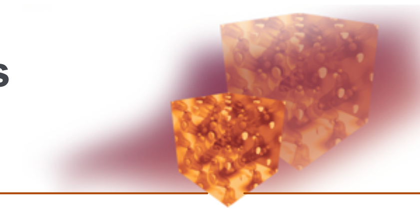
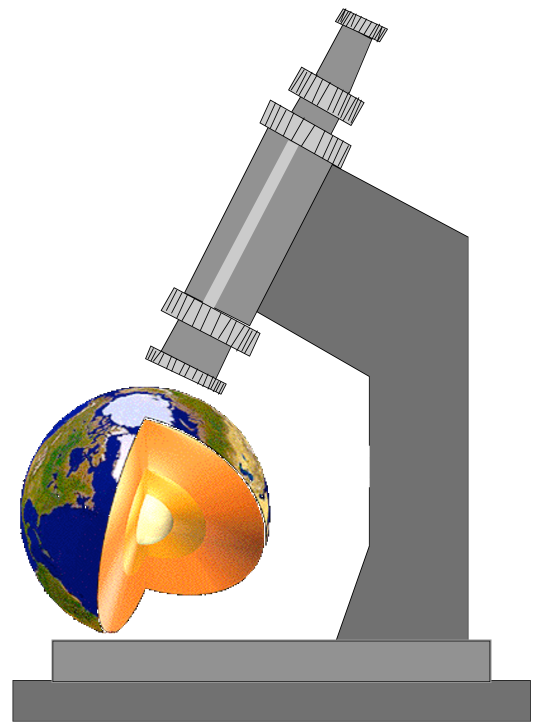


# Geophysics, Mineral Physics, and QMC

**Lars Stixrude**
[University of Michigan]

# Earth as a laboratory sample?

Compositionally complex and inhomogeneous
Multiple phases
Pressure and temperature inhomogeneous
Produced by adiabatic gravitational self-compression
Internal heat source
Internal motion
Largely intangible (spatially and temporally!)



# What would we like to know?

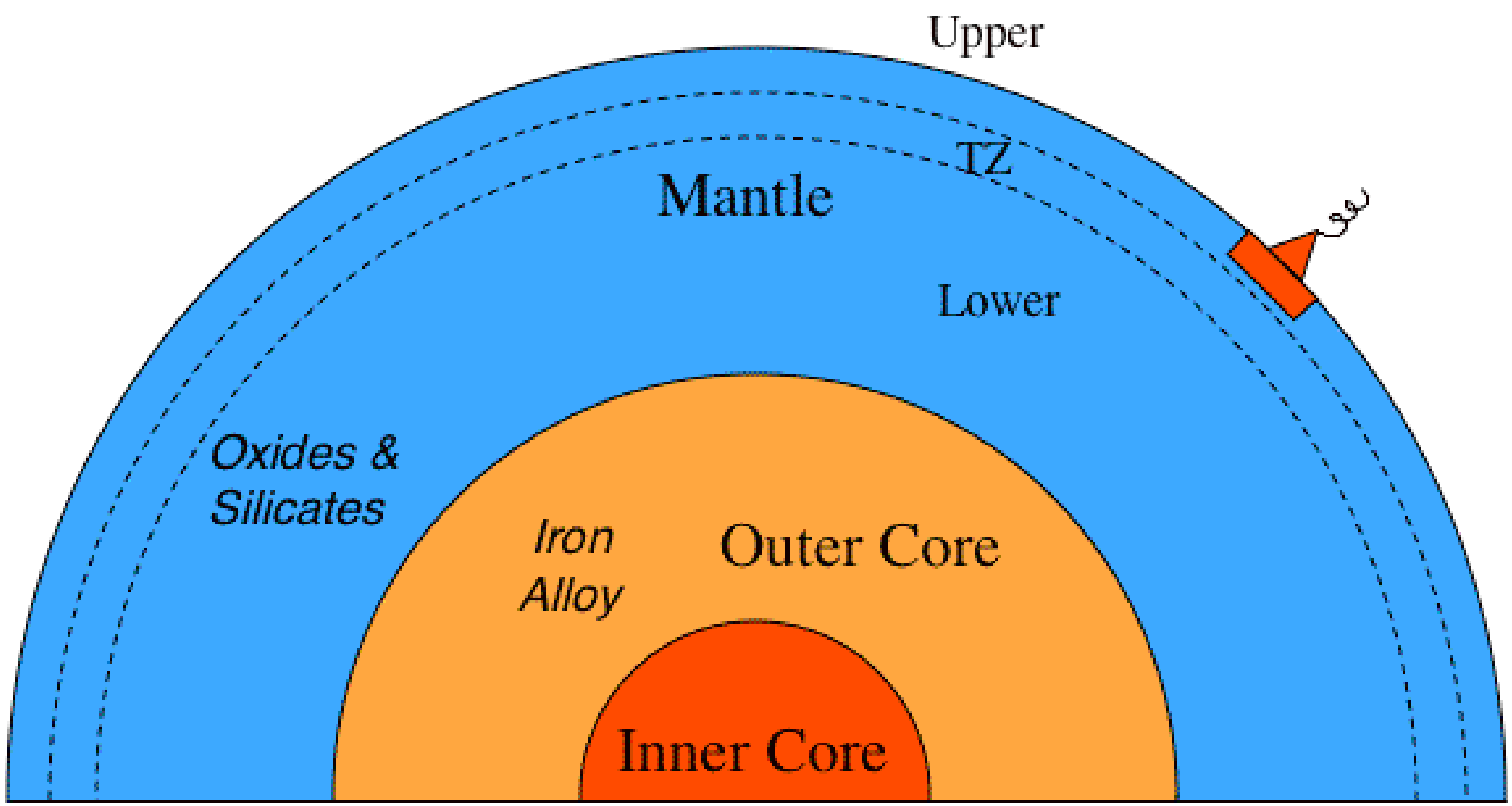
How did it form?
How did it evolve?
How does it work today?

Process

Earth subject to various thermal and mechanical forcings throughout its history

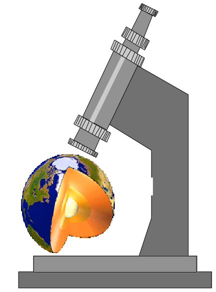
Response depends on material properties at extreme conditions

# Pressure, temperature, composition



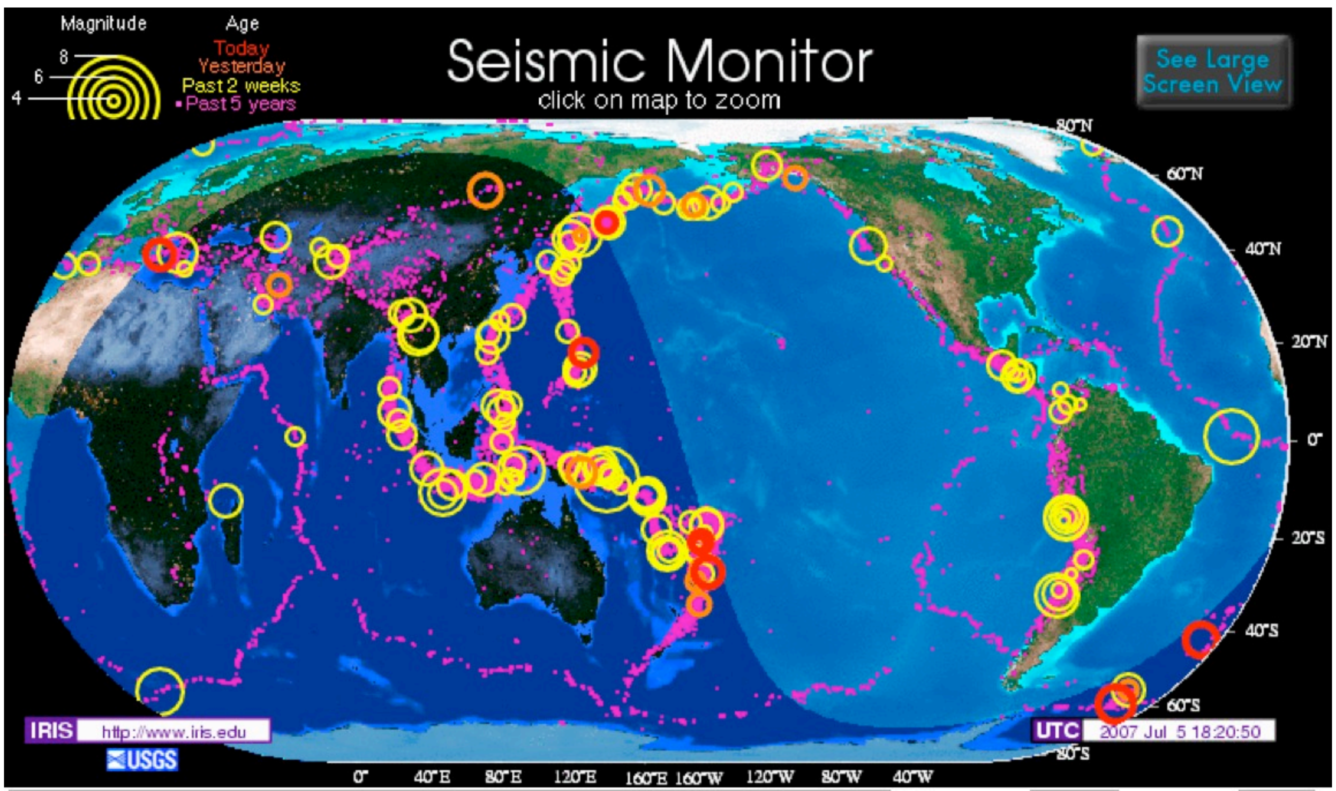

| | | | | | | |
|---|---|---|---|---|---|---|
| Depth | 0 | 660 | 2890 | 5150 | 6371 | km |
| Pressure | 0 | 24 | 136 | 329 | 363 | GPa |
| Temperature | 300 | 1800 | 3000 | 5500 | 6000 | K |

# Probe: Earthquakes



Many each year strong enough to generate signal at antipodes

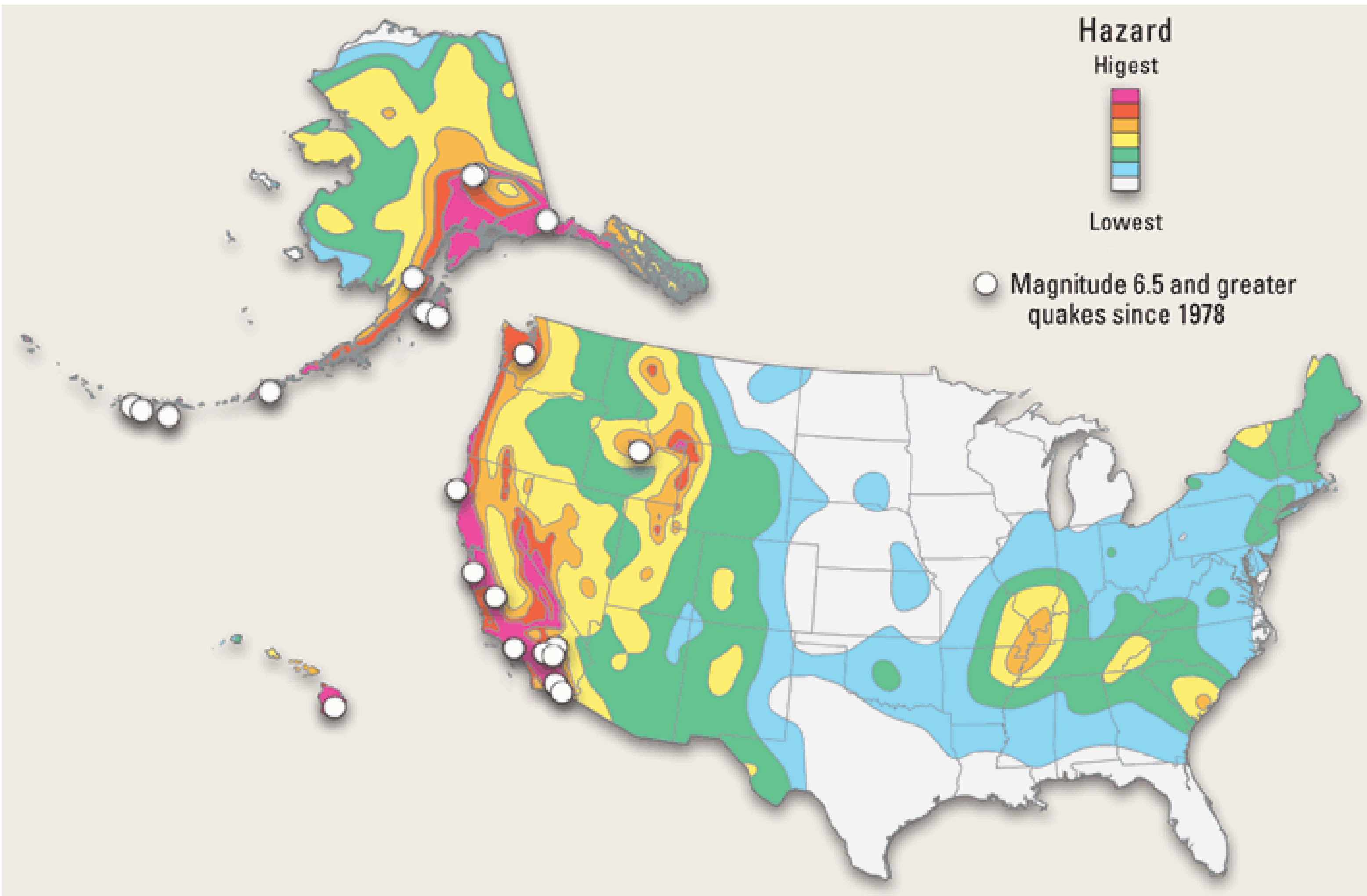
| | | |
|---|---|---|
| 10 major (magnitudes 7-8) | 32 megaton | ~ Largest test |
| 100 large (6-7) | 1 megaton | |
| 1000 damaging (5-6) | 32 kiloton | ~ Trinity |



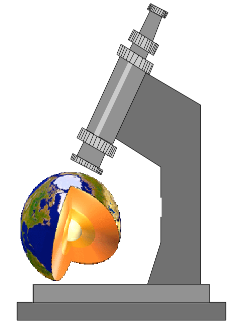

www.iris.edu

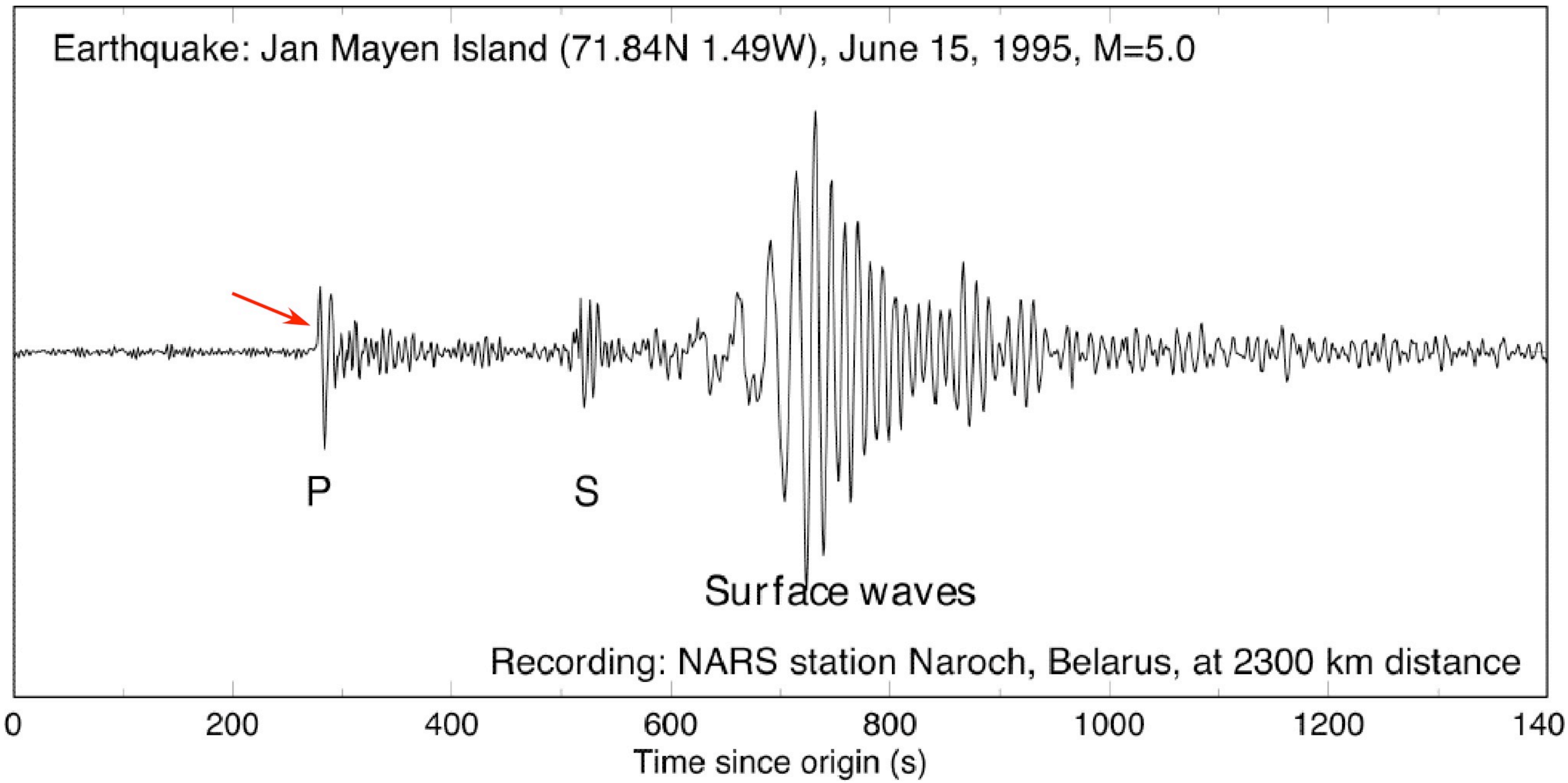
# U.S. earthquakes

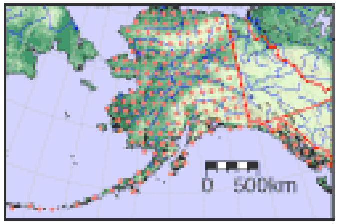
New Madrid, Missouri, 4 earthquakes magnitude > 7.0
Dec. 16, 1811 to Feb. 7, 1812



