

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

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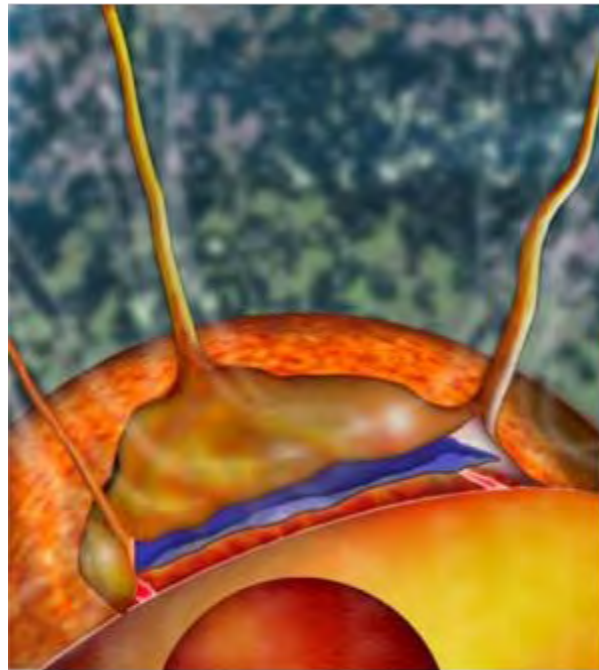
*Katedra geofyziky
Matematicko-fyzikální fakulta
Univerzita Karlova v Praze*

*přednášky na podzim 2011
7. lekce 23.11.*

The Core-Mantle Boundary Region:

$CMB, D''[\Delta V_{P,S}, \partial V_{P,S}/\partial z, \nabla(V_P/V_S), V_{P,S}(\theta, \phi)], ULVZs, LLSVPs$

phase change(s)?, melting? lateral δT ?, lateral $\delta X_{Fe,Al,Si}$? $^3Fe^{metal}$?



(Ed Garnero, 2006)

CMB Heterogeneity

Some early signs suggesting lateral heterogeneity at the base of the mantle: Velocity anomalies might arise from ΔT , but anticorrelated changes in V_P and V_S suggested probable compositional variations (or very special ∇T).

TABLE 4. Velocity Variations Due to Changes in Temperature

Temperature, K	ΔV_P	ΔV_S	Δv
3100	+1.6%	+1.1%	+1.6%
3300	+0.8%	+0.6%	+0.9%
3500	-----	-----	-----
3700	-0.9%	-0.6%	-1.0%
3900	-1.7%	-1.2%	-2.0%

CMB Diffracted Waves

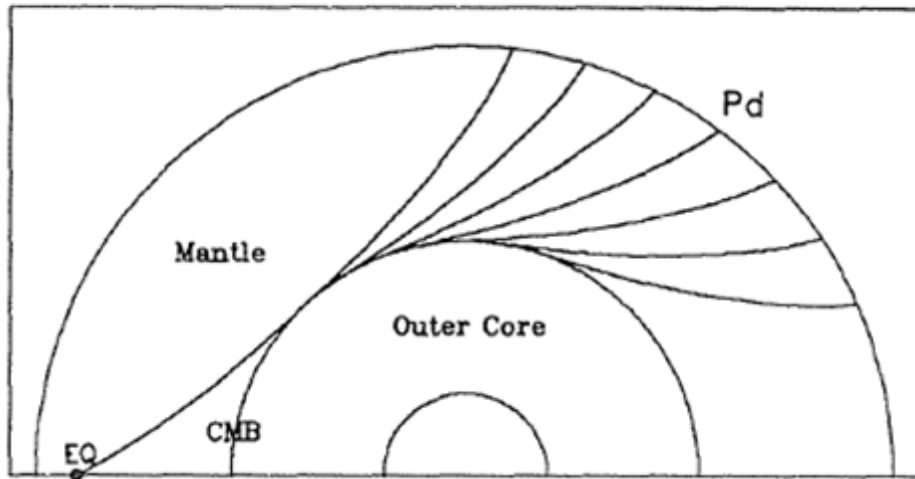


TABLE 5. Velocity Variations Due to Mg/Fe Variations

Mg/(Mg+Fe)	ΔV_P	ΔV_S	Δv
1.0	+1.9%	+1.8%	+0.3%
0.9	-----	-----	-----
0.8	-1.8%	-1.7%	-0.3%
0.7	-3.5%	-3.3%	-0.5%

TABLE 6. Velocity Variations Due to Oxide/Silicate Ratio Changes

Model	ΔV_P	ΔV_S	Δv
Pv	+0.2%	-0.9%	+3.6%
2Pv + Mw	-----	-----	-----
Pv + 2Mw	-0.1%	+1.6%	-5.8%

(Wyssession, Bina, and Okal, 1993)

CMB Heterogeneity

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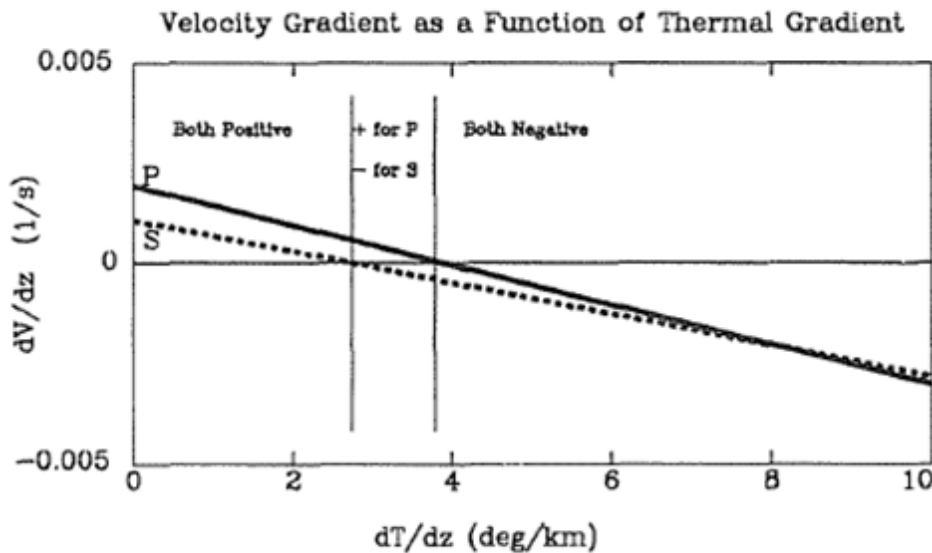


Figure 3. An example of the P and S velocity gradients as functions of the thermal gradient at the base of the mantle. The thermoelastic parameters used for the calculation are $K_S = 685$ GPa; $\mu = 291$ GPa; $\alpha = 1.3 \times 10^{-5} \text{ K}^{-1}$; $\partial K_S/\partial T = -0.015$ GPa/K; $\partial \mu/\partial T = -0.035$ GPa/K; $K_S' = 4.0$; $\mu' = 1.9$; $T = 3000$ K (sources are given in the text). Note that the shear velocity gradient becomes negative before the P velocity gradient, creating a layer in D'' in which P velocities are still increasing but S velocities are decreasing.

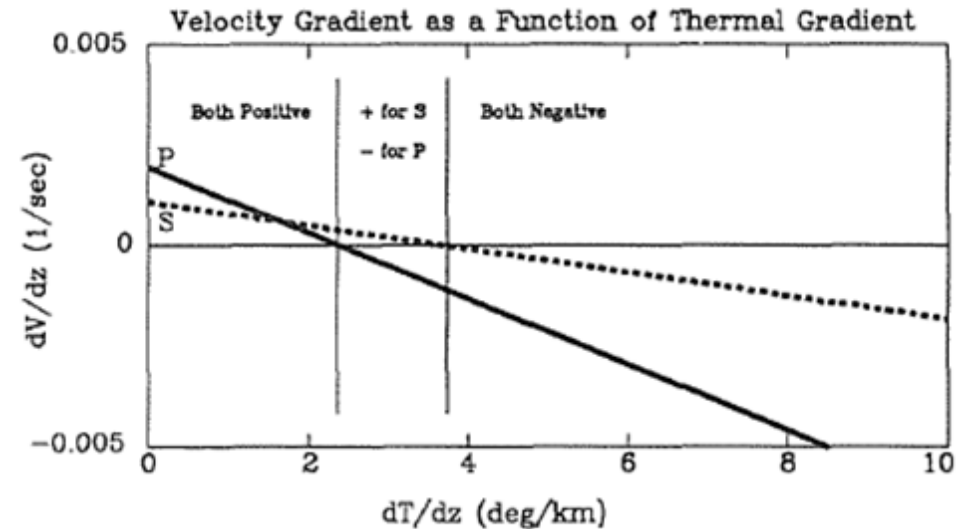


Figure 4. An example of the P and S velocity gradients as functions of the thermal gradient at the base of the mantle. The thermoelastic parameters used for the calculation are $K_S = 685$ GPa; $\mu = 291$ GPa; $\alpha = 4.0 \times 10^{-5} \text{ K}^{-1}$; $\partial K_S/\partial T = -0.035$ GPa/K; $\partial \mu/\partial T = -0.035$ GPa/K; $K_S' = 4.0$; $\mu' = 1.9$; $T = 3000$ K (sources are given in the text). Note that in this case the P velocity gradient becomes negative before the S velocity gradient, creating a layer in D'' in which S velocities are still increasing but P velocities are decreasing. This is the opposite of the case represented in Figure 3.

(Wyssession, Bina, and Okal, 1993)

Recall ...

CMB Heterogeneity

More recent observations of regions where $\delta\rho>0$ but $\delta V_S<0$ (and $\delta V_P\approx 0$) at the base of the mantle ...

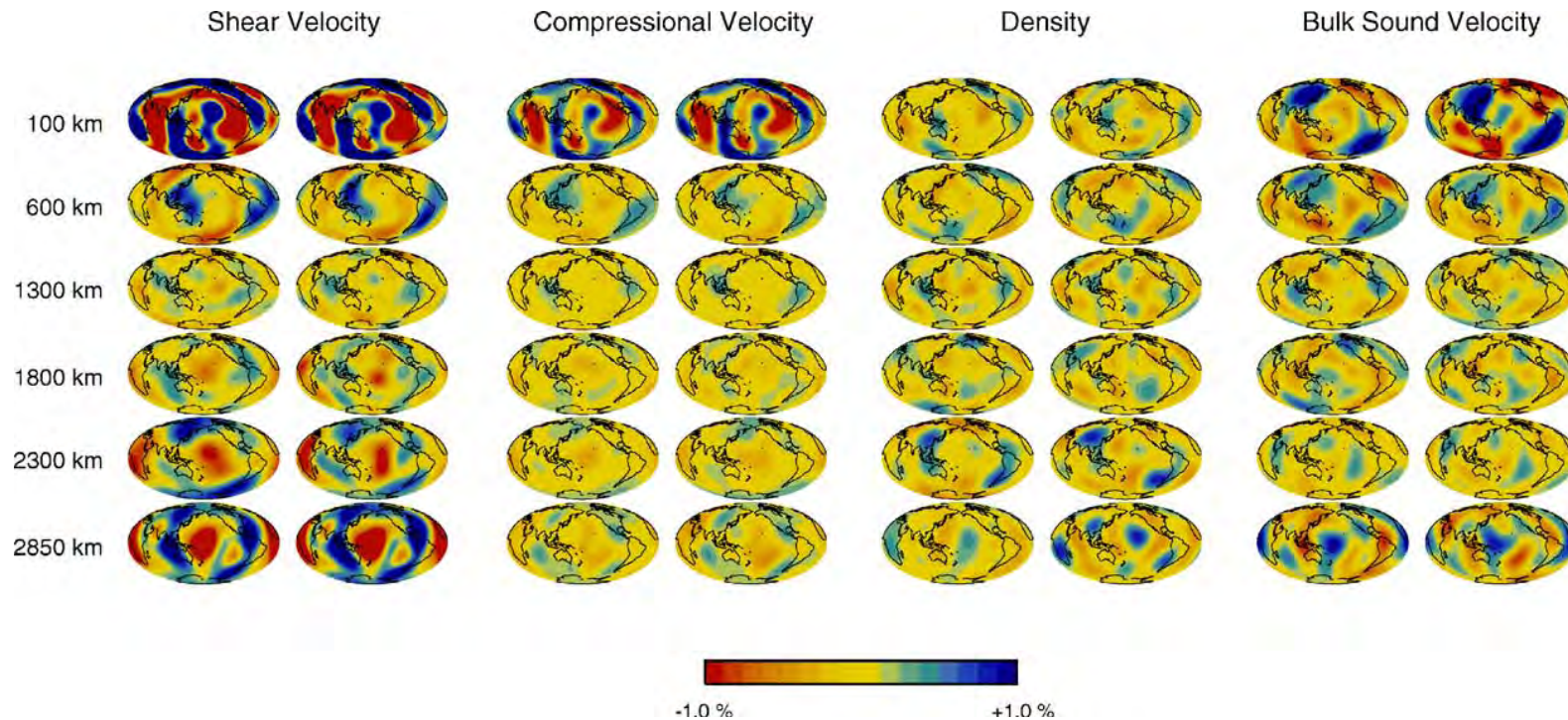
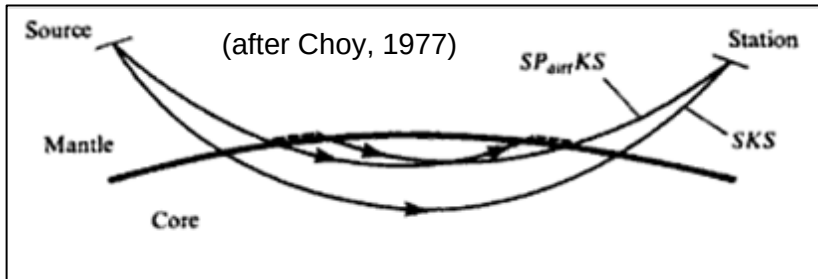


Fig. 2. Models of shear velocity, compressional velocity, density, and bulk-sound velocity within the mantle. Three-dimensional models of the mantle plotted in map view at six discrete depths. Blue indicates regions where the relative perturbation is higher than average and red indicates values that 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 (right). (Ishii and Tromp, 2004)

Ultra-Low Velocity Zones (ULVZs)



Some early signs of very low velocities at the base of the mantle: Anomalous $SKKS/SKS$ amplitude ratios

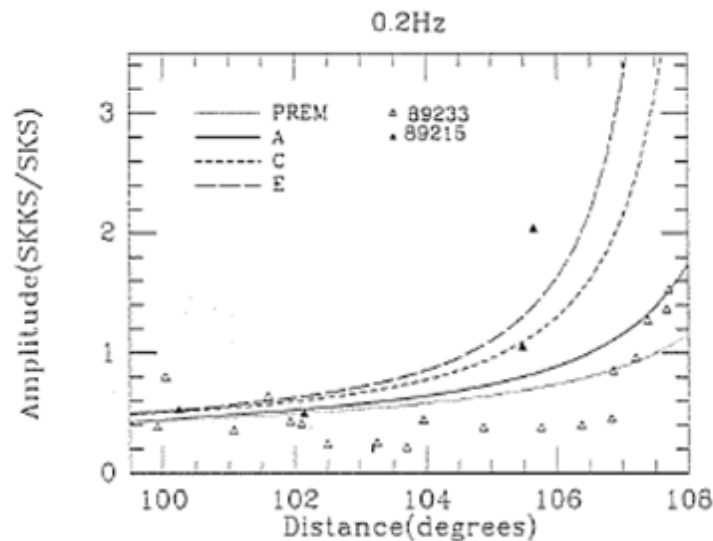


Fig. 3. Ratio $R_o(\omega)$ as a function of distance for event 89215 (solid triangles, Table 1) and 89233 (open triangles) at a frequency of 0.2 Hz. Note the apparent 2° shift in the profile for 89215 relative to 89233. Also shown are predicted values $R_s(\omega)$ for models PREM (dotted), A (solid), C (short-dash), and E (long-dash) at the same frequency. Models C and E are PREM with α_{cmb} decreased 3.3% and 4.0%, respectively. Calculations were made using Full Wave theory.

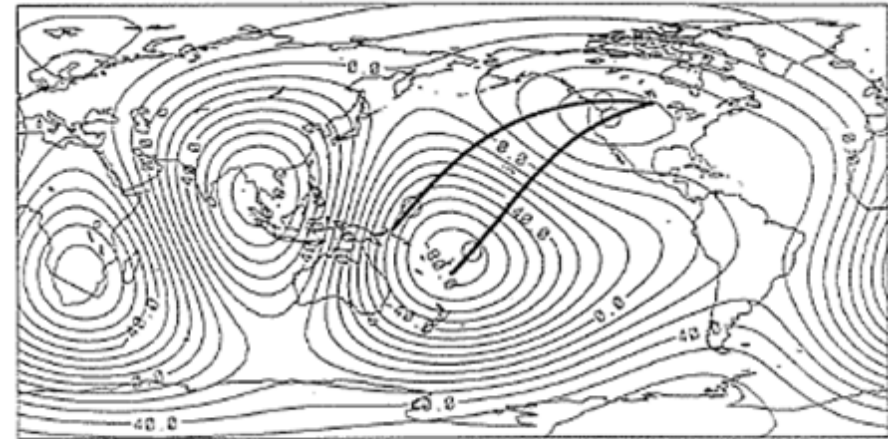


Fig. 4. World map showing event locations, event-station paths, the center of the array (station FVNR), and interaction points of SKS phases at the CMB. Also shown is the laterally varying P-velocity model L0256 (Dziewon-ski, 1984) evaluated at the CMB for angular orders 2 and 3 (units: m/s). Note that the interaction point for 89215 (just north of Tonga) is centered on the velocity minimum for this map, while the point for 89233 (Solomon Is.) is off to the side of this minimum. The difference in P-velocity at the base of the mantle between these two points is estimated to be 2.0–2.5% (89215 has slower velocity) based on the value of $R(\omega)$. This is in the same sense as indicated by L0256, although much greater in magnitude.

(Silver and Bina, 1993)

Ultra-Low Velocity Zones (ULVZs)

More recent analyses of anomalous *SKKS*/*SKS* amplitude ratios require thin (10-20 km) ULVZs with 20-30% V_S reduction.

