CIDER 12 Deep Time

Earth Materials I Introduction to Earth Materials (Hirschmann)
Earth Materials II Exp. Studies Related to Early Earth Proc (Rubie)
Earth Materials III The Mantle (Li)
Tutorial IV: Equations of State (Li)
Earth Materials IV Accretion, Magma Oceans, Core Formation (Rubie)
Tutorial V: Molecular Dynamics (Caracas)
Earth Materials V Transport Properties (Williams)
Earth Materials VI The Core (Li)

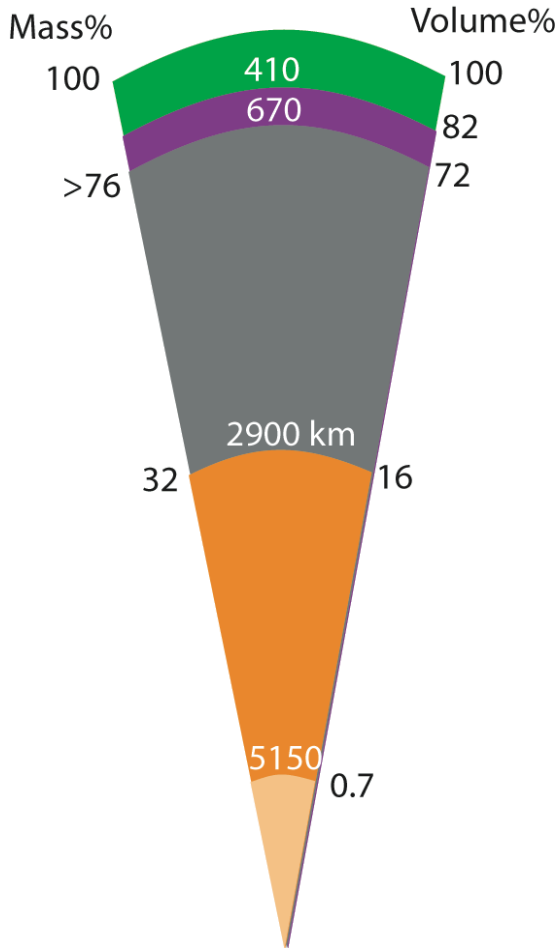
KITP, Santa Barbara CA

July 16-28, 2012

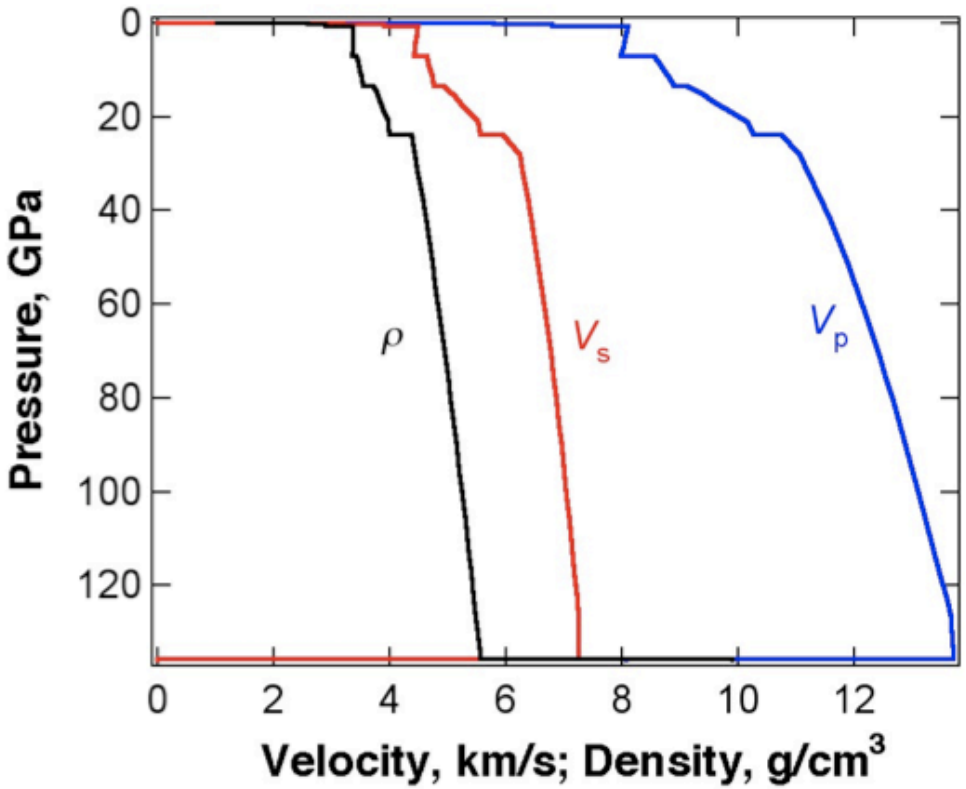
Earth's Mantle

How are Earth processes controlled by material properties?

P: 136 GPa
T: 3000 K
x: ?
t: ?