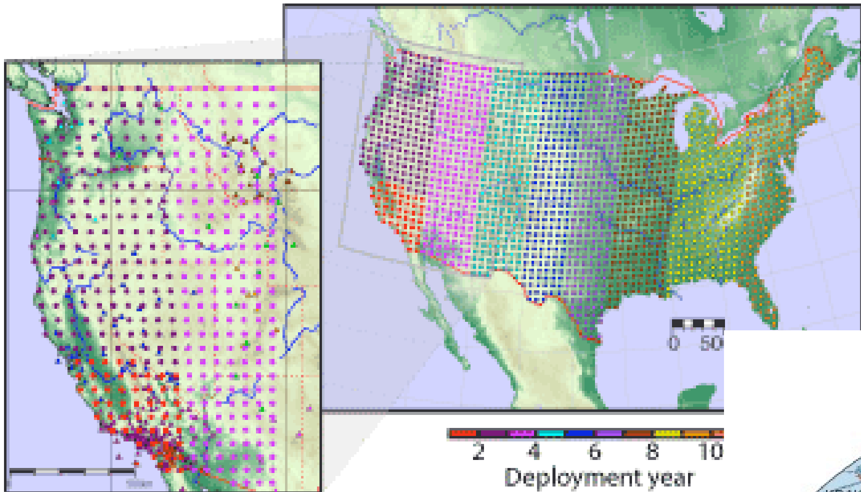
# Detector: seismograph



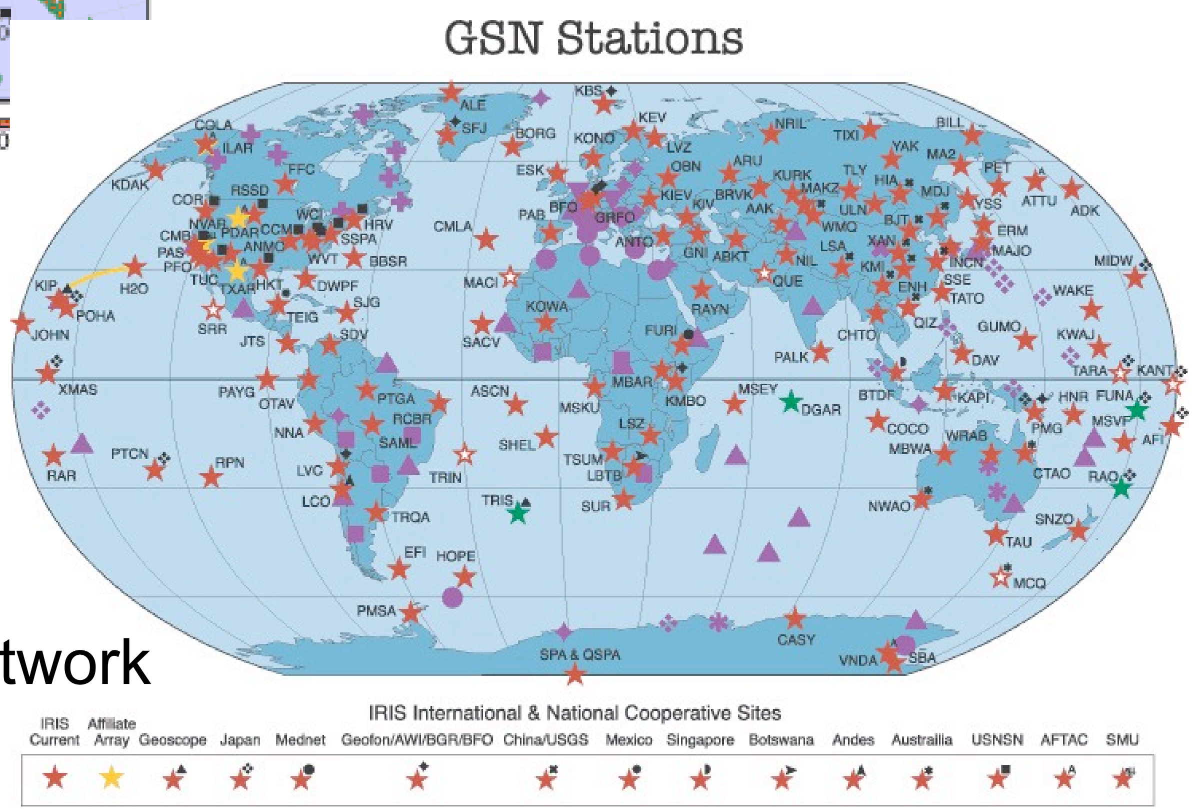





# Seismic networks



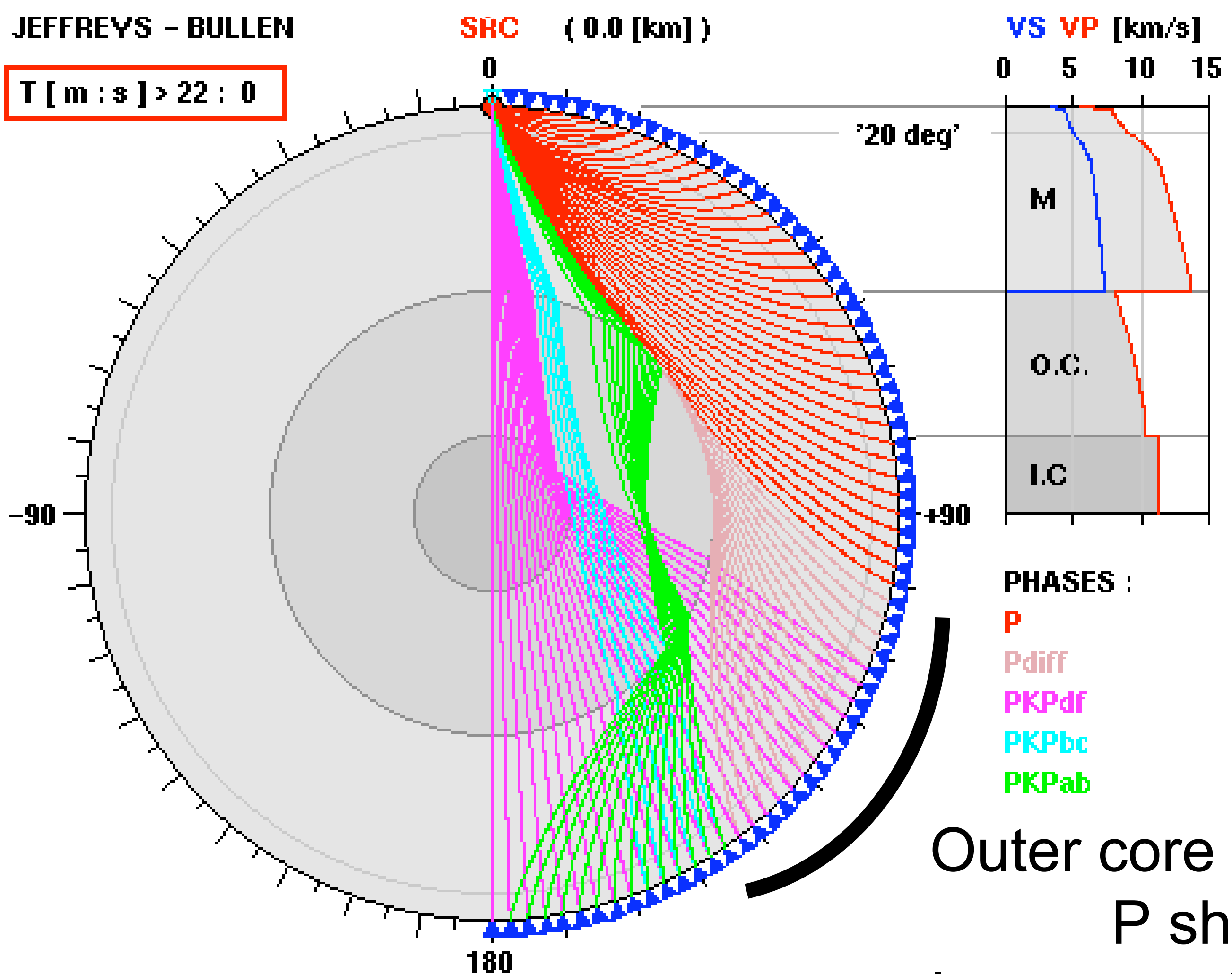

USArray




Global Seismic Network

# Seismic phases

*Earthquake*




Shown:
P
PKP
PKIKP (or PKPdf)

Many not shown
e.g. PcP (reflection off core-mantle boundary

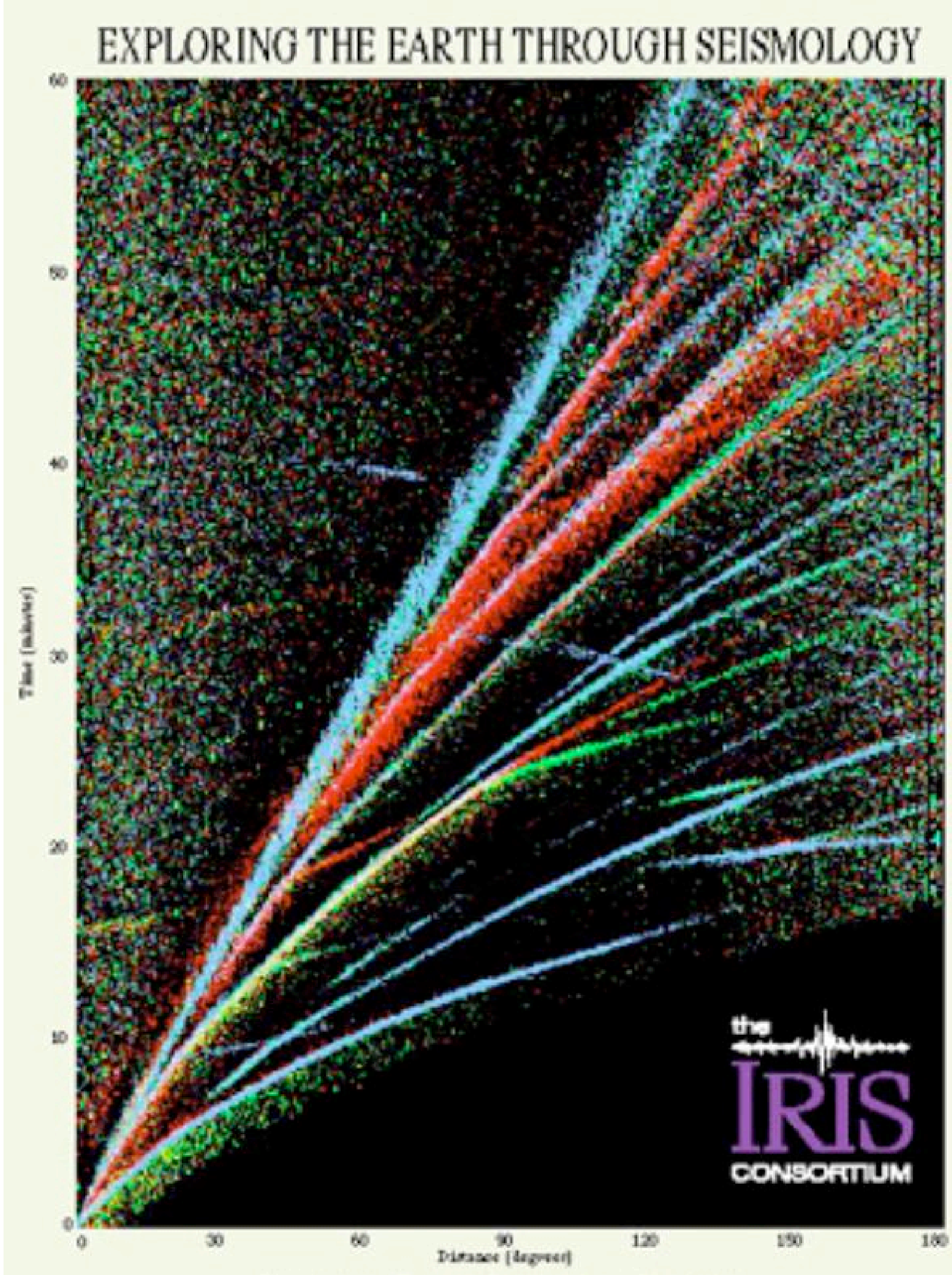
Outer core (Gutenberg, 1913)
P shadow zone
Inner core (Lehmann, 1936)
Weak arrivals in shadow zone

*Antipodal travel time ~20 minutes*

*TU Clausthal*

# Travel time curves

- Travel time increases with distance
- Shape requires velocity to increase with depth
- “Scatter” reflects asphericity
- “Shadow zone” caused by core

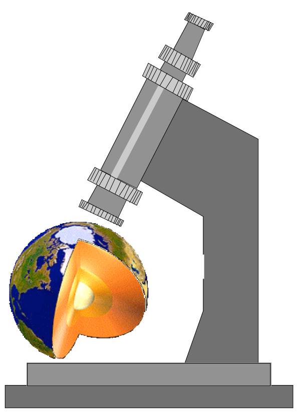


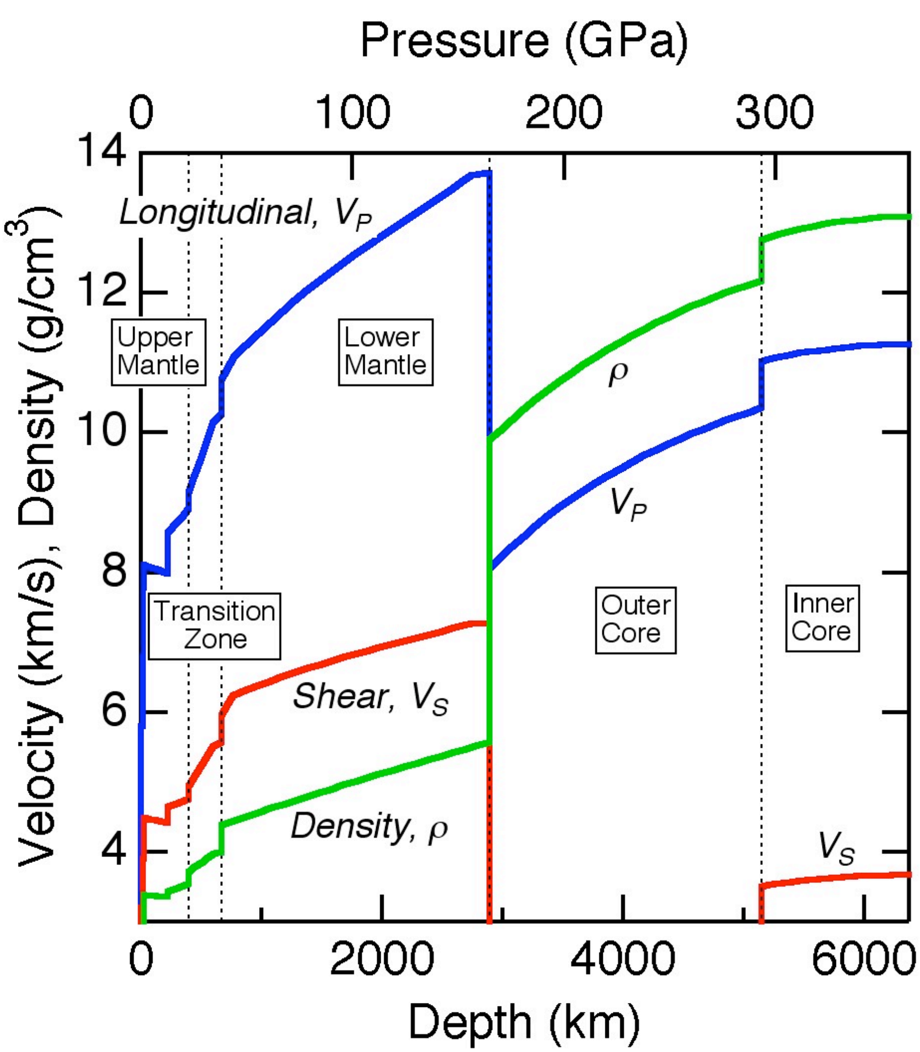
# Observable: elastic wave velocities and density

~radially homogeneous,
Isotropic

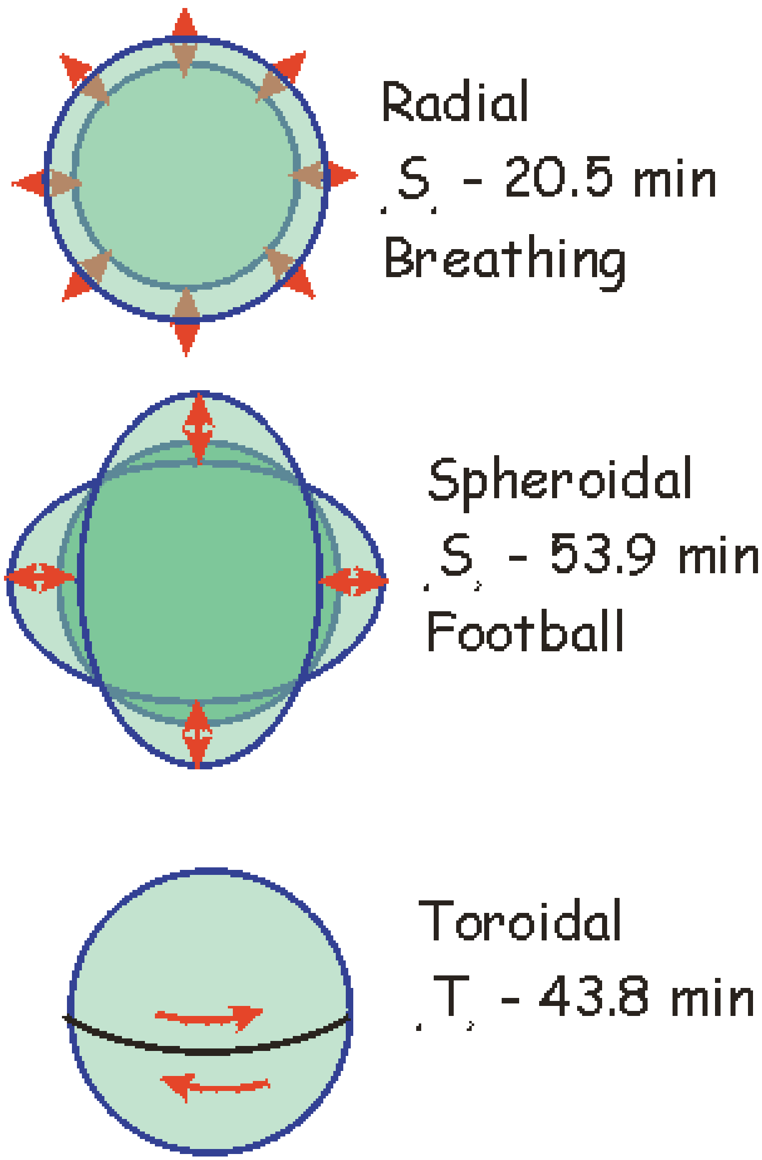
Monotonic and smooth increase with depth except:

