(\text{Mg}+\text{Fe}) (=X_{Pv})$, in 10 km depth slices through the lower mantle. Shaded region at $X_{Pv} > 1$ indicates free silica. Dotted lines (at $X_{Pv} = 0.67$ and $X_{Mg} = 0.89$) denote pyrolite. Roots of lower-mantle adiabats are 1,800 K (red), 2,000 K (green), and 2,200 K (blue) at 660 km depth.

(Figure 9 of Bina, 2003)

(C.Bina, 9/2011)

Electronic spin transitions in Fe-bearing minerals at lower mantle pressures and temperatures

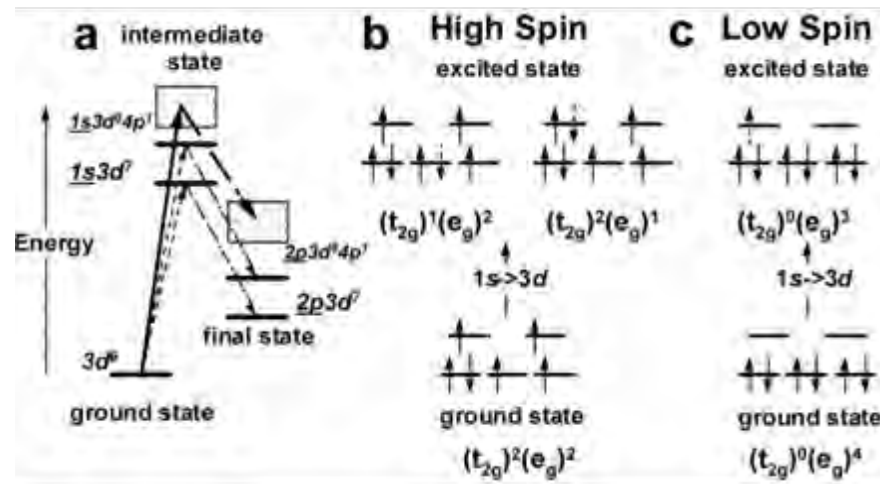


FIGURE 1. Schematic representation of 1s2p RXES transitions for octahedrally coordinated Fe²⁺ in ferropericlase at the Fe K pre-edge based on crystal field theory (after Caliebe et al. 1998; Rueff et al. 2004). (a) A two-step RXES transition process within a mono-electronic picture. The quadrupolar and dipolar transitions are indicated by thick and thin lines, respectively. (b) Ground and excited states of the octahedrally coordinated high-spin Fe²⁺. (c) Ground and excited states of the octahedrally coordinated low-spin Fe²⁺. The dashed arrows in **b** and **c** represent the excited electron. (Lin et al., *Amer. Mineral.*, 2010)

broadening of transition at high temperatures

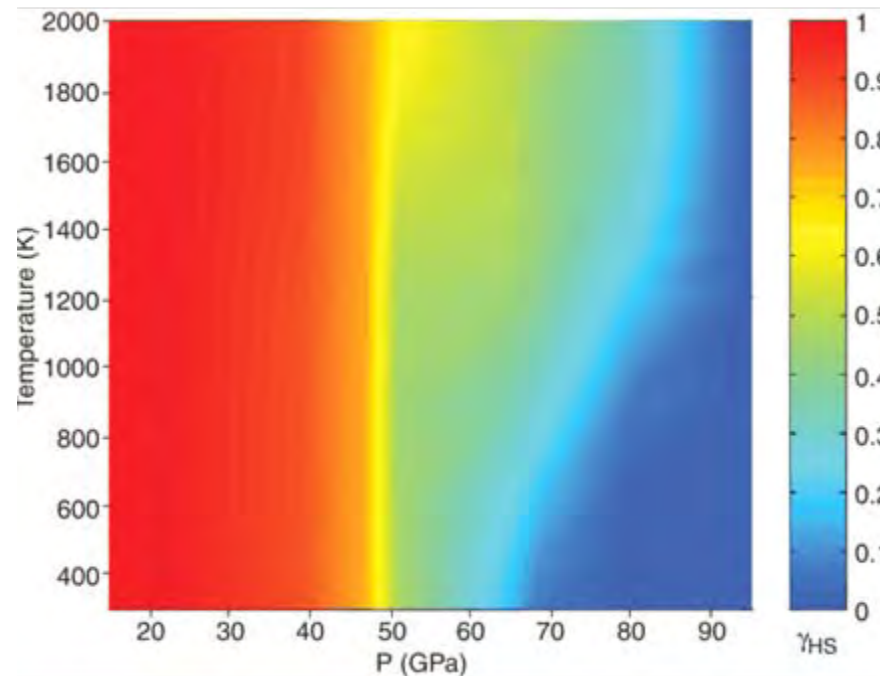


Fig. 3. Isosymmetric spin crossover of Fe^{2+} in $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$. The phase diagram is constructed from the interpolation and extrapolation of the derived fractions of the high-spin state in the sample (fig. S2). Colors in the vertical column on the right represent fractions of the high-spin iron, γ_{HS} , in $(\text{Mg}_{0.75}, \text{Fe}_{0.25})\text{O}$. (Li et al., *Science*, 2007)