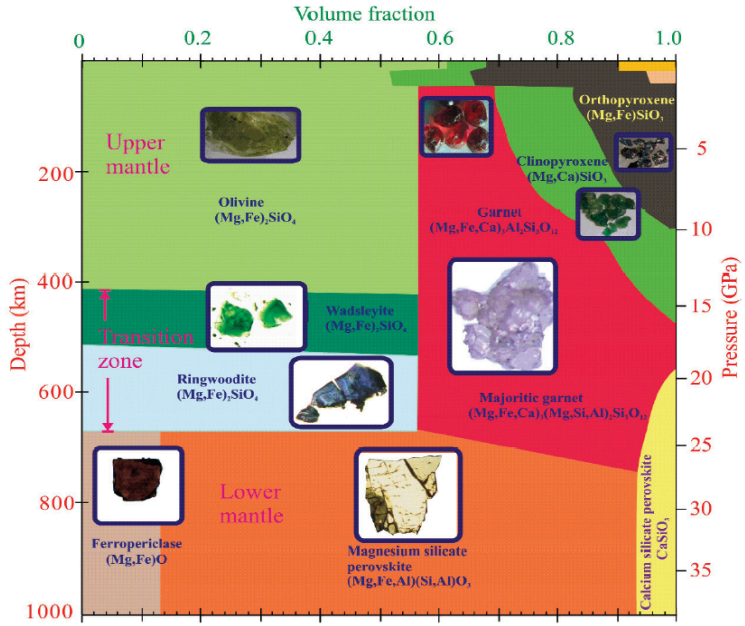


Interpret 1D Seismic Profile + Rock Records: *X-T-t*



Dziewonski and Anderson 81 PEPI

Frost 08 Element



LAB Melt, water

TZ Discontinuities

Depth: Phase transitions

Width: Fe partition, phase equilibria

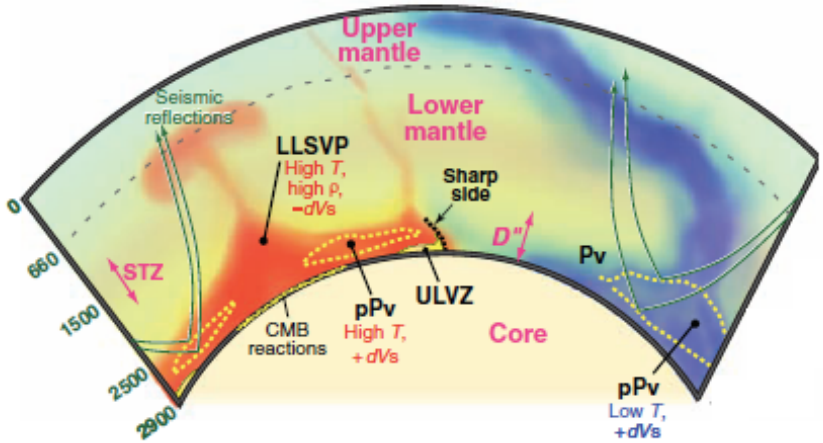
Magnitude: Density, velocity

Topography: Clapeyron slope, kinetics

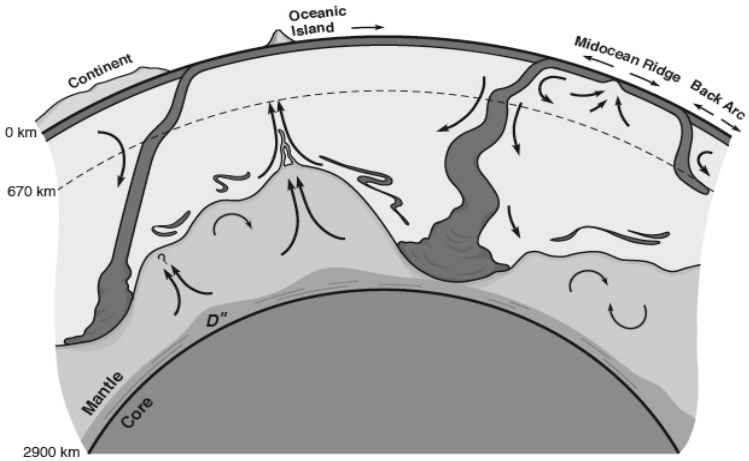
D” Phase transitions

Deep time MO overturn: Density

Explain Seismic Tomography + Geochemical Domains: *X-T-t*



Garnero/McNamara 08 Science



Kellogg et al. 99

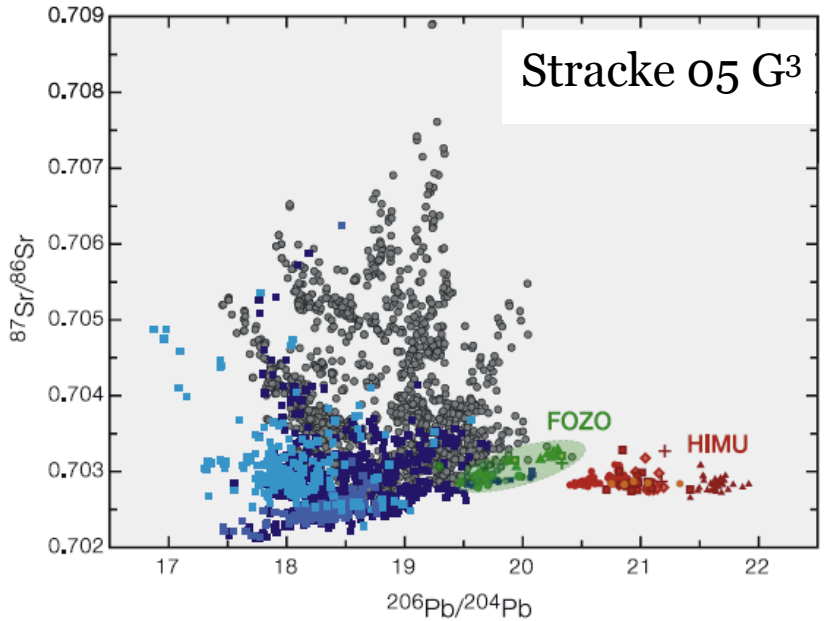


Plate Tectonics

Slab, Plume: Density, viscosity, conductivity

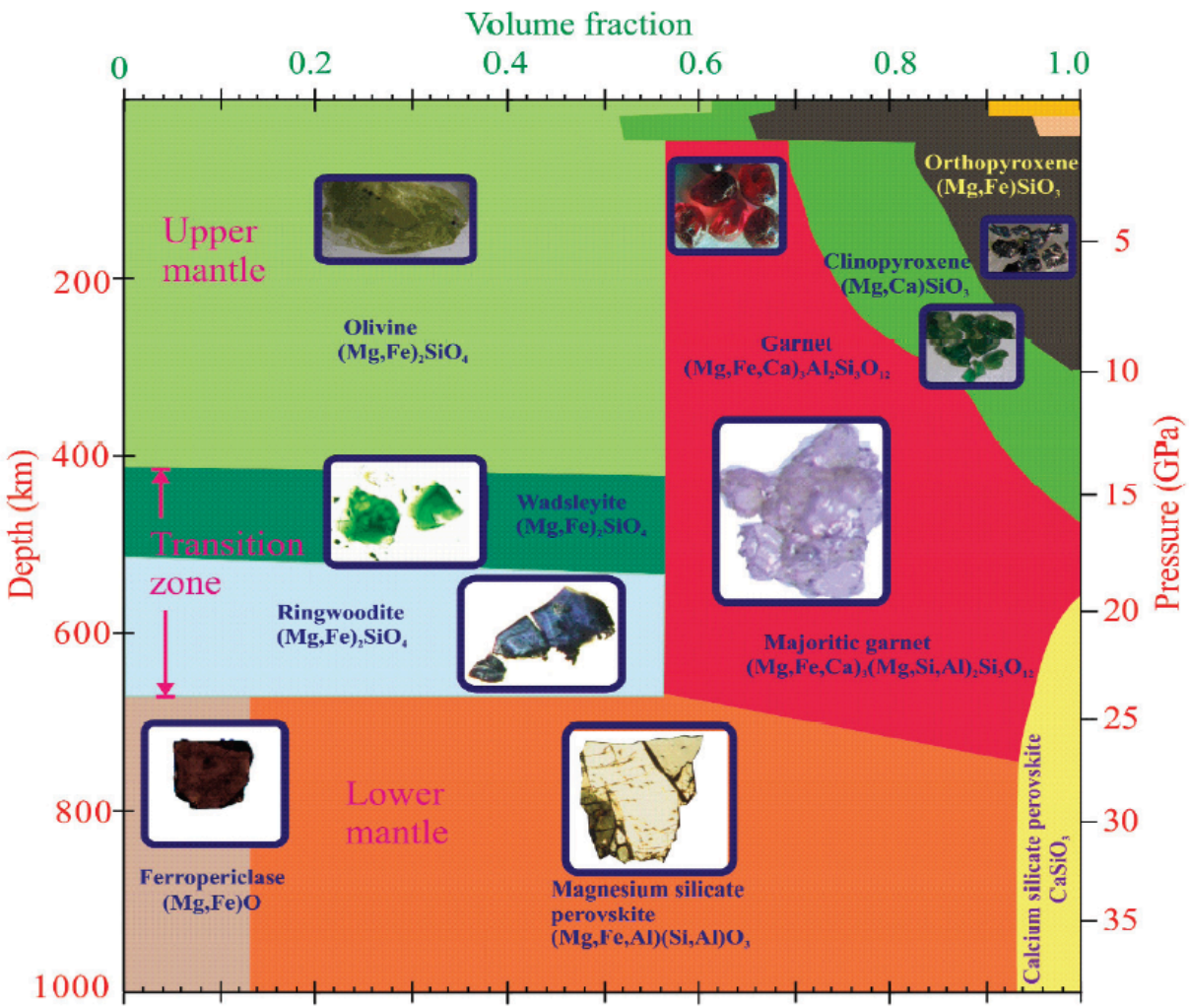
Mantle Convection

Rayleigh #: Density, viscosity, conductivity, heat capacity

CMB Interaction

Partition, transport

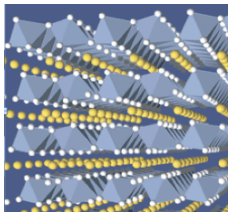
Iron Plays a Critical Role in Mantle Evolution



Phase transition
Partitioning
Oxidation state
Spin crossover
Density, velocity, elasticity
Transport properties

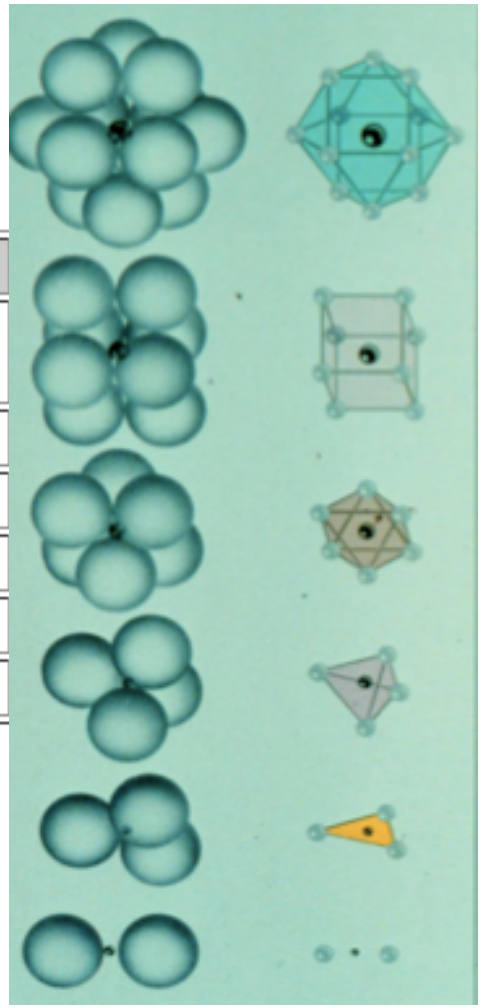
Jie (Jackie) Li, University of Michigan

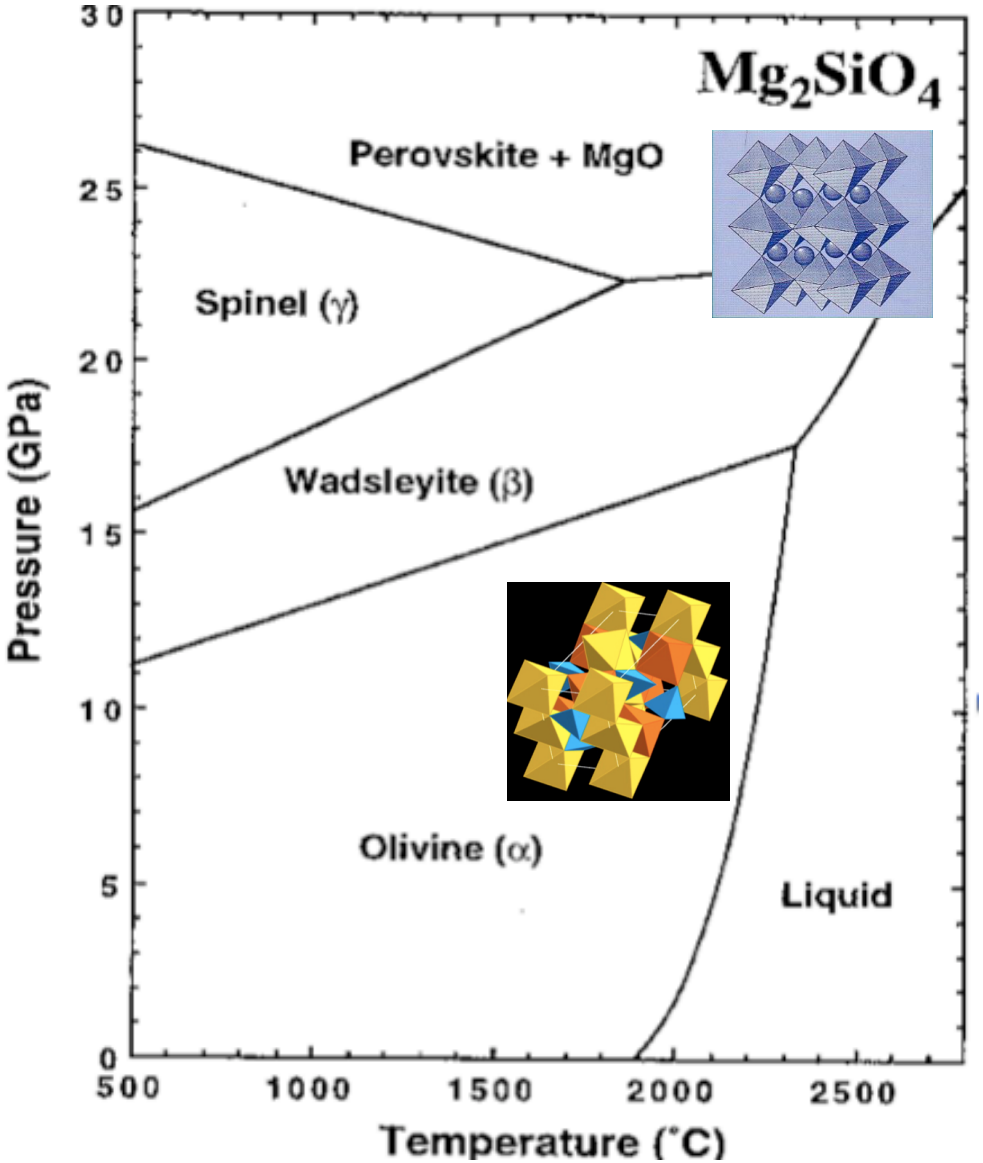
Phase Transition: Coordination Number



Pauling's Rules

Rx/Rz	C.N.
1.0	12
1.0 - 0.732	8
0.732 - 0.414	6
0.414 - 0.225	4
0.225 - 0.155	3
<0.155	2





Fei 98 UHPM

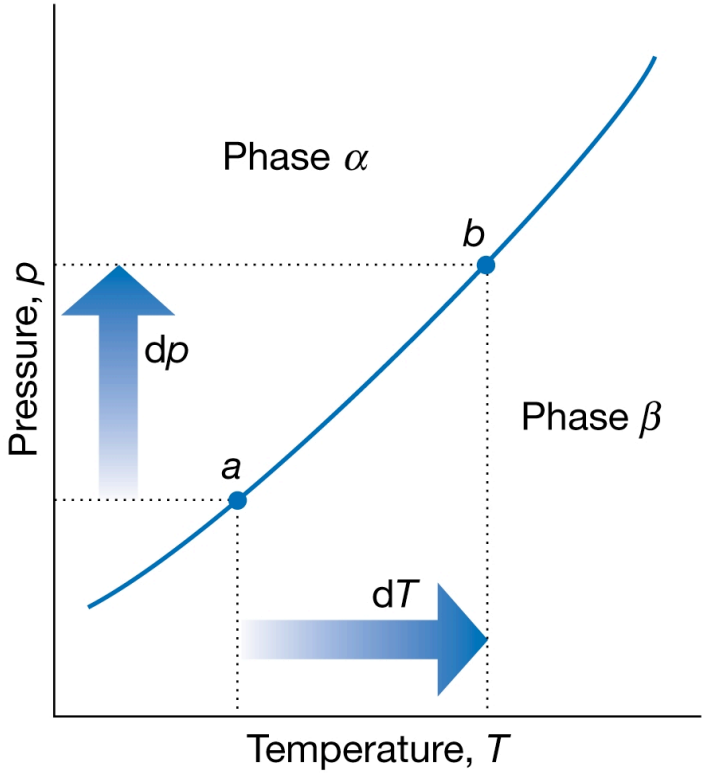
Phase Transition Affects Density and Velocities

Phase	Density (g/cm^3)	Bulk Modulus, K (GPa)	Rigidity, μ (GPa)	V_P (km/s)	V_S (km/s)
α olivine Mg_2SiO4	3.222	129	82	8.60	5.05
β wadseyite Mg_2SiO4	3.47	174	114	9.69	5.73
γ ringwoodite Mg_2SiO4	3.56	184	119	9.81	5.78
Perovskite ($MgSiO_3$)	3.81	253	175	11.29	6.78
Periclase (MgO)	3.59	163	131	9.70	6.04

Phase Transition in Mg_2SiO_4 Produces Density/Velocity Jumps

	$\Delta\rho$ (%)	ΔV_P (%)	ΔV_S (%)
$\alpha(0 \rightarrow 14GPa)$	10%	10%	6%
α (300 → 1700 K)	-5%	-9%	-11%
$\alpha \rightarrow \beta$	8%	13%	14%
AK135 410 km	--	**3.7%**	**4.3%**
$\beta \rightarrow \gamma$	3%	1%	1%
$\gamma \rightarrow$ Pv+Per	5%	8%	11%
AK135 660 km	--	**5.8%**	**6.2%**