- Core-mantle boundary
- Smaller discontinuities
- Near surface





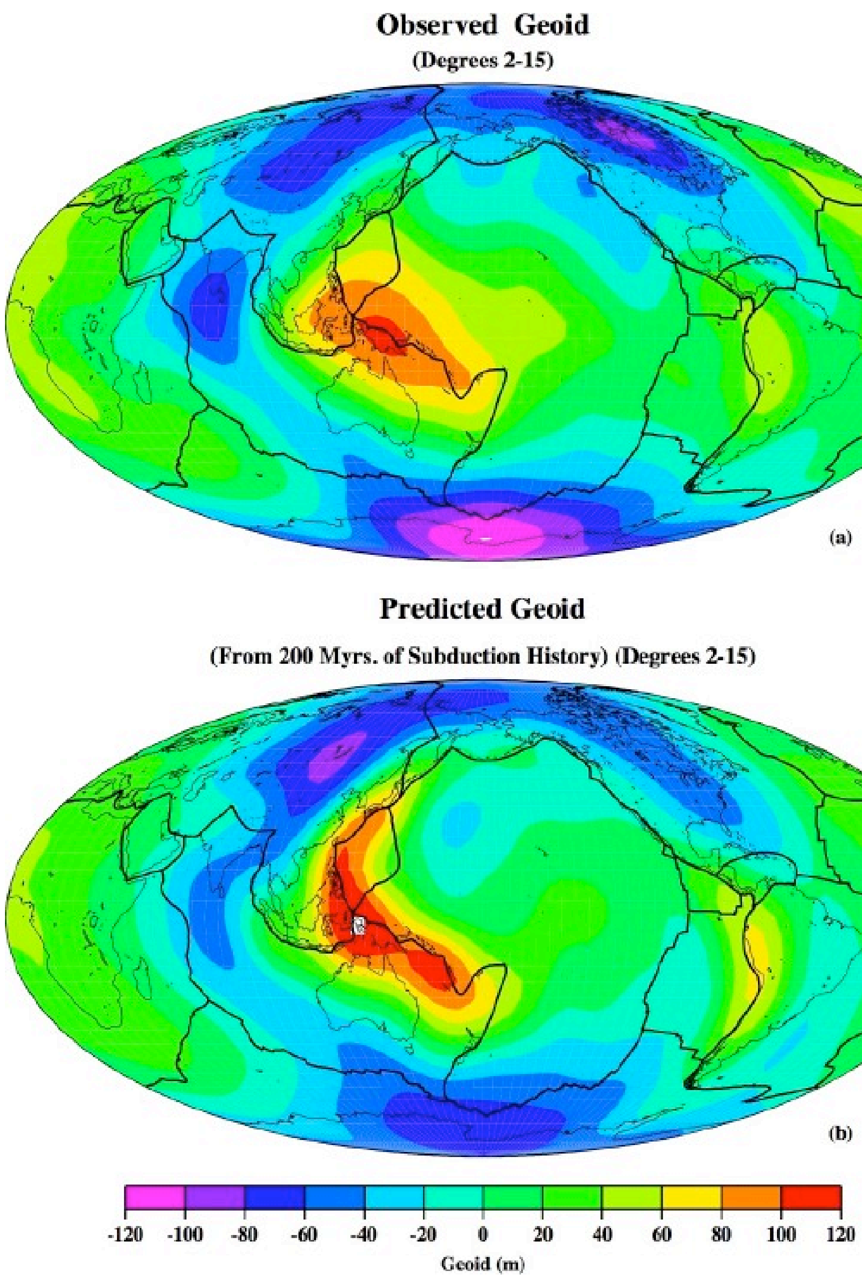
# Density

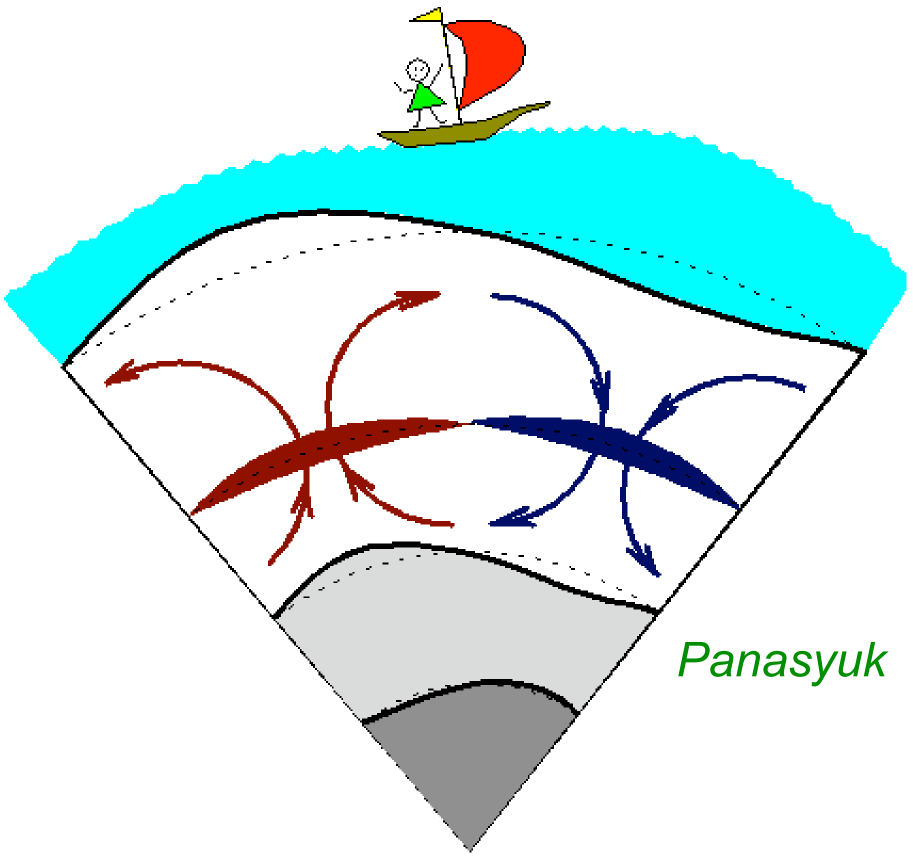



- Normal modes of oscillation
- Frequency depends on velocity and density distribution
- Excited by earthquakes
- Most normal modes undetectable except after largest earthquakes
- Rigidity of inner core

# Geoid

equipotential surface of the gravity field




*Lithgow-Bertelloni and Richards (1998) Rev. Geophys.*

# Radial inhomogeneity

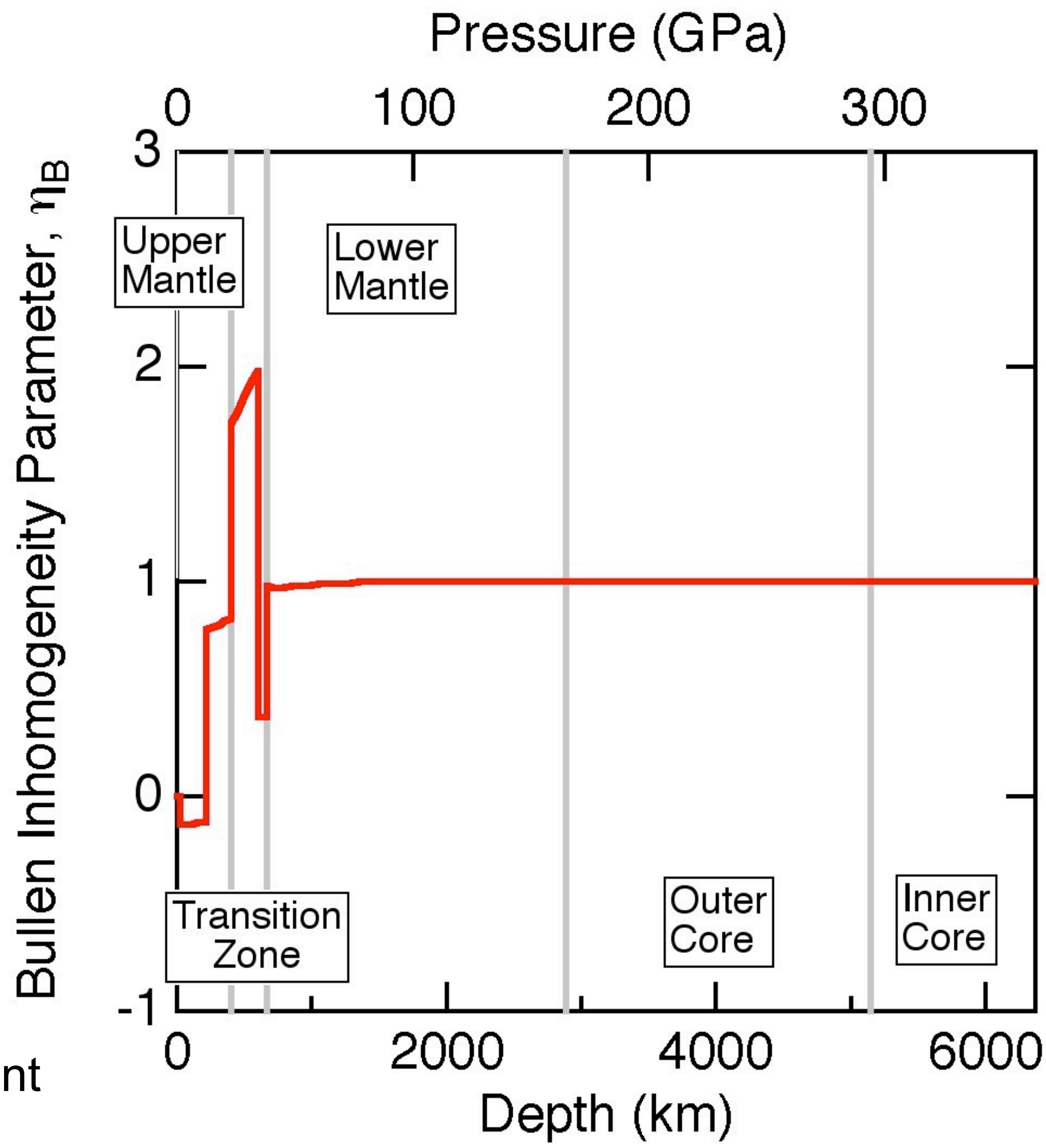
$$V_P = \sqrt{\frac{K_S + 4/3G}{\rho}}$$

$$V_S = \sqrt{\frac{G}{\rho}}$$

$$\Phi = V_P^2 - \frac{4}{3}V_S^2 = \frac{K_S}{\rho} = \left(\frac{\partial P}{\partial \rho}\right)_{S,\vec{n}}$$

$$\frac{\Phi}{\rho g}\left(\frac{\partial \rho}{\partial z}\right)_{Earth}$$

- Unity for homogeneous, adiabatic layers
- Deviations from unity:
  - –Inhomogeneous chemical composition
  - –Phase transformations
  - –Non-adiabatic temperature gradient



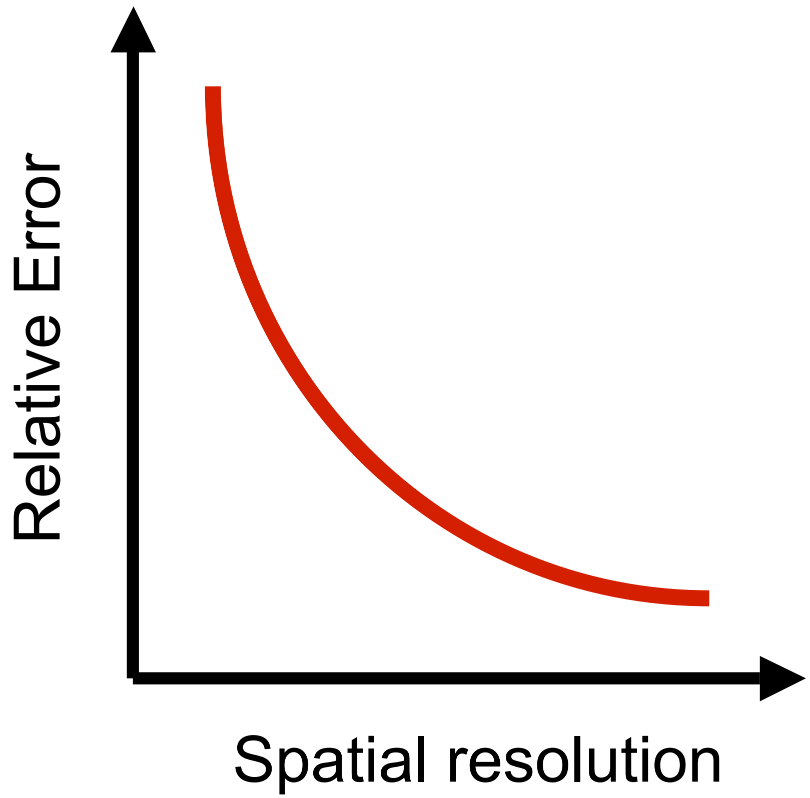

PREM: Dziewonski and Anderson (1981) PEPI

# Overdetermined inversion of inaccurate, incomplete data

Resolution - Error tradeoff curve

Higher spatial resolution means larger uncertainty

Better resolution and higher accuracy?  More data!