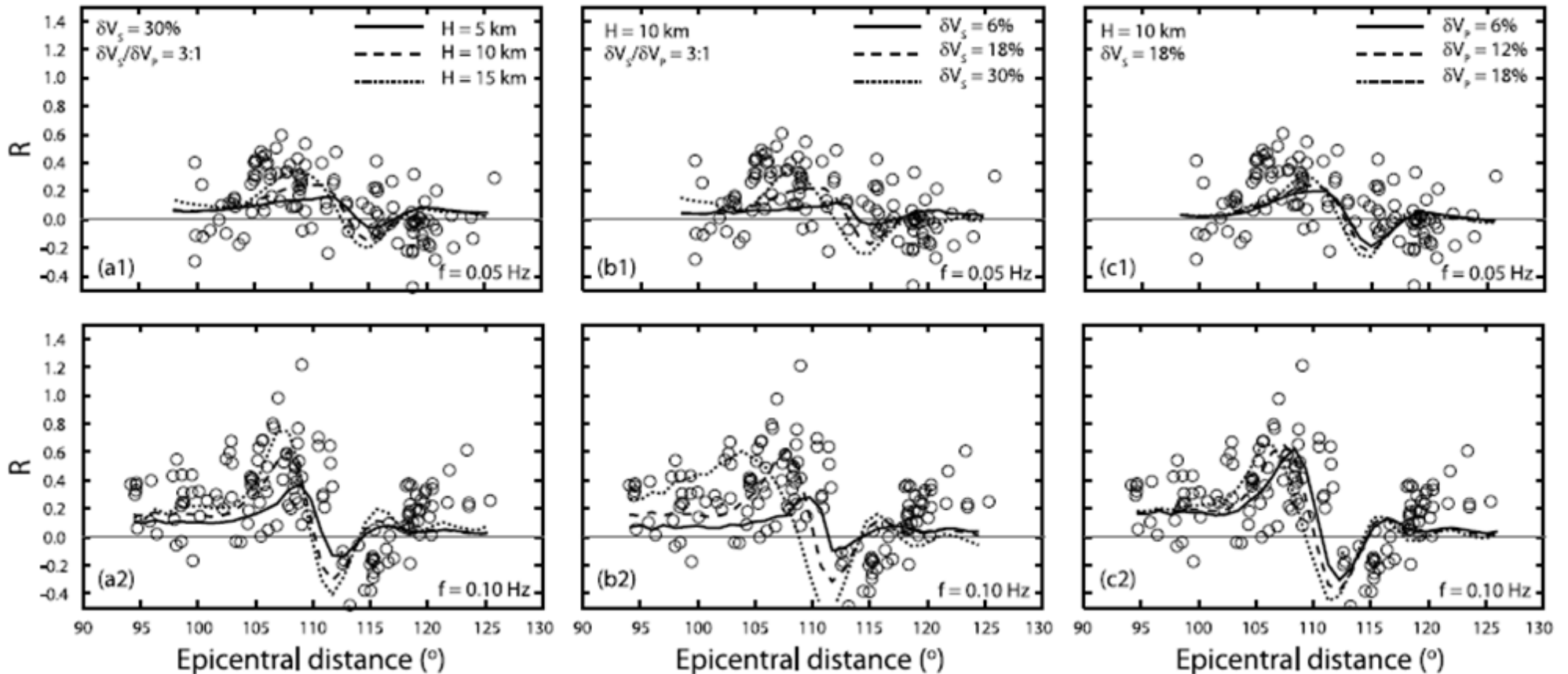
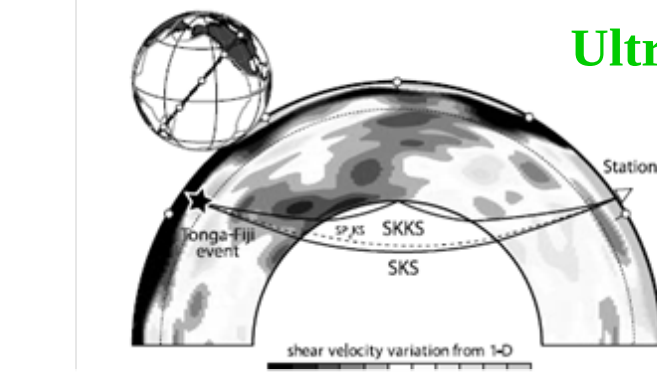


Figure 5. Measurements (circles) and model predictions (lines) of R at (top) 0.05 Hz and (bottom) 0.1 Hz for ULVZs at the SKS and SKKS core-entry points. Varied are (a) ULVZ thickness, (b) V_S reduction, and (c) the ratio of the V_S and V_P reductions.

(Zhang, Ritsema, and Thorne, 2009)

Ultra-Low Velocity Zones (ULVZs)

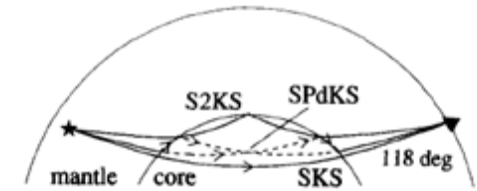


Fig. 1. Earth cross-section displaying raypaths of SKS and SKKS (continuous lines), and SP_dKS (dashed lines) for an event at 500 km depth at 118°.

Early signs of very low velocities at the base of the mantle: Anomalous SKS, SKKS, SV_{diff} , and SP_dKS travel times and amplitudes

(Garnero and Helmberger, 1995)

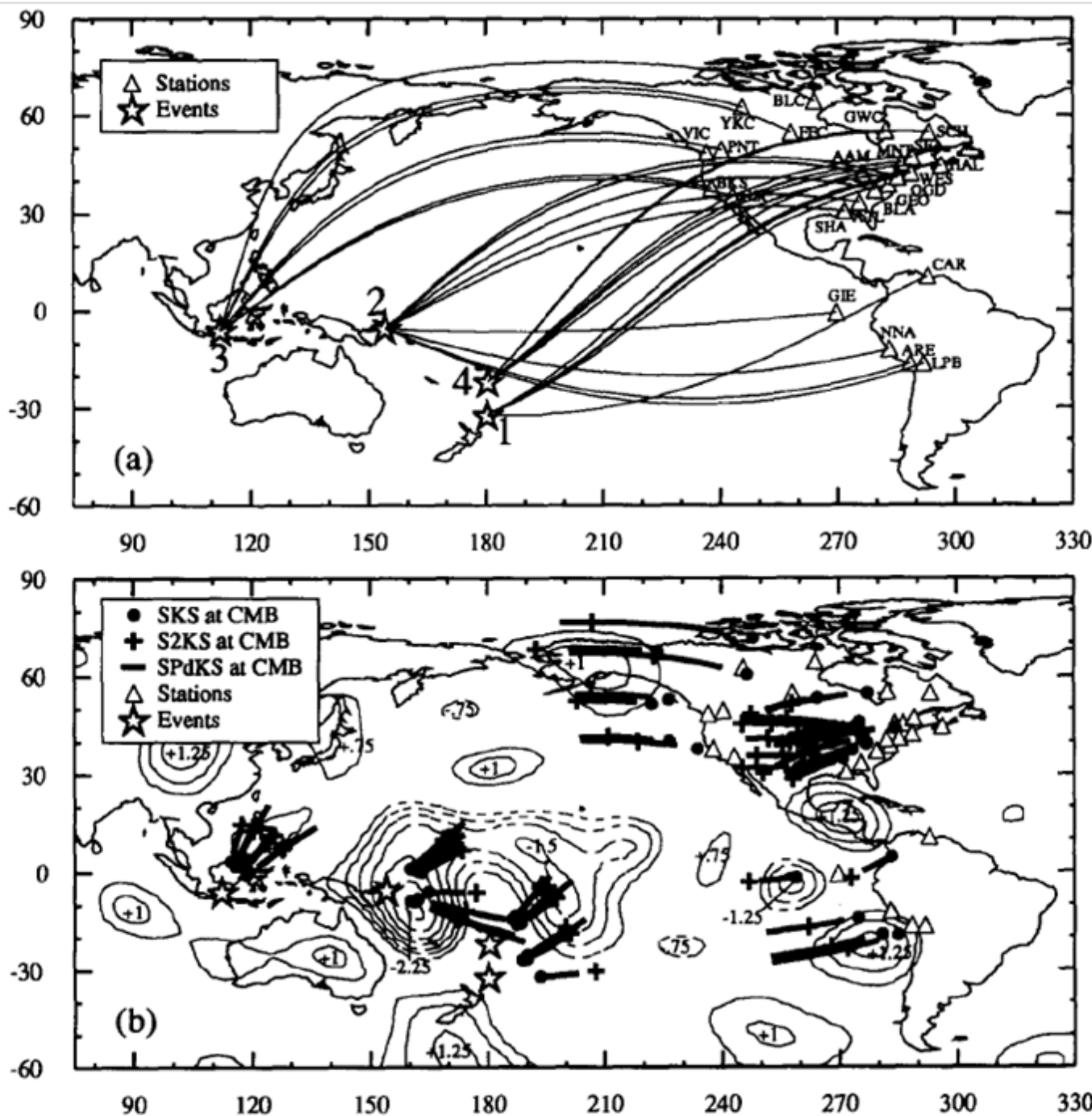
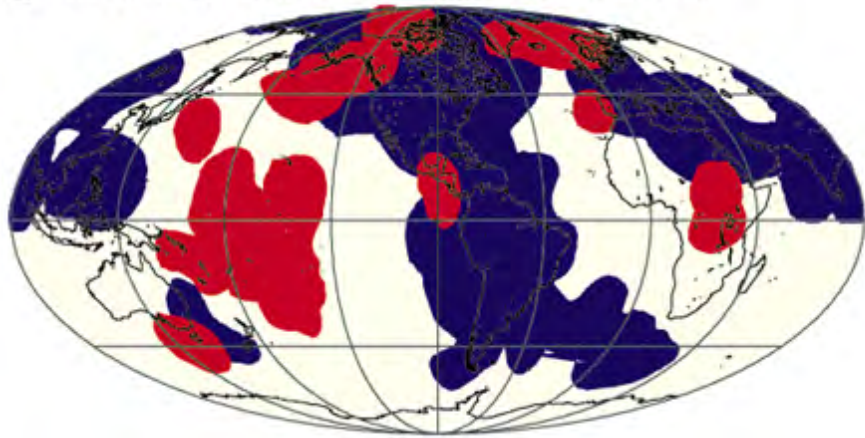
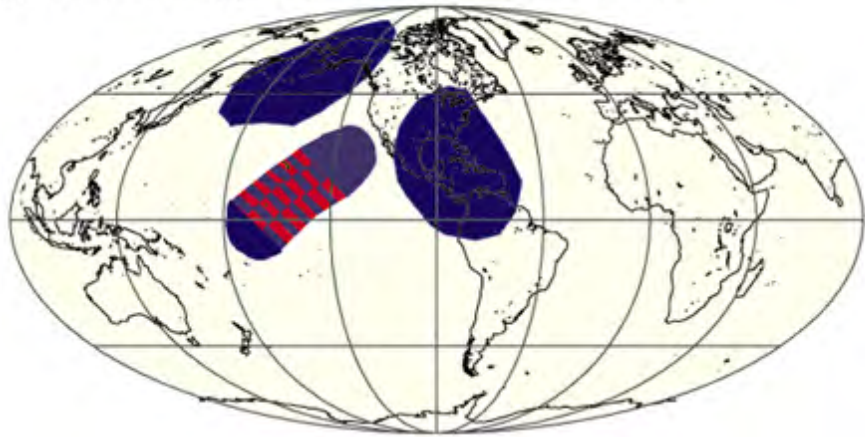


Fig. 2. (a) Great-circle raypaths projected to the Earth's surface between events (☆) and stations (Δ). Only paths for records with clearly measurable SKS, SP_dKS and SKKS are shown. (b) CMB crossing locations of SKS (●) and S2KS (+), and P-diffraction segments in SP_dKS. Also displayed are δV_s perturbations of magnitude greater than or equal to $|\pm 0.75|\%$ as given by model SH12_WM13 (Su et al., 1994).

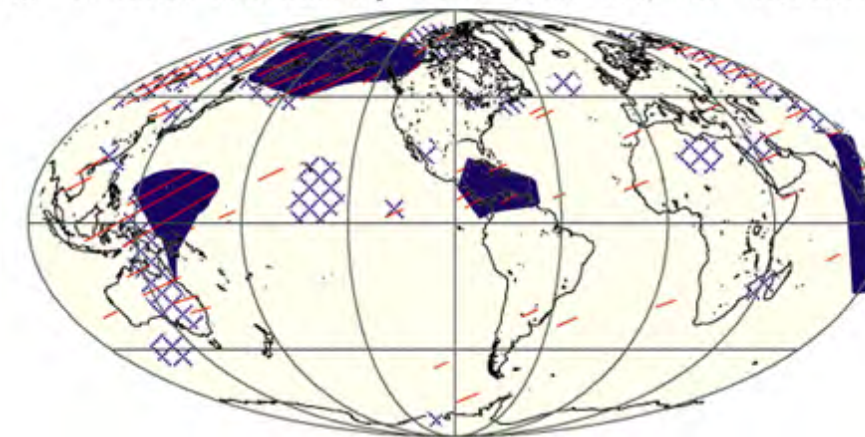
a ULVZ: red - observed, blue - not observed



b D" anisotropy: red - SV>SH, blue - SH>SV



c D" shear discontinuity: blue - observed, red - not observed



Global mapping of V_s reductions (ULVZs), V_s anisotropy, and V_s discontinuities at the CMB ...

Figure 3: Recent high-resolution global seismic tomography models for P-wave³¹ and S-wave³⁰ velocity heterogeneity near depths (Z) of 1,350 km (top row) and 2,750 km (bottom row). **a**, Regions with detectable ultra-low-velocity zone (ULVZ) structure are shown in red, and sampled regions that lack evidence of any ULVZ are shown in blue²⁹. **b**, Regions with shear-wave anisotropy in D" are shown²⁶. Transverse isotropy, caused by horizontal layers with strong velocity contrasts (as indicated schematically) or by hexagonally symmetric minerals with aligned vertical symmetry axes, could account for SH waves traveling faster than SV waves in these regions. The central Pacific region has a mix of no anisotropy and general anisotropy (possibly triclinic, or hexagonal symmetric minerals with variably orientated symmetry axes, or lamellae with variable orientation) with relatively small lateral coherence. **c**, Regions with shear-wave discontinuities near the top of the D" layer. Several regions show large-scale coherence (solid blue), with mixed areas lacking extra reflections (red stripes), while in some areas the reflection from D" is highly variable and intermittent (cross-hatched)²¹.

← (... long ago half-jokingly referred to as the "Thorne Layer"...) →

(Lay, Williams, and Garnero, 1998)

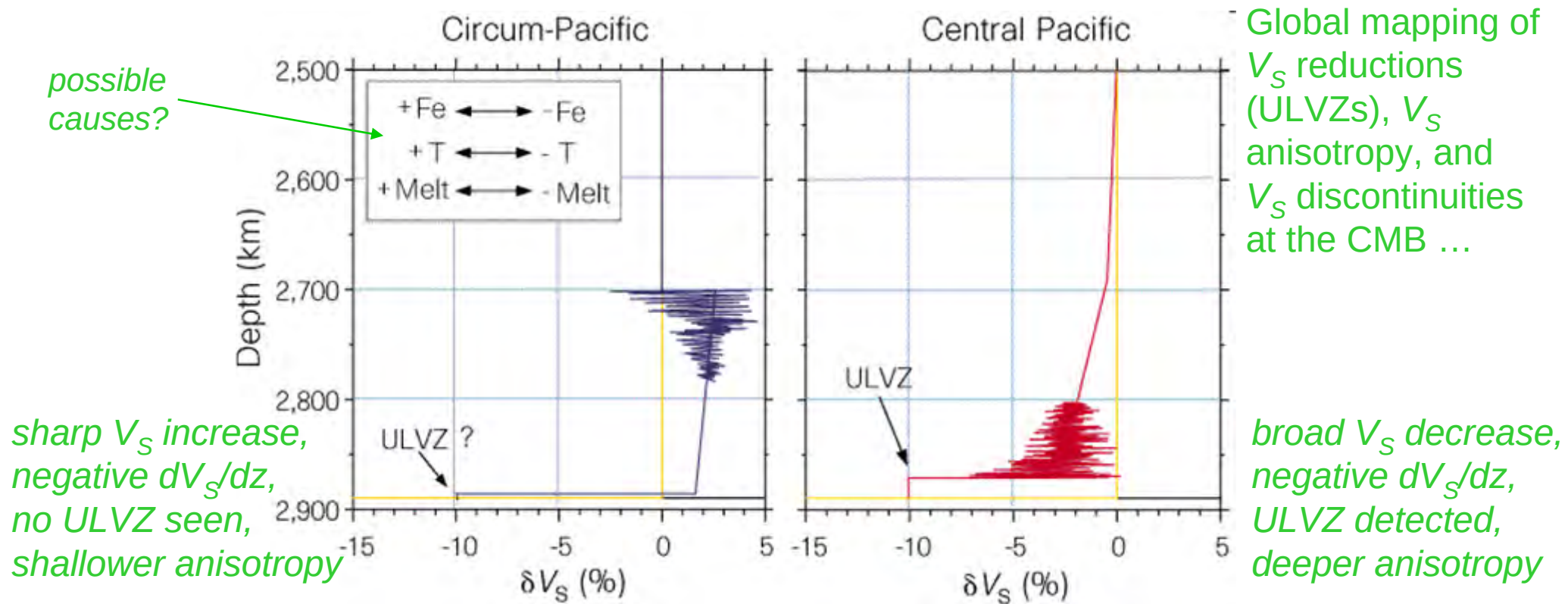


Figure 4: The main classes of D" shear-wave velocity structures. Schematic shear-wave velocity structures (shown as per cent deviations (δV_S) relative to a standard reference Earth model which has smoothly varying structure in the lower mantle) for circum-Pacific (**left**) and central Pacific (**right**) regions. The circum-Pacific regions under Alaska and the Caribbean are well characterized to have relatively abrupt shear velocity increases near 250 km above the CMB, with mild negative gradients throughout the D" layer. The blue model indicates that these high-velocity regions are relatively cold. These regions also have shear-wave splitting consistent with transverse isotropy, which is represented here by thin horizontal lamellae of strongly varying material properties (possibly involving melt), concentrated near the depth of the discontinuity. Any ULVZ in these regions is so thin as to not be detectable in most cases, and it may not be present. The central Pacific region is characterized by strong negative gradients of shear velocity extending over 200–300 km above the CMB, with little evidence for any discontinuity. The red model indicates that these low-velocity regions are relatively hot. This region has a thick, pronounced ULVZ, with shear velocity decreases that are of the order of 5–30%. There appears to be laterally variable general anisotropy, concentrated towards the base of the D" region (and possibly in the ULVZ as well). The sense of velocity perturbation with respect to increasing or decreasing Fe concentration, temperature (T) or partial melt is indicated by the inset box.