Clausius-Clapeyron Slope



Phase boundary (curve)
dP/dT = Slope of tangent to curve
Sign and value of slope

$G = U + PV - TS$
$G_A = U_A + PV_A - TS_A$
$G_B = U_B + PV_B - TS_B$

For an infinitesimal change in P and T
$dG_A = V_A dP - S_A dT$
$dG_B = V_B dP - S_B dT$

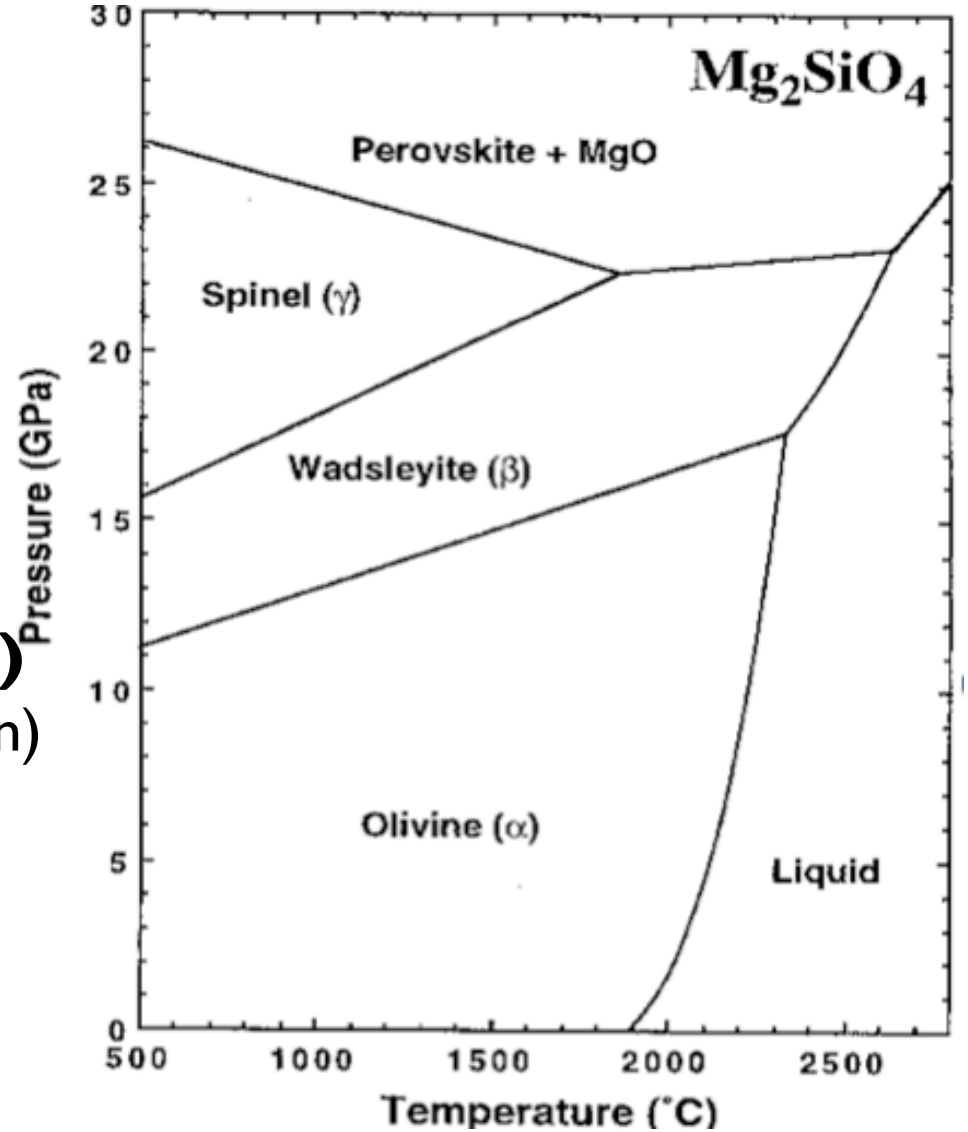
Along the boundary
$G_A = G_B$
$dG_A = dG_B$
i.e.
$V_A dP - S_A dT = V_B dP - S_B dT$
$\Delta V_{B\text{-}A} dP = \Delta S_{B\text{-}A} dT$
$dP/dT = \Delta S_{B\text{-}A}/\Delta V_{B\text{-}A}$

Sign of Clapeyron Slope Indicates Thermal Effect

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

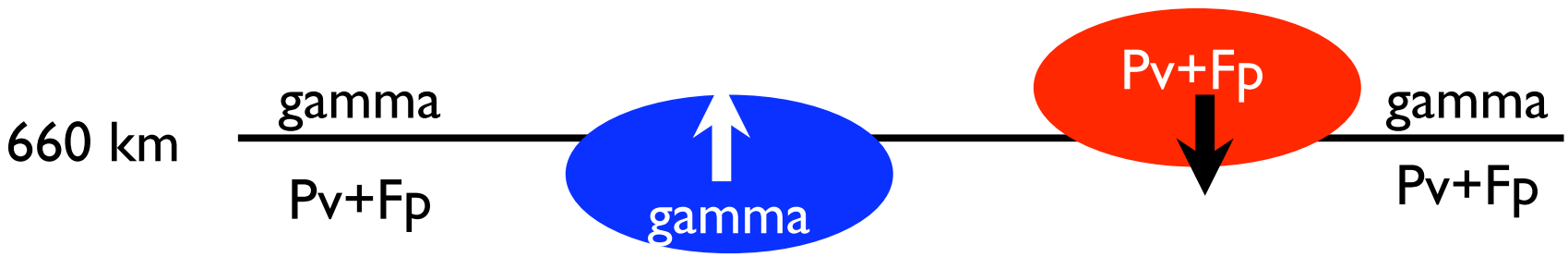
α to β transition (410 km)
Positive Clapeyron slope (common)
β smaller molar volume,
smaller molar entropy
Exothermic

γ to PV+FP transition (660 km)
Negative Clapeyron slope (uncommon)
PV+FP smaller molar volume
larger molar entropy
Endothermic



TZ Topography / Barriers to Convection

resistance to plume rising
boundary pushed upwards

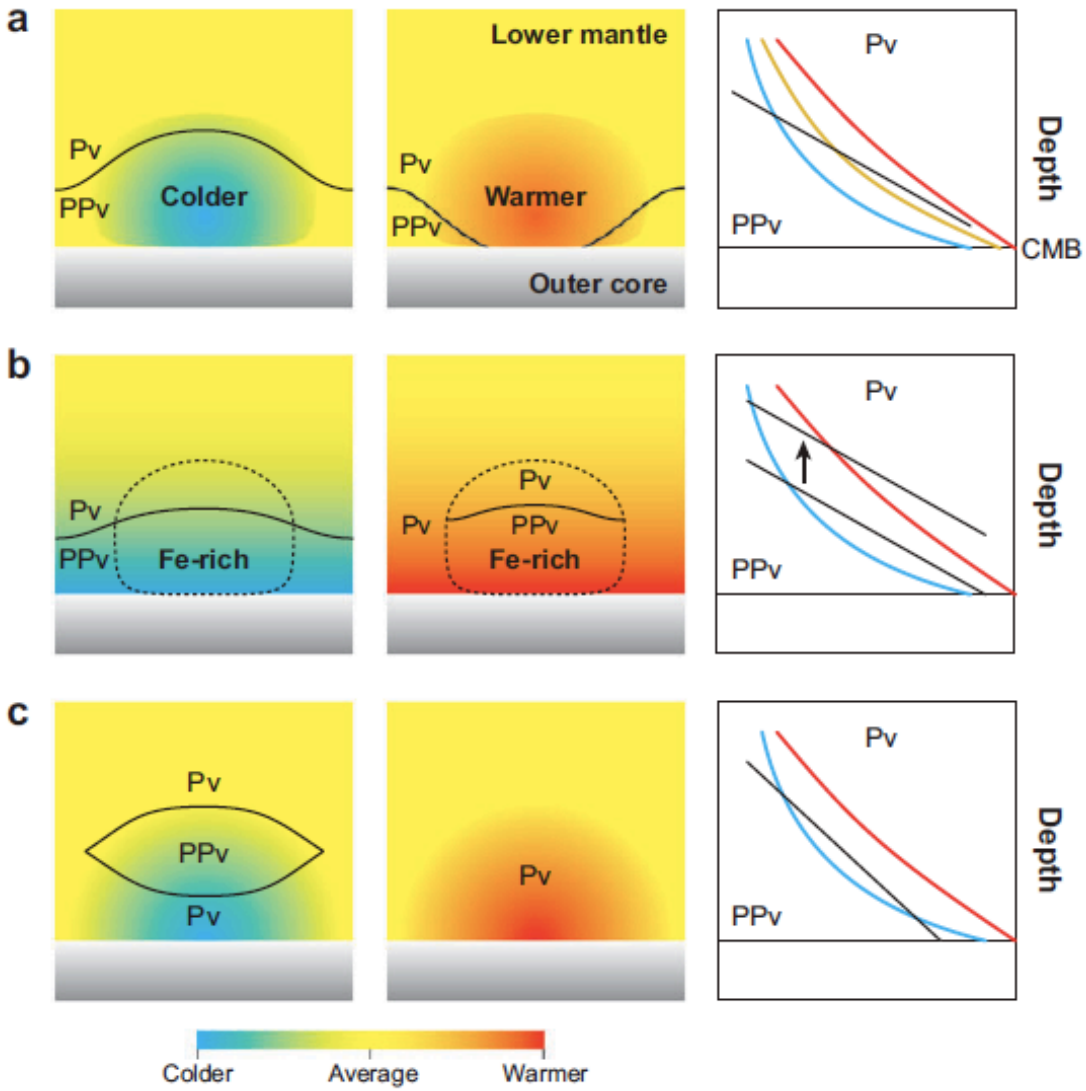


boundary pushed downwards
resistance to slab sinking

$dT/dP = \Delta V/\Delta S = 769$ K/GPa
Assuming linear slope
For slab $dT \sim -500$ K, $dP \sim 0.6$ GPa (15 km)
For plume $dT \sim +200$ K, $dP \sim -0.3$ GPa (7.5 km)