broadening of transition at high temperatures

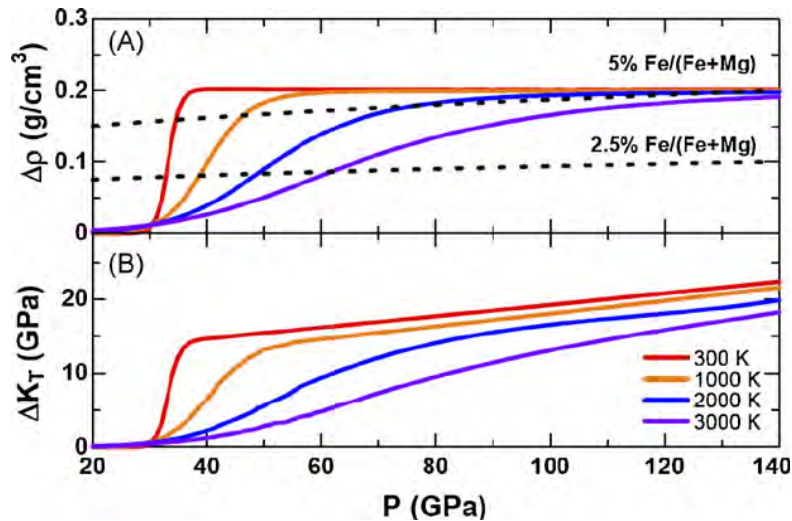


Fig. 8. Calculated density (A) and bulk modulus (B) differences for $(\text{Mg}_{0.8125}, \text{Fe}_{0.1875})\text{O}$. The differences are calculated using the spin crossover model at 300, 1000, 2000 and 3000 K (same colors in Fig. 6) (Tsuchiya et al., 2006a) as compared with that without the spin crossover (Figs. 6 and 7). Dotted lines represent density variation produced by adding 2% and 5% FeO into MgO at 300 K. The density variation by considering the spin crossover is about 0.19 g/cm^3 ($\pm 3.5\%$) at 2000 K and 100 GPa which is equivalent to adding 5.0% FeO into MgO. Bulk modulus variation is estimated within the model shown in Fig. 7(B). (Lin et al., *PEPI*, 2008)

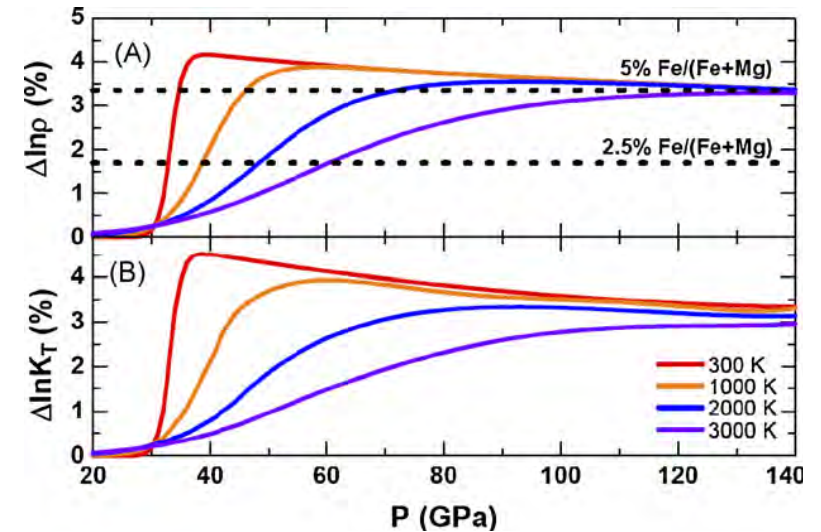
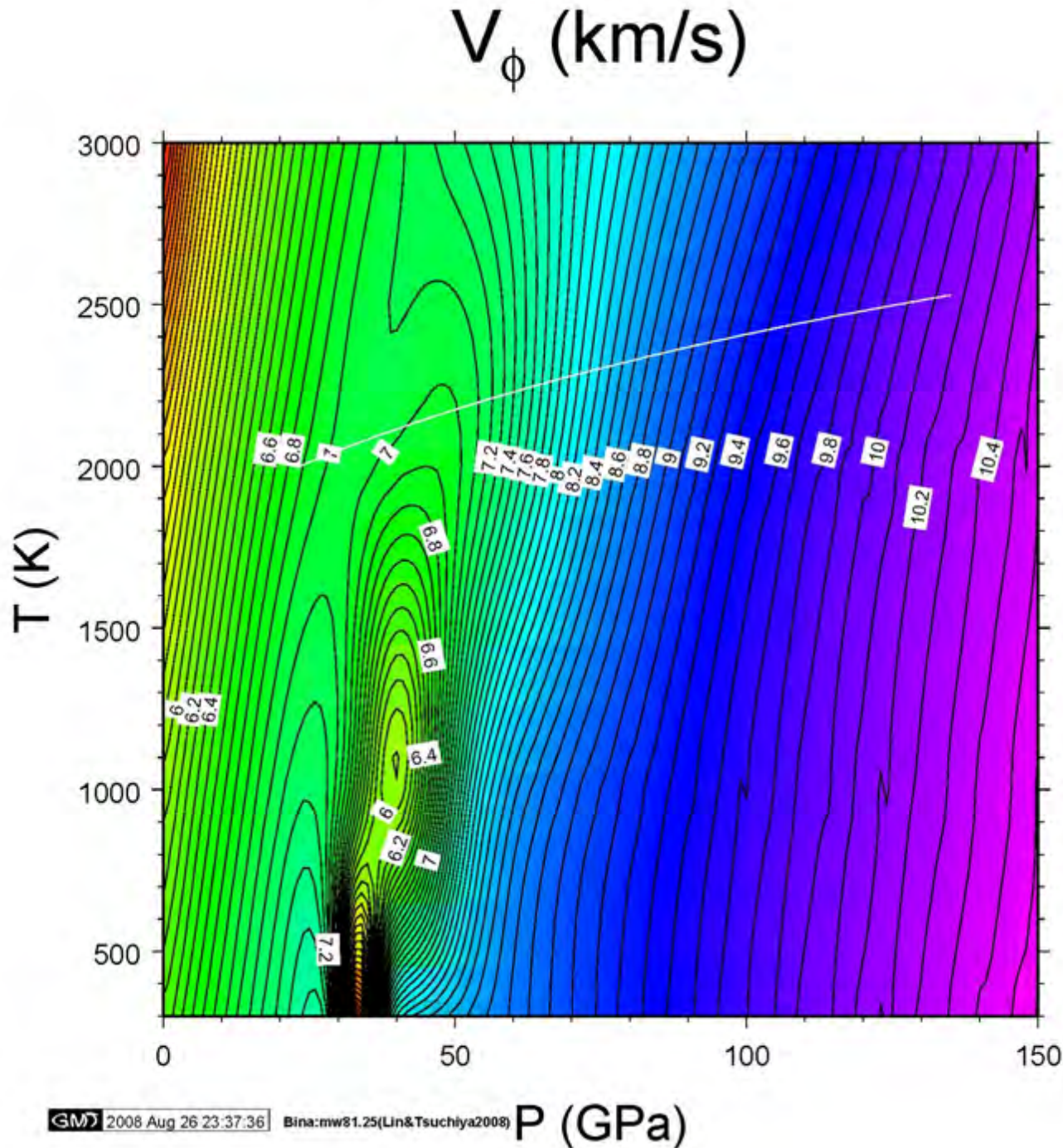