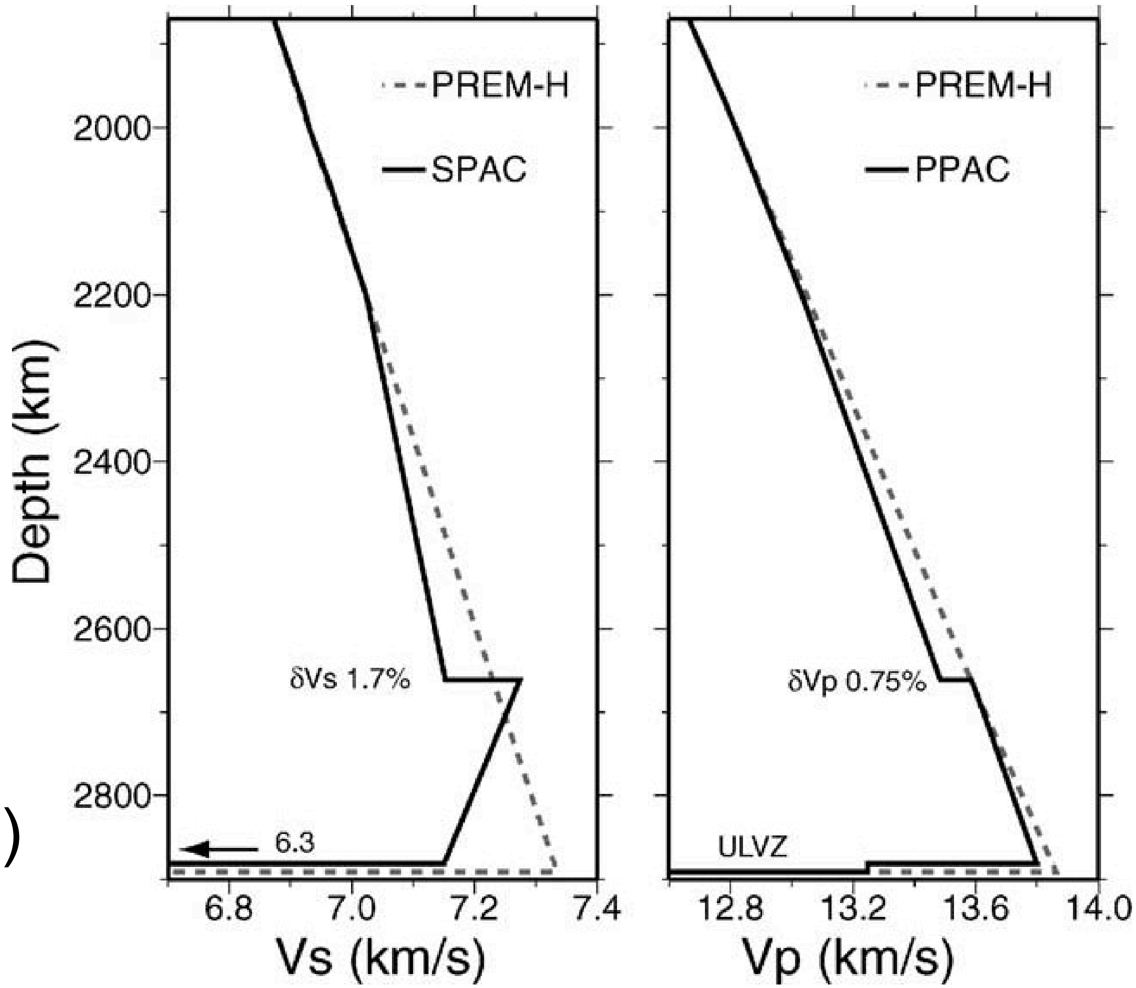

*Backus and Gilbert (19&) Phil. Trans. A*

# Waveforms

Waveforms contain information on velocity gradients

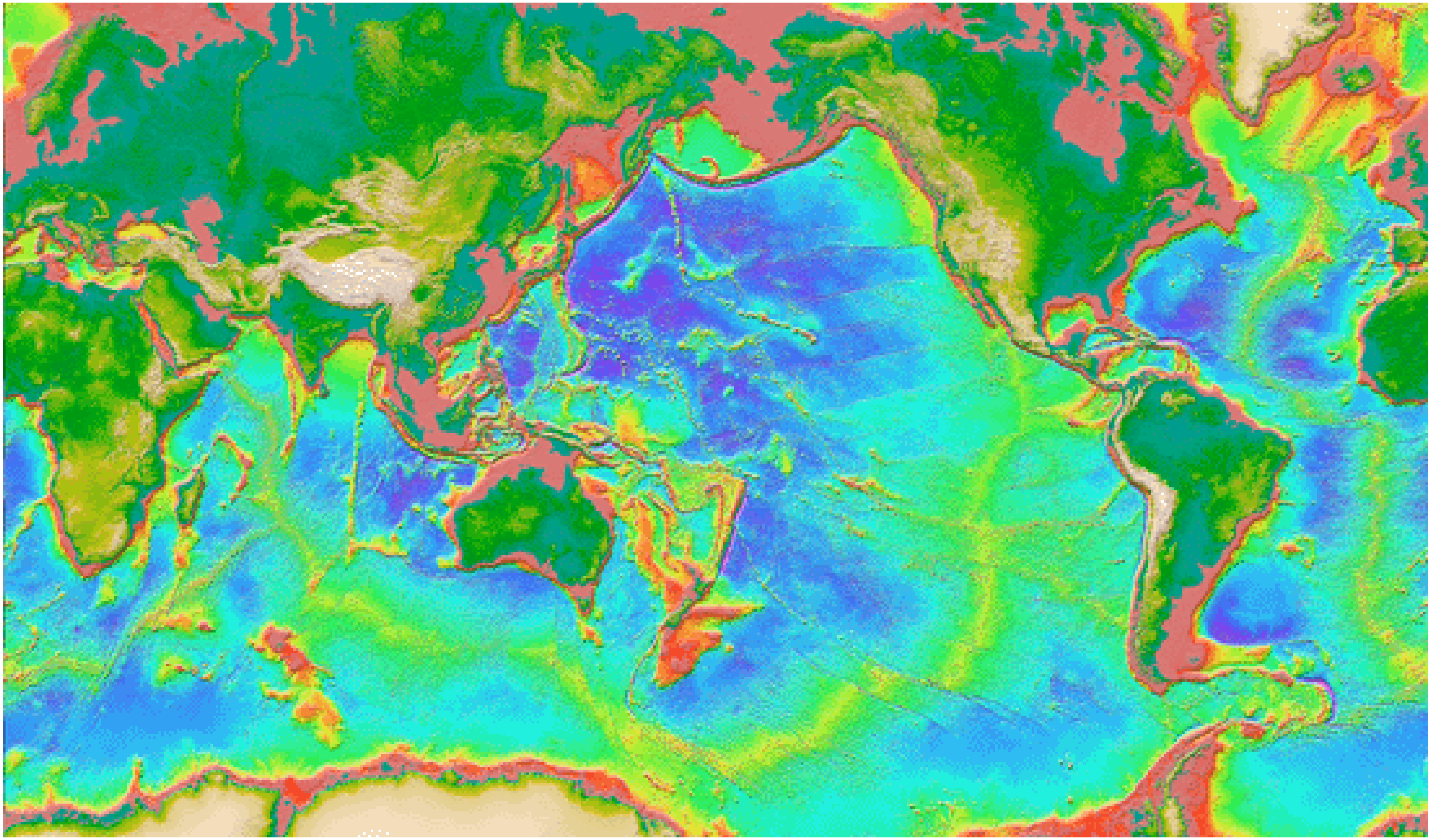
Regional studies with dense arrays can dramatically improve spatial resolution

D'' layer bounded by Velocity discontinuity (top) Ultra-low velocity zone (bottom)




*Lay et al. (2004) PEPI*

# Spherically symmetric Earth?



*Smith and Sandwell (1997) Science*

# Seismic tomography

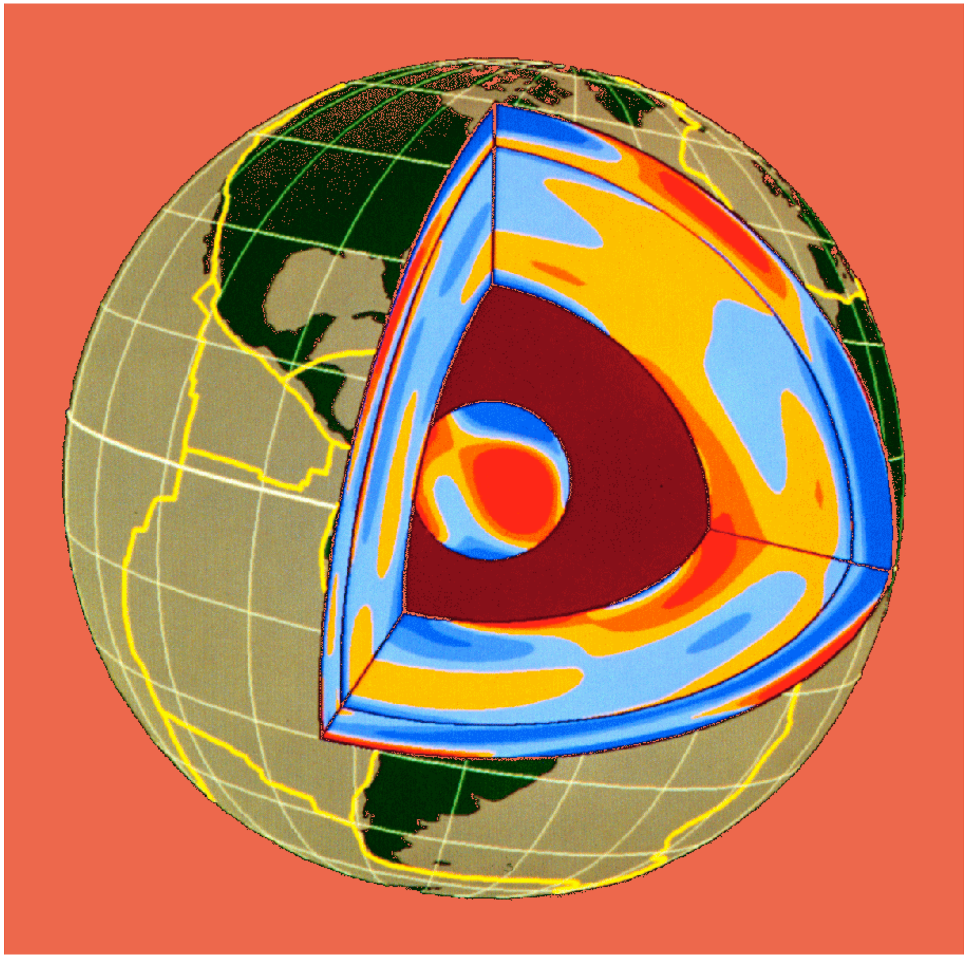
Systematic spatial variations in travel times at the same distance

Conventions:

Plot relative lateral variations about the average velocity at a given depth, i.e.

Average spherical structure removed

Blue: fast
Red: slow

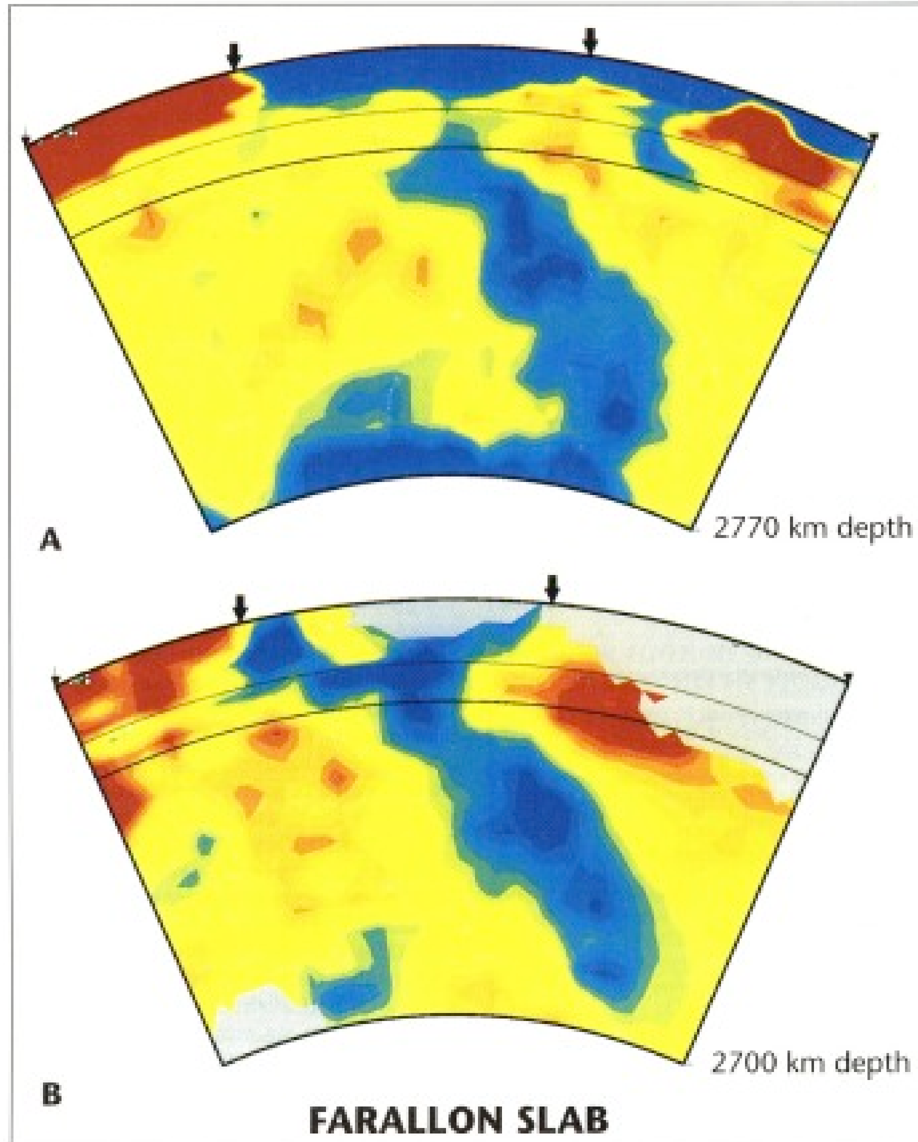


# Seismic tomography

Blue tabular feature interpreted as a subducted slab

Supported by geologic evidence for subduction of Pacific seafloor beneath California

This part of now subducted Pacific seafloor was called the Farallon plate




*Grand et al., (1997) GSA Today*

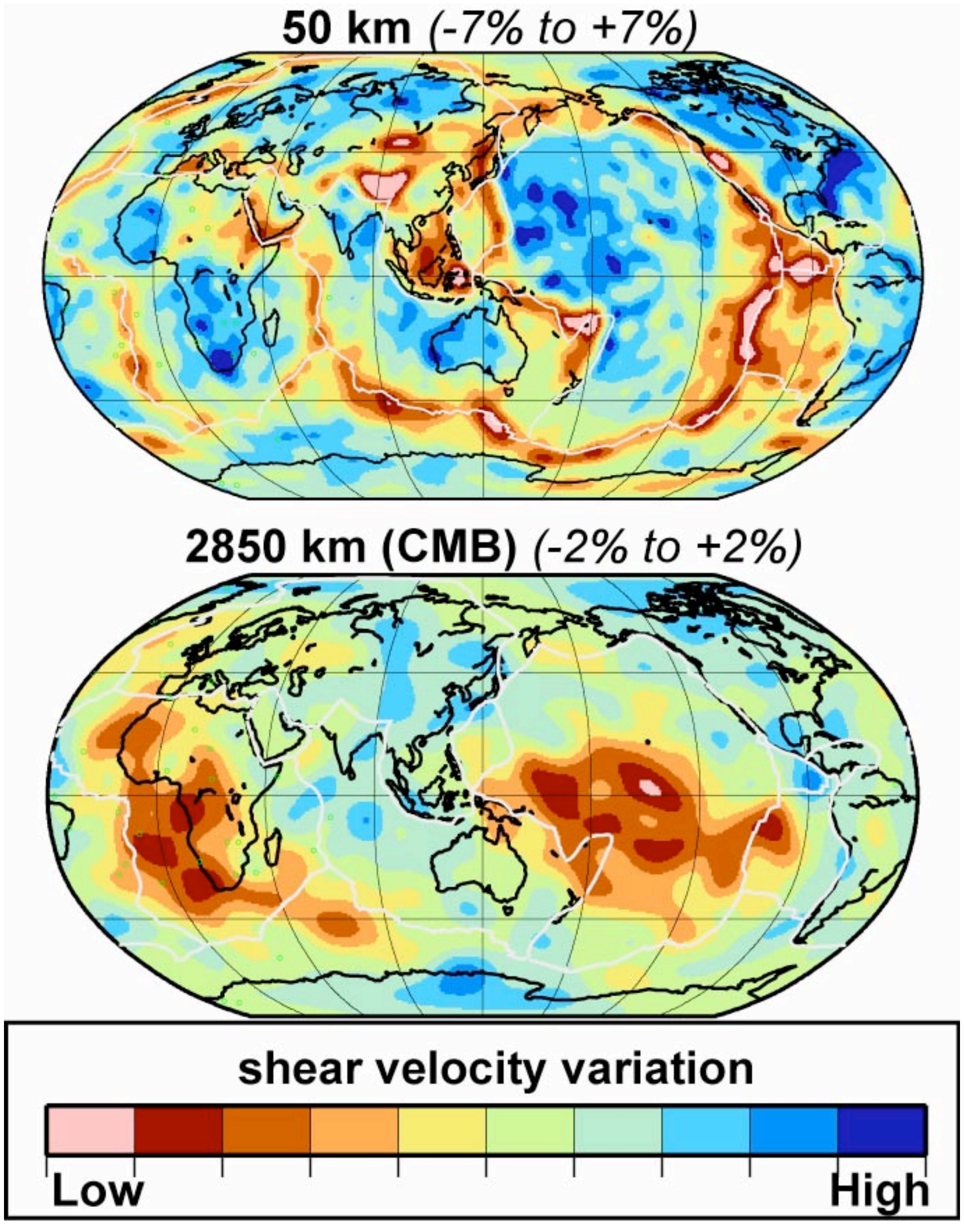
# Seismic tomography

<u>Near surface</u>
Old oceans fast
Young oceans slow
Cratons (old parts of continents) fast

<u>Core-mantle boundary</u>
Past subduction fast
African and Pacific anomalies slow

Cause?

*Ritsema*



# Anisotropy

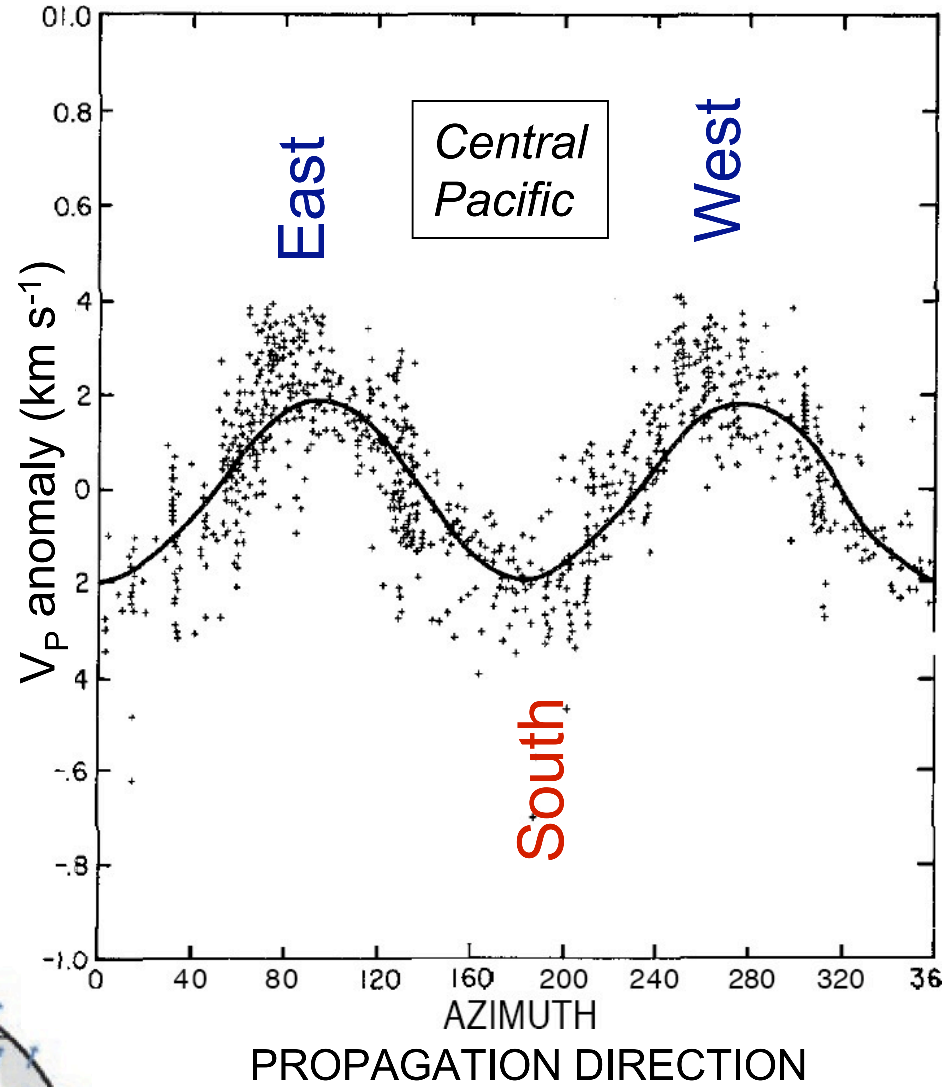
Seismic wave velocity depends on direction of:

Propagation (P- & S-waves)