(Lay, Williams, and Garnero, 1998)

ULVZ thickness and V_p reduction: Modeled dependence upon thickness of chemically distinct layer (d_{ch}), T_{CMB} , and ΔT_{CMB} – without invoking partial melt

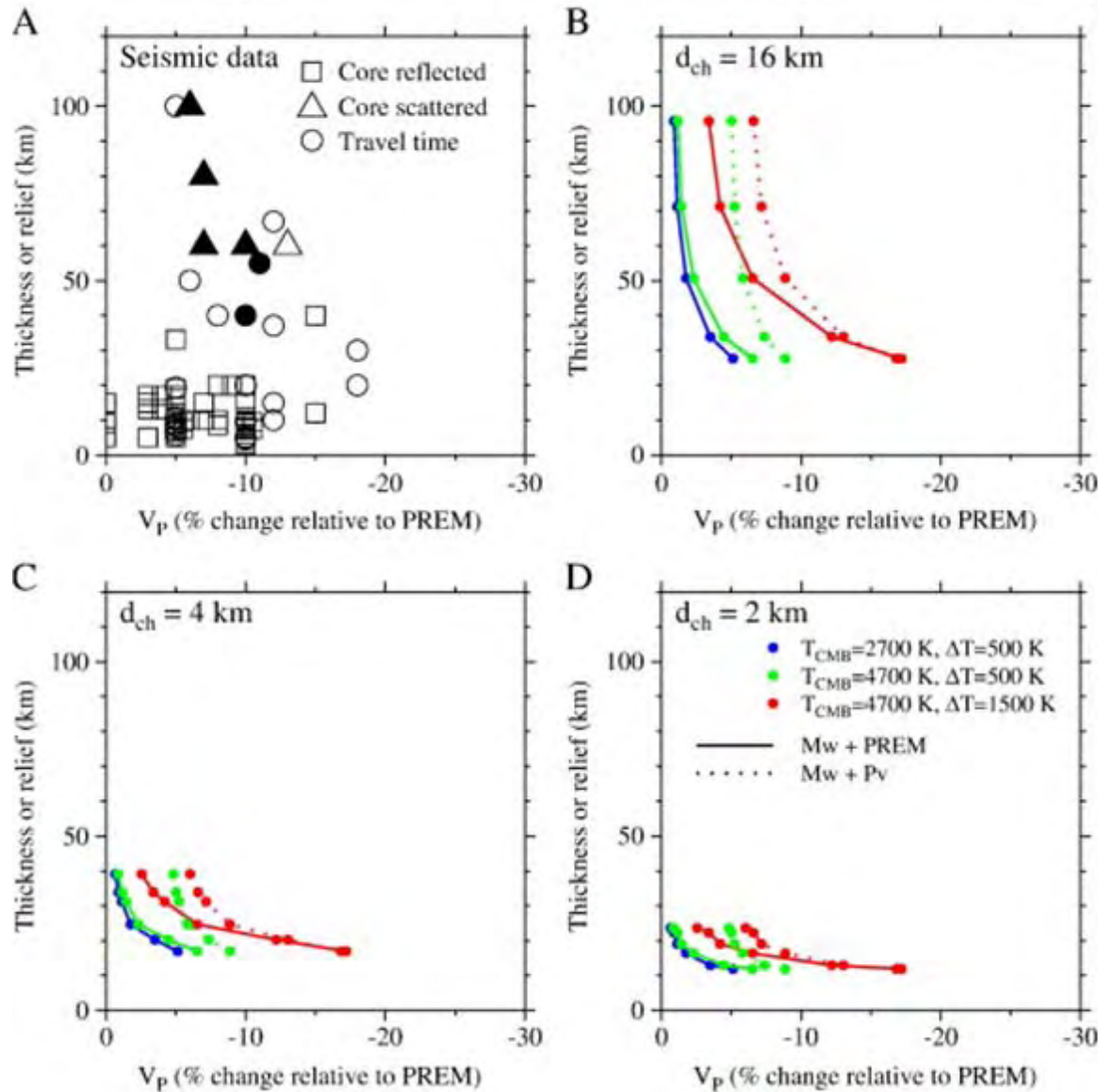


Fig. 8. (A) Summary of seismically inferred ULVZ thicknesses and P-wave velocity reductions found globally. Following the nomenclature of Garnero and Thorne (2004): $\square$ precursors to core reflected phases ([Garnero and Vidale, 1999], [Havens and Revenaugh, 2001], [Hutko et al., 2009], [Kohler et al., 1997], [Mori and Helmberger, 1995], [Reasoner and Revenaugh, 2000], [Rost and Revenaugh, 2003], [Rost et al., 2005], [Rost et al., 2006] and [Rost et al., 2010a]), $\triangle$ scattered core phases ([Ni and Helmberger, 2001b], [Niu and Wen, 2001], [Vidale and Hedlin, 1998] and [Wen and Helmberger, 1998a]), $\circ$ travel time and waveform anomalies ([Garnero and Helmberger, 1995], [Garnero and Helmberger, 1996], [Garnero et al., 1993], [Helmberger et al., 1996], [Helmberger et al., 1998], [Helmberger et al., 2000], [Luo et al., 2001], [Ni and Helmberger, 2001a], [Rondenay and Fischer, 2003], [Simmons and Grand, 2002], [Thorne and Garnero, 2004], [Wen, 2001] and [Wen and Helmberger, 1998b]). Filled symbols denote 2-D studies. (B, C, and D) Models using the Hill bound, for various d_{ch} , temperature at the CMB (T_{CMB}), and temperature drop (ΔT). Solid lines are the "Mw + PREM" model and dotted lines are the "Mw + Pv" model.

(Bower et al., *EPSL*, 2011)

ULVZ thickness and V_S reduction: Modeled dependence upon thickness of chemically distinct layer (d_{ch}), T_{CMB} , and ΔT_{CMB} – without invoking partial melt

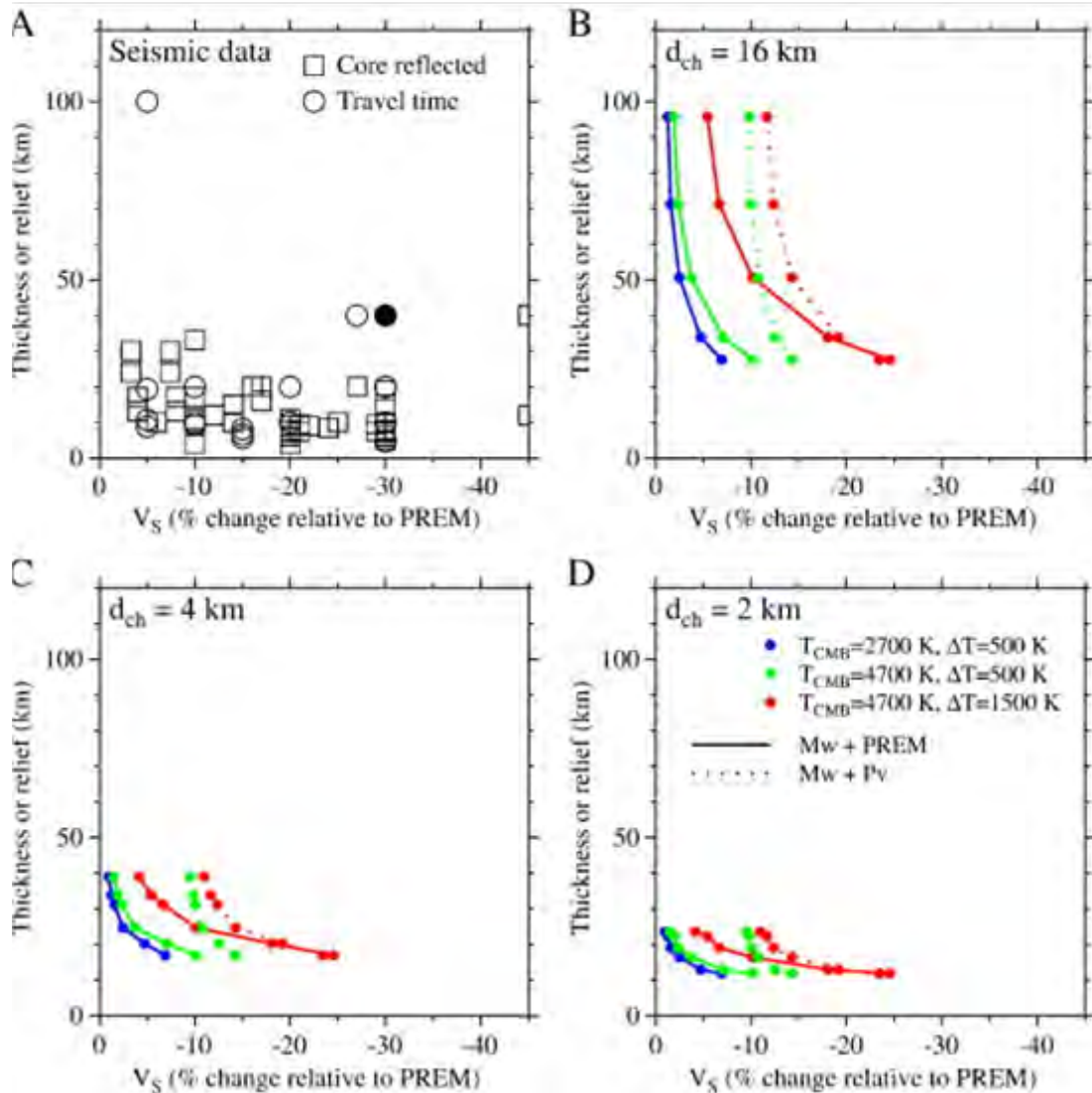


Fig. 9. (A) Seismically inferred ULVZ thicknesses and S-wave velocity reductions found globally. Following the nomenclature of Garnero and Thorne (2004): $\square$ precursors to core reflected phases ([Avants et al., 2006], [Garnero and Vidale, 1999], [Havens and Revenaugh, 2001], [Hutko et al., 2009], [Kohler et al., 1997], [Reasoner and Revenaugh, 2000], [Rost and Revenaugh, 2003], [Rost et al., 2005], [Rost et al., 2006] and [Rost et al., 2010a]), $\circ$ travel time and waveform anomalies ([Garnero and Helmberger, 1995], [Helmberger et al., 1998], [Helmberger et al., 2000], [Ni and Helmberger, 2001a], [Rondenay and Fischer, 2003], [Simmons and Grand, 2002], [Thorne and Garnero, 2004], [Wen and Helmberger, 1998b] and [Zhang et al., 2009]). Filled symbols denote 2-D studies. (B, C, and D) Models using the Hill bound, for various d_{ch} , temperature at the CMB (T_{CMB}), and temperature drop (ΔT). Solid lines are the “Mw + PREM” model and dotted lines are the “Mw + Pv” model.

(Bower et al., *EPSL*, 2011)

“Post-Perovskite”: The $pv \rightarrow ppv$ phase transition

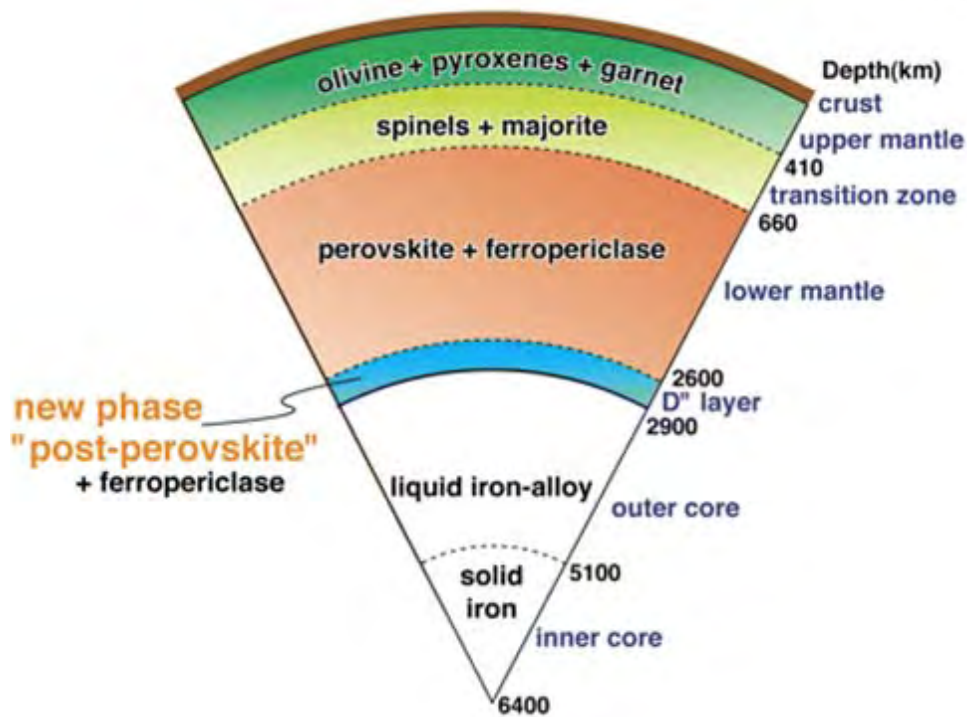


FIGURE 1. Simplified cross-section of the Earth. The main constituent minerals in the mantle change from olivine + pyroxenes + garnet (or Al-rich spinel) in the upper mantle, to spinels + majorite in the transition zone, to perovskite + ferropericlasite in the lower mantle, and to post-perovskite + ferropericlasite in the D" layer. The boundaries between the layers are characterized by seismic-wave discontinuities.

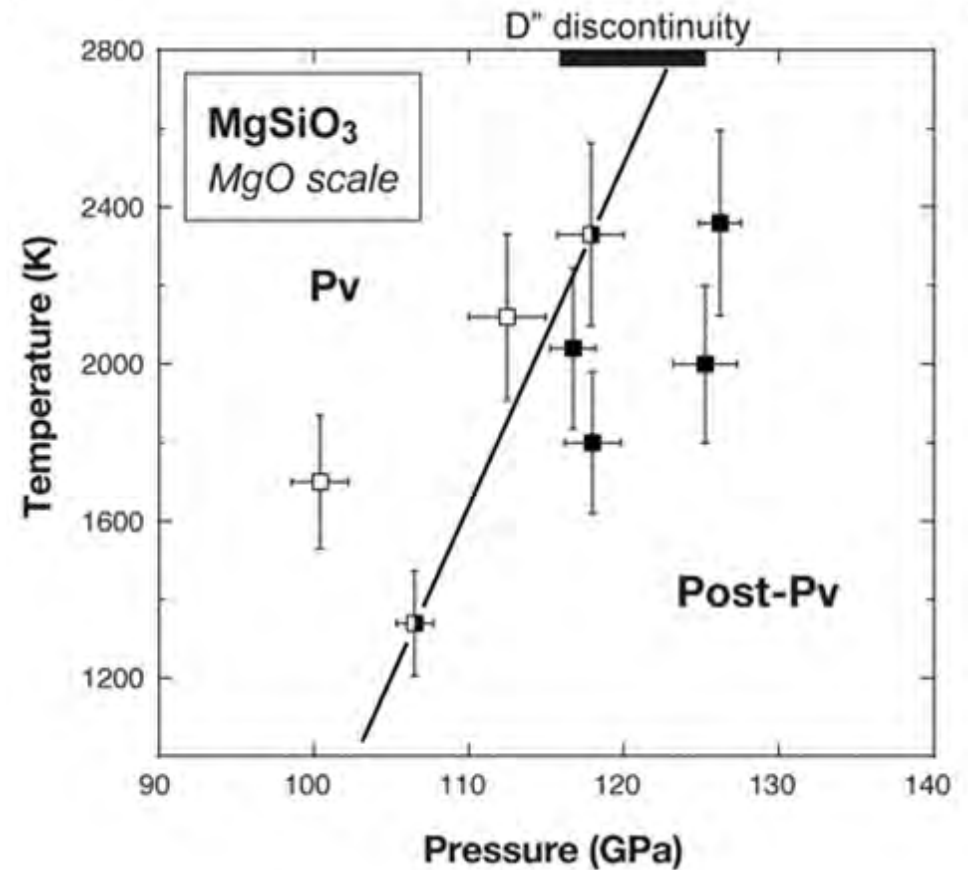


FIGURE 4. Phase diagram of MgSiO_3 based on the MgO pressure scale. Open symbols, perovskite; solid symbols, post-perovskite; half-filled symbols, coexistence of perovskite and post-perovskite. The post-perovskite phase transition occurs at 119 GPa and 2500 K, matching the general depth range of the D" discontinuity (2550 to 2700 km depth).

(Hirose and Lay, *Elements*, 2008)

Recall ...

vyšoký tlak

(Mg,Fe)SiO₃
orthopyroxene
(Mg,Fe)^{VI}Si^{IV}O₃



Wikipedia

akimotoite
(ilmenite-type)

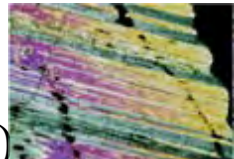


N.Tomioka
& K.Fujino

(Mg,Fe)^{VI}Si^{VI}O₃

majorite

(garnet-type)



J.Smyth

(Mg,Fe)^{VIII}₃[(Mg,Fe)^{VI}Si^{VI}]₂Si^{IV}₃O₁₂

silicate perovskite

(CaTiO₃-type)

(Mg,Fe)^{VIII}Si^{VI}O₃

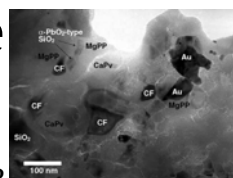


HACTO

post-perovskite

(CaIrO₃-type)

(Mg,Fe)^{VIII}Si^{VI}O₃



K.Hirose +

pv→ppv phase transition

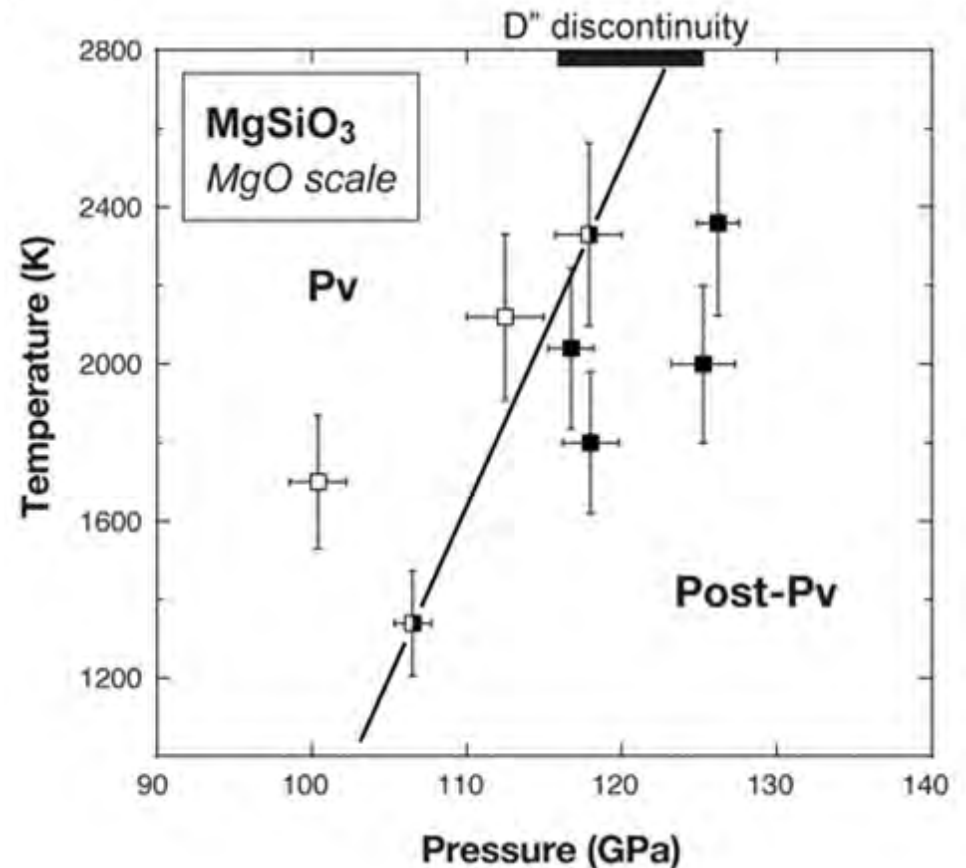


FIGURE 4. Phase diagram of MgSiO₃ based on the MgO pressure scale. Open symbols, perovskite; solid symbols, post-perovskite; half-filled symbols, coexistence of perovskite and post-perovskite. The post-perovskite phase transition occurs at 119 GPa and 2500 K, matching the general depth range of the D'' discontinuity (2550 to 2700 km depth).