Fig. 9. Calculated density (A) and bulk modulus (B) variations in percentage for $(\text{Mg}_{0.8125}, \text{Fe}_{0.1875})\text{O}$ as derived from Fig. 8. (Lin et al., *PEPI*, 2008)

broadening of transition at high temperatures

FeO



This shows my own attempt to combine Tsuchiya's information on $K_T(P,T)$ and $\rho(P,T)$ to show $V_{\phi}(P,T)$, with a superimposed lower mantle adiabat.

broadening of transition at high temperatures
possible shear-wave anisotropy

FeO

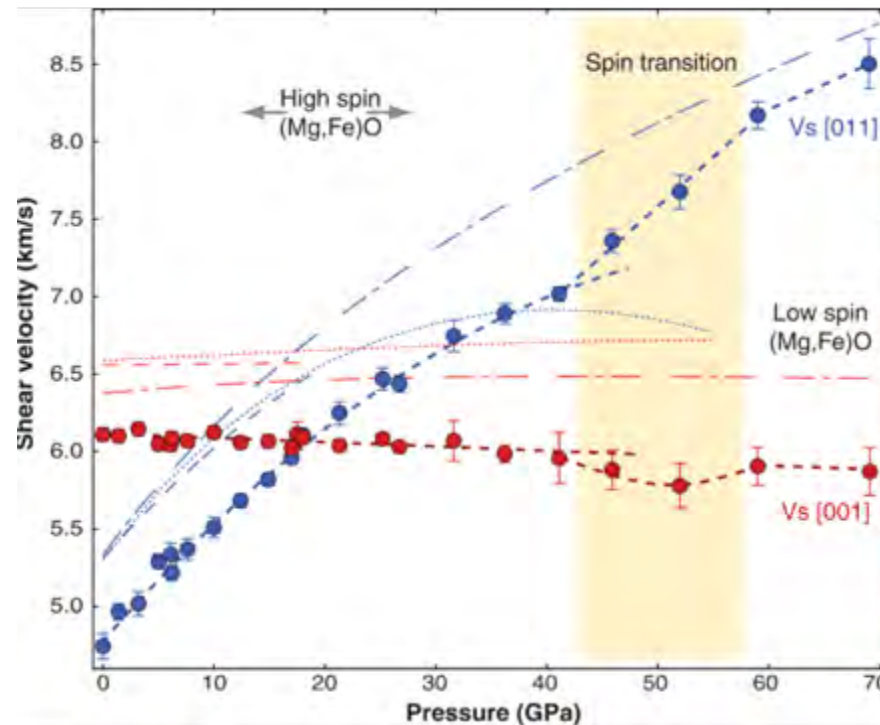


Fig. 1. Maximum and minimum shear velocities in $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{O}$ as a function of pressure. Shear velocities were measured in the (100) plane at different angles (at least seven directions) at each pressure and inverted for the two effective elastic shear constants $(c_{11} - c_{12})/2$ and c_{44} , which were used to calculate maximum and minimum shear velocity. Uncertainties are based on the propagation of the uncertainties in every measured velocity, taking into account the positions of Stokes and anti-Stokes peaks, their uncertainties, and the broadness of the peaks. The thin dashed, dotted, and dash-dotted lines are calculated from experimental (17, 18) and computational (11) data of MgO. (Marquardt et al., *Science*, 2009)