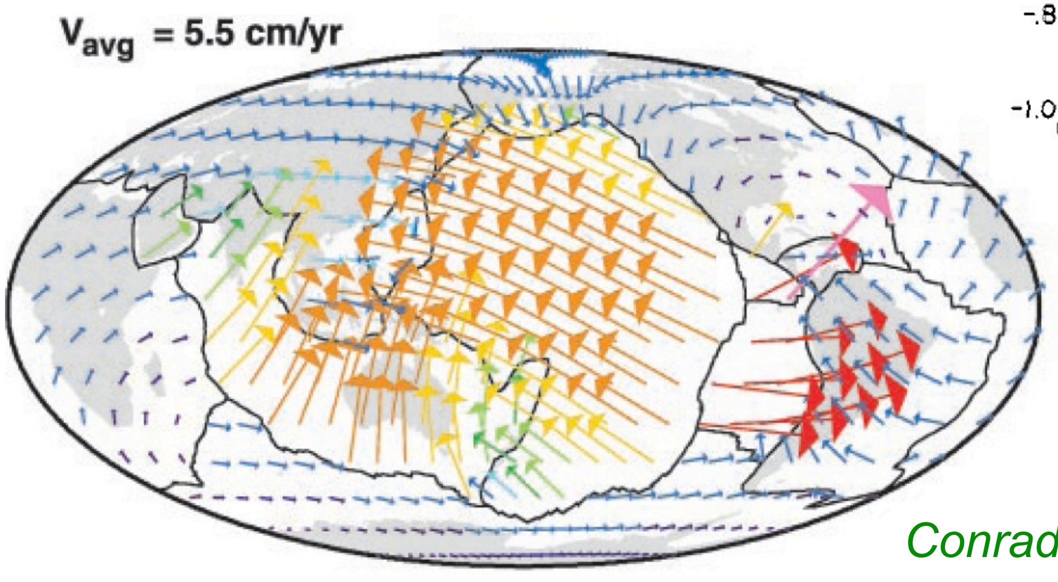
Polarization (S-waves)

Explaination

- Elastic anisotropy of olivine
- Alignment of olivine crystals

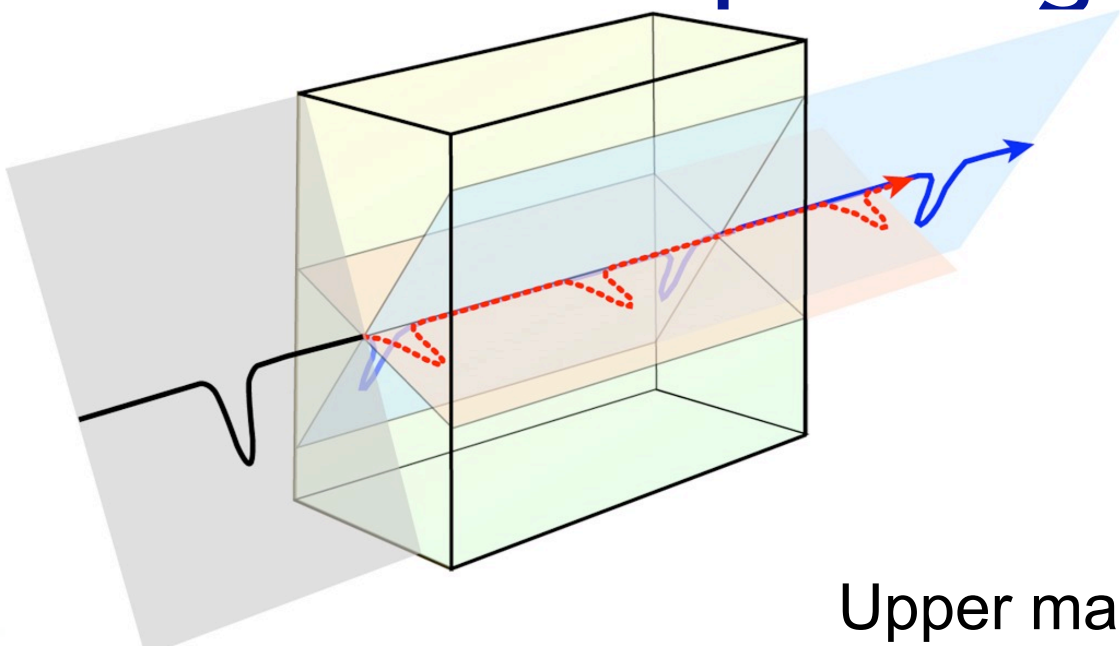


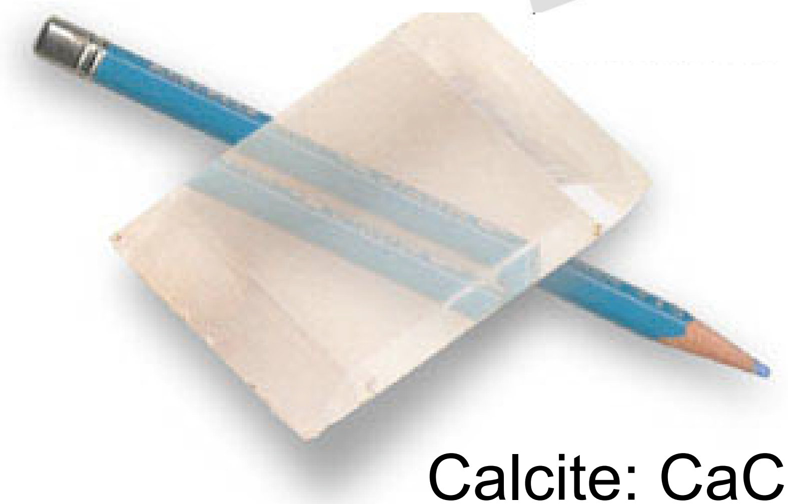

*Christensen & Salisbury (1979) JGR*




*Conrad & Lithgow-Bertelloni (2002) Science*

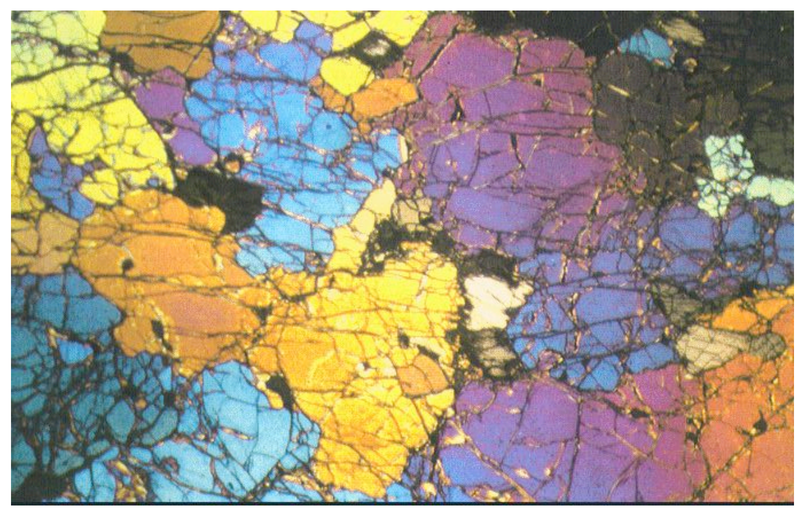
# Polarization anisotropy aka shear-wave splitting





Calcite: $CaCO_3$

Upper mantle xenolith



# Polarization anisotropy

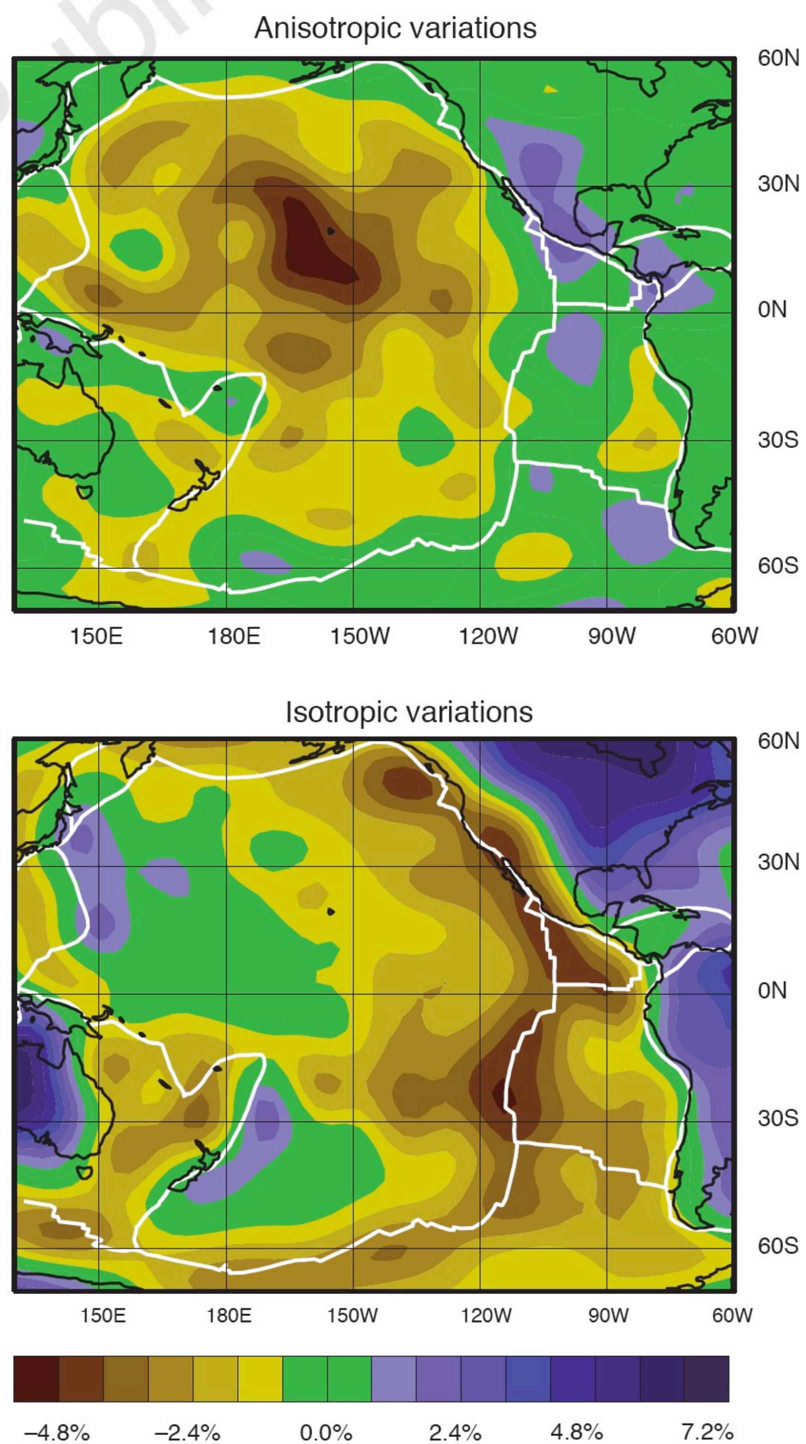
Most of shallow Pacific mantle:

Horizontally polarized shear wave faster than vertically polarized shear wave

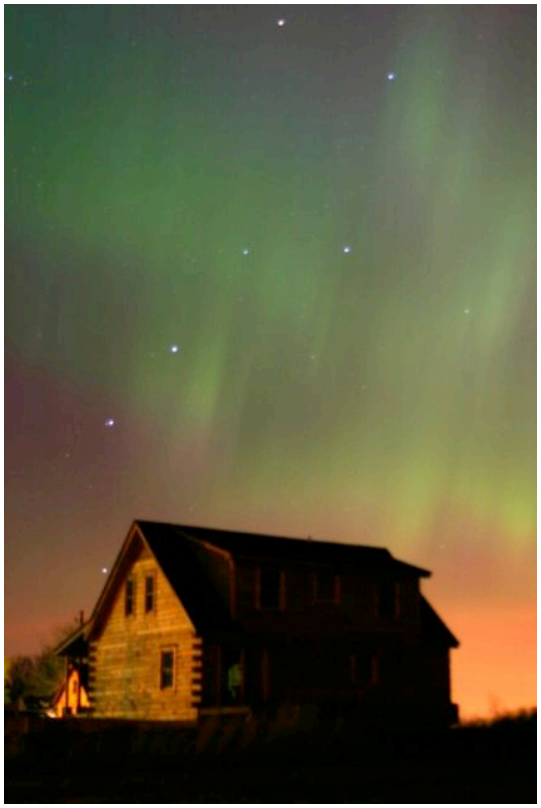
$V_{SH} > V_{SV}$

If origin of anisotropy is related to plate motion, might expect $V_{SH}-V_{SV}$ to increase systematically westward. It doesn't!

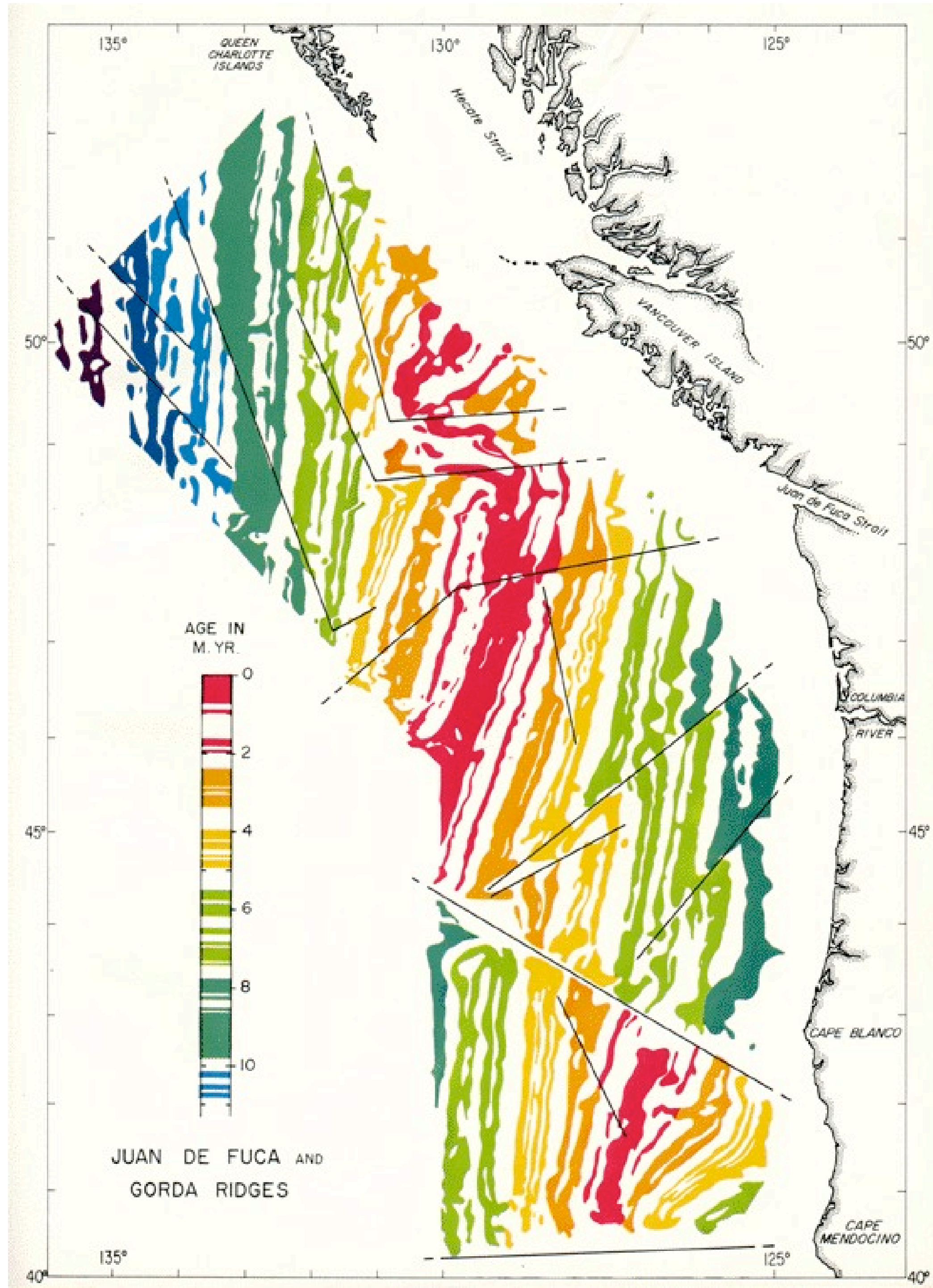
*Ekstrom and Dziewonski (1999) Nature*



# Geomagnetic field

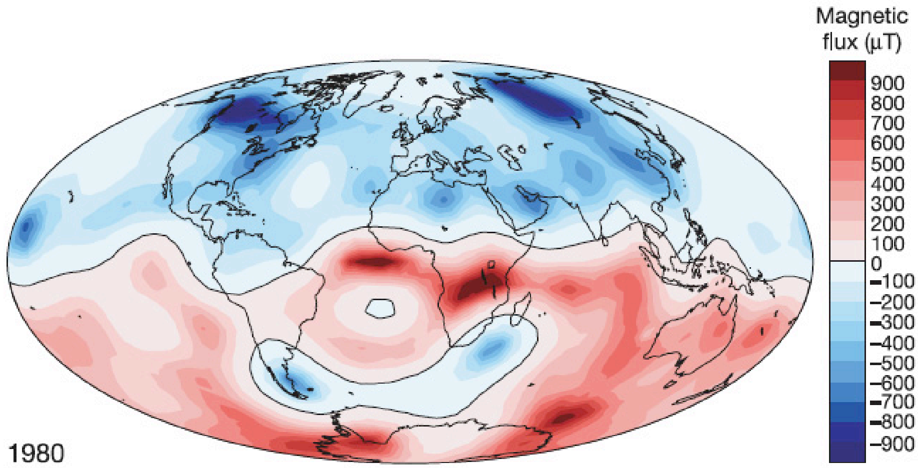


Elburn, IL
Latitude: 42 degrees N

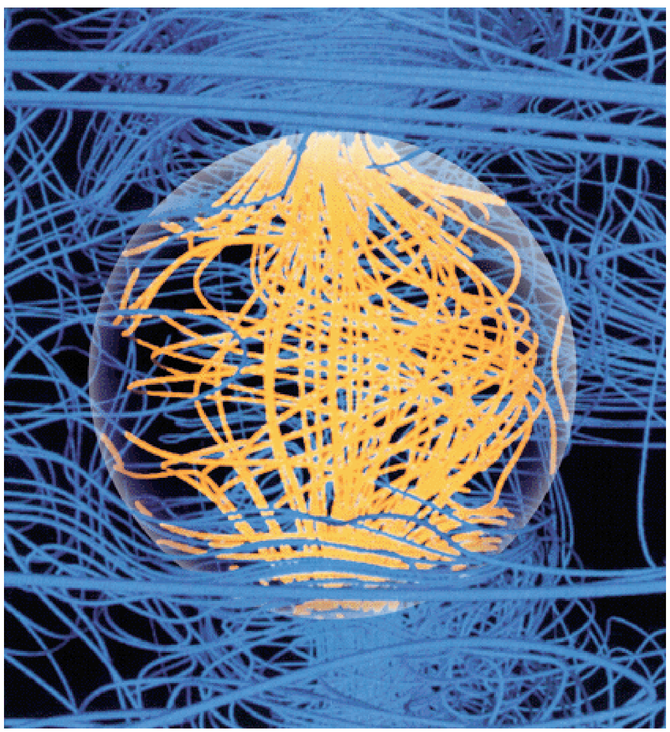



*Vine (1966) Science*

# Geomagnetic field

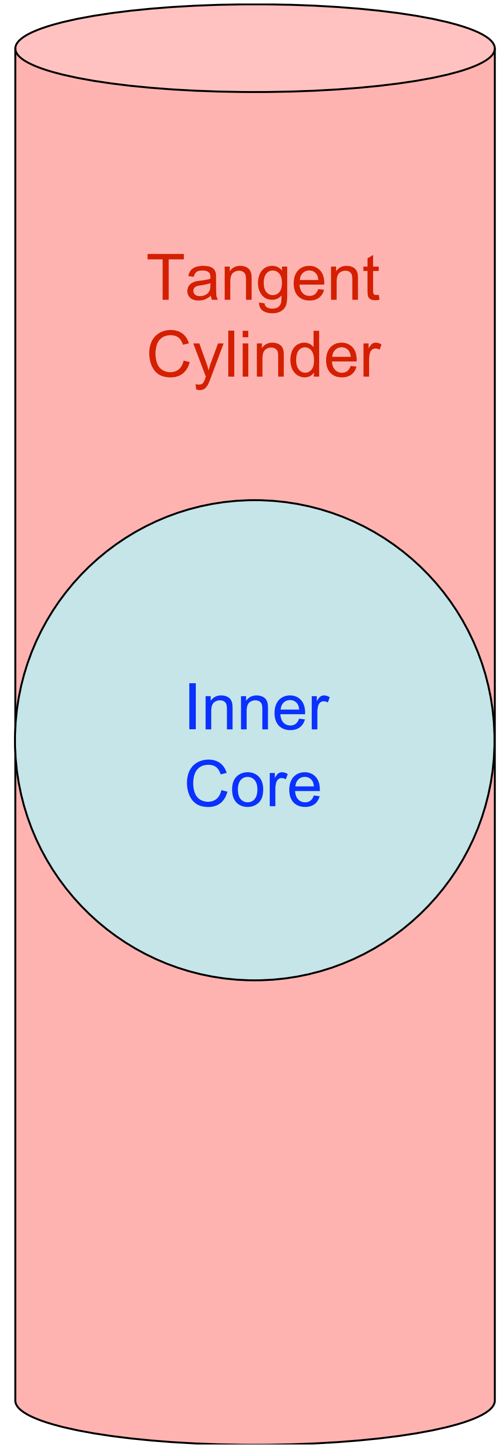



Field at core-mantle boundary



Inner core may
- Be an important heat source for the field
- Stabilize field against reversals
- Influence shape of field