(Hirose and Lay, *Elements*, 2008)

Double crossing of $pv \rightarrow ppv$ phase boundary? ∇T dependence?

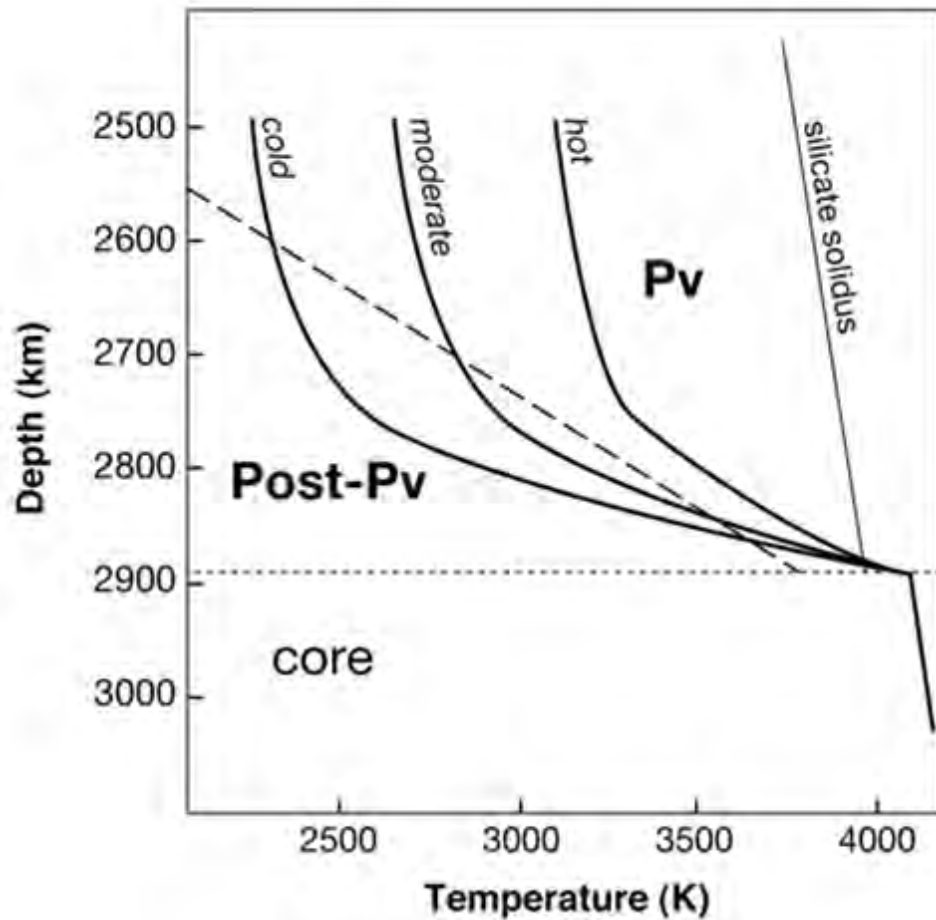


FIGURE 5. Possible thermal structure in D'' (Hernlund et al. 2005). The CMB temperature may be higher than a silicate solidus and perhaps higher than a solidus temperature for MORB composition (Hirose et al. 1999), thus accounting for partial melting in the ultralow-velocity zone. The geotherm (dashed line) intersects a post-perovskite phase-transition boundary twice in D'', except in hot regions, where post-perovskite may not be present.

(Hirose and Lay, *Elements*, 2008)

Double crossing of $pv \rightarrow ppv$ phase boundary? ∇T dependence?

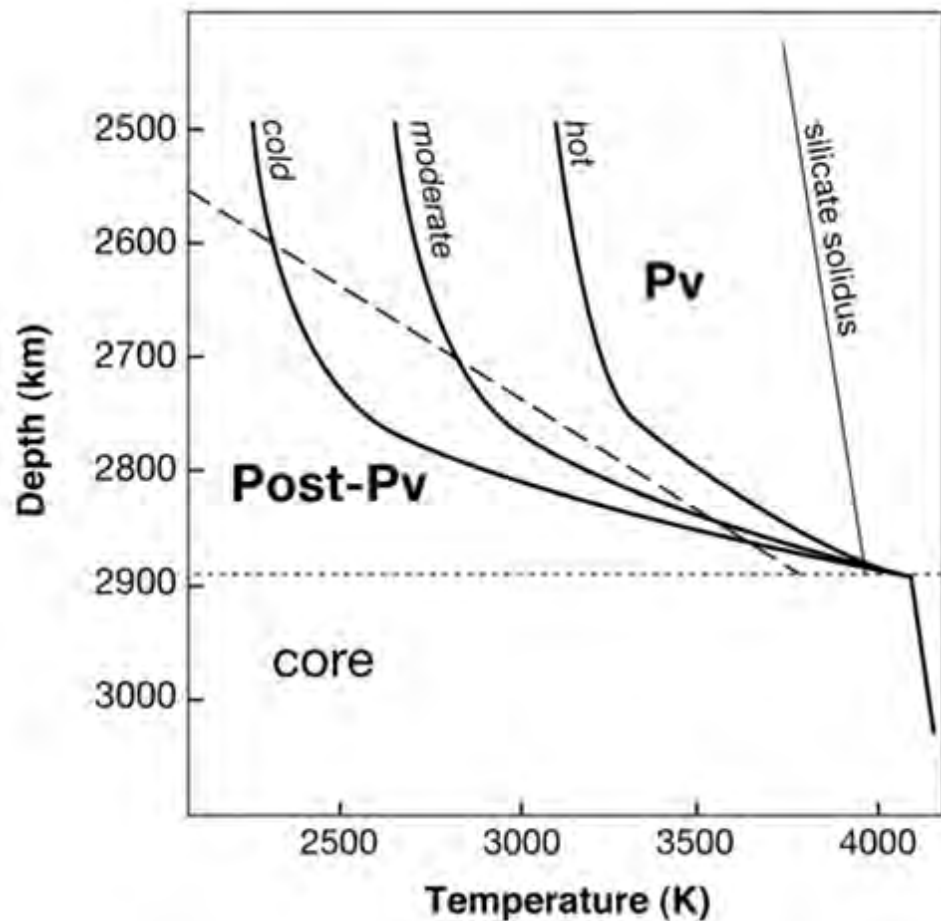
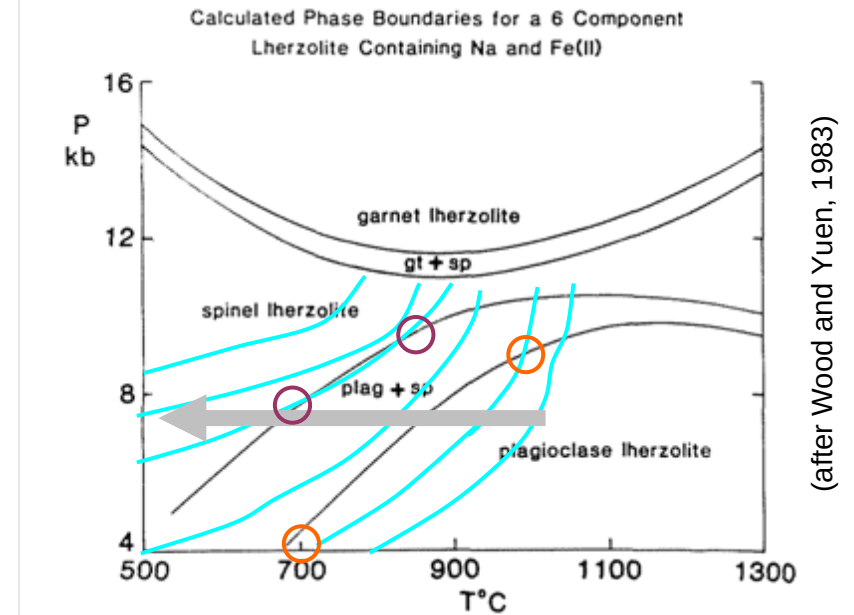


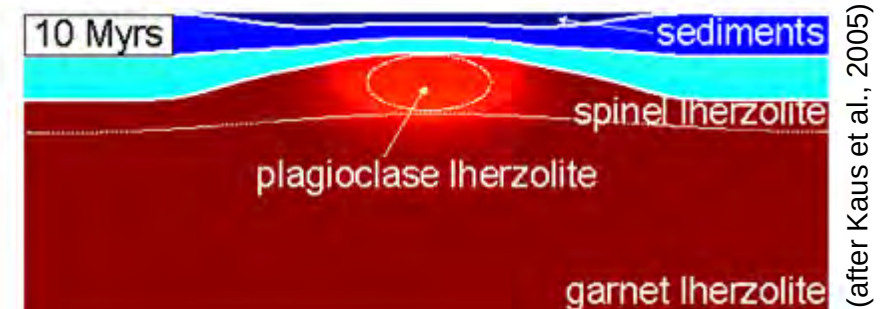
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(Hirose and Lay, *Elements*, 2008)

Recall ...



Warm (young) geotherms may intersect plagioclase lherzolite field twice.



Double crossing of $pv \rightarrow ppv$ phase boundary? ∇T dependence?

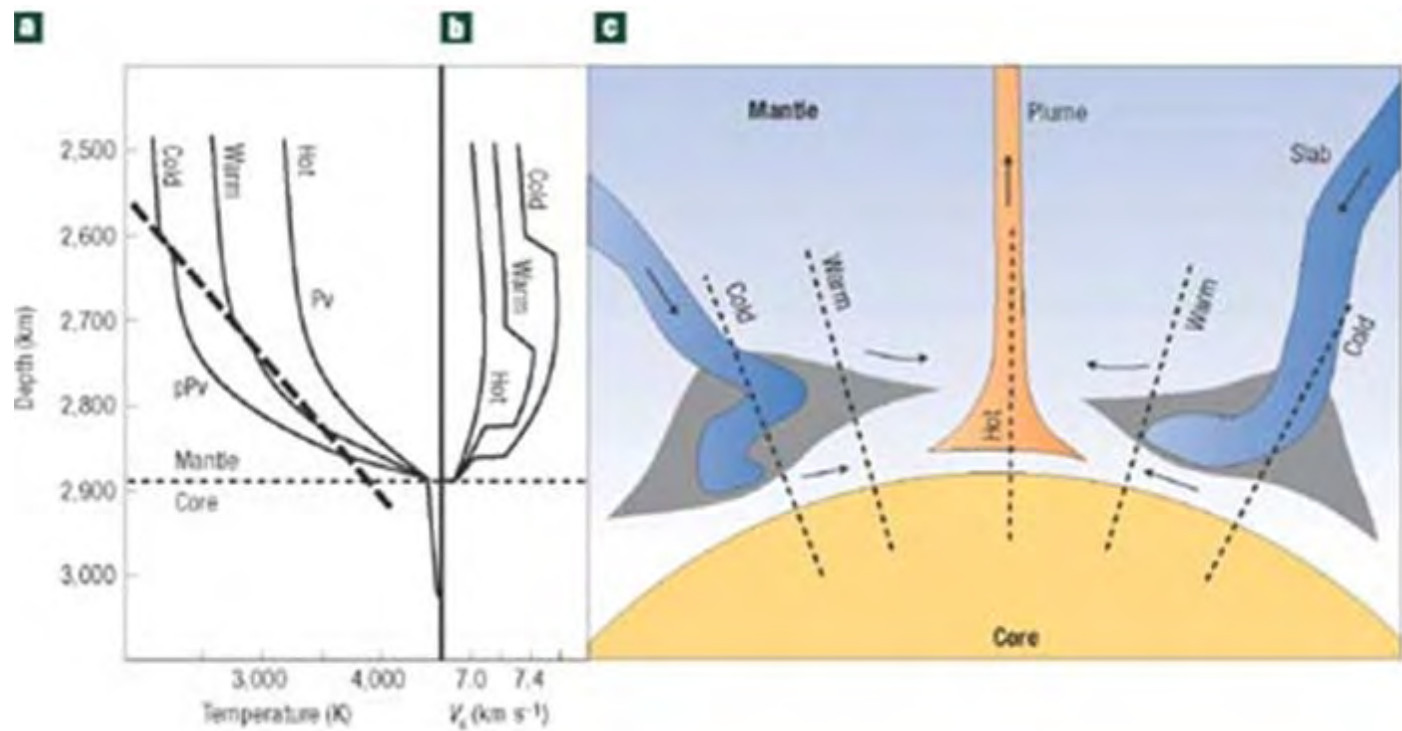


Figure 4 - Post-perovskite occurrence. The presence of the perovskite to post-perovskite phase transition in the lower mantle may account for observed increases in S-wave velocity (V_s) several hundred kilometres above the CMB, and thermal variations may produce the observed topography at the boundary. If the temperature at the CMB exceeds the temperature at which the phase transition boundary intersects the CMB, a double crossing could occur, with reversion to perovskite at the base of the mantle. This could be detected by occurrence of a velocity decrease below the S-velocity increase in D'', and the occurrence of post-perovskite that may pinch out laterally, producing lenses of material (grey zones).

(Lay, Hernlund, and Buffett, *Nature Geoscience*, 2008)

Double crossing of $pv \rightarrow ppv$ phase boundary?

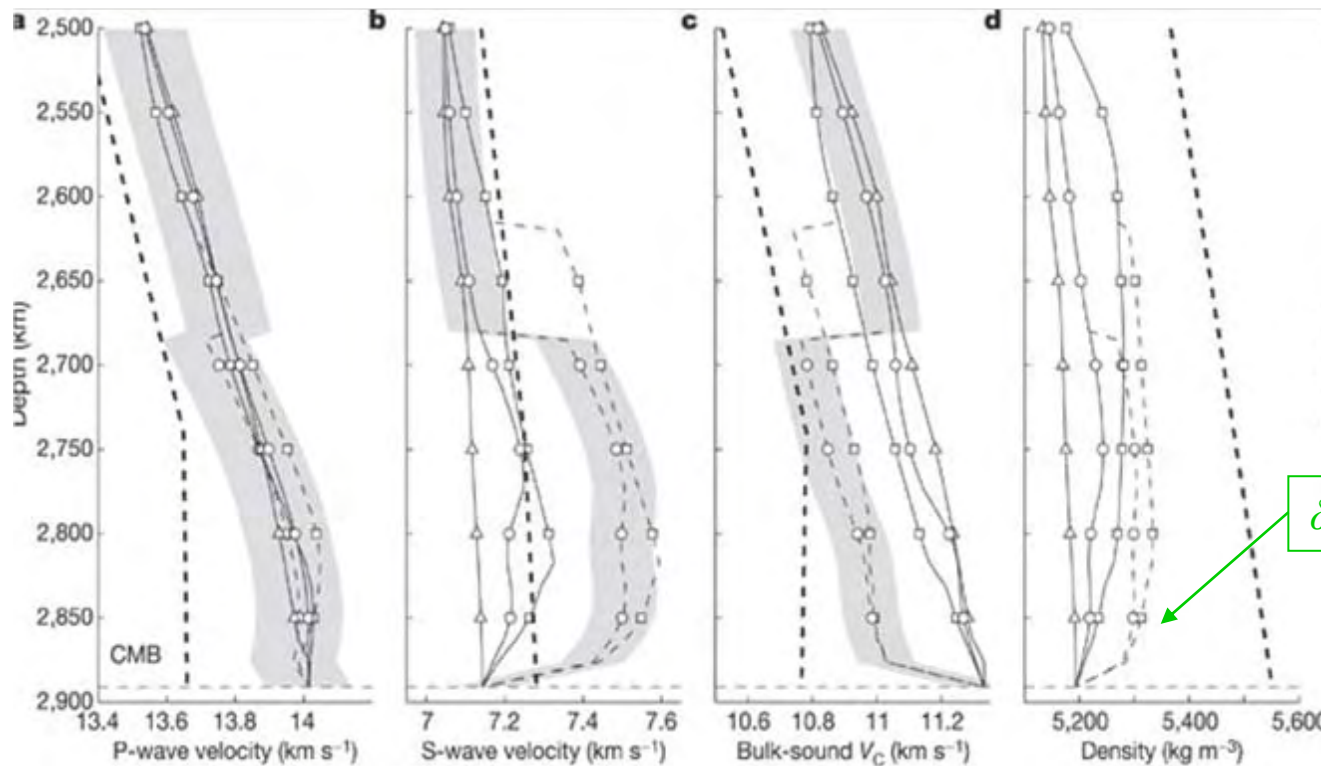


FIGURE 2. Seismic properties interpolated from *ab initio* calculations.

These show the P-wave (a) and S-wave (b) velocities, the bulk-sound speed (c) and the density (d) for the 'hot' (triangles), 'average' (circles) and 'cold' (squares) mantle convection profiles. These are converted from the temperature profiles in Fig. 1 into variation of the seismic properties with depth by interpolation of our *ab initio* results. The solid traces are the variation solely due to temperature (in perovskite), and the dashed lines are where a phase-transformation is included. The shaded area shows the estimated constraint for the average profile (other profiles are similarly constrained). For comparison the velocities and density from the reference model ak135 (ref. 15) are included (black dashed trace).