broadening of transition at high temperatures
possible shear-wave anisotropy

FeO

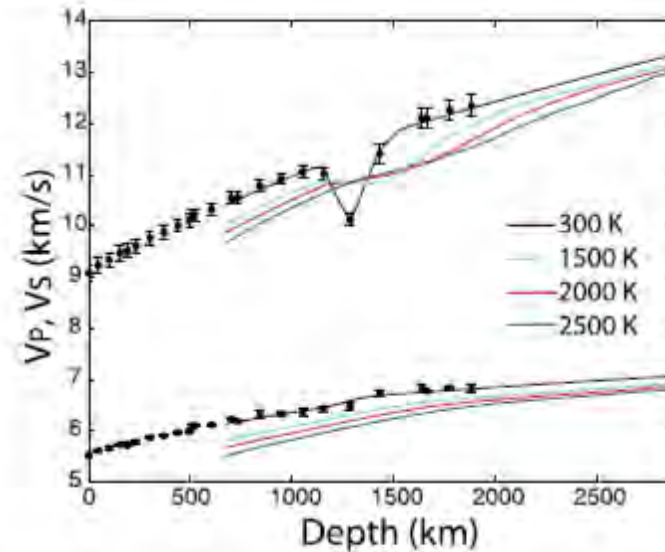


Figure 1. Seismic velocities of $(\text{Mg}_{0.9}, \text{Fe}_{0.1})\text{O}$ as a function of depth and temperature. Data points and error bars refer to measurements at ambient temperature [Marquardt *et al.*, 2010]. Pressures are converted to depths by using the PREM [Dziewonski and Anderson, 1981] pressure profile. Velocities are computed along 4 isotherms (see legend). The broadening of the iron-spin transition with temperature is modeled on the basis of a theoretical computation [Tsuchiya *et al.*, 2006]. The elastic properties are corrected at high temperature using the Debye model with parameters from Matas *et al.* [2007].

(Cammarrano *et al.*, 2010)

possible shear-wave anisotropy

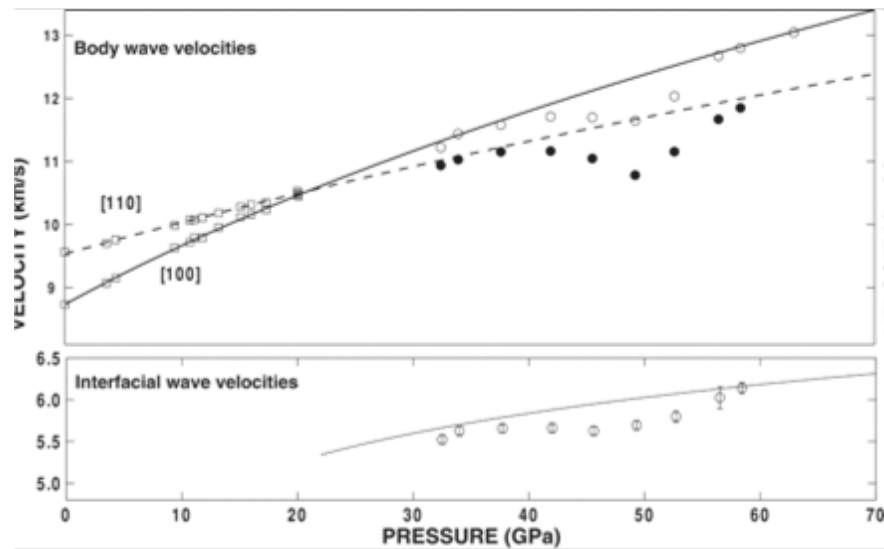
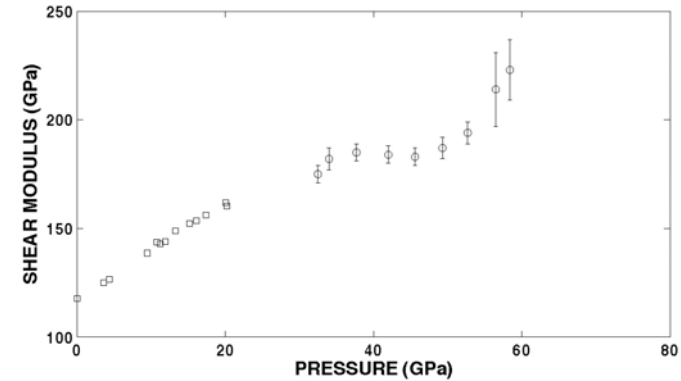