*Glatzmaier & Roberts (1996) Science*



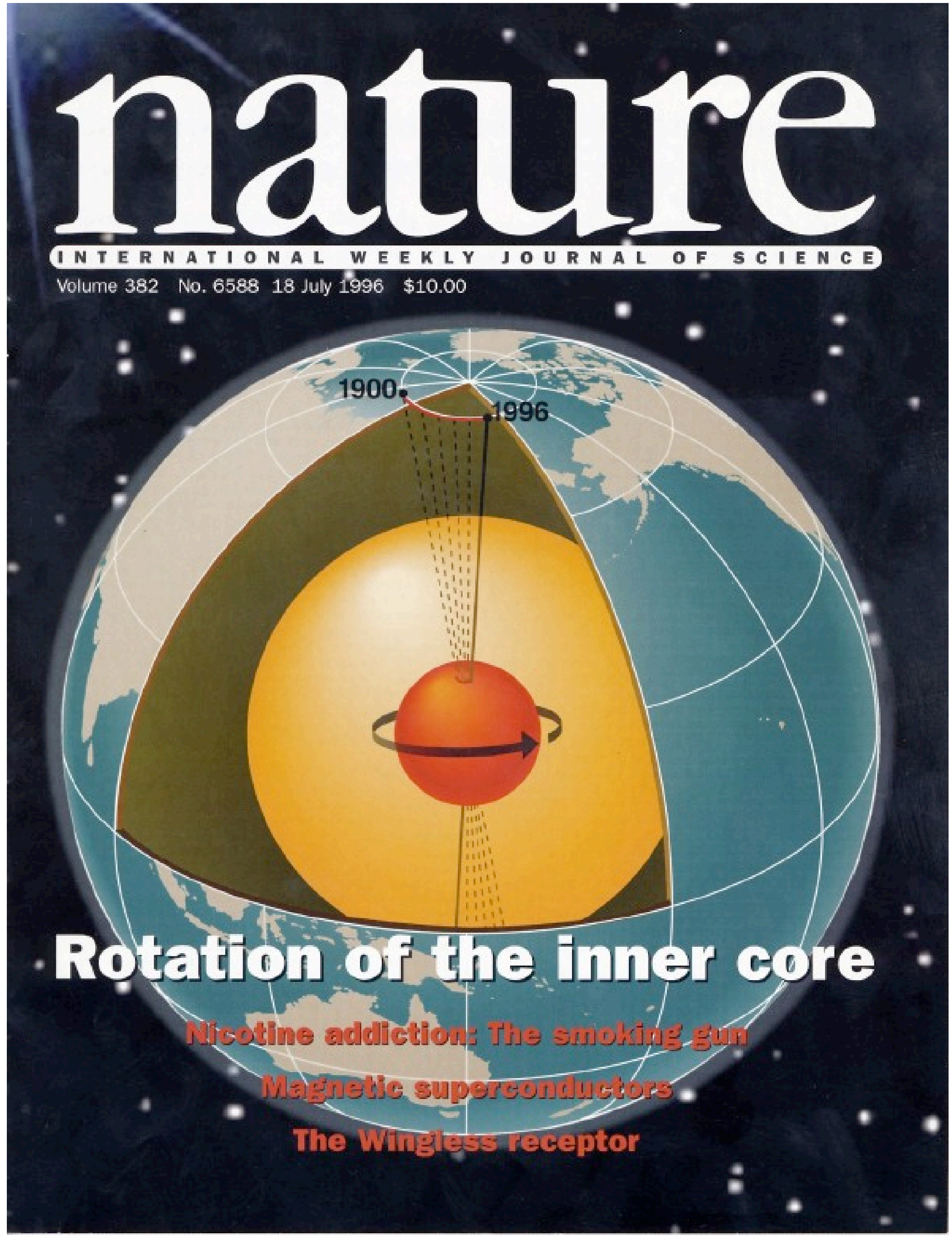
# Inner core

- 1200 km radius
- Nearly pure iron
- P-wave anisotropy!
- 3 % faster along rotation axis
- Fast axis slightly tilted

Other recent findings:

- Heterogeneous
- Layered (innermost inner core)

*Song & Richards (1996) Nature*



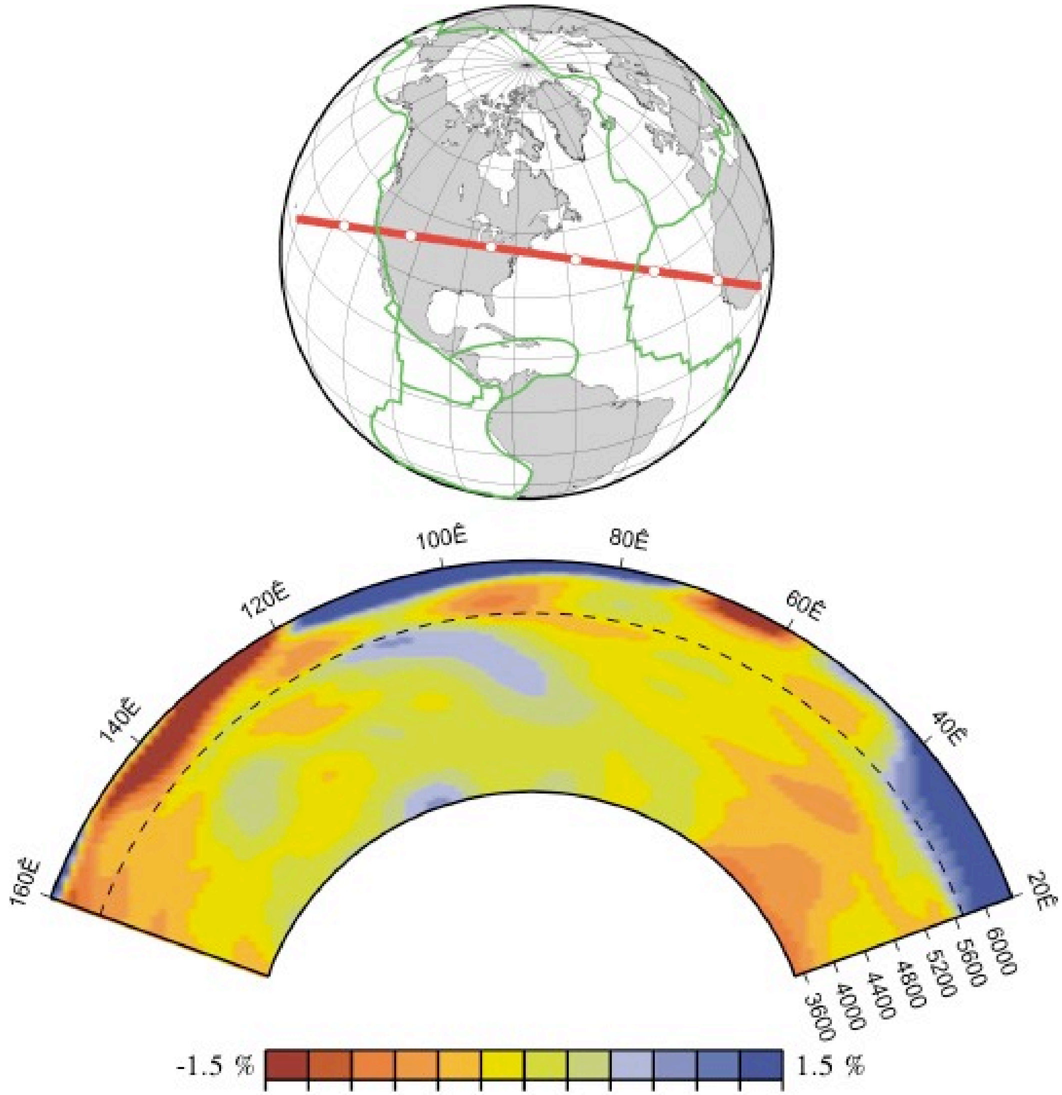
# Earth structure

Seismology can tell us
$V_P$, $V_S$, $\rho(r,\theta,\phi)$

What about temperature and composition?

Dynamics, differentiation, …

Connection through mineralogical models

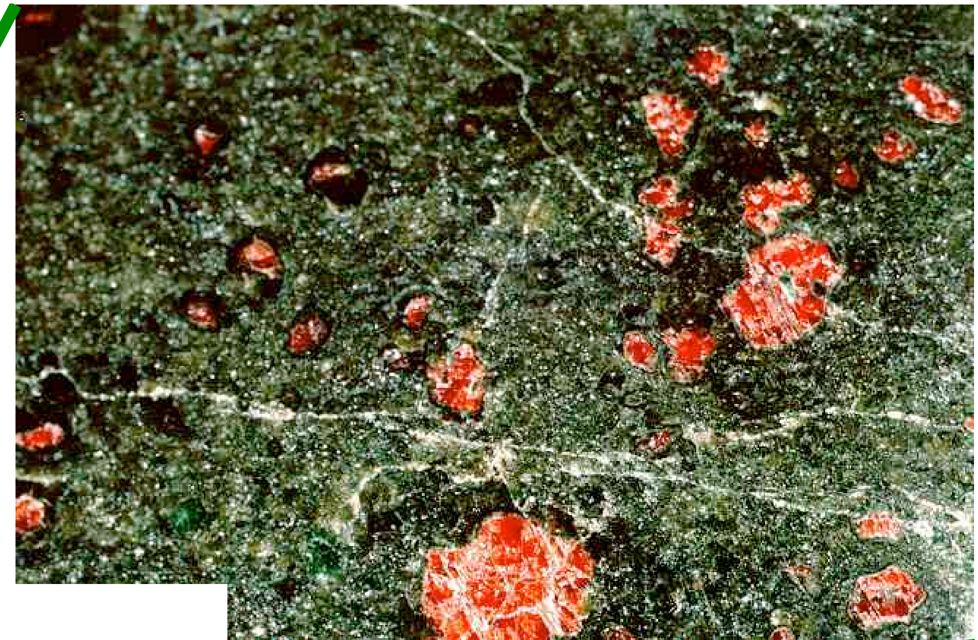


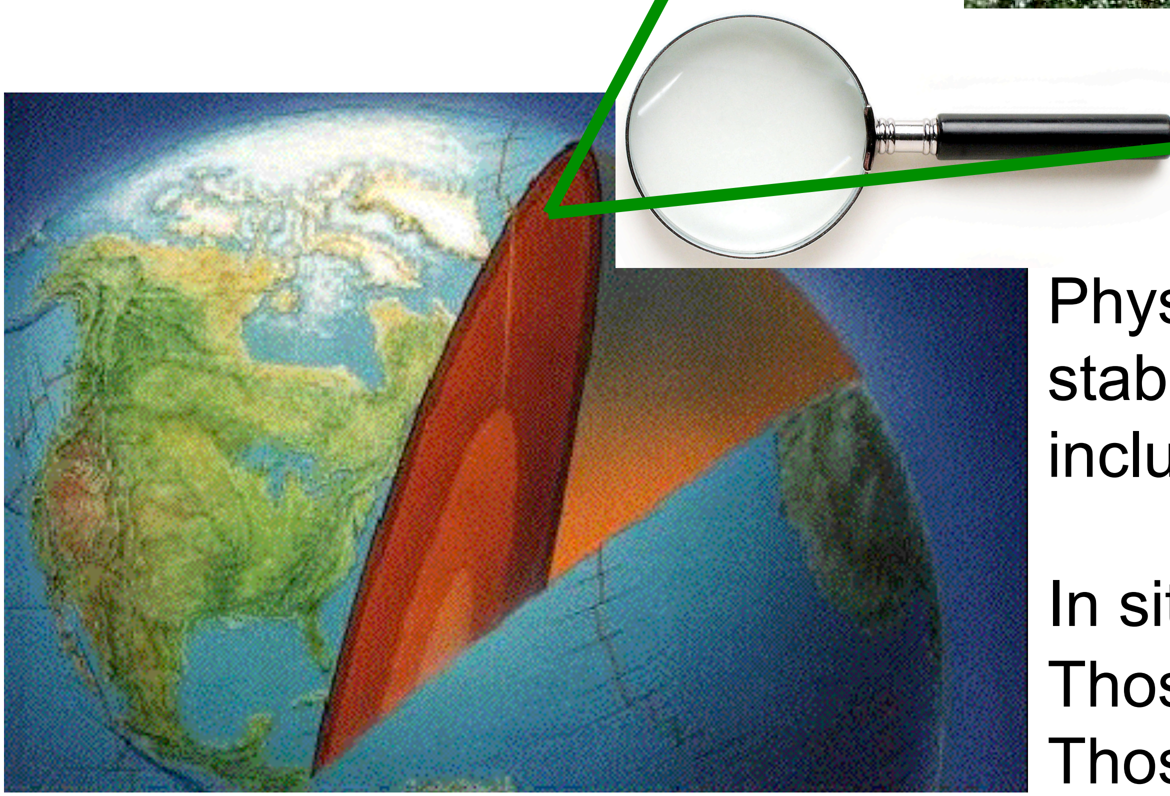

Van Heijst, Ritsema, and Woodhouse [1999]

*Van Heijst, Ritsema, Woodhouse (1999)*

# Central problem

Given a point in a planet of known pressure, temperature, and bulk composition, compute…





*Press & Siever*

Physical properties of the stable multi-phase assemblage including

In situ observables ($V_P$, $V_S$, $\rho$)
Those governing dynamics
Those governing energy transfer

# What is Earth made of?

# Xenoliths

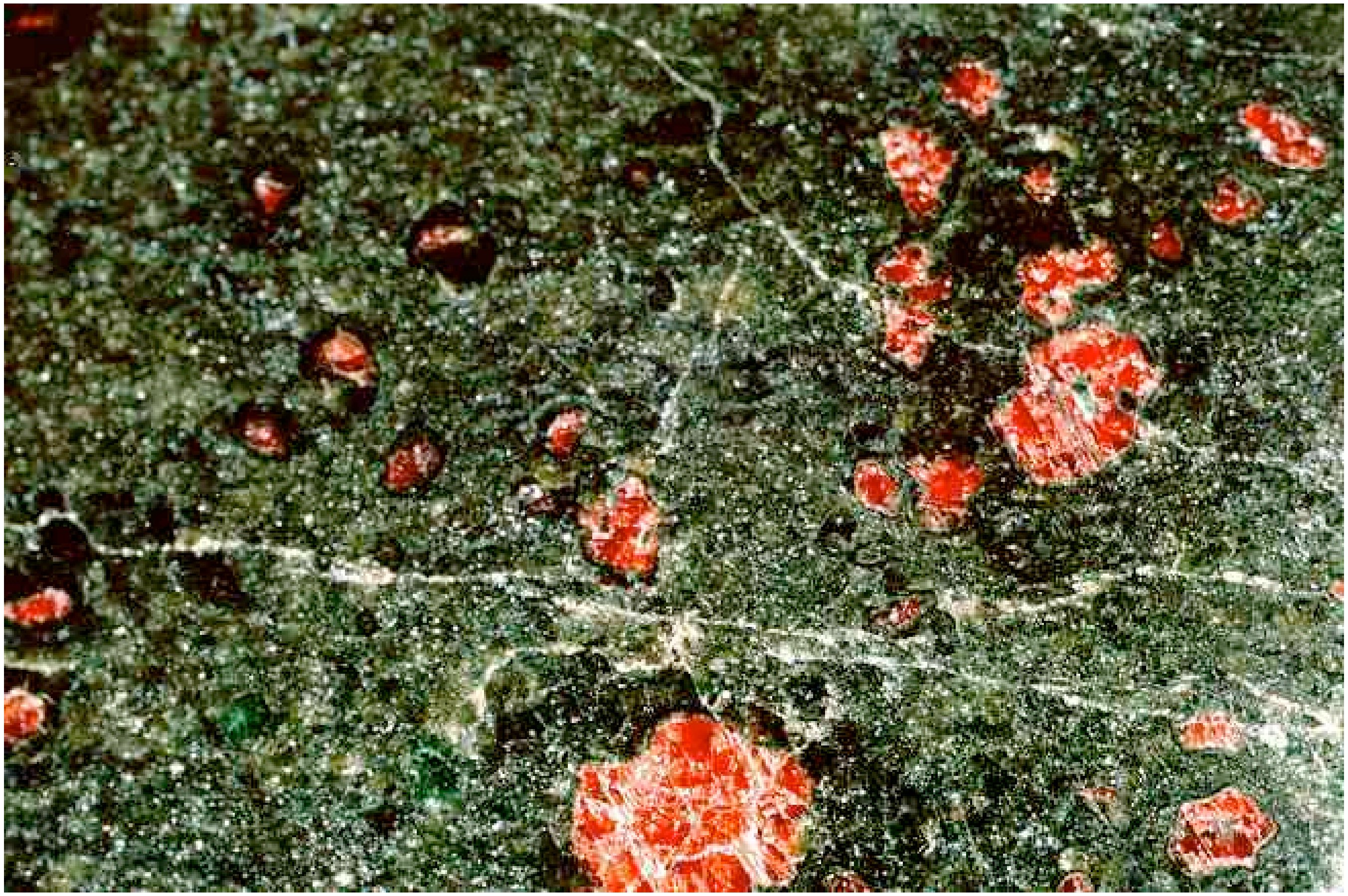
Eruption of Mt. Etna,
October 28, 2002

Mantle xenoliths
from San Carlos,
Arizona

# Upper mantle xenolith: depth ~ 100 km

| | | |
|---|---|---|
| yellow-green | olivine (ol) | $Mg_2SiO_4$ |
| black | orthopyroxene (opx) | $Mg_2Si_2O_6$ |
| green | clinopyroxene (cpx) | $CaMgSi_2O_6$ |
| red | garnet (gt) | $Mg_3Al_2Si_3O_{12}$ |