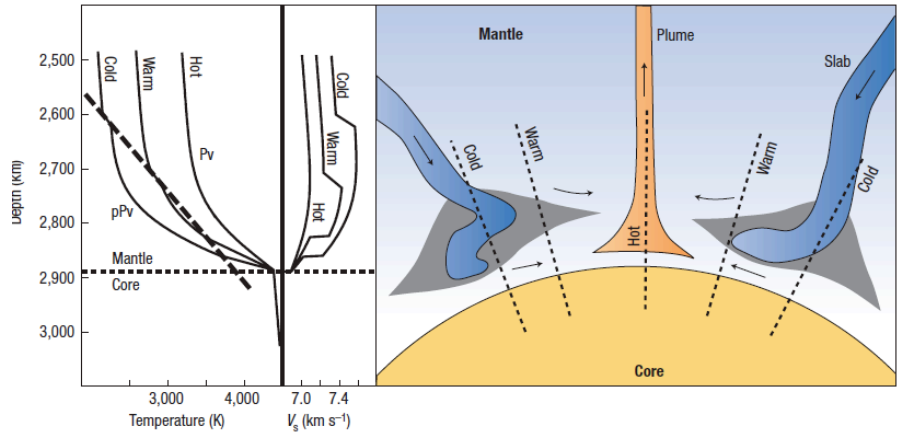
Fei et al. 2004

D” Topography and Structure



Double Crossing PPv lens

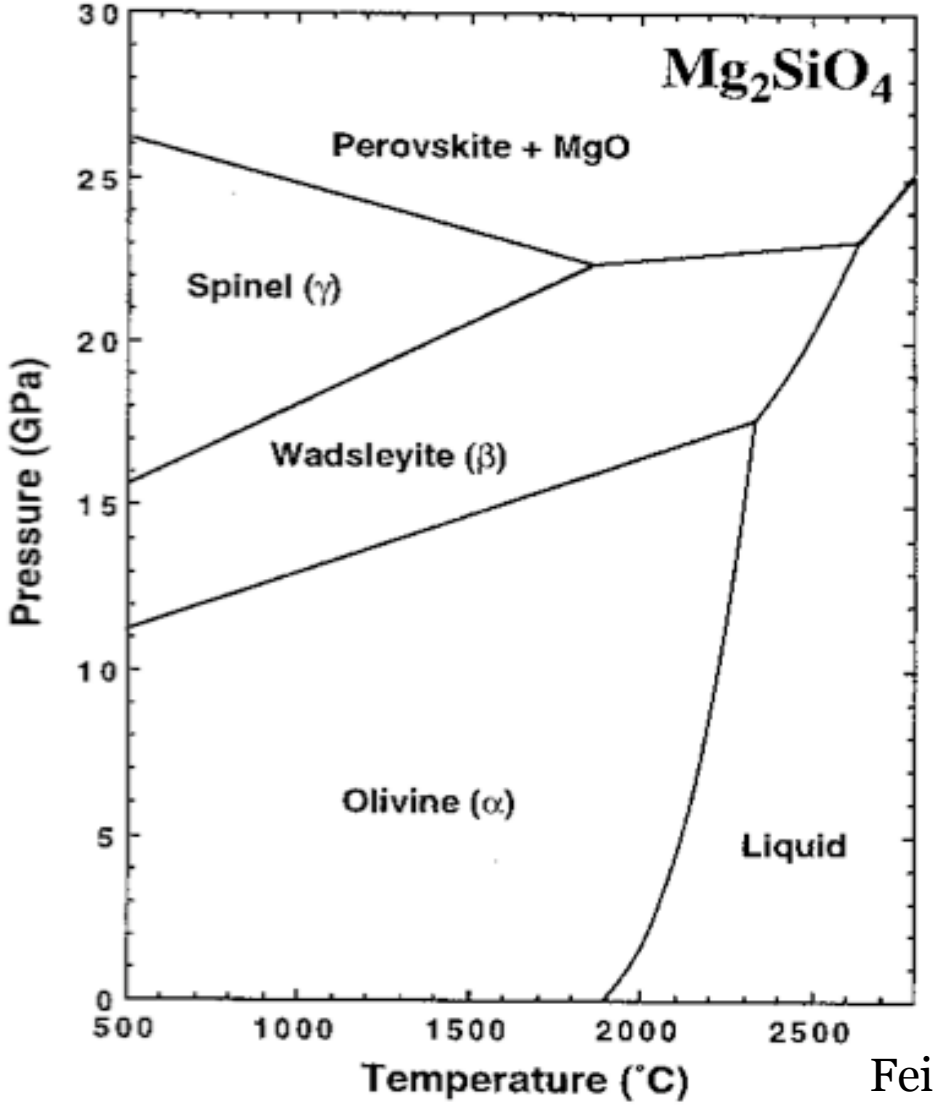
Shim 08 AREPS
Lay et al. 08 Nature Geo.

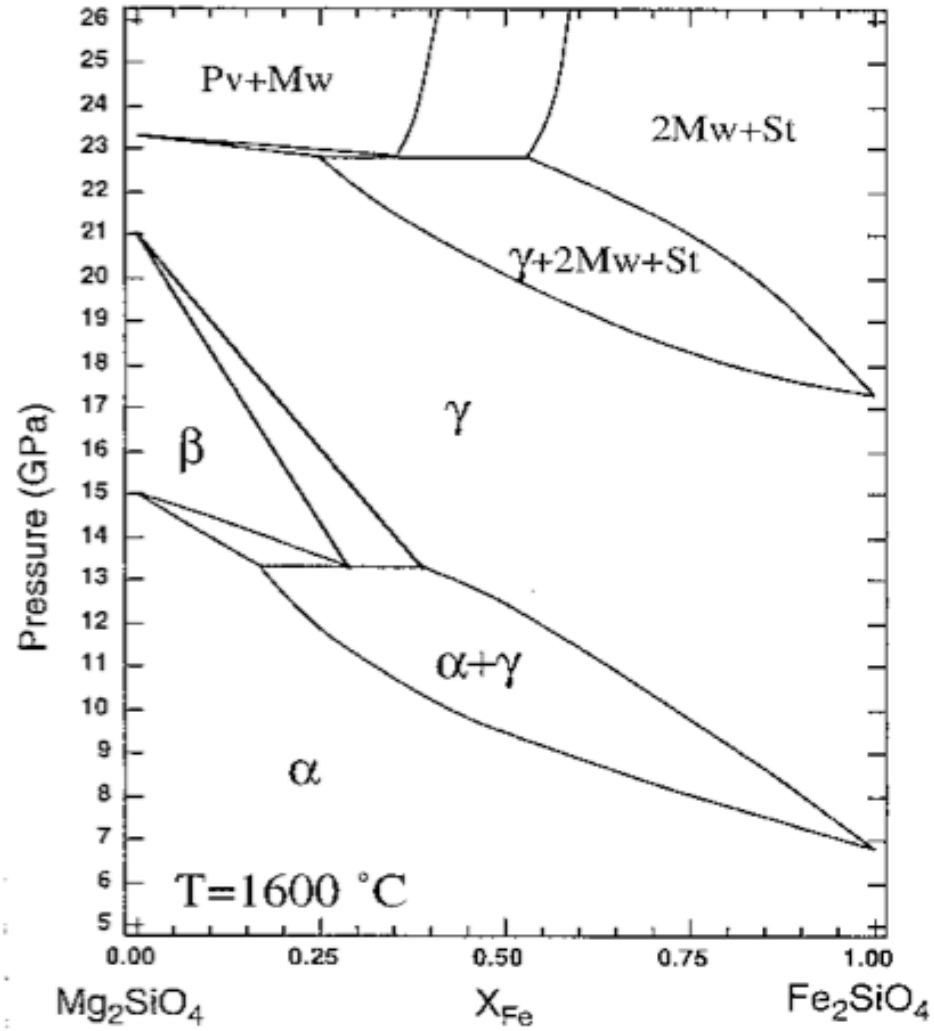


Iron Lowers and Broadens Phase Boundaries

Phase Rule $f = c + 2 - p$

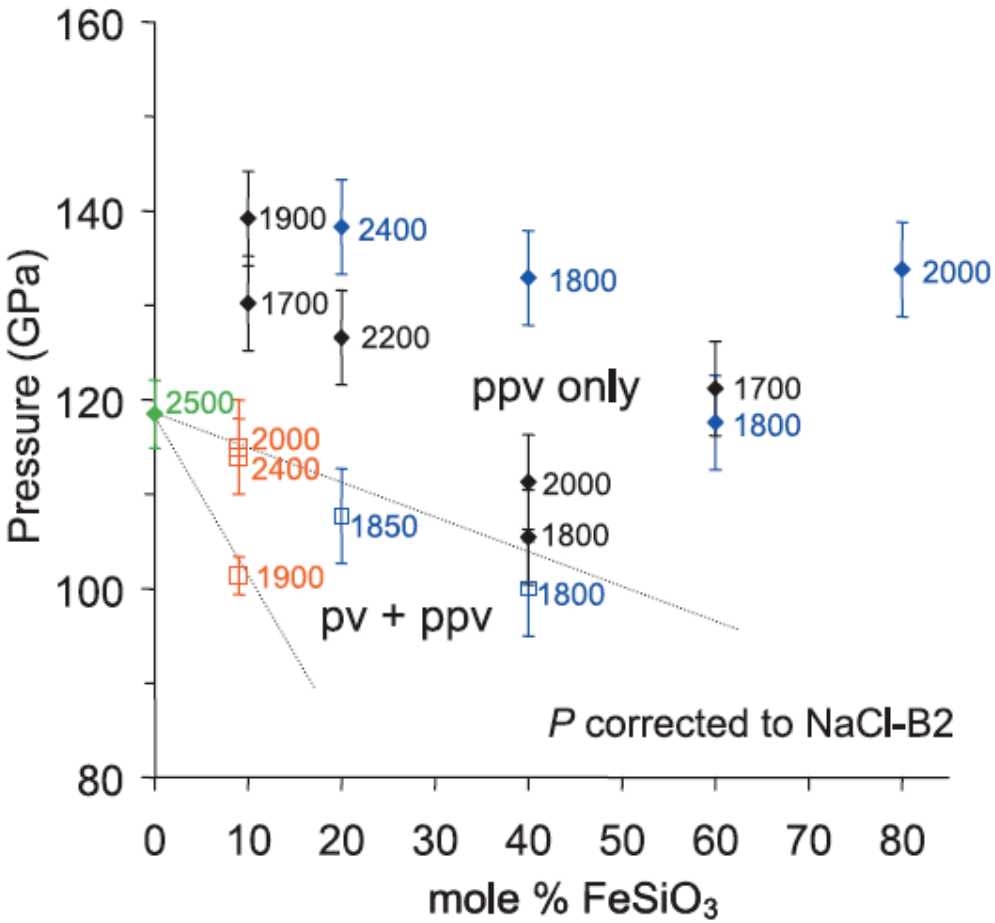
Mw or Fp





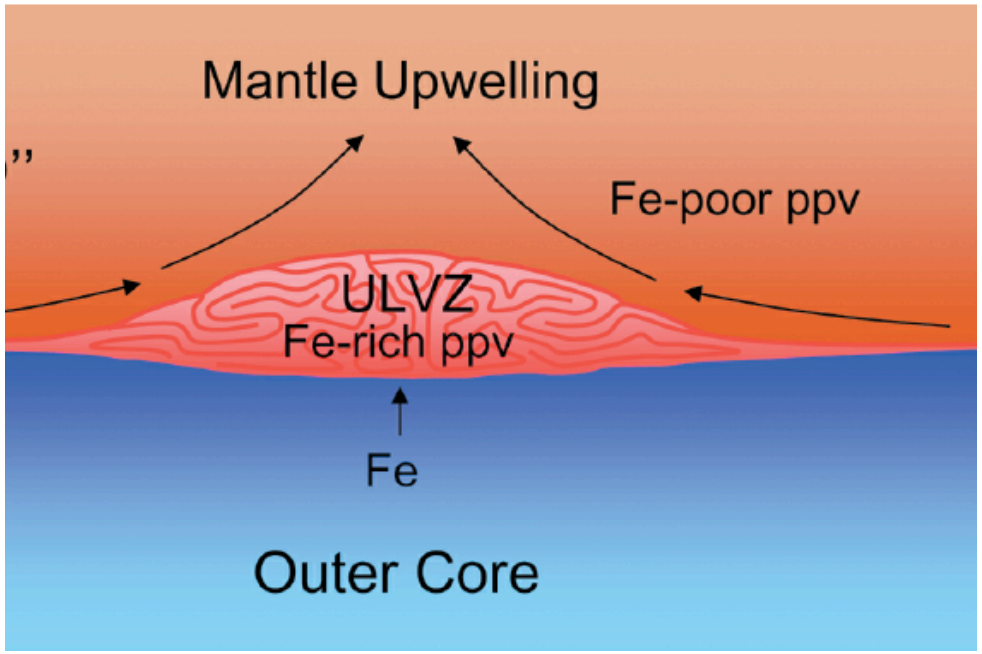
Fei 1998 UHPM

Iron Shifts and Broadens Pv-PPv Transition



Pv contains more iron than PPv

Hirose 08 AM



Mao 07 AGU mono
Mao et al. 06 Science
Mao et al. 06 PNAS

Iron Increases Density and Lowers Sound Velocities

$\rho = m/V$ $\rho V_p^2 = K + 4G/3$ $\rho V_S^2 = G$

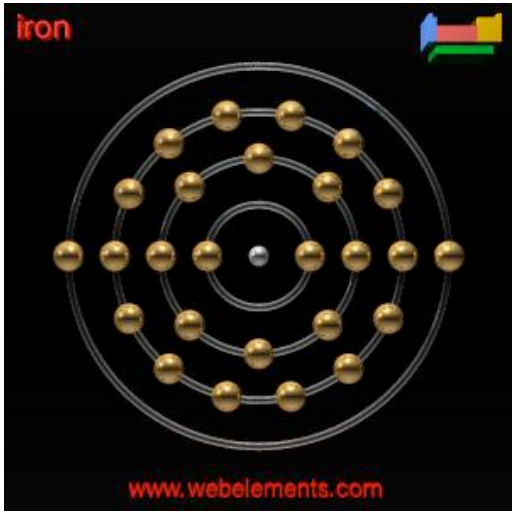
Table 1 Elastic properties of major mantle phases