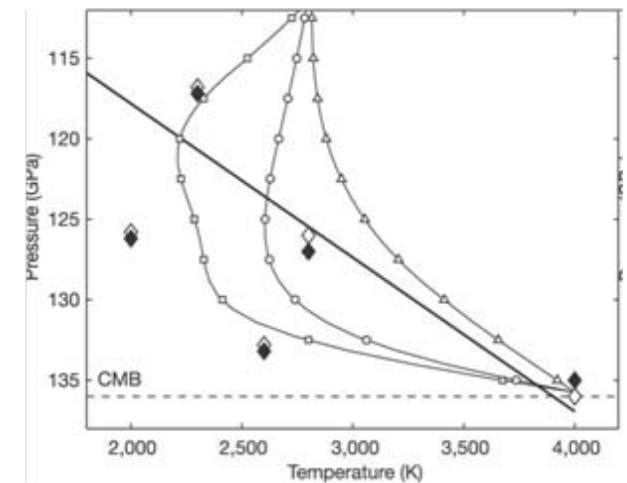


FIGURE 1. Phase boundary⁷ and calculation points for the perovskite and post-perovskite polymorphs of MgSiO₃. We show the variation of temperature with pressure for three vertical profiles in a mantle convection model⁴. These come from 'hot' (triangles), 'cold' (squares) and 'average' (circles) parts of the mantle. Also plotted is the phase boundary from ref. 7; MgSiO₃ has a perovskite structure above this line, and a post-perovskite form below it. The 'cold' and 'average' profiles cross this boundary twice, thus predicting a thick post-perovskite layer underlain by a thin perovskite layer (similar to ref. 5). The 'hot' profile does not cross the phase boundary at all. It should be noted that this linear phase boundary is approximate; deviation from this will change the transition pressure. The dashed line indicates the CMB. The open and solid diamonds show the positions for which we have *ab initio* calculations of the seismic properties of the perovskite and post-perovskite, respectively.

(Wookey et al., *Nature*, 2005)

(C.Bina, 9/2011)

Large Low Shear-Velocity Provinces (LLSVPs)

chemical compositional variation,
high ρ but low V_s , combined with
 $pv \rightarrow ppv$ phase transitions?

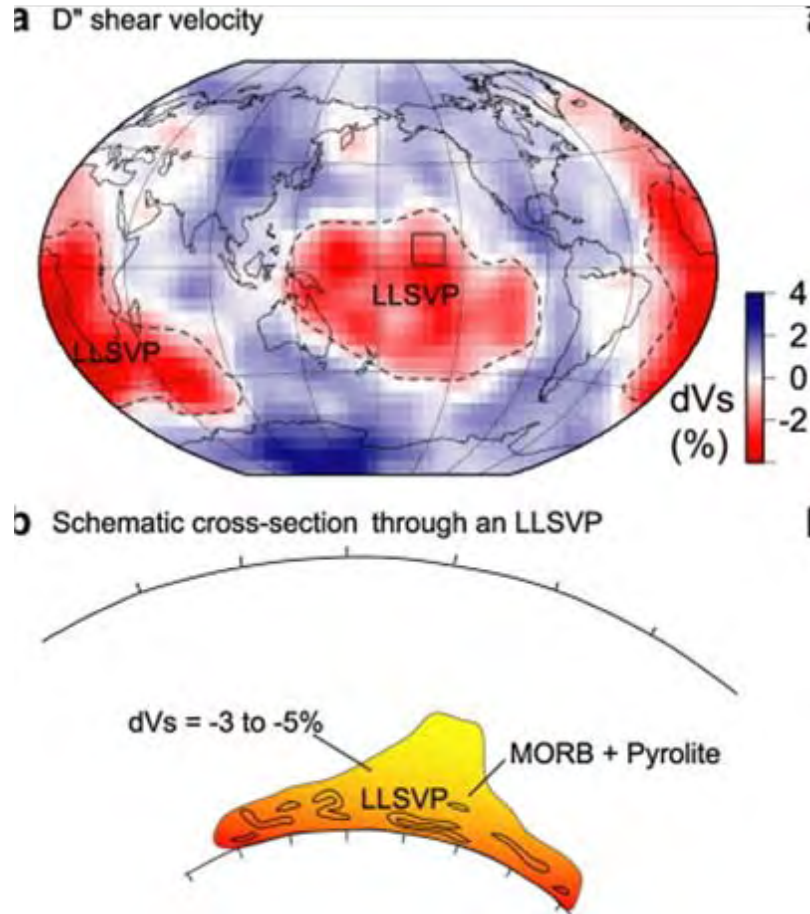


Fig. 1. (a) S-wave velocity variations in the lowermost 200-km of the mantle in the seismic tomography model of Grand (2002). The large low shear velocity provinces (LLSVP) regions appear to be dense and chemically distinct from surrounding mantle (Lay and Garnero, 2004). (b) Schematic cross-section through an LLSVP, suggesting that a mix of dense, separated MORB and pyrolitic mantle comprises the pile. Phase transitions within the pile give rise to the reflectivity (Fig. 8) shown for the northern edge of the Pacific LLSVP (see small box in (a) corresponds to Fig. 2c).

(Ohta et al., *EPSL*, 2008)

A Combined Picture of D'' ?

Double crossing of $pv \rightarrow ppv$ phase boundary? Lateral ∇T variations?
Lateral compositional variations? Partial melting?

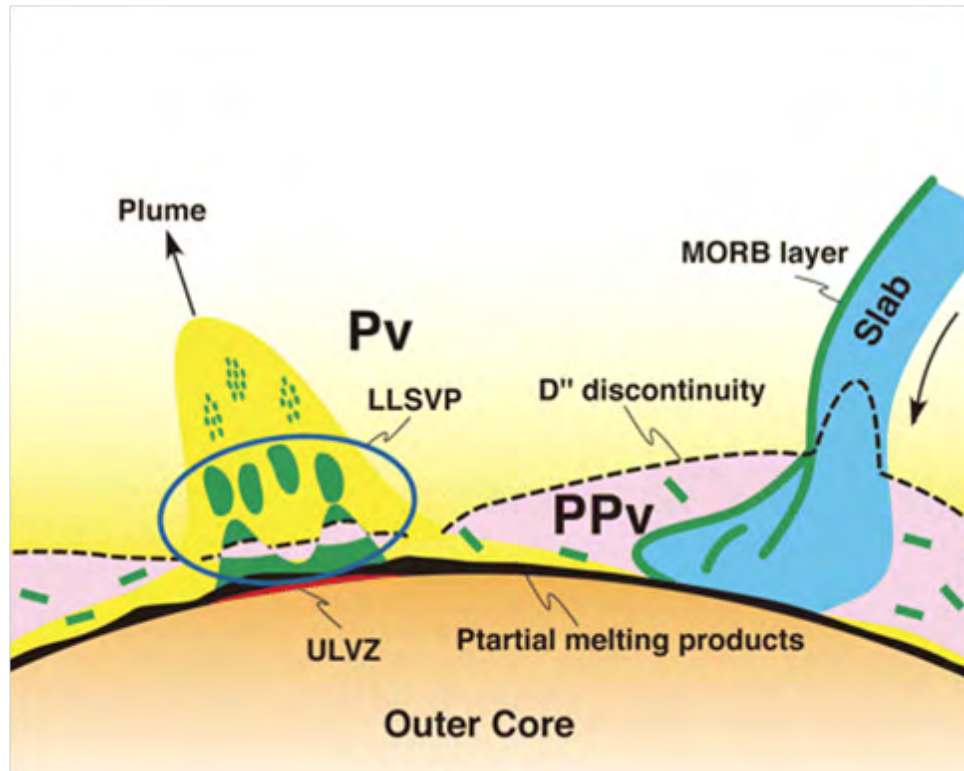


FIGURE 6. Cartoon scenario for the D'' region. The D'' seismic discontinuity is caused by the perovskite (Pv) to post-perovskite (PPv) phase transition. Post-perovskite may transform back to perovskite in the bottom thermal boundary layer with a steep temperature gradient. The large low-shear-velocity provinces (LLSVP) underneath upwellings (forming plumes) possibly represent large accumulations of dense MORB-enriched materials. The solid residue formed by partial melting in the ULVZ might also be involved in upwelling plumes.

(Hirose and Lay, *Elements*, 2008)

pv→*ppv* phase boundary shifted to lower *P* for *Al,Fe*-rich compositions?
*CaCl*₂→*α-PbO*₂ transition in *SiO*₂ largely invisible for *Si*-rich basalt?

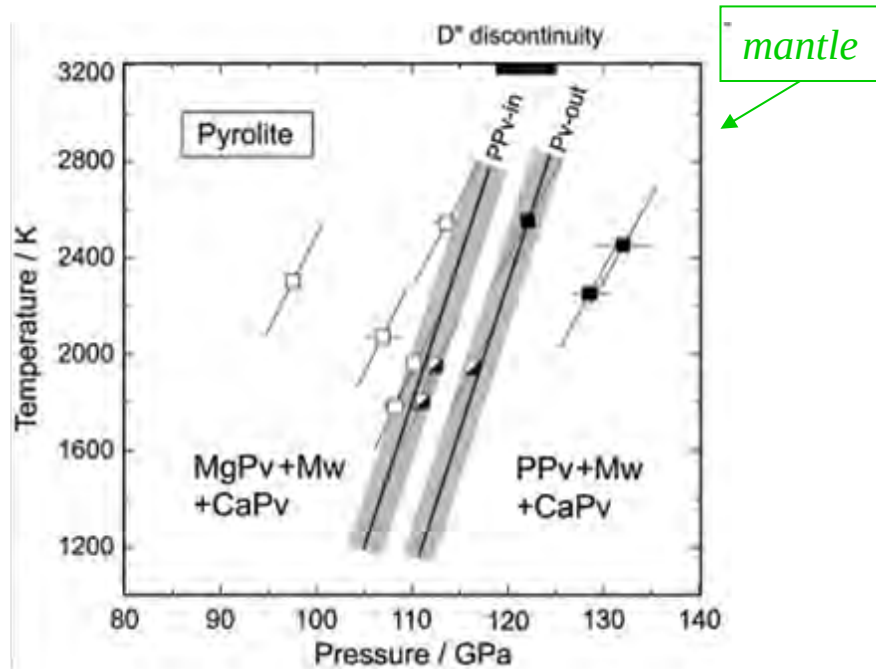


Fig. 4. Phase relations in a pyrolitic lowermost mantle. Open and solid symbols indicate the stabilities of Mg-perovskite and post-perovskite, respectively. Half-filled symbols show the coexistence of perovskite and post-perovskite. Magnesiowüstite and Ca-perovskite were observed in all the experiments. The horizontal error bars indicate pressure uncertainty due to the error in unit-cell volume of pressure standard. The oblique bars represent a pressure gradient corresponding to a temperature gradient ($\pm 10\%$) in the sample. The uncertainties in the locations of post-perovskite (PPv)-in and perovskite (Pv)-out curves are shown by gray. A general depth range of the D'' discontinuity (2600 to 2700-km depth) is indicated by a bar (Wyssession et al., 1998).

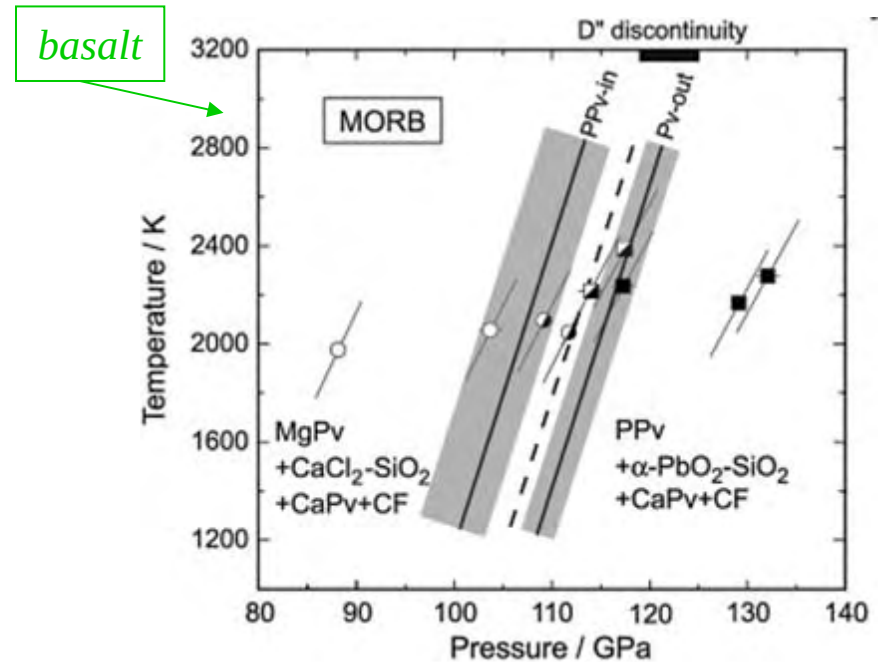


Fig. 5. Phase relations in a subducted MORB crust at lowermost mantle conditions. The stabilities of Mg-perovskite and post-perovskite were shown by open and solid symbols, respectively. Half-filled symbols indicate the coexistence of perovskite and post-perovskite. The boundaries are assumed to have the same pressure/temperature slope as that for pyrolite, and the gray indicates the uncertainties in their locations. The dashed line indicates the phase transition boundary between *CaCl*₂-type (circles) and *α-PbO*₂-type (squares) *SiO*₂ phases.

(Ohta et al., *EPSL*, 2008)

$pv \rightarrow ppv$ phase boundary shifted to lower P for Al, Fe -rich compositions?
 $CaCl_2 \rightarrow \alpha\text{-}PbO_2$ transition in SiO_2 largely invisible for Si -rich basalt?

Recall ...

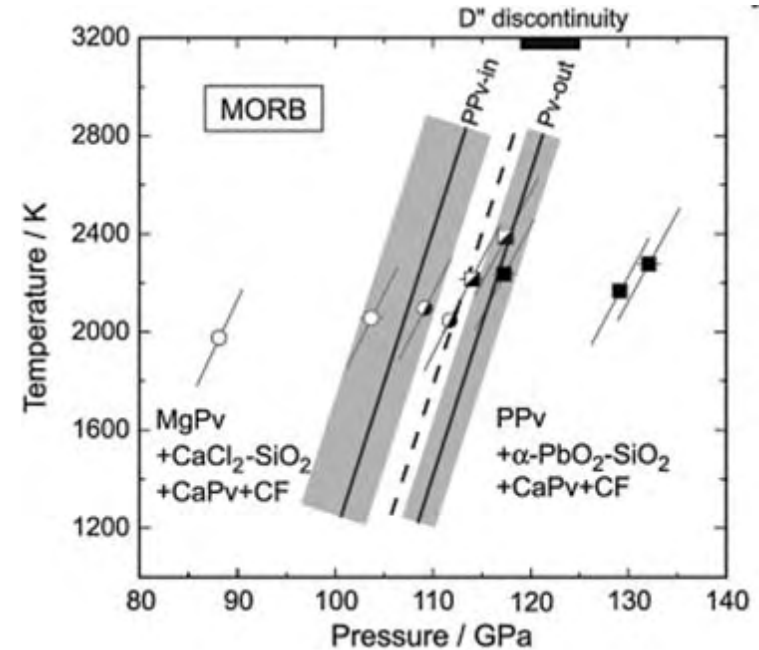
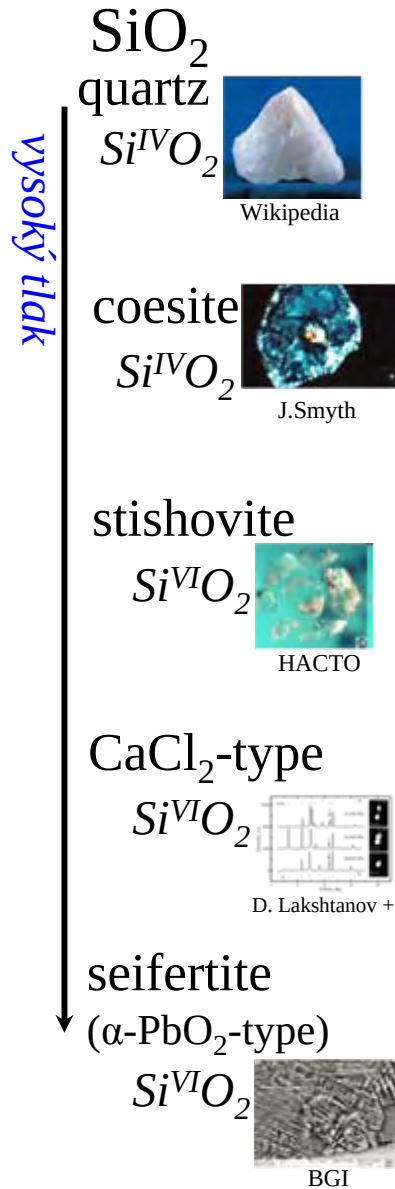


Fig. 5. Phase relations in a subducted MORB crust at lowermost mantle conditions. The stabilities of Mg-perovskite and post-perovskite were shown by open and solid symbols, respectively. Half-filled symbols indicate the coexistence of perovskite and post-perovskite. The boundaries are assumed to have the same pressure/temperature slope as that for pyrolite, and the gray indicates the uncertainties in their locations. The dashed line indicates the phase transition boundary between $CaCl_2$ -type (circles) and $\alpha\text{-}PbO_2$ -type (squares) SiO_2 phases.

(Ohta et al., *EPSL*, 2008)

$pv \rightarrow ppv$ phase boundary shifted to lower P and broadened for Al-rich compositions

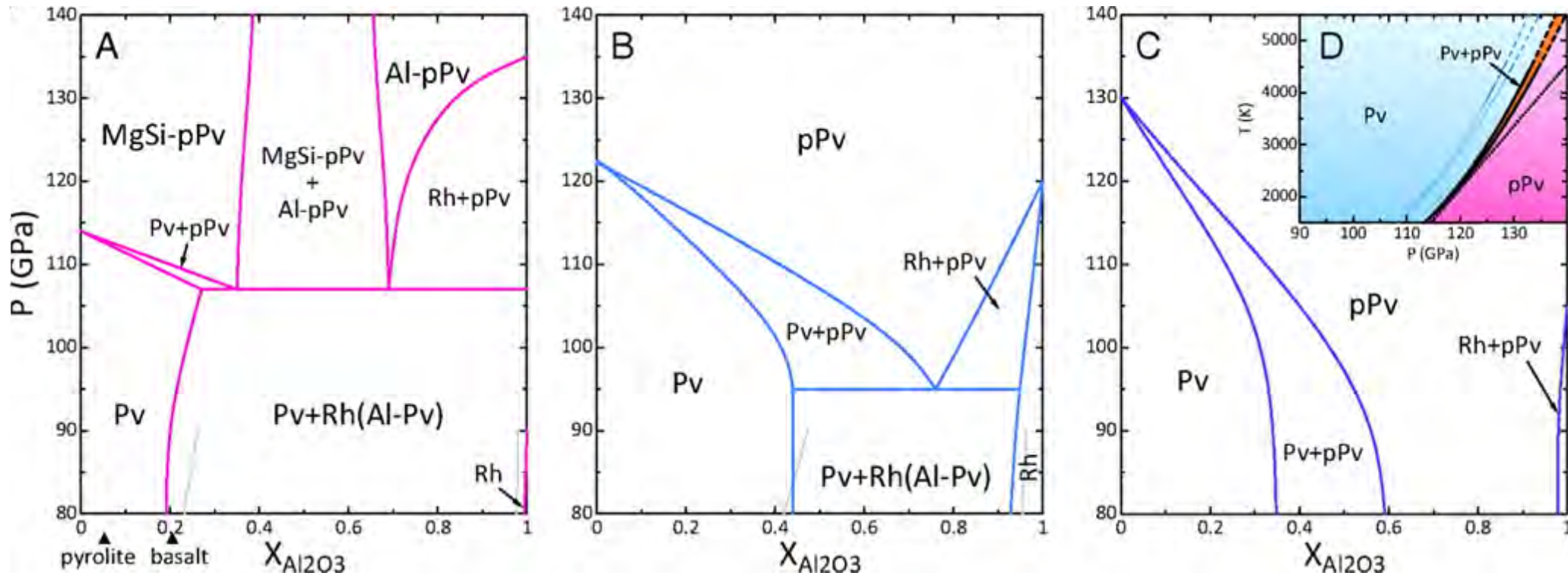


Fig. 3. Calculated phase equilibria in the $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ system. (A–C) at 2,000 K (A), 3,000 K (B), and 4,000 K (C) with low-pressure results of the Pv -Corundum system (gray lines) (26). (D) A P,T section at pyrolitic concentration $x_{\text{Al}_2\text{O}_3} = 6$ mol% is shown, where thin, thick, and dotted lines are the bare phase boundaries calculated within LDA, the shifted boundaries after the corrections for exchange correlation energy (32), and the phase boundary for pure MgSiO_3 with a Clapeyron slope of 7.5 MPa/K (2), respectively. Those are drawn by dashed lines over the QHA limit (12, 23). (Tsuchiya and Tsuchiya, *PNAS*, 2008)

$pv \rightarrow ppv$ phase boundary shifted to lower P and broadened for Al-rich compositions

Recall ...