} + 10 %Fe for Mg



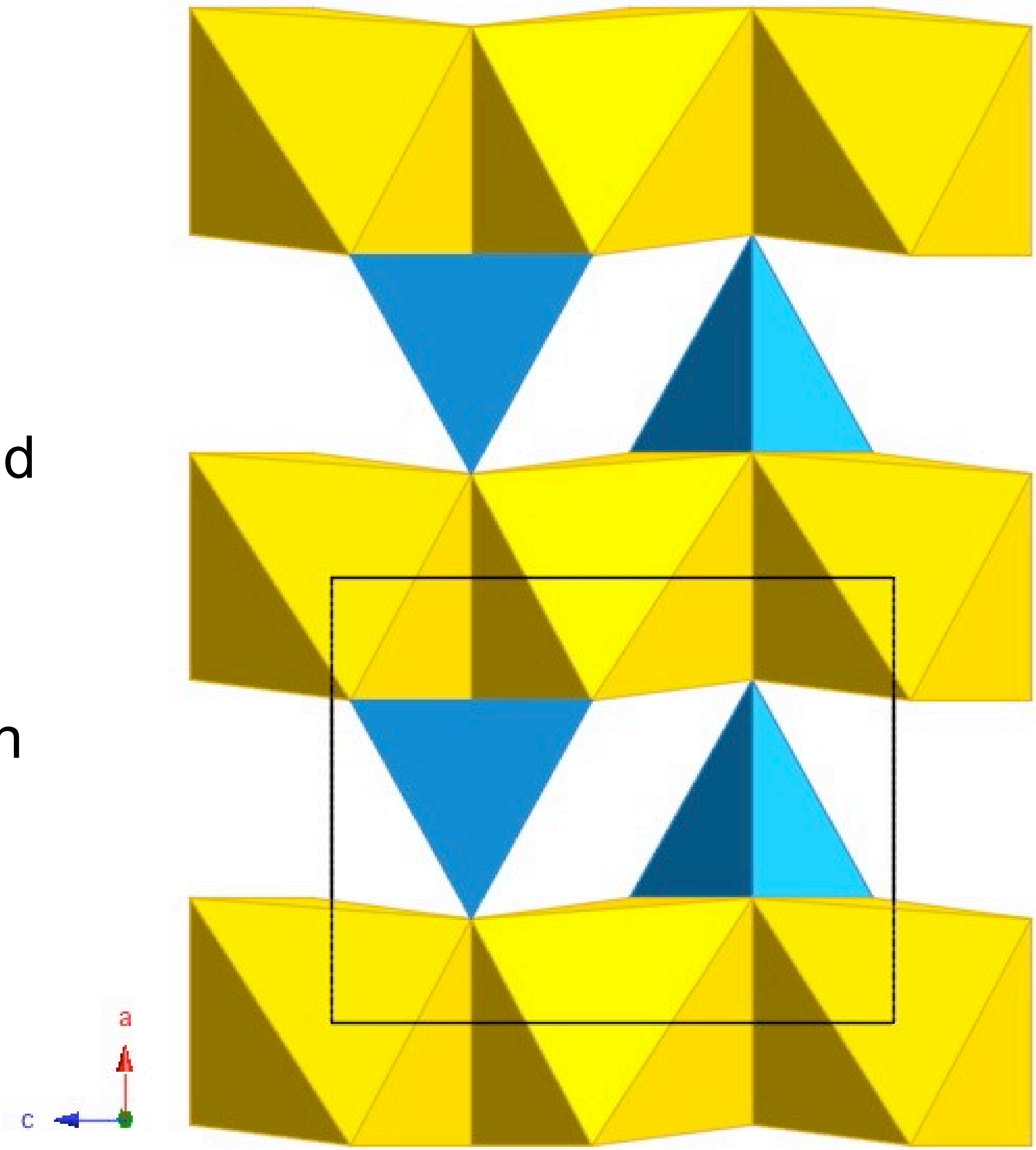
# Olivine, $Mg_2SiO_4$

Fastest direction

Compress Mg- and Si-polyhedra

Easiest dislocation glide direction

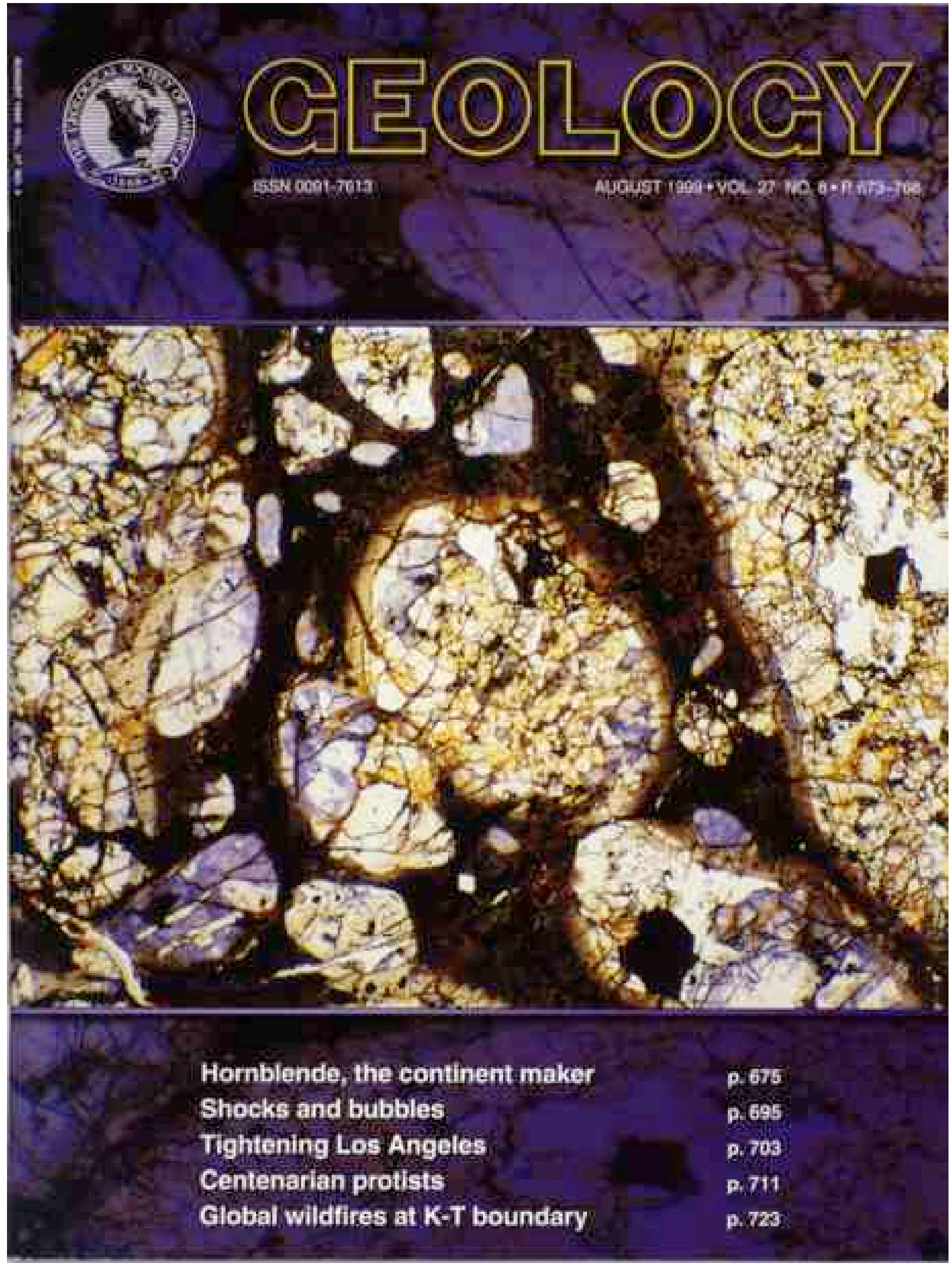
Shortest repeat distance



# High pressure polymorphs

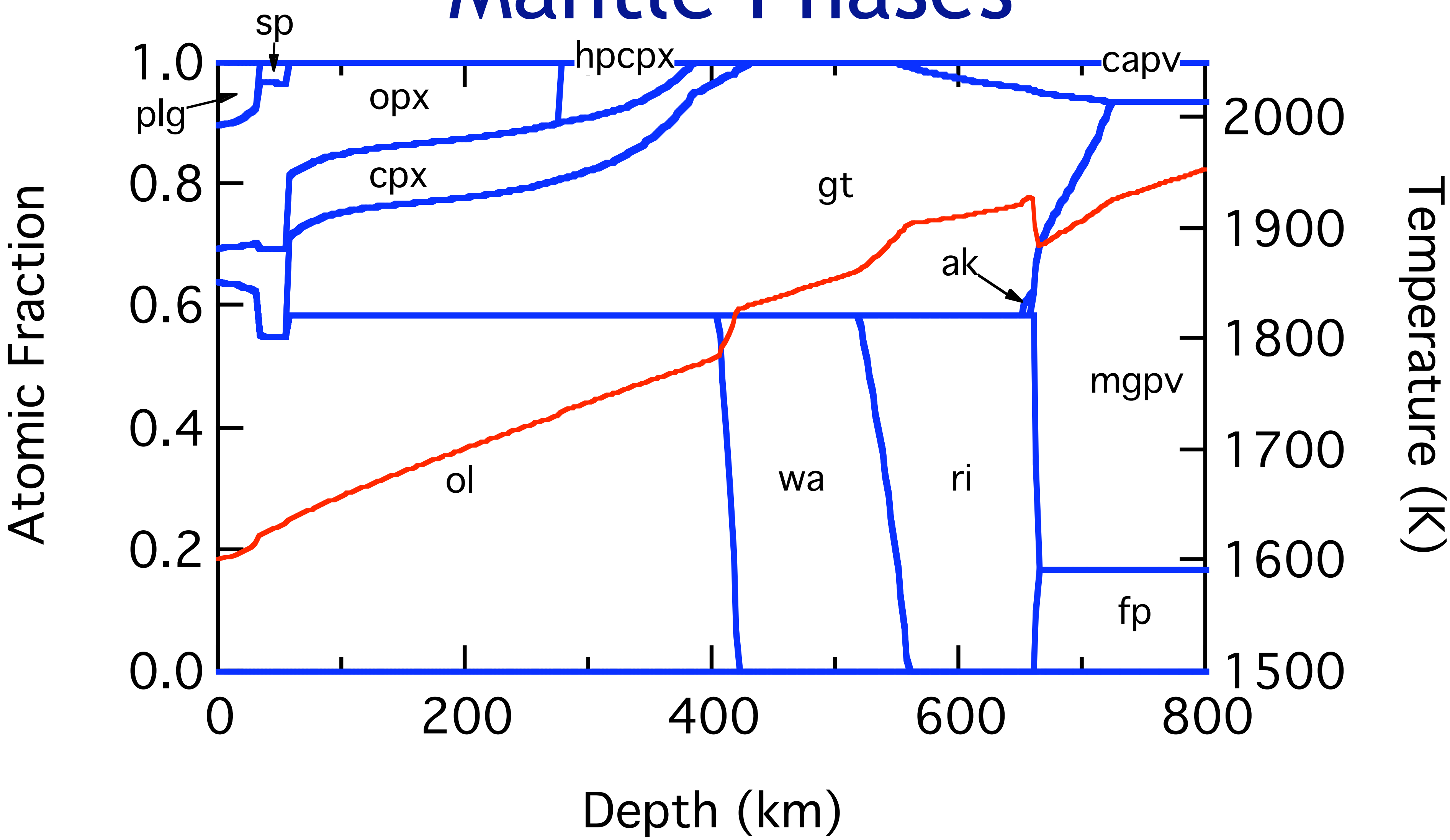
Many found in meteorites

Originally discovered in laboratory




Purple ringwoodite, high pressure polymorph of olivine, in the Tenham chondrite (Spray, 1999)

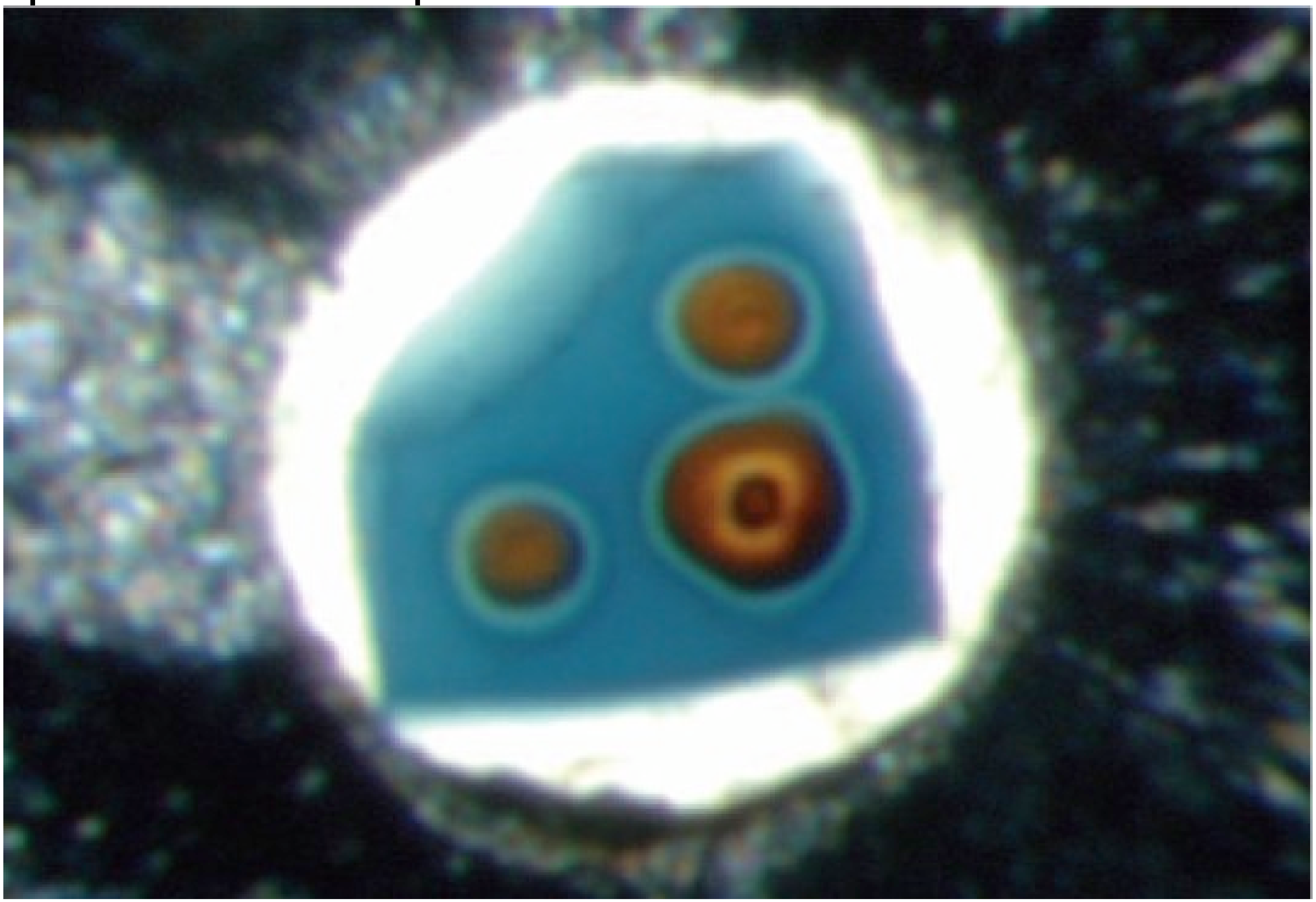
# Mantle Phases




Plagioclase (plg); Spinel (sp); Wadsleyite (wa); Ringwoodite (ri); akimotoite (ak); Mg-perovskite (mgpv); Ca-perovskite (capv); Ferropericlase (fp)

*Stixrude et al. (2007) EPSL*

Blue hydrous ringwoodite viewed in situ through the diamond anvil cell, transformed in laser-heated spots to perovskite+ferropericlase