Phase	K_0	dK_0/dX	K_0'	$-dK/dT$	G_0	dG/dX	G_0'	$-dG/dT$
plg	84(5)	-	4.0(10)	*4*(1)	40(3)	-	*1.1*(5)	*6*(3)
sp	197(1)	12(2)	5.7(2)	29(3)	109(10)	−24(16)	0.4(5)	13(2)
ol	128(2)	7(2)	4.2(2)	18(1)	82(2)	−31(2)	1.4(1)	14(1)
wa	169(3)	0(13)	4.3(2)	22(6)	112(2)	−40(12)	1.4(2)	18(1)
ri	183(2)	16(7)	4.1(2)	23(2)	120(2)	−25(10)	1.3(1)	17(2)
opx	107(2)	−7(4)	7.0(4)	19(5)	77(1)	−25(5)	1.6(1)	13(2)
cpx	112(5)	7(6)	5.2(18)	18(9)	67(2)	−6(2)	*1.4*(5)	*11*(4)
hcpcx	121(1)	*0*(10)	5.5(3)	20(3)	90(1)	−19(10)	1.5(1)	17(2)
capv	236(4)	-	3.9(2)	22(13)	165(12)*	-	2.5(5)*	*26*(4)
ak	211(4)	*0*(10)	4.5(5)	*20*(6)	132(8)	*25*(12)	1.6(5)*	*21*(4)
gt	170(2) − 9Y	7(3)	4.1(3) + 0.1Y	16(2)	94(2)	4(3)	1.3(2) + 0.1Y	10(1) − 2Y
st	314(8)	-	4.4(2)	31(18)	220(12)	-	*1.6*(5)	*36*(5)
pv	251(3)	30(40)*	4.1(1)	23(4)	175(2)	−37(40)*	1.7(2)*	25(3)*
fp	161(3)	18(3)	3.9(2)	21(1)	130(3)	−83(3)	2.2(1)	26(1)

Symbols and Units: K, adiabatic bulk modulus (GPa); *G*, shear modulus (GPa), *X*, Fe/(Mg + Fe); *Y*,*mj*/(*py* + *mj*); subscript o indicates values at zero pressure, primes indicate pressure derivatives; d*K*/d*T* and d*G*/d*T* in MPa K^{-1}. Italicized entries are unconstrained by experiment. Asterisk indicates values taken from density functional theory calculations.After Stixrude and Lithgow-Bertelloni (2005b) and references therein.

Stixrude 07 ToG

Iron's Valence State / Oxidation State

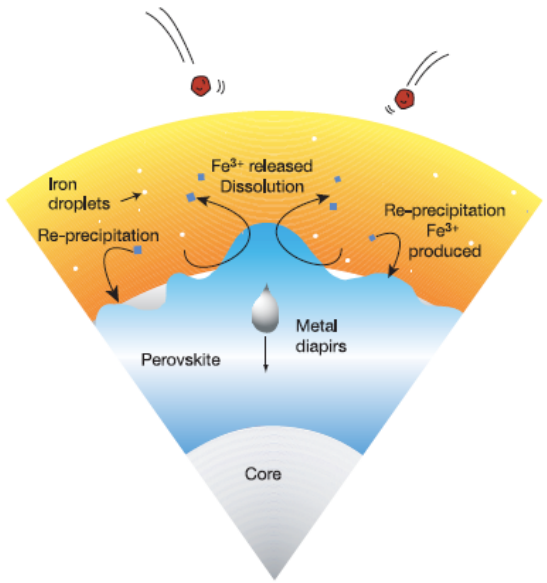


$$3Fe^{2+} = 2Fe^{3+} + Fe^{0}$$

$$Fe^{3+} + Al^{3+} = Mg^{2+} + Si^{4+}$$

$$Fe^{3+} + Fe^{3+} = Mg^{2+} + Si^{4+}$$

Fe	$[Ar]3d^6 4s^2$
metallic	
Fe^{2+}	$[Ar]3d^6$
ferrous	
Fe^{3+}	$[Ar]3d^5$
ferric	

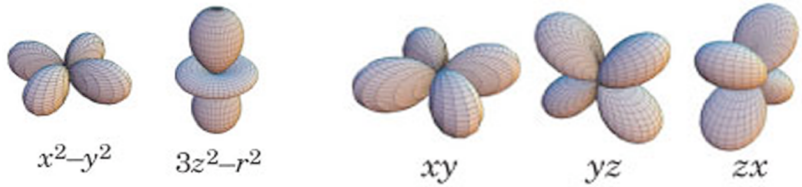


McCammon 97 Nature

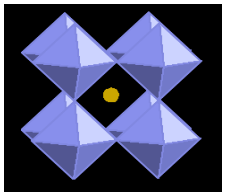
Wood et al. 06 Nature

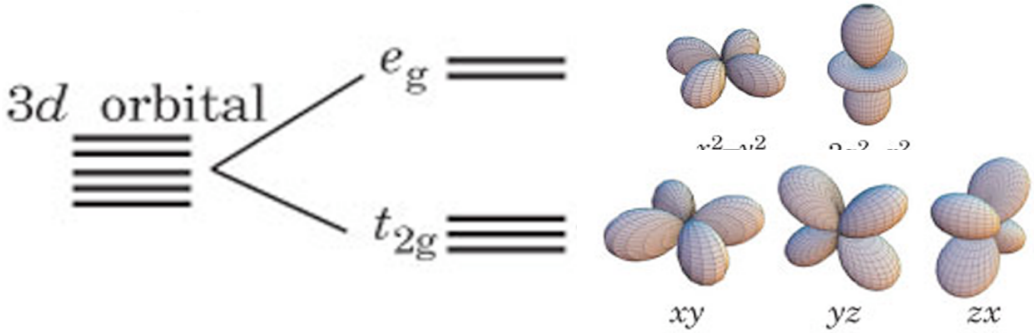
Crystal Field Splitting in Iron

Spherical, degeneracy

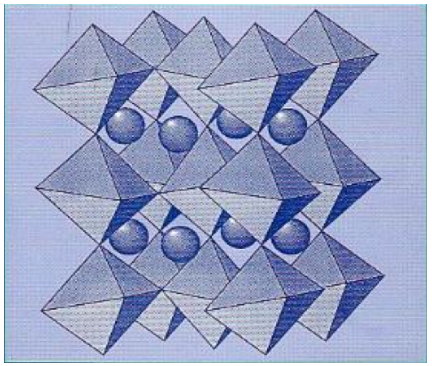


Cubic, octahedral site

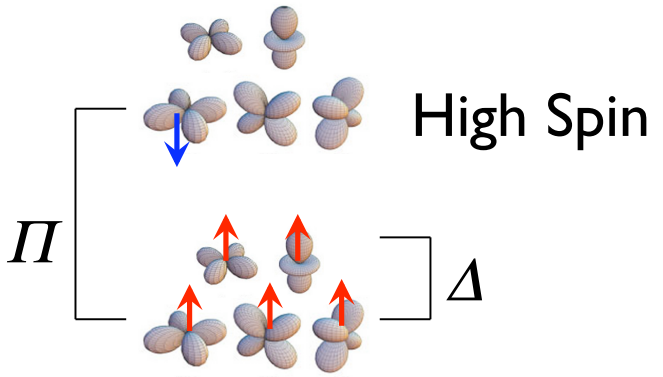


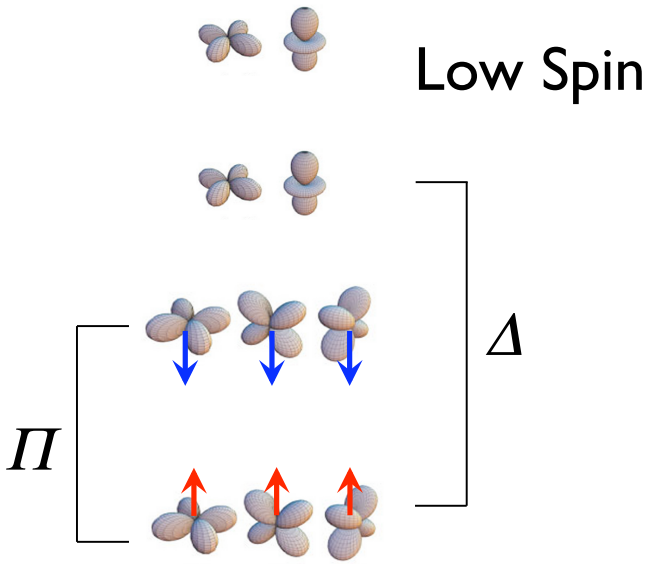


Orthorhombic
8-12 C.N. site

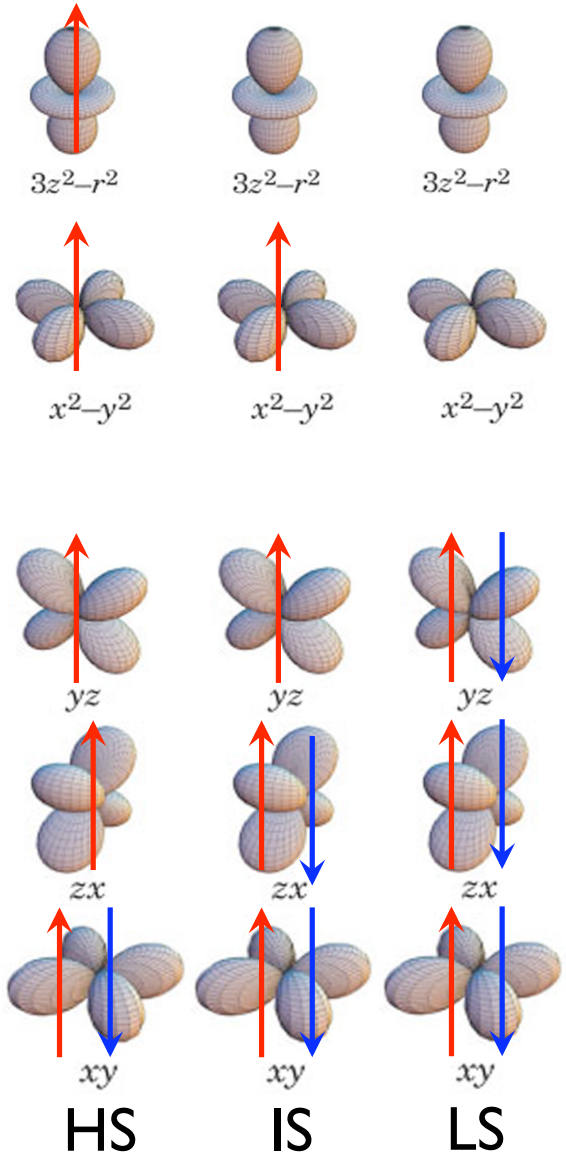


Pressure-Induced Spin Crossover in Fe^{2+}





Intermediate Spin



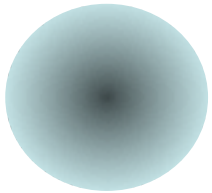
Probe Electronic Structure

Mössbauer spectroscopy

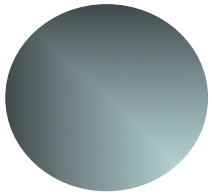
- Conventional
- Synchrotron
  - Energy domain
  - Time domain