$N=2, R=2: F'=1$

$N=2, R=3: F'=0$

**The
Phase
Rule**

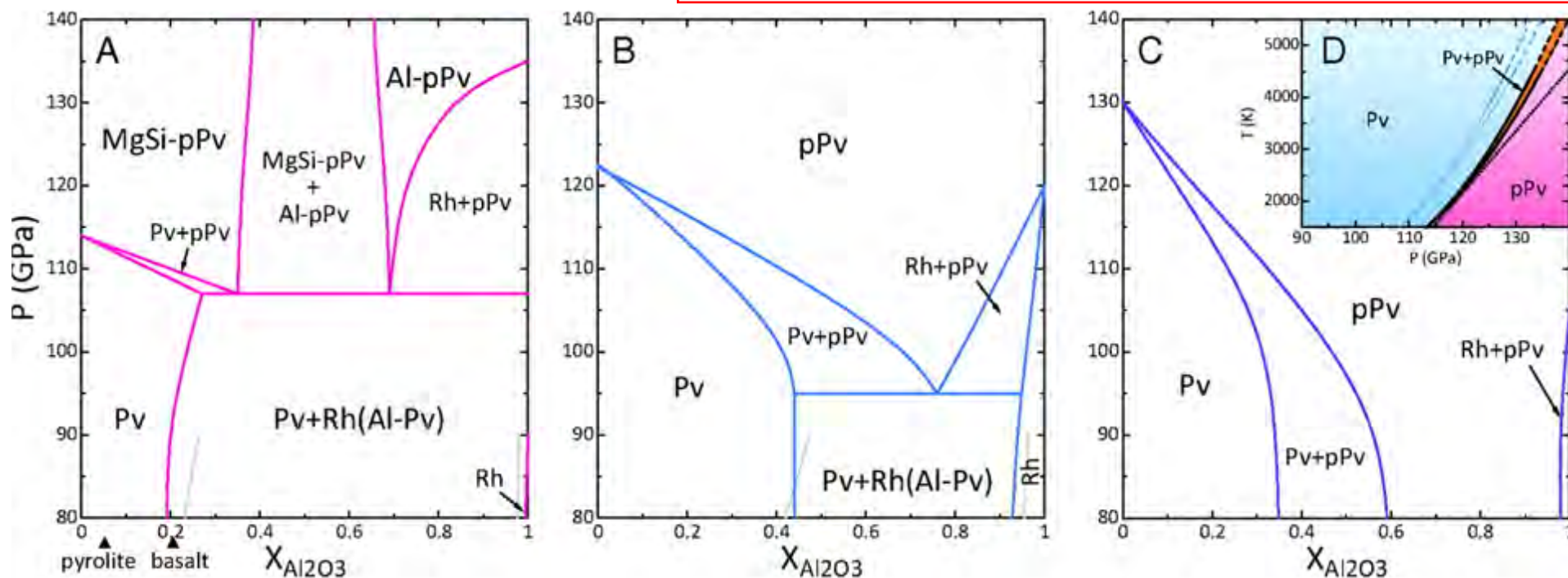
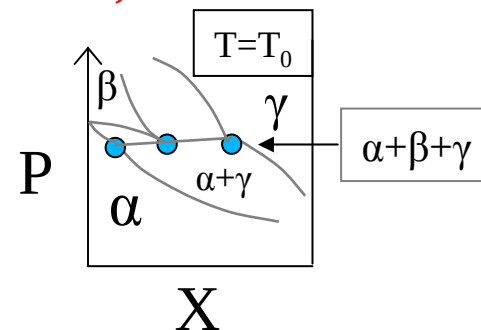
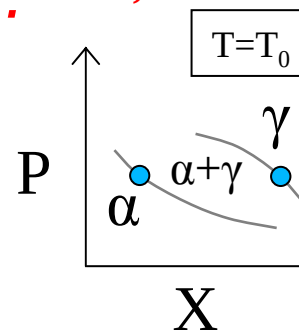
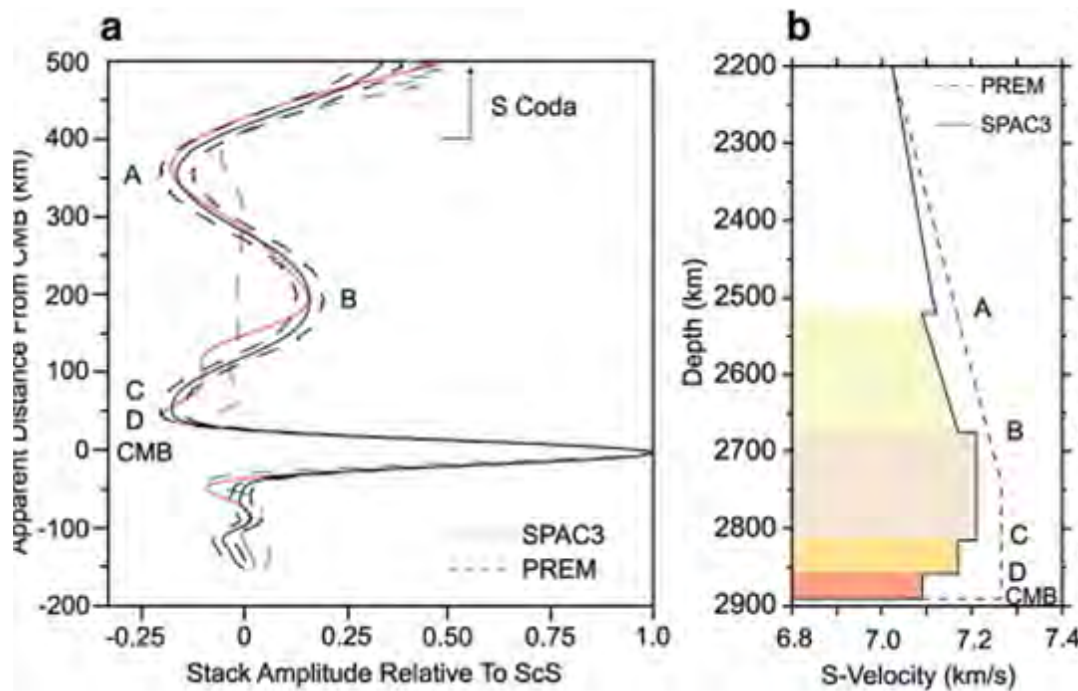


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Further Complexity ...



Double crossing of $pv \rightarrow ppv$ phase boundary is invoked to explain two discontinuities in V_S ... but how to explain four?

Fig. 8. Seismogram stack and velocity profile for the northern margin of the Pacific LLSVP. (a) Double-array stack of 444 transverse component (SH) recordings of Tonga–Fiji earthquakes made at broadband stations in California (see example waveforms in Fig. 6 and Fig. 7). The traces were aligned and normalized on the core–mantle boundary (CMB) reflected phase ScS , and stacked to determine reflectivity of energy as a function of depth relative to the CMB (solid black line). Bootstrap uncertainties on the stack are shown by dashed lines (Avants et al., 2006). The stacked data for depths more than 450-km above the core are contaminated by coda from direct S arrivals that turn at shallower depths. The blue dashed curve shows the results of stacking of similarly processed synthetics for model PREM (Dziewonski and Anderson, 1981). The red curve shows the results of stacking synthetics for model SPAC3. (b) The velocity profiles for PREM and SPAC3. SPAC3 had four velocity discontinuities (A, B, C, D) that produce reflectivity associated with the corresponding labeled peaks on the left. For the interpretation of this region as a MORB-pyrolite mixed pile, discontinuity A results from post-perovskite and SiO_2 phase transitions in the MORB component, discontinuity B from post-perovskite phase transition in the pyrolitic component, discontinuity C from back transformation of the post-perovskite to perovskite in the pyrolitic material due to rapid temperature increase (Lay et al., 2006), and discontinuity D from onset of partial melting just above the CMB.

(Ohta et al., *EPSL*, 2008)

Further Complexity ...

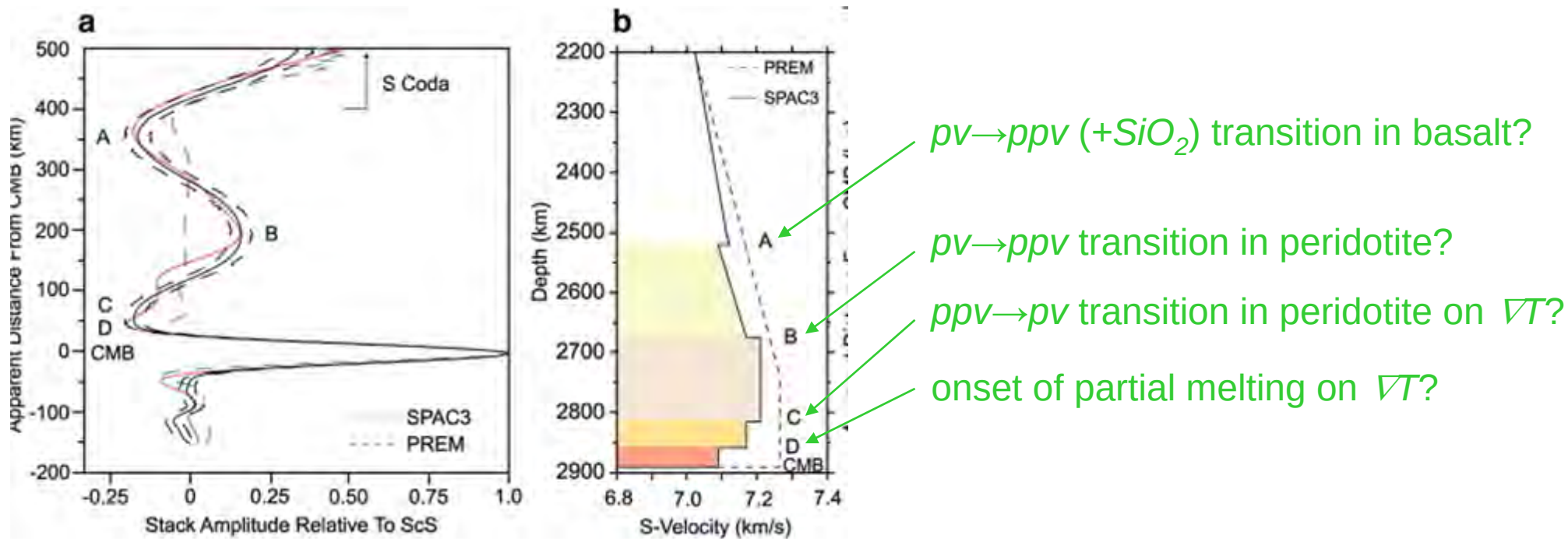
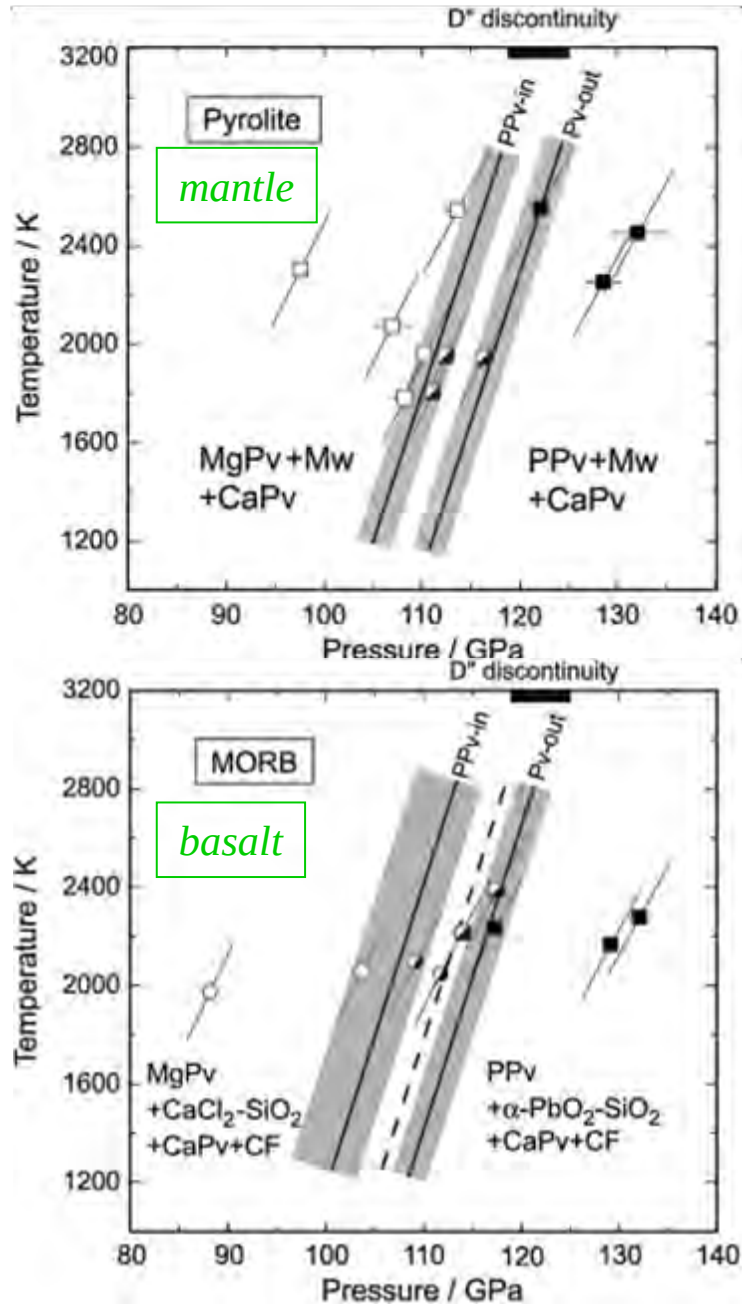


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(Ohta et al., *EPSL*, 2008)

pv → *ppv* phase boundary shifted to lower *P* for *Al, Fe*-rich compositions?
*CaCl*₂ → *α-PbO*₂ transition in *SiO*₂ largely invisible for *Si*-rich basalt?

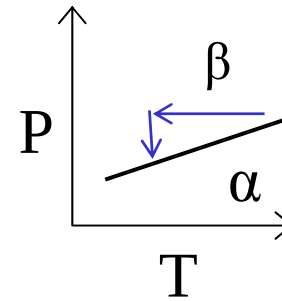
(Ohta et al., EPSL, 2008)



Clapeyron Slopes and Convection

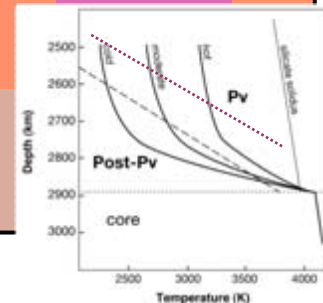
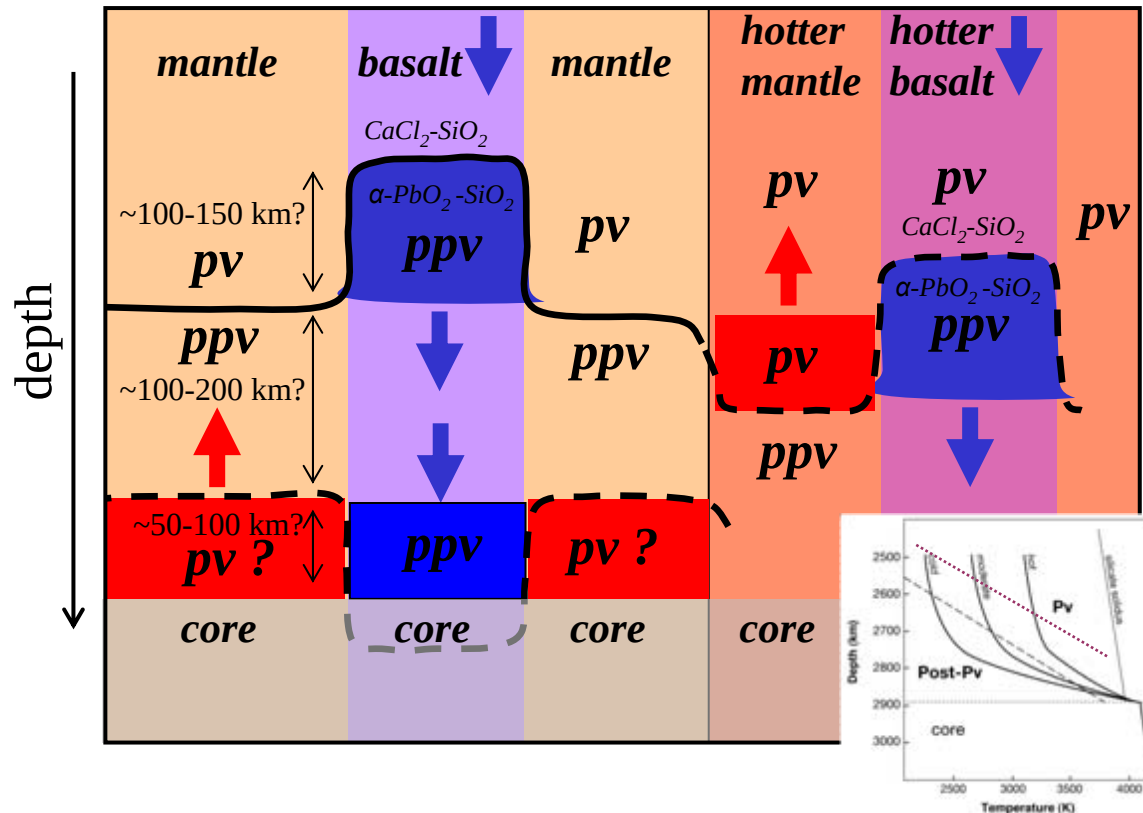
Recall ...

$$dP/dT > 0$$



... but now we have dP/dX_i as well as dP/dT ...