Fig. S1

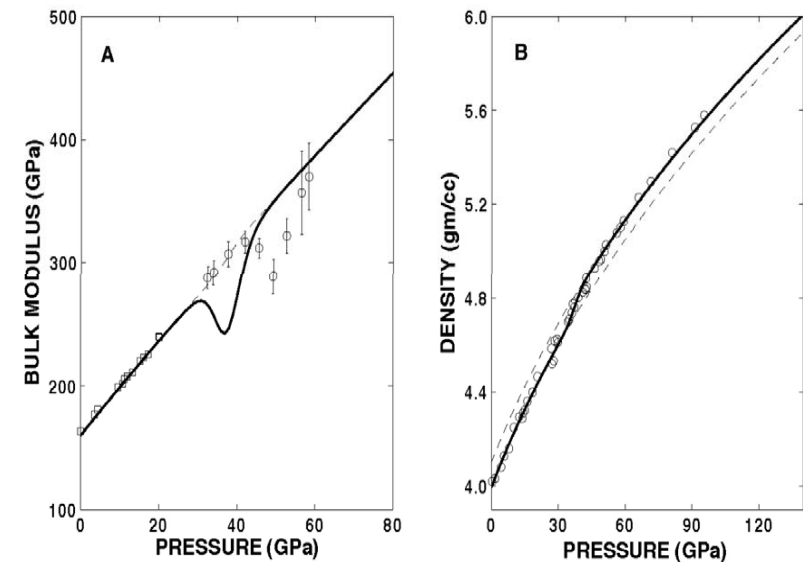


Fig. S2

Fig. 1. Acoustic wave velocities as a function of pressure for propagation in the (001) plane of single-crystal $(\text{Mg}_{0.94}\text{Fe}_{0.06})\text{O}$ in an argon pressure-transmitting medium. Circles indicate present data acquired by impulsive stimulated scattering. Uncertainties are given by $\pm 2\sigma$, where σ is the formal SE. Squares indicate data obtained by Jackson *et al.* via Brillouin scattering (19). Lines are calculated velocities based on linear extrapolations of the elastic moduli obtained by Jackson *et al.* (19). **(Top)** Body wave velocities. Solid circles and open circles are data for propagation along [110] and [100], respectively. **(Bottom)** Velocities of the wave that propagates at the interface between the sample and the pressure-transmitting medium. The interfacial wave has no dependence on direction under these conditions. (Crowhurst *et al.*, *Science*, 2008)

no significant impact upon aggregate velocities
only upon shear-wave anisotropy

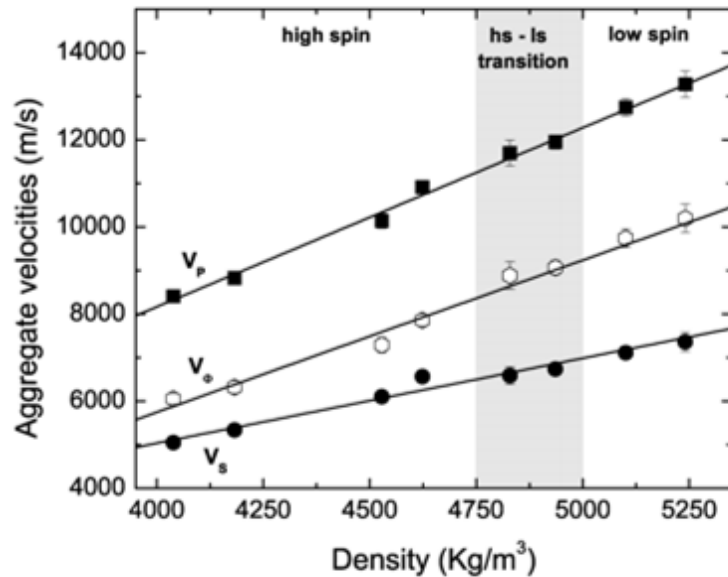


Fig. 2. Density evolution of the aggregate sound velocities (Voigt-Reuss-Hill average) (15). Solid squares, compressional sound velocity (V_p); solid circles, shear sound velocity (V_s); open hexagons, bulk sound velocity ($V_\phi = \sqrt{K/\rho}$). The lines are linear fits to the experimental data. The density range corresponding to the spin-transition zone (4750 to 5000 kg/m³) is shaded. Error bars on the aggregate velocities come from the propagation of the uncertainties on the elastic moduli and the difference between the Voigt and Reuss average (15). (Antonangeli et al., *Science*, 2011)

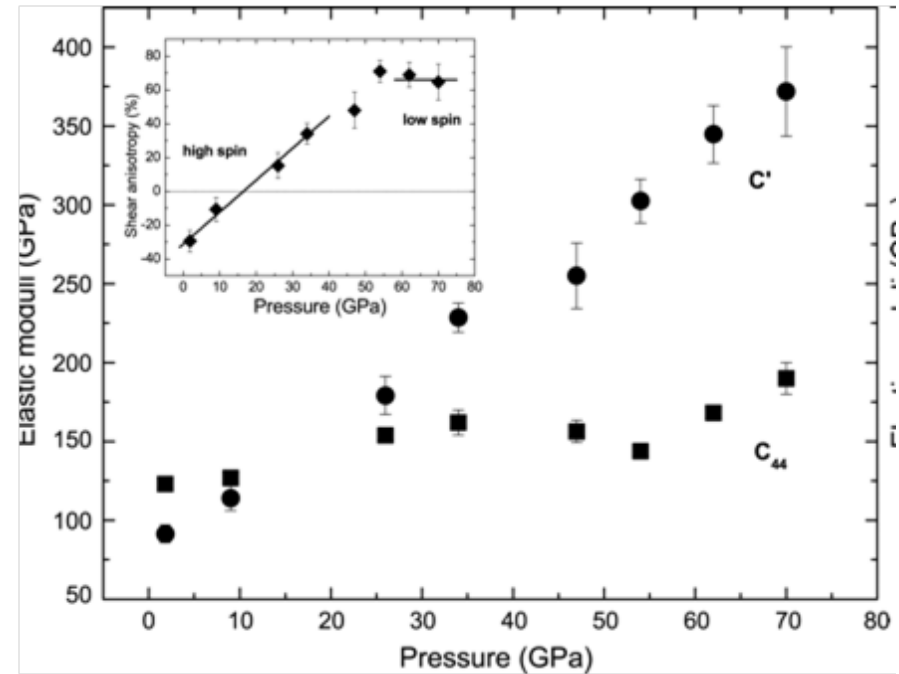


Fig. 3. Comparison of the pressure evolution of C_{44} (squares) and C' (circles), corresponding to the two different polarizations of the shear mode in the diagonal plane of a cubic lattice. (Inset) Shear anisotropy as a function of pressure. The lines are guides for the eye. Error bars account for the uncertainties on the measured velocities and densities (15). (Antonangeli et al., *Science*, 2011)

Schematic diagrams of electronic spin configuration of Fe^{2+} in the A site of perovskite based on crystal field theory (4).