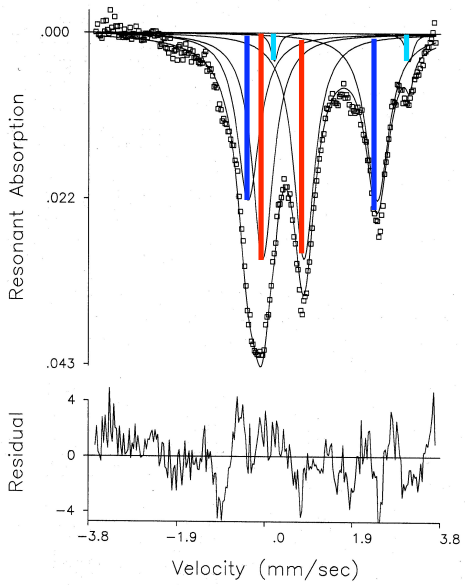
  Nuclear Forward Scattering

Isomer shift



Quadrupole splitting





X-ray emission spectroscopy

- Local moment
- K_β'/K_β

Struzhkin 04, JPCM

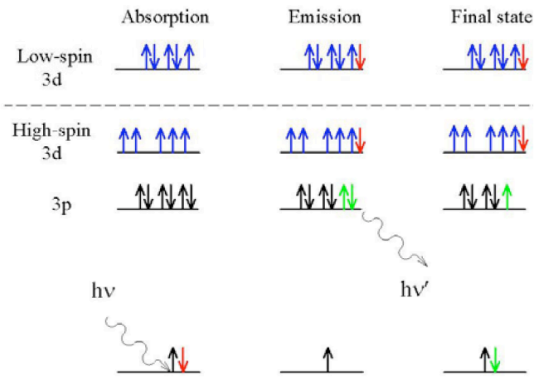
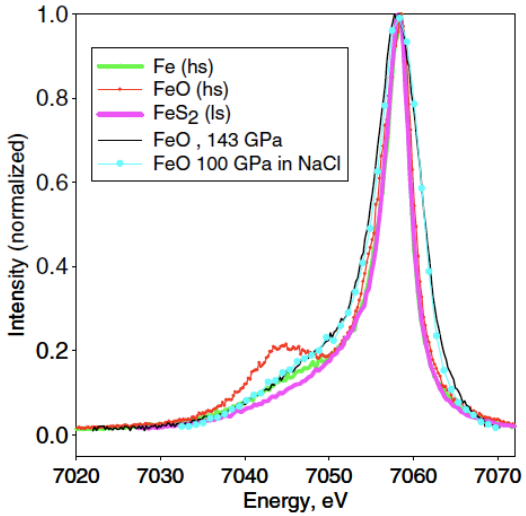
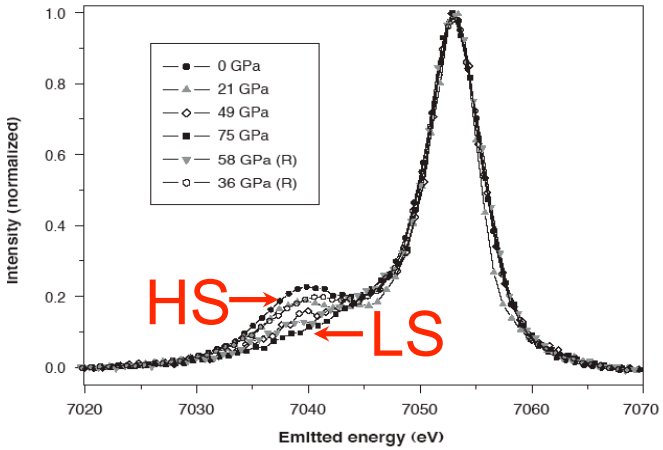


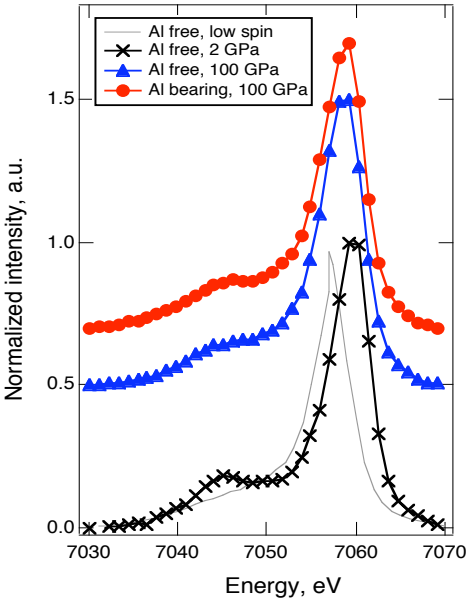
Figure 5. The schematic diagram of the Kβ emission process.



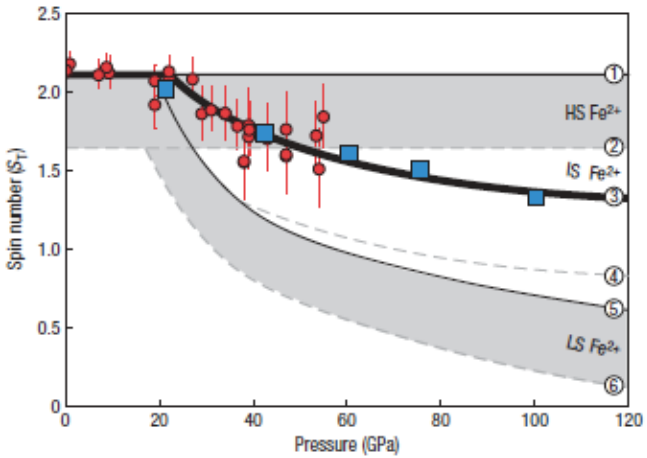
Pressure-Induced Spin Crossover in Fp and Pv



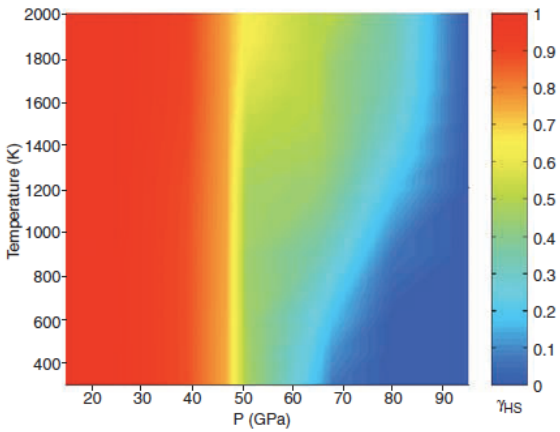
Badro et al. 03 Science



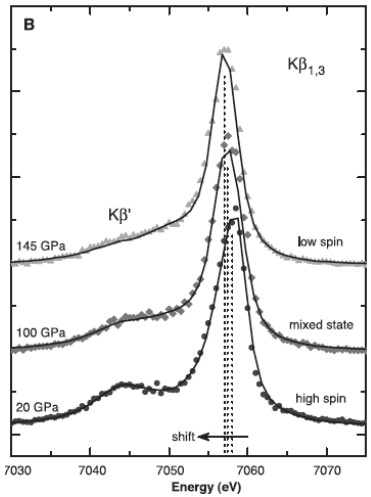
Li et al. 04 PNAS



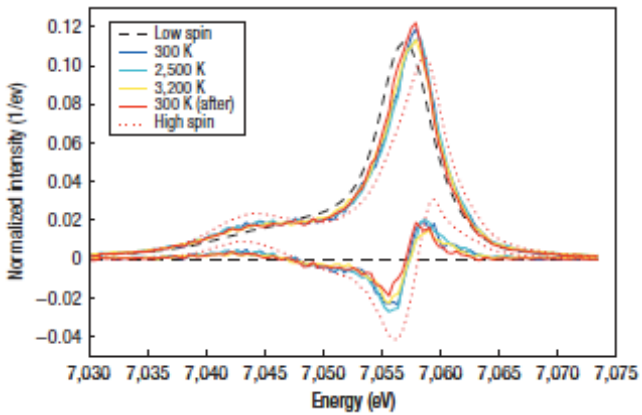
McCammon et al. 08 Nature Geo



Lin et al. 07 Science



Badro et al. 04 Science



Lin et al. 08 Nature Geo

Spin Crossover Influences Physical Properties

Density & elasticity
Lin et al. 05, 07 - Fp
Fei et al. 05 – Pv

Radiative conductivity - Fp
Badro et al 04 - blue shift
Tsuchiya et al. 06 - red shift
Goncharov et al 06 - red shift

Electric conductivity - Fp
Ohta et al. 07

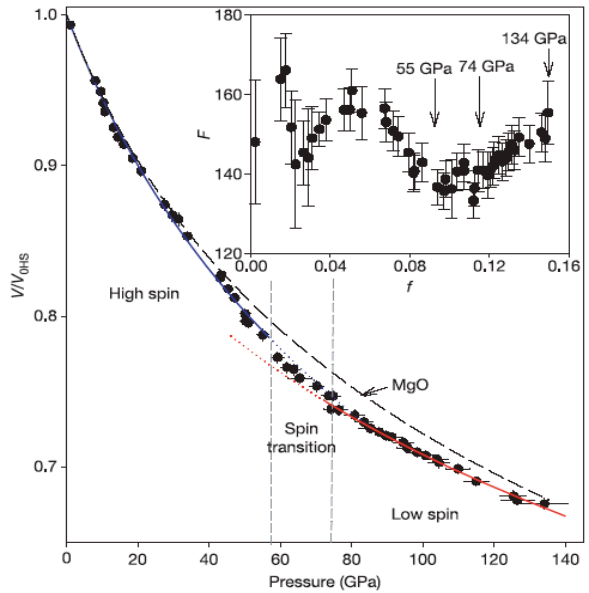
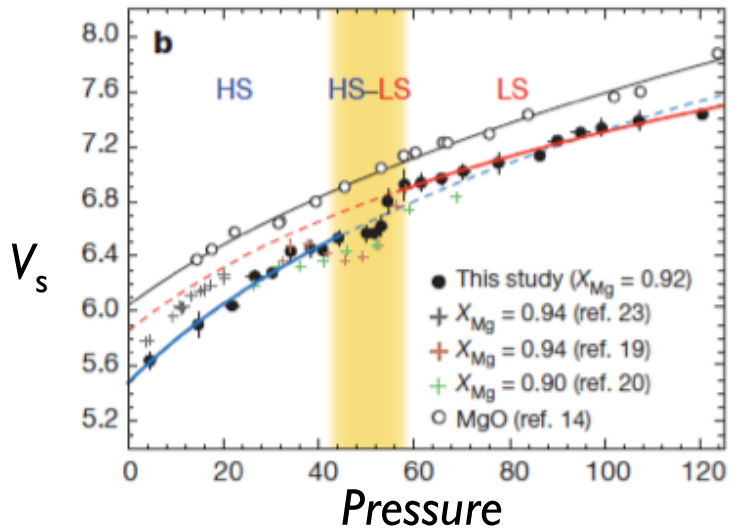
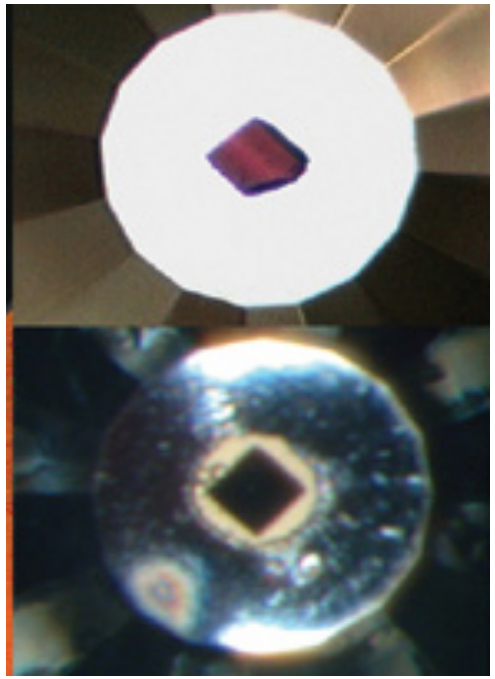