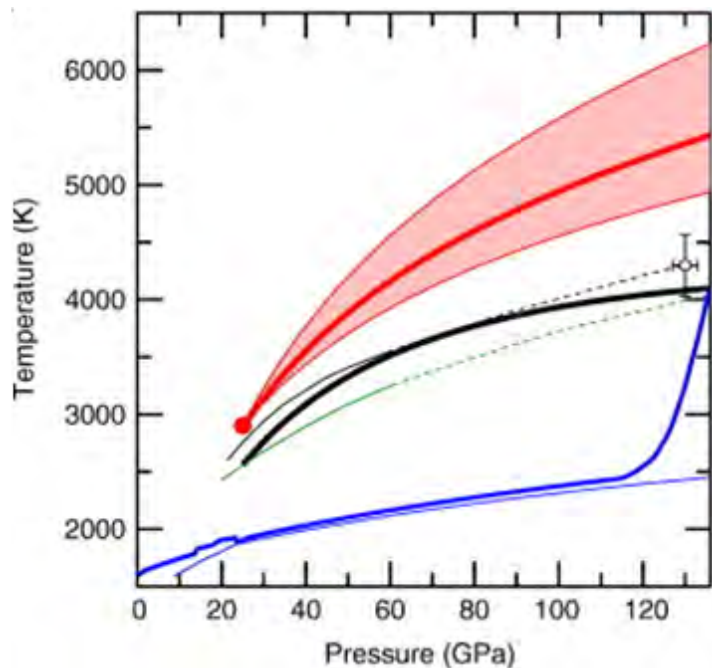
My rough sketch of some possible buoyancy implications...



(C.Bina, 9/2011)

Partial melting in ULVZs?

Is it hot enough?



(Stixrude et al., *EPSL*, 2009)

Fig. 1. Predicted melting curve of MgSiO_3 perovskite (red line with shaded uncertainty envelope) compared with a modern mantle geotherm (blue thick line) represented by the $T_0 = 1600$ K isentrope (Stixrude and Lithgow-Bertelloni, 2007) and a lower thermal boundary layer that reaches a temperature of 4100 K at the core–mantle boundary ([Nimmo et al., 2004] and [Steinle-Neumann et al., 2002]). The form of the thermal boundary layer shown is consistent with models based on observed seismic discontinuities in D'' and the location of the perovskite to post-perovskite phase boundary (Lay et al., 2006). For comparison (blue thin line), we also show the geotherm of Brown and Shankland (1981). The mantle solidus $T_{\text{sol}}(P)$ (bold black solid line) is estimated as $T_{\text{sol}}(P) = T_{\text{pv}}(P) - T_{\text{fp}}(P)$ where T_{pv} is the melting curve of MgSiO_3 perovskite from our simulations, and T_{fp} is the freezing point depression which is assumed to vary linearly with pressure from the experimental value at 25 GPa (340 K) (Tronnes and Frost, 2002) to 1300 K at 136 GPa (Zhou and Miller, 1997). For comparison we show previous experimentally-based estimates of the mantle solidus including upper bounds on the peridotite solidus (symbol: (Holland and Ahrens, 1997); thin black line: (Zerr et al., 1998)), and the basalt solidus (thin green line: (Hirose et al., 1999)). The thin lines are drawn as solid over the range of measurements, and dashed in extrapolation.

Partial melting in ULVZs?

Is it hot enough?

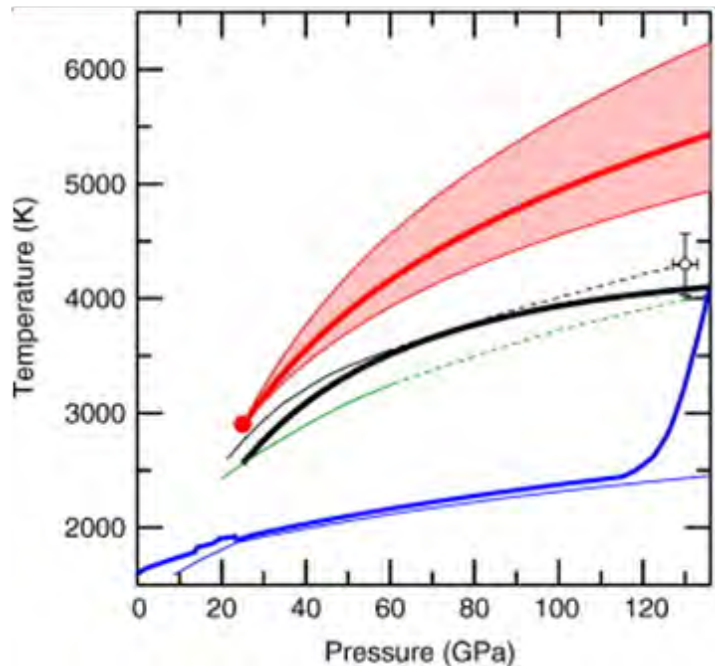
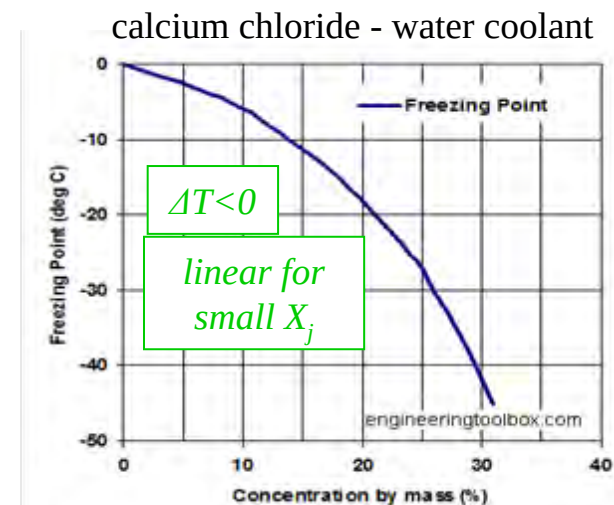
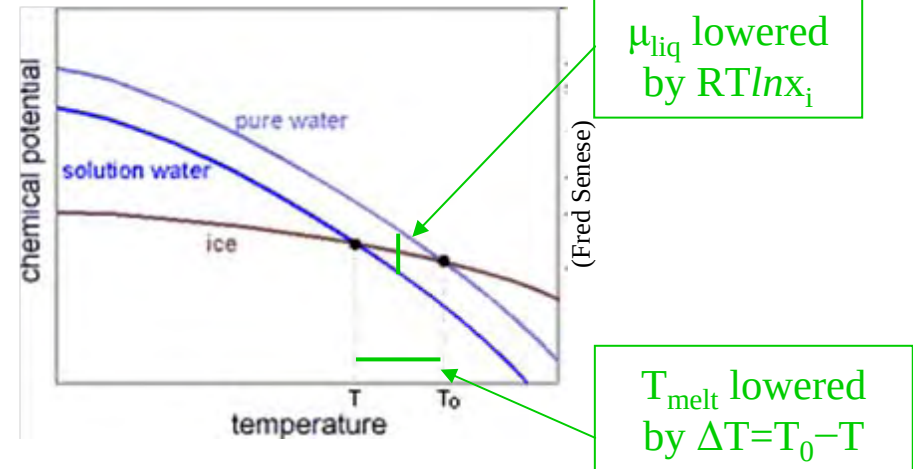


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(Stixrude et al., *EPSL*, 2009)

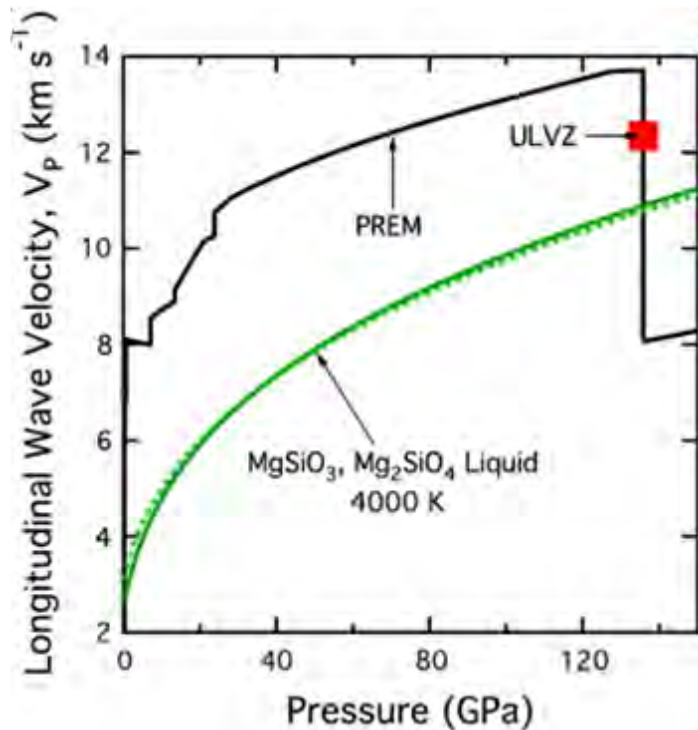
Recall ...

Melting-Point Depression



Partial melting in ULVZs?

Is it slow enough?



(Stixrude et al., *EPSL*, 2009)

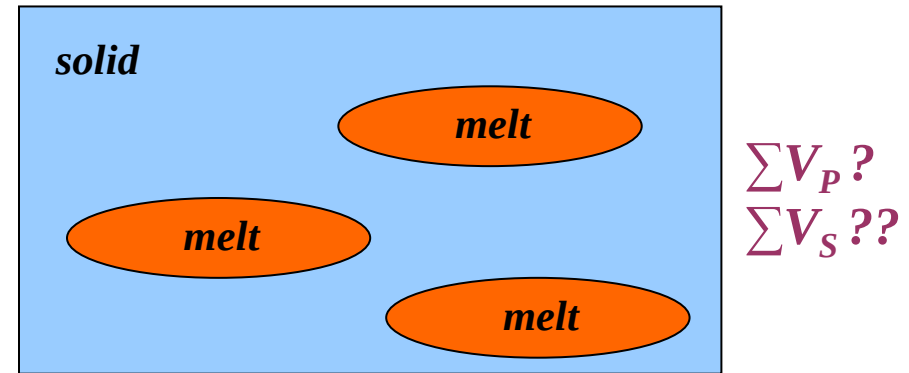


Fig. 4. The longitudinal wave velocity of $MgSiO_3$ (green solid line), and Mg_2SiO_4 (green dashed line) liquid at 4000 K from our FPMD simulations compared with that of the global seismic model PREM (Dziewonski and Anderson, 1981) (black) and a representative value for ultra-low velocity zones (red square) (Williams and Garnero, 1996).

Partial melting in ULVZs?

Is it stable enough?

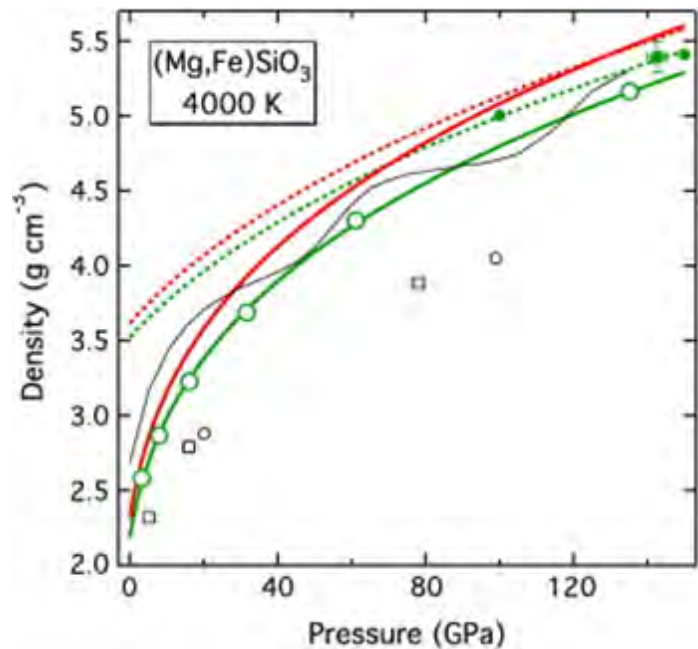
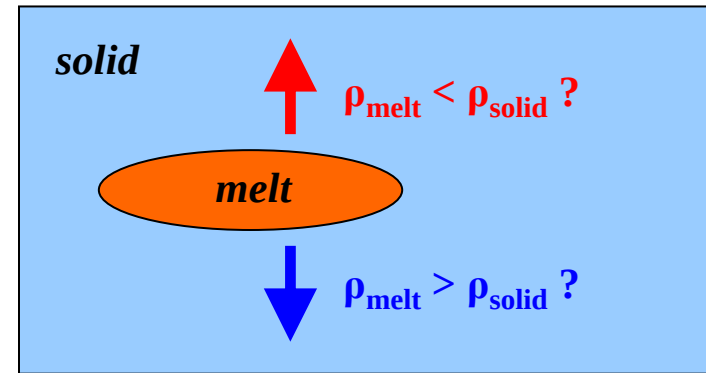


Fig. 3. Density of liquid (solid lines) and perovskite (dashed lines) of MgSiO_3 composition (green) and with added iron as described in the text (red) at 4000 K based on our FPMD results compared with our FPMD results for MgSiO_3 liquid (open green circles) and MgSiO_3 perovskite (solid green circles) at 4000 K, the experimental measurement of perovskite by Luo et al. (2004) at 4130 K (green square with error bars, P. D. Asimow, personal communication), the results of non-first principles rigid ion molecular dynamics simulations of MgSiO_3 liquid by Wasserman et al. (1993) at 4500 K (open black squares) and Zhou and Miller (Zhou and Miller, 1997) at 5000 K (open black circles), and a speciation model calculation at 1673 K (Ghiorso, 2004) (thin black line).

(Stixrude et al., *EPSL*, 2009)

Oxidation States: Fe^{2+,3+,0}

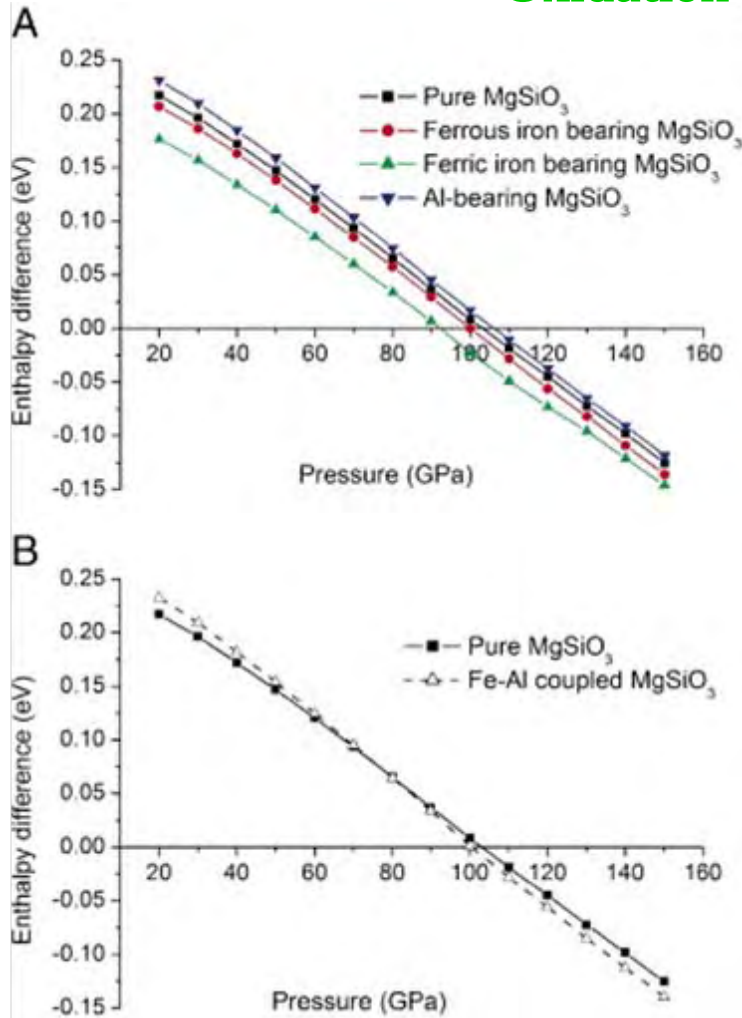


Fig. 3. *Pv*–*PPv* enthalpy difference as a function of chemistry and pressure. (A) Pure MgSiO_3 , $(\text{Mg,Fe})\text{SiO}_3$ with 3.125 mol% FeO , $(\text{Mg,Fe})(\text{Si,Fe})\text{O}_3$ with 3.125 mol% Fe_2O_3 and $(\text{Mg,Al})(\text{Si,Al})\text{O}_3$ with 3.125 mol% Al_2O_3 . (B) $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ with 3.125 mol% FeAlO_3 , taking the most favourable coupled substitutions: $\text{Fe}^{3+}\text{--Al}^{3+}$ in *Pv* and $\text{Fe}^{3+}\text{--Fe}^{3+}$ and $\text{Al}^{3+}\text{--Al}^{3+}$ in *PPv*.