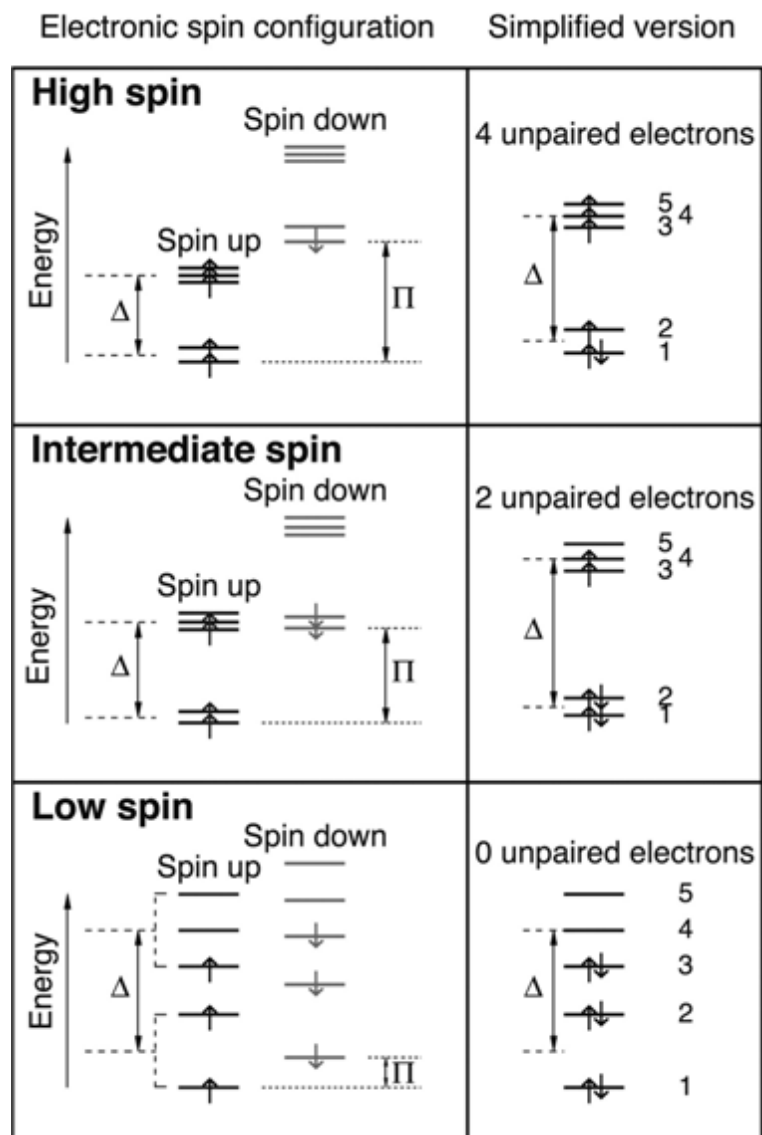


Fig. 4. Schematic diagrams of electronic spin configuration of Fe^{2+} in the A site of perovskite based on crystal field theory (4). On the right are the simplified pictures that are commonly found in the literature. The 3d subshell of iron contains five orbitals, each capable of accommodating two electrons with opposite spins. The energy difference between the opposite spins on each orbital (dotted lines) is called spin-pairing energy (π). According to the crystal field theory, in a cubic environment, the 3d orbitals split into the t_{2g} and e_g levels (dashed lines). The energy difference between the two levels is called crystal field splitting energy (Δ). In a noncubic environment, additional splitting occurs between the t_{2g} levels and between the e_g levels, resulting in five different energy levels. At ambient condition, the 1st spin-down level is higher than the 5th spin-up level. Only one electron is forced to pair. Fe^{2+} has the largest number of unpaired electrons (high-spin state). Upon compression, crystal field splitting energy increases with increasing density (decreasing ligand bond lengths) and possibly increasing degree of distortion. Given fixed spin-pairing energy (5), certain lower spin-down levels will cross higher spin-up levels. When the 2nd spin-down level crosses the 5th spin-up level, the electron at the 5th orbital will switch spin and move to the 2nd orbital (intermediate-spin state, intermediate number of unpaired electrons). When the 3rd spin-down level crosses the 4th spin-up level, the electron at the 4th orbital will switch spin and move to the 3rd orbital (low-spin state, smallest number of unpaired electrons). In other words, each iron species goes through two pressure-induced partial spin-pairing transitions: Upon the first partial spin-pairing transition the number of unpaired 3d electrons drops to two, forming the intermediate-spin state. After the second partial transition, the number becomes zero, reaching the final low-spin state. Similar diagrams can be drawn for Fe^{3+} in either the A or the B site. (Li et al., *PNAS*, 2004)