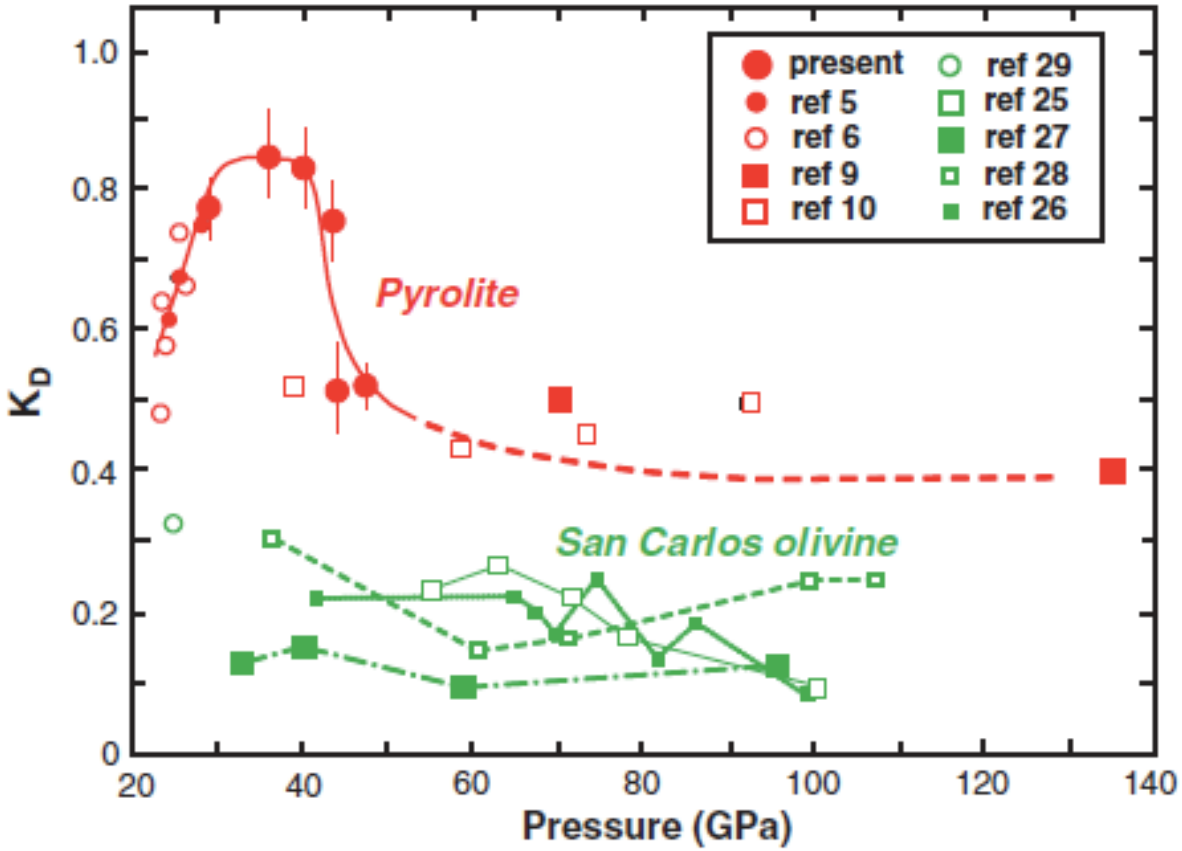
Figure 2 | Normalized volume of magnesiowüstite, $(Mg_{0.83},Fe_{0.17})O$, as a function of pressure at 300 K. A weighted least-squares fit to the high-spin





Limited Effects of Spin Crossover on Partitioning

$$K_D = (Fe/Mg)_{Mg\text{-}Pv}/(Fe/Mg)_{Mw}$$



Spin crossover gradual

Fe^{3+} strongly prefers pV

Badro et al 03, 05 - Pv/Fp
Li et al. 04; Li 07 - Pv/Fp
Irifune et al. 10 - Pyrolite

Birch-Murnaghan EoS

Finite strain theory: Eulerian strain
Thermodynamics
Macroscopic view

$$f = \frac{1}{2}\left(\left(\frac{V_0}{V}\right)^{2/3} - 1\right)$$

$$K = (1+2f)^{5/2} K_0 \left[1 + (3K_0' - 5)f\right]$$

$$G = (1+2f)^{5/2} G_0 \left[1 + (3\frac{K_0}{G_0}G_0' - 5)f\right]$$

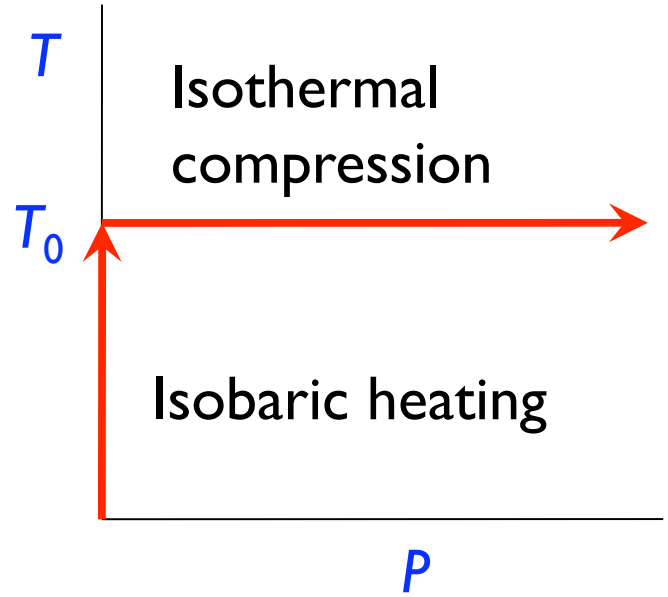
$$P = 3K_0 f (1+2f)^{5/2}\left(1 + \frac{3}{2}(K'-4)f + \frac{3}{2}\left(K_0K'' + (K'-4)(K'-3) + \frac{35}{9}\right)f^2\right)$$

$$= \frac{3}{2}K_0\left(\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right)\left(1 + \frac{3}{4}(K'-4)\left(\left(\frac{V_0}{V}\right)^{2/3} - 1\right)\right)$$

“Hot” BM EoS

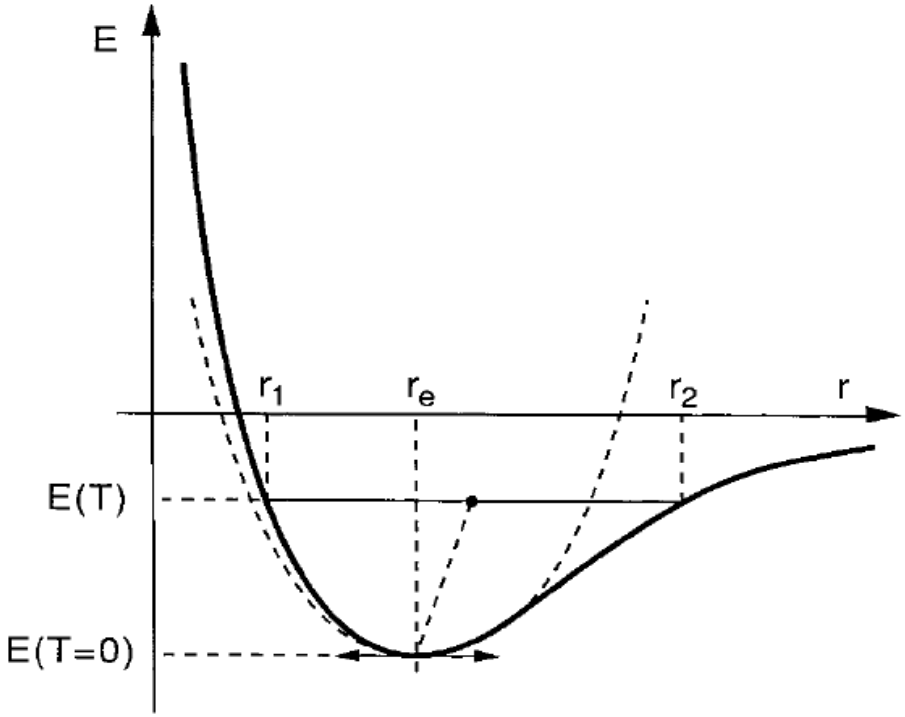
$$V_{0,T} = V_0 \exp\left(\int_{300}^{T} (\alpha_1 + \alpha_2 T)\mathrm{d}T\right)$$

$$K_T' = K' + \frac{\partial K'}{\partial T}(T - 300)$$

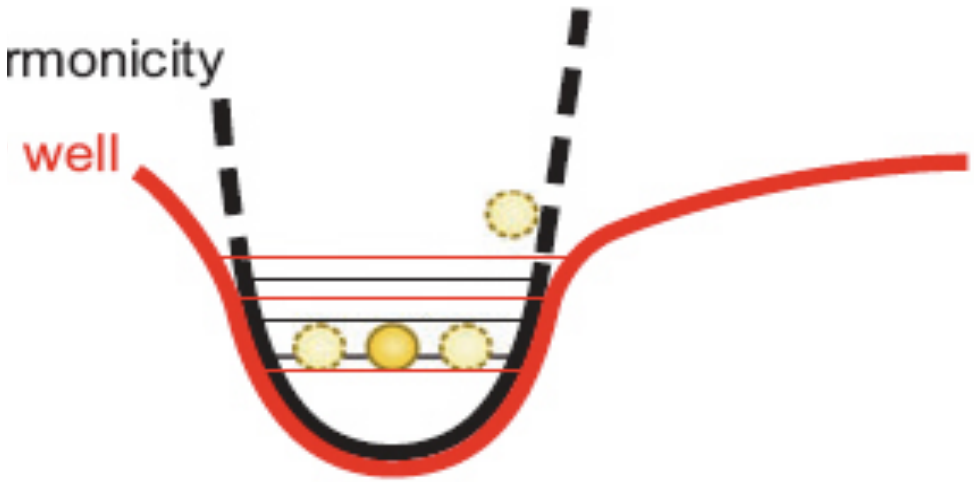


$$P(V,T) = \frac{3}{2} K_{0,T} \left(\left(\frac{V_{0T}}{V}\right)^{7/3} - \left(\frac{V_{0T}}{V}\right)^{5/3} \right) \left(1 + \frac{3}{4}(K'_T - 4)\left(\left(\frac{V_{0T}}{V}\right)^{2/3} - 1 \right) \right)$$

Elasticity: Atomic Potential and Lattice Dynamics



Microscopic view
Bulk modulus
Thermal expansion



Lattice dynamics: The Core

Mie-Grüneisen-Debye EoS - γ

$$P(V, T) = P(V, T_0) + P_{\mathrm{th}}(V, T)$$

$$P_{\mathrm{th}}(V, T) = \frac{\gamma(V)\{E_{\mathrm{th}}(\theta, T) - E_{\mathrm{th}}(\theta, T_0)\}}{V}$$

$$\gamma = -\frac{\mathrm{d}\ln\Theta}{\mathrm{d}\ln V}$$

$$E_{\mathrm{th}}(\theta, T) = 9nRT\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{t^3}{(e^t - 1)}\,\mathrm{d}t$$

Mie-Grüneisen-Debye EoS – γ, q

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0} \right)^q$$

$$\theta(V) = \theta_0 \, \exp \left\{ \frac{[\gamma_0 - \gamma(V)]}{q} \right\}$$