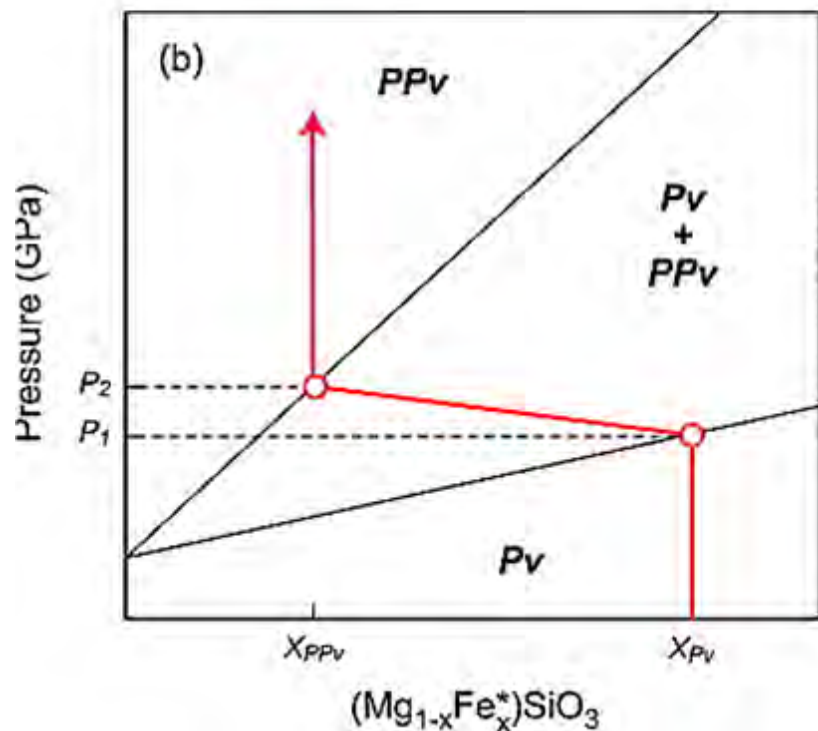
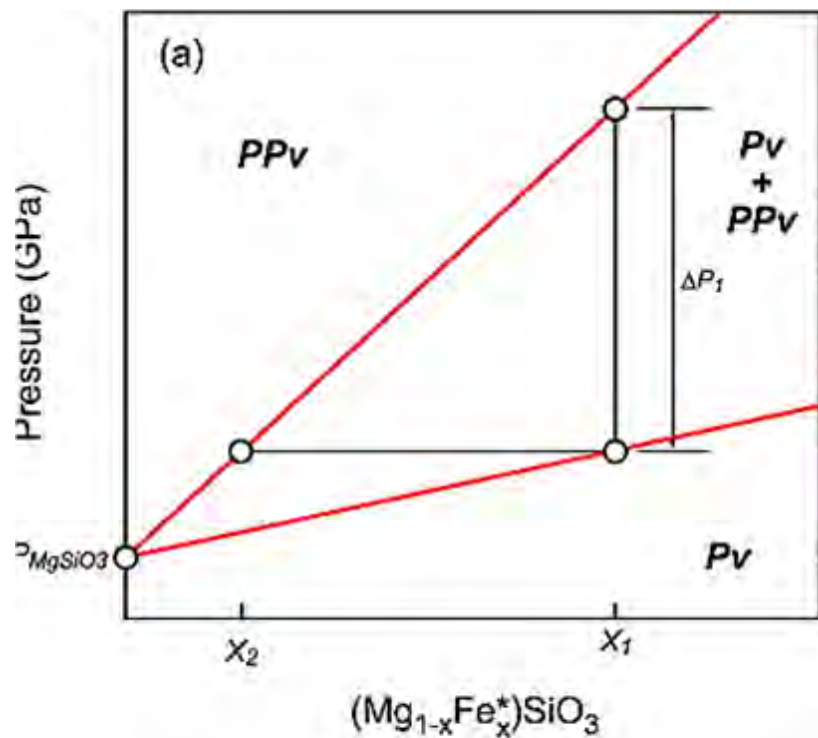


(Frost et al., *Nature*, 2004)

Chemical compositional variation:
It is commonly assumed that CMB mantle should be *Fe*-enriched, due to diffusion from the core, but what if auto-oxidation of *pv* and *ppv* phases yields *Fe* metal?

“At lower mantle conditions, it is energetically favorable for Fe^{2+} in *Pv* and *PPv* to ‘self-oxidize’ by the reaction $3\text{Fe}^{2+} \rightarrow \text{Fe}(\text{metal}) + 2\text{Fe}^{3+}$ without needing external oxygen pump and leading to the formation of free iron metal phase. We have performed the first theoretical study of this reaction and, quite surprisingly, found it to be strongly exothermic.”

(Zhang and Oganov, *EPSL*, 2006)



Experiments suggest auto-oxidation to *Fe* metal occurs in *pv* but not in *ppv* ... partitioning Fe^{2+} into *fp*-(*Mg,Fe*)O ... thus depleting *Fe* from *ppv* ... and sharpening the *pv*→*ppv* transition.

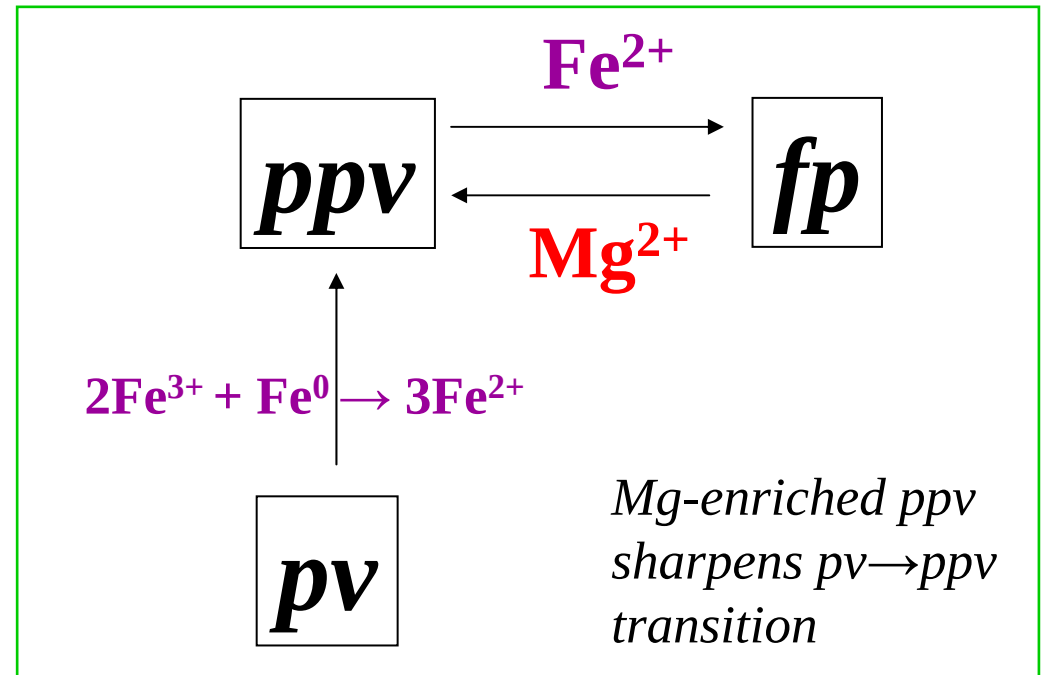


Figure 7. Schematic illustration of Pv-PPv transition in $MgSiO_3$ - Fe^*SiO_3 binary system, describing (a) PPv-in and Pv-out lines and (b) iron content in Pv and PPv coexisting with Fp in pyrolite. See section 4.3.

(Sinmyo et al., *JGR*, 2011)

Experiments suggest auto-oxidation to *Fe* metal occurs in *pv* but not in *ppv* ... partitioning Fe^{2+} into *fp*-(*Mg,Fe*)O ... thus depleting *Fe* from *ppv* ... and sharpening the *pv*→*ppv* transition.

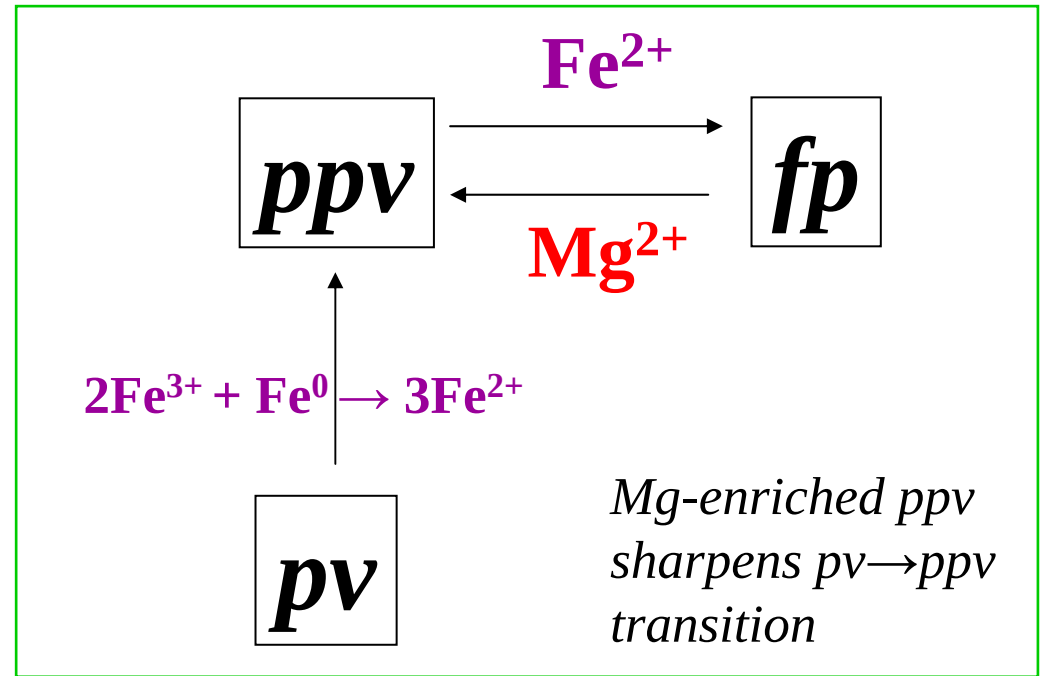
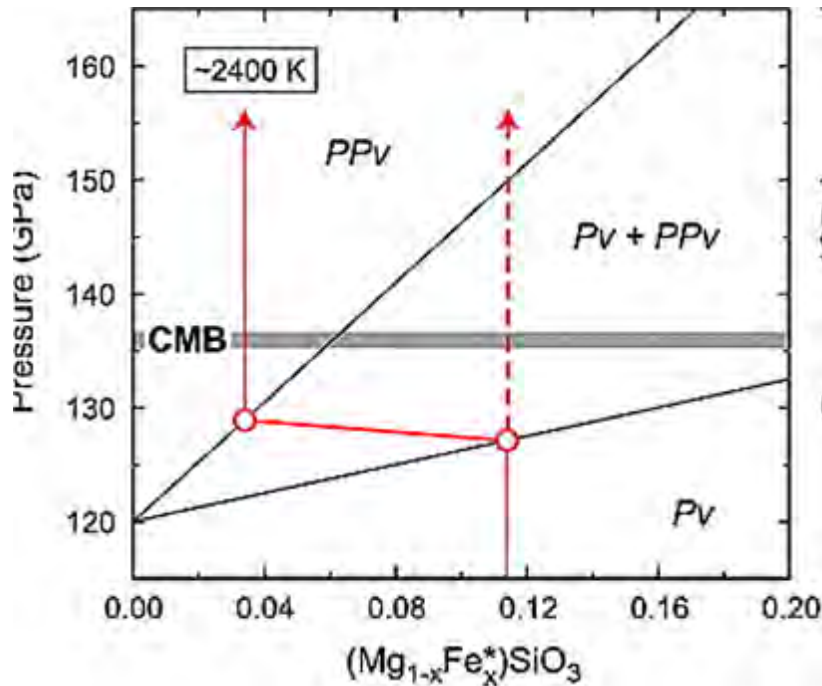
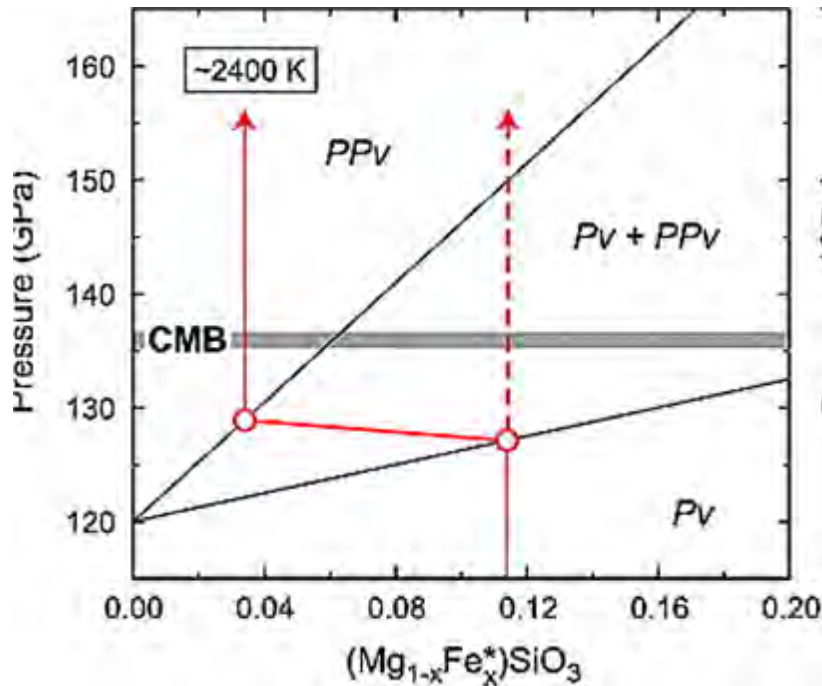


Figure 8. Schematic phase diagram in $MgSiO_3$ – Fe^*SiO_3 binary system at 2400 K, demonstrating the thickness of *Pv* + *PPv* two-phase coexisting region. Fe^* indicates either Fe^{2+} or Fe^{3+} , assuming that both have a similar effect on the stabilities of *Pv* and *PPv*. See section 4.3 for details. Note that the thickness of the two-phase coexisting region is much narrower when iron content decreases across the phase transition from *Pv* to *PPv* (solid arrow) than for a fixed *Fe* content (dashed arrow). CMB, core-mantle boundary.

(Sinmyo et al., *JGR*, 2011)

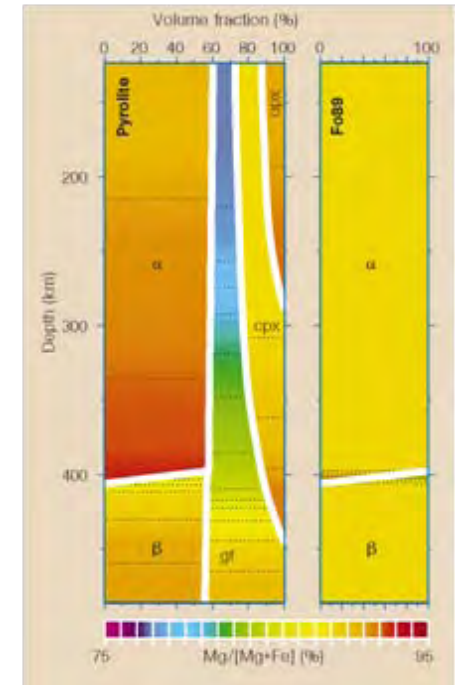
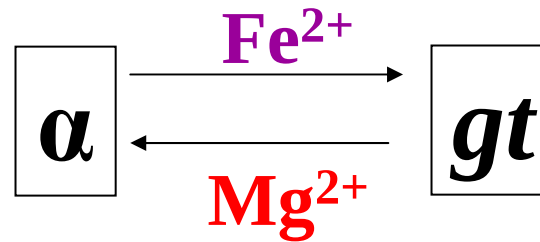
(C.Bina, 9/2011)

Experiments suggest auto-oxidation to *Fe* metal occurs in *pv* but not in *ppv* ... partitioning Fe^{2+} into *fp*-(*Mg,Fe*)O ... thus depleting *Fe* from *ppv* ... and sharpening the *pv*→*ppv* transition.



Recall ...

Mg-enriched olivine sharpens $\alpha \rightarrow \beta$ transition



(Figure 1 of Bina, 1998; after Irifune and Isshiki, 1998)

Figure 8. Schematic phase diagram in $MgSiO_3-Fe^*SiO_3$ binary system at 2400 K, demonstrating the thickness of Pv + PPv two-phase coexisting region. Fe^* indicates either Fe^{2+} or Fe^{3+} , assuming that both have a similar effect on the stabilities of Pv and PPv. See section 4.3 for details. Note that the thickness of the two-phase coexisting region is much narrower when iron content decreases across the phase transition from Pv to PPv (solid arrow) than for a fixed Fe content (dashed arrow). CMB, core-mantle boundary.

(Sinmyo et al., *JGR*, 2011)

(C.Bina, 9/2011)

The Core-Mantle Boundary Region:

$CMB, D''[\Delta V_{P,S}, \partial V_{P,S}/\partial z, \nabla(V_P/V_S), V_{P,S}(\theta, \phi)], ULVZs, LLSVPs$



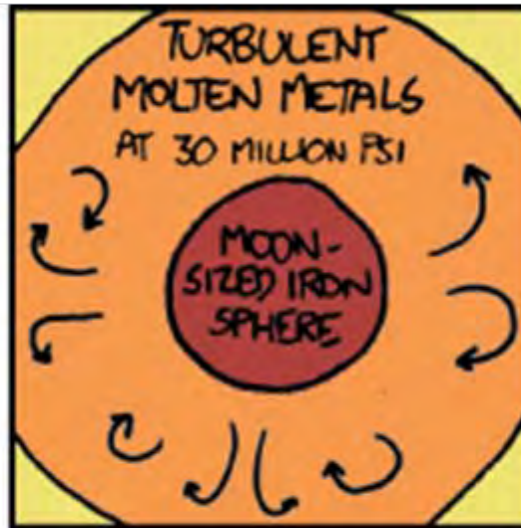
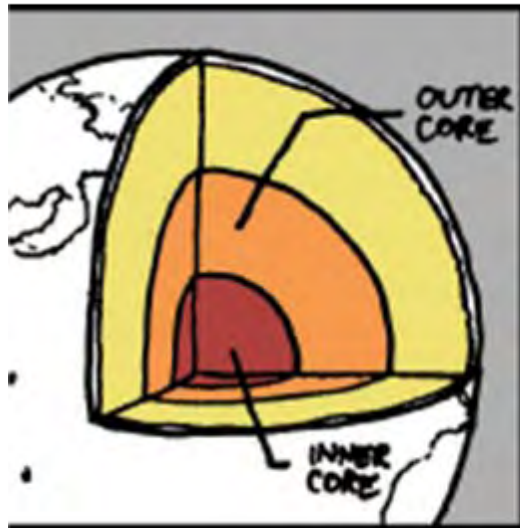
Phase change(s): $pv \rightarrow ppv$ likely, but P - T uncertainties remain; double-crossing requires narrow range of $T(z)$; triple- or quadruple-crossing also requires proximally coexisting basalt and peridotite.

Partial melting: possible with sufficient freezing point depression; unclear if melts are gravitationally stable; unclear if melt assemblages exhibit suitable seismic velocities; melting apparently not strictly necessary, due to strong $V_{P,S}(X_{Fe})$ effects.

Lateral δT : almost certainly; will affect presence of $pv \rightarrow ppv$ transition(s).

Lateral $\delta X_{Fe,Al,Si}$: probable; will directly induce $\delta V_{P,S}$, as well as shifting depth and sharpness of $pv \rightarrow ppv$ transition(s).

$\exists Fe^{metal}$: probable, but Fe likely to remain unseparated and disconnected; reaction preference in pv over ppv may shift Mg - Fe partitioning with coexisting fp , thereby sharpening $pv \rightarrow ppv$ transition(s).



I FREAK OUT ABOUT FIFTEEN MINUTES INTO
READING ANYTHING ABOUT THE EARTH'S CORE
WHEN I SUDDENLY REALIZE IT'S *RIGHT UNDER ME*.

If you're a geologist or geophysicist and you don't introduce yourself by saying your name, then gesturing downward and saying "... and I study that", I don't know what you're doing with your life.

<<http://xkcd.com/913/>>

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

Craig R. Bina



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



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

přednášky na podzim 2011

Poslední přednáška: Děkuju mnohokrát!