increase in bulk modulus for high Fe contents

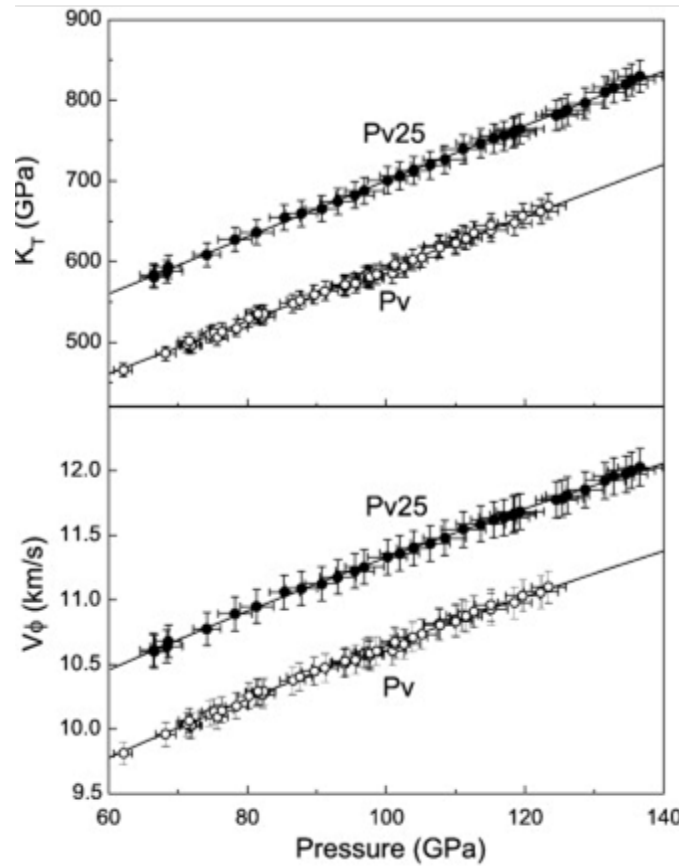
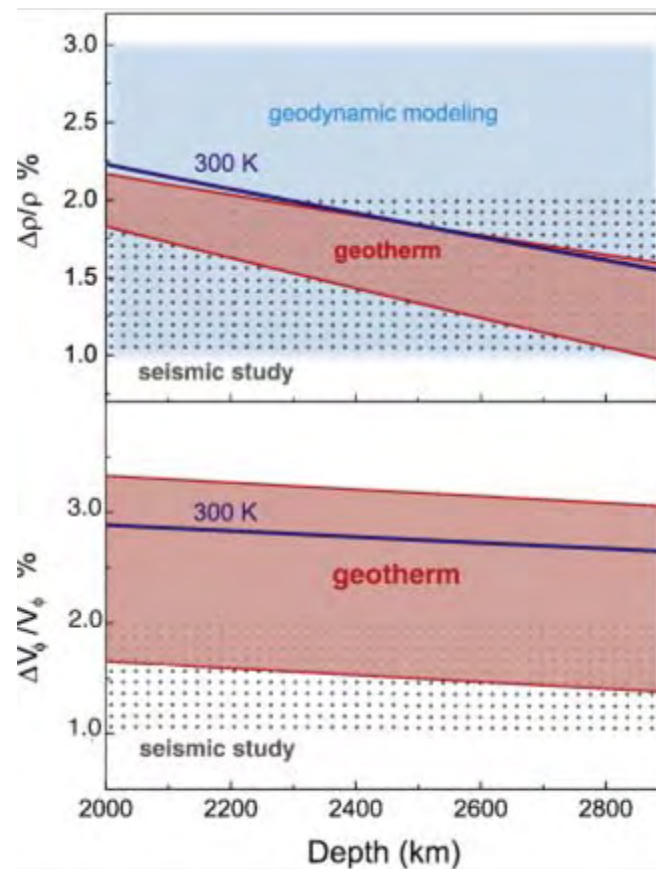


Fig. 6. K_T and V_ϕ of perovskite as a function of pressure at 300 K. Open circles: Pv; solid circles: Pv25. Corresponding lines represent modeled EoS fits to the experimental results. Uncertainties are approximately 2% for K and 1.2% for V_ϕ when fixed $K_0' = 4$ for Pv25. Varying the K_0' value of Pv25 by ± 0.5 can lead to the uncertainty of K and V_ϕ up to 14% and 4%, respectively. (**Mao et al., *EPSL*, 2011**)



*increase in bulk modulus
for high Fe contents:
possible source of
positive density and P-
velocity anomalies with
negative S-velocity
anomalies due to lateral
compositional variation?*

Fig. 8. Modeled ρ and V_ϕ deviation of Pv25 relative to Pv10 along a model mantle geotherm (Brown and Shankland, 1981). $\Delta\rho/\rho$ ($\Delta V_\phi/V_\phi$) represents the density (V_ϕ) difference between Pv25 and Pv10. Blue lines: estimates based on our experimental data at 300 K; red lines and shaded area: calculated deviation along the mantle geotherm (Brown and Shankland, 1981); gray dotted areas: observed maximum seismic anomalies in the LLSVPs ([Ishii and Tromp, 2004] , [Ishii and Tromp, 1999] , [Su and Dziewonski, 1997] and [Trampert et al., 2004]); blue areas: estimated ρ anomalies in the LLSVPs from thermodynamic modelings ([McNamara and Zhong, 2005] and [Tan and Gurnis, 2005]). Uncertainties of the calculated ρ and V_ϕ deviations are plotted as red areas by taking various thermoelastic parameters of perovskite from the literature into account ([Fiquet et al., 2000] and [Ricolleau et al., 2009]). **(Mao et al., *EPSL*, 2011)**

regions of positive density anomalies but negative S-velocity anomalies at the base of the mantle