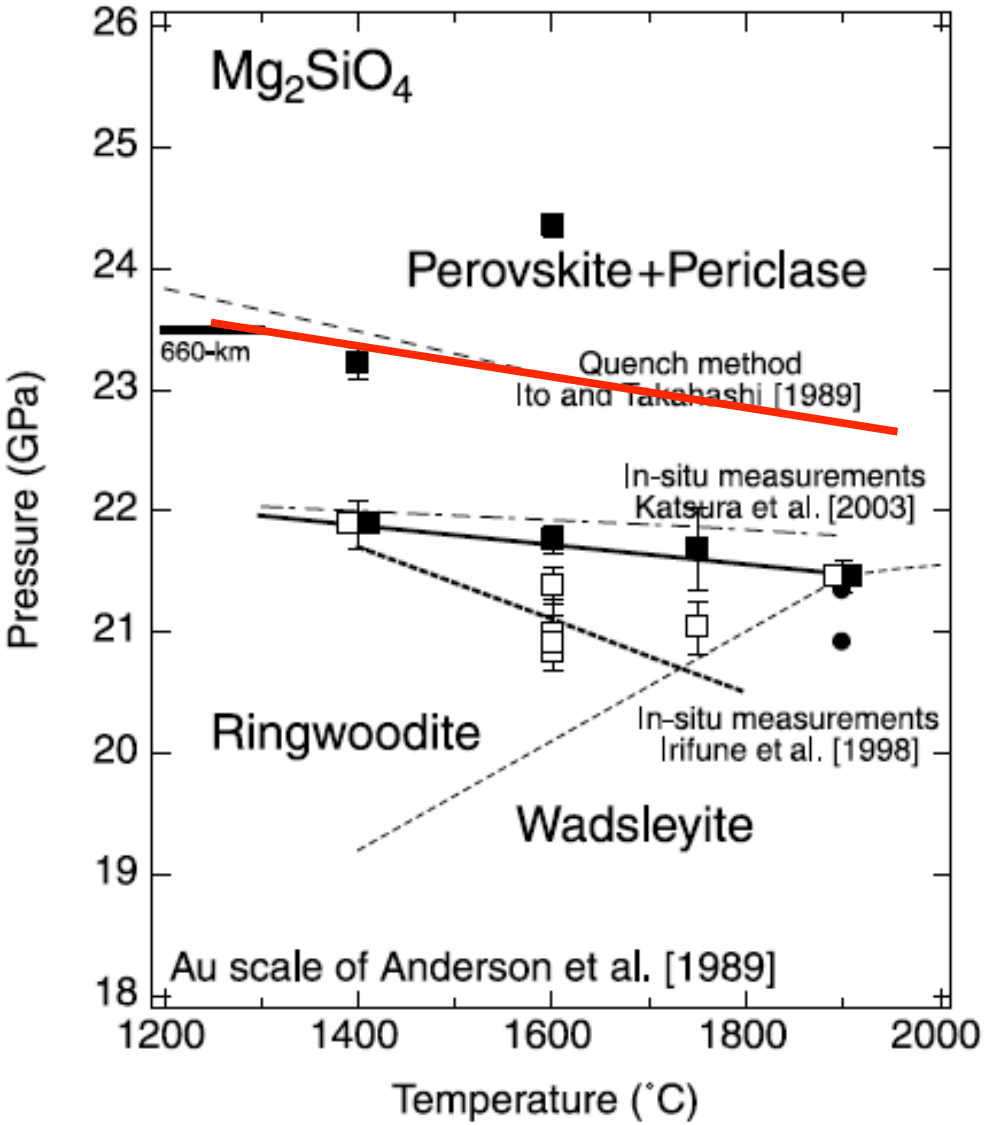
Modified Mie-Grüneisen-Debye EoS – γ, q0, q1

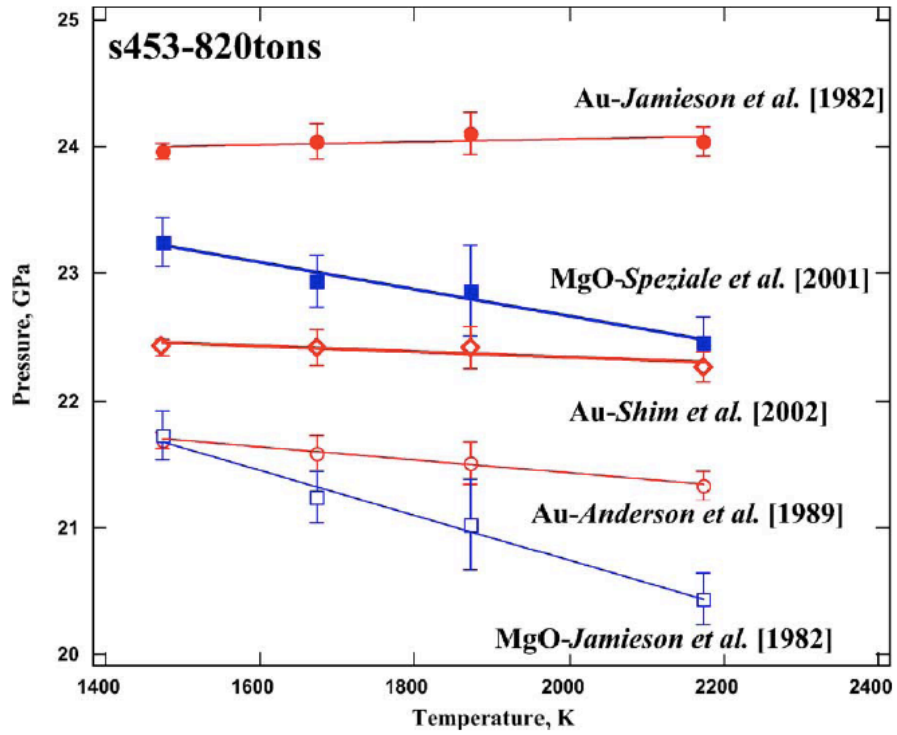
$$q = q_0 \left(\frac{V}{V_0} \right)^{q_1}$$

$$\gamma = \gamma_0 \exp\left(\frac{q_0}{q_1} \left(\left(\frac{V}{V_0} \right)^{q_1} - 1 \right) \right)$$

$$\Theta = \Theta_0 \exp\left(-\int_{V_0}^{V} \frac{\gamma(V)}{V} \mathrm{d}V \right)$$

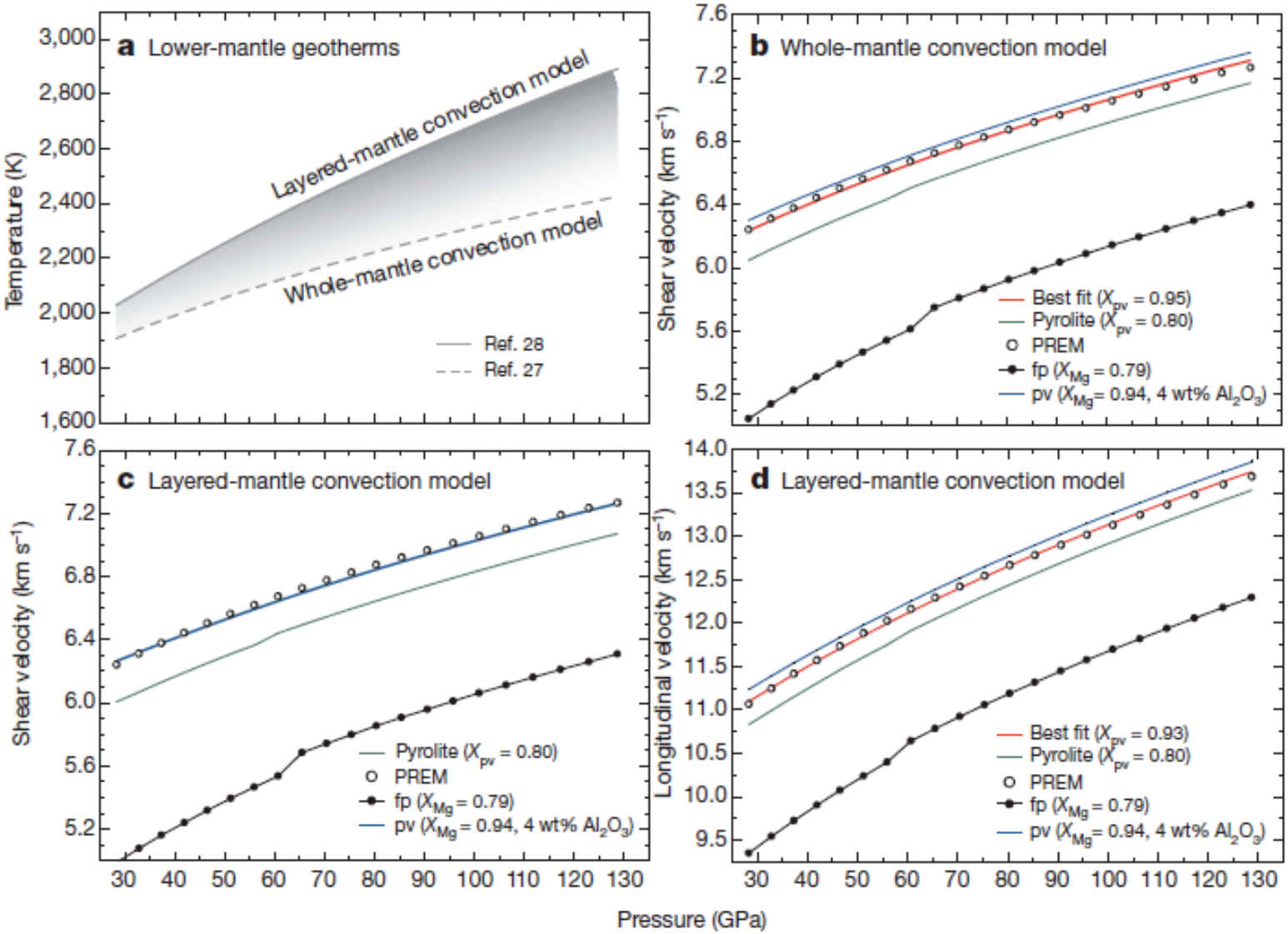
Post-Spinel Transition and 660-km Discontinuity





Fei et al. 04 JGR
Fei et al. 04 PEPI

Perovskitic Lower Mantle



Murakami et al. 12 Science

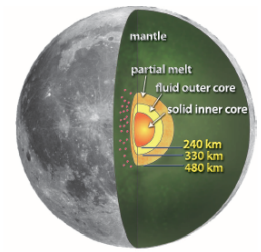
Conclusions and Outlook

Material properties under deep mantle *P-T-x-t* conditions key to understanding the state and history of the mantle but poorly constrained

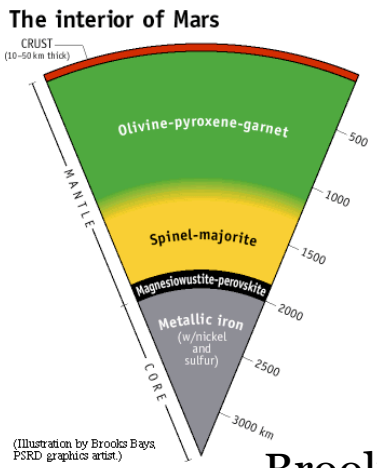
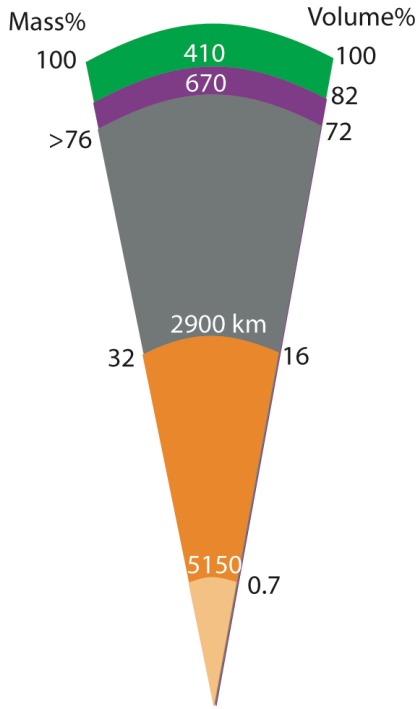
State of the art
Experimental: ~ 4 Mbar (400 GPa), ~ 6000 K
Analytical: time second spatial 10 nm

Planetary perspectives

CIDER



Weber et al. 11 Science



Brooks Bays