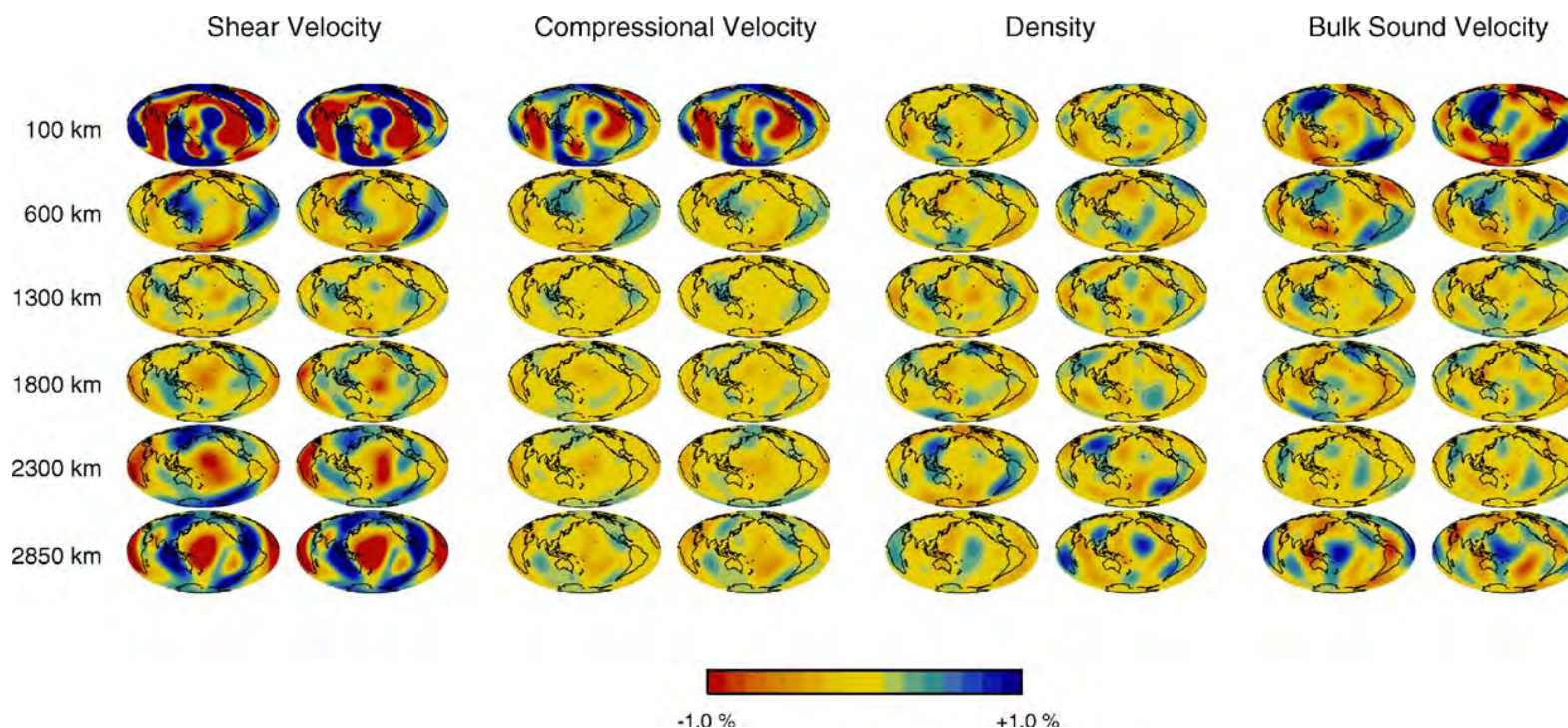


Fig. 2. Models of shear velocity, compressional velocity, density, and bulk-sound velocity within the mantle. Three-dimensional models of the mantle plotted in map view at six discrete depths. Blue indicates regions where the relative perturbation is higher than average and red indicates values that are lower than average. The scale is fixed at a saturation level of $\pm 1\%$ for all maps. These maps are plotted using even spherical harmonic degrees 2, 4, and 6, hence some of the common features seen in tomographic maps such as the contrast between oceans and continents at shallow depths is not obvious. (Shear Velocity) Comparison of the shear-velocity model derived from mantle and inner-core sensitive modes (left) and SKS12WM13 (right). (Compressional Velocity) Comparison of the compressional-velocity model derived from mantle and inner-core sensitive modes (left) and P16B30 (right). (Density) Comparison of density models based upon mantle and inner-core sensitive modes (left) and SPRD6 (Ishii and Tromp, 2001) which is constrained only by mantle sensitive modes (right). (Bulk Sound Velocity) Comparison of bulk-sound velocity models derived using shear- and compressional-velocity models from this study (left) and from SPRD6 (Ishii and Tromp, 2004)