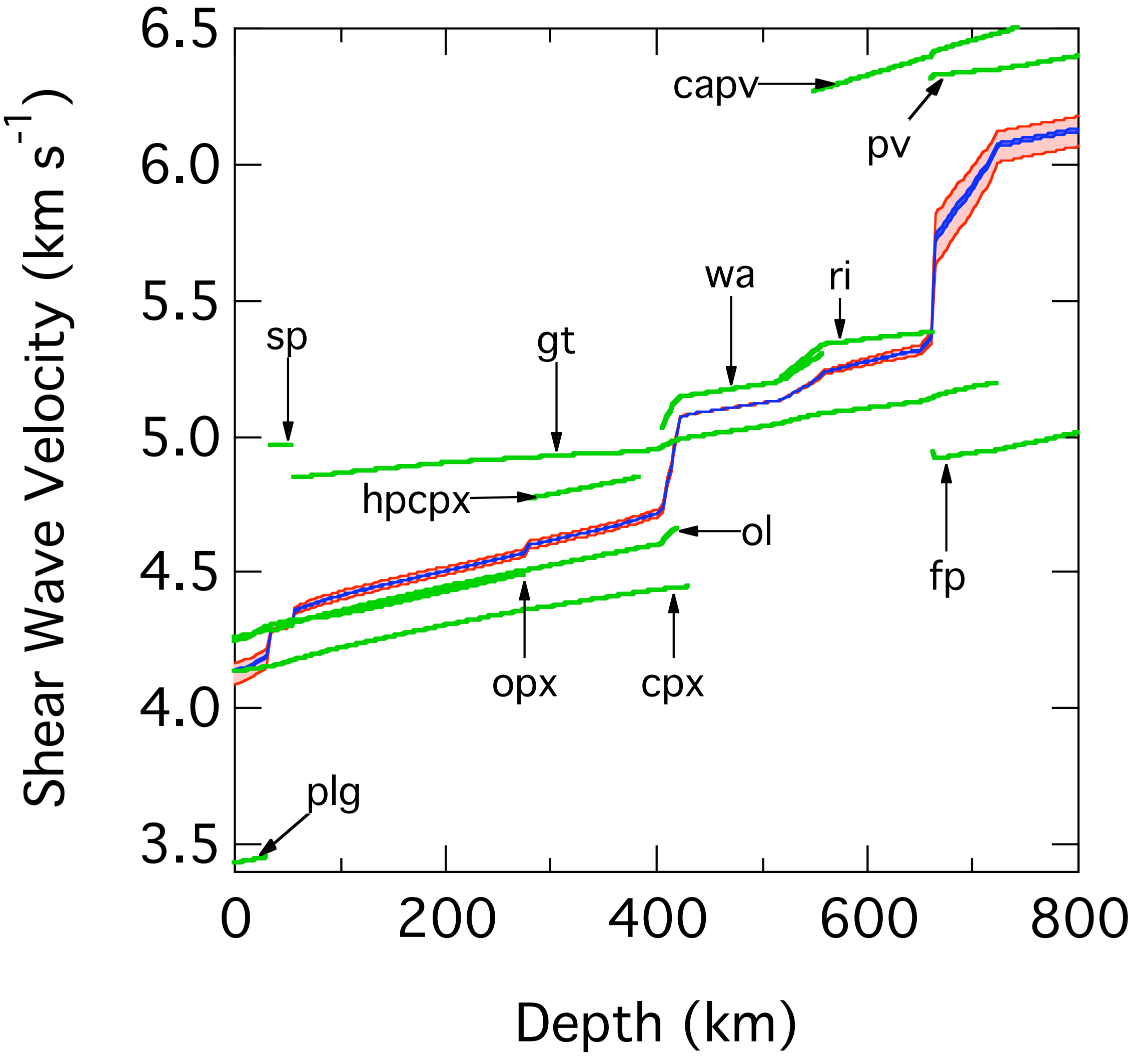


*Jacobsen and Lin (2005) Elements*

# Earth structure

Phase transformations
•Produce discontinuities
•Thermometers
•Influence dynamics

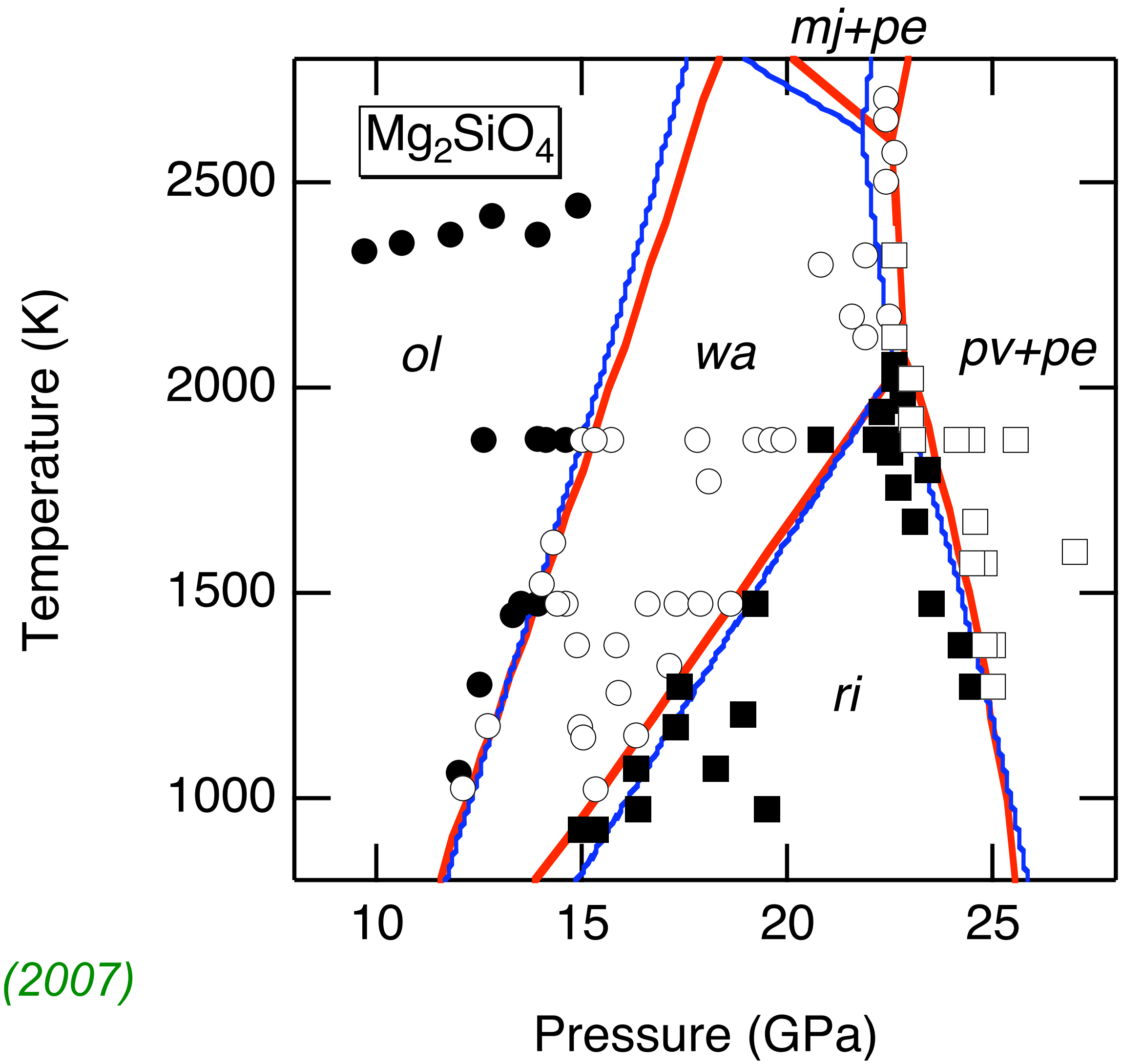
Computation
•Global Gibbs free energy minimization
•New self-consistent method
  –Phase equilbria
  –Physical properties
  –Elasticity




*Stixrude & Lithgow-Bertelloni (2005) GJI*
*Stixrude & Jeanloz (2007) Treatise on Geophysics*

# Phase equilibria

- Invert phase equilibria data for reference free energy, characteristic vibrational frequency
- Experimental Data
  - N~1000
  - CaO-FeO-MgO-$Al_2O_3$-$SiO_2$
  - One-component, two-component phase equilibria
  - Element partitioning




*Stixrude and Lithgow-Bertelloni (2007)*

$$\chi^2 = \sum_i^{stability} \left[ G(P_i, T_i, \vec{n}_i) - G(P_i, T_i, \vec{n}_{\min}) \right]^2 + \sum_i^{reactions} \left[ \Delta G_{0i}^{calc} - \Delta G_{0i}^{\exp} \right]^2$$

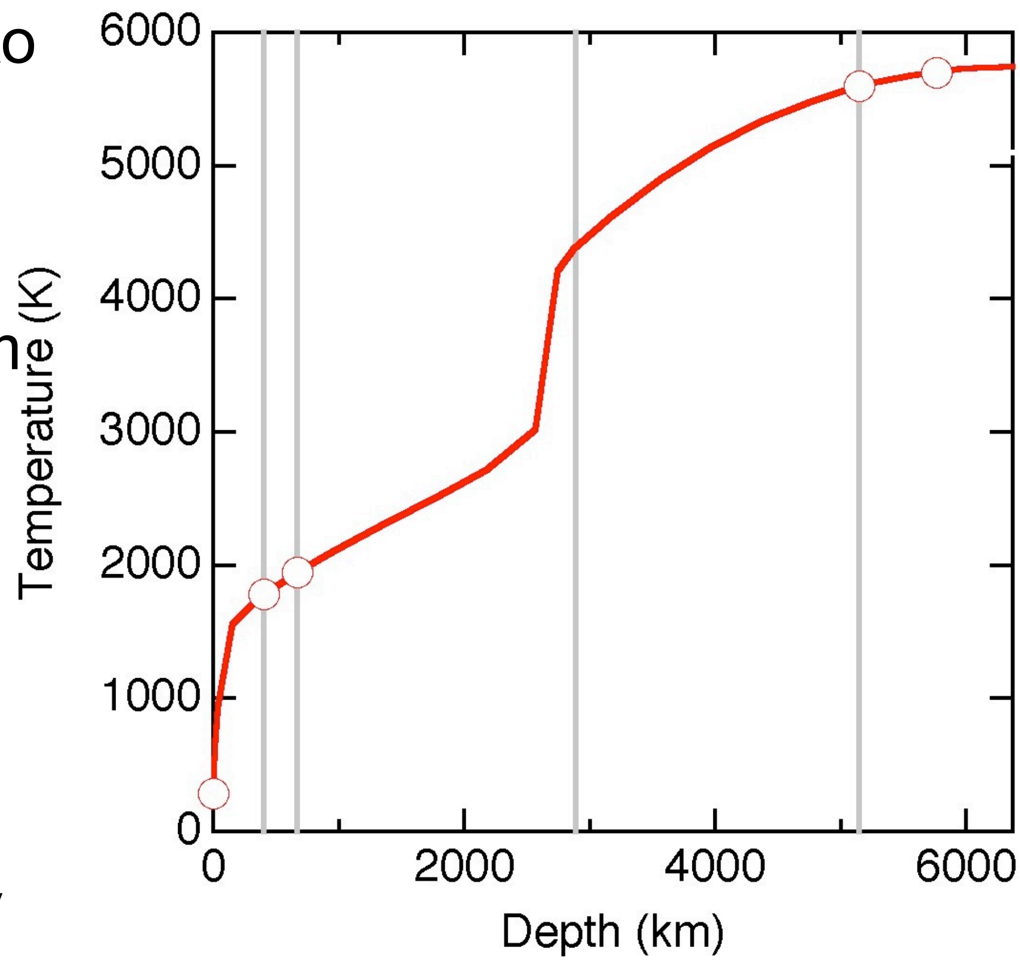
# Thermometers

Phase transitions
- Clapeyron slope
- Relate pressure of transition to depth of seismic discontinuity

Grüneisen parameter
- Determines slope of geotherm in adiabatic regions via

$$\left(\frac{\partial \ln T}{\partial P}\right)_S = \frac{\gamma}{K_S}$$

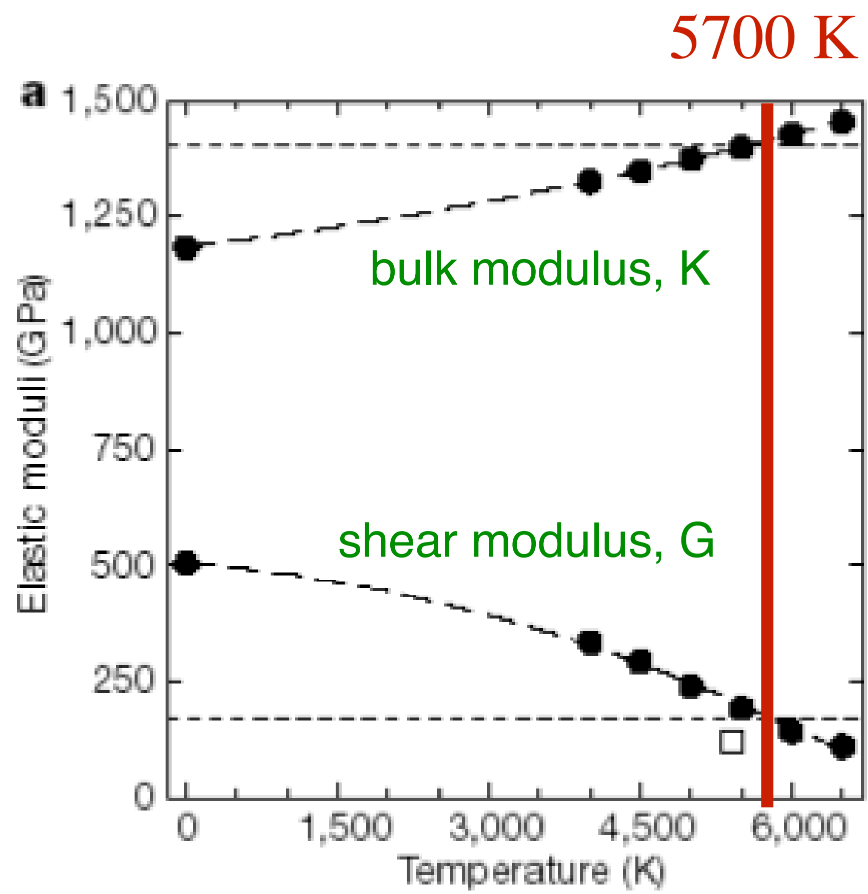
Elastic wave velocity
- V of assumed bulk composition = seismologically observed




Core
*Alfe et al. (2002) EPSL: Fe-X melting*
*Steinle-Neumann et al. (2001) Nature: V of inner core*

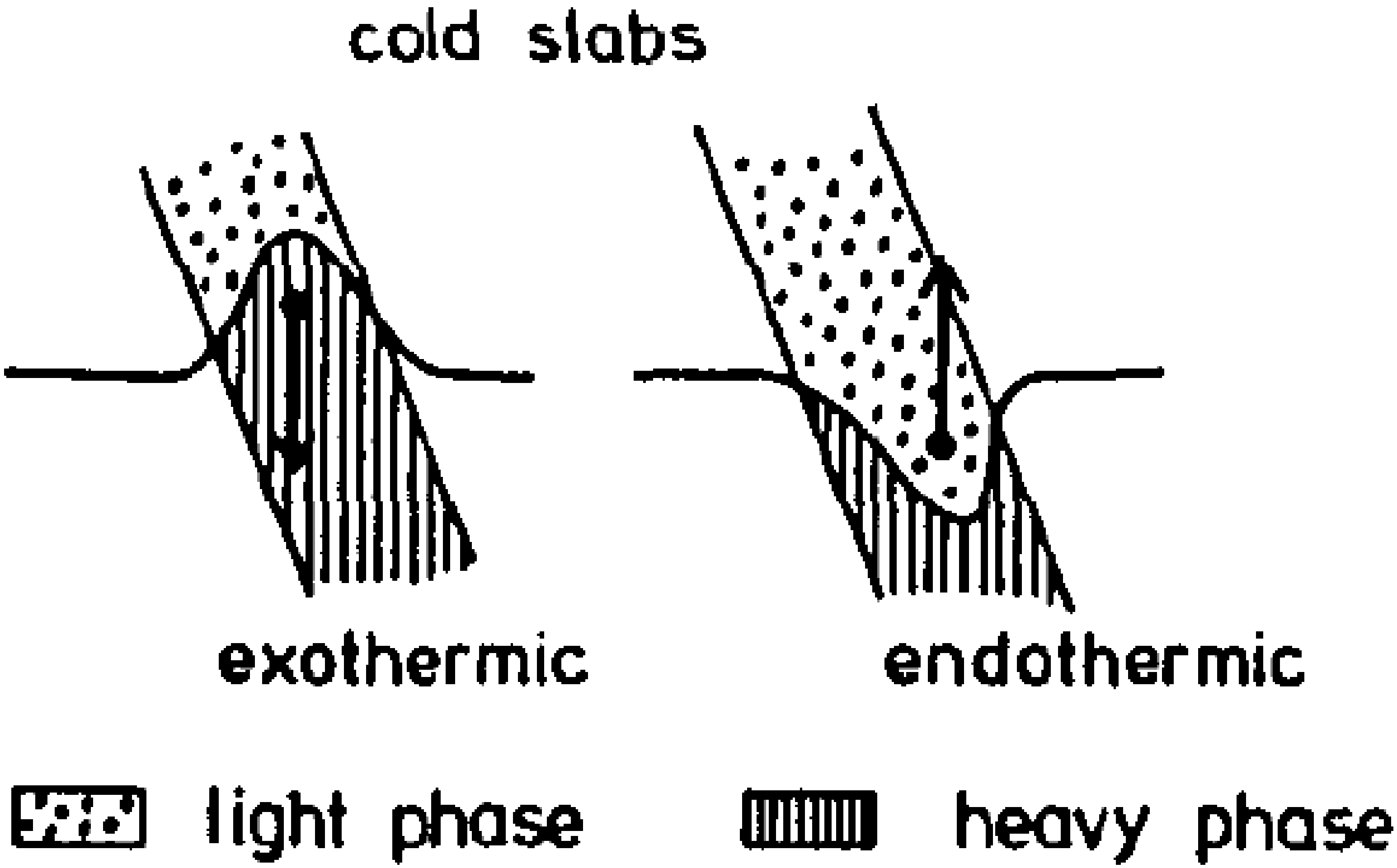
# Temperature of the inner core

- Compare elastic moduli of
  - hcp iron (theory)
  - inner core (seismology)
- Estimate consistent with those based on
  - Iron melting curve
  - Mantle temperatures, adiabatic outer core, …
- Implies relatively large component of basal heating driving mantle convection
- Low Poisson ratio (G/K) of inner core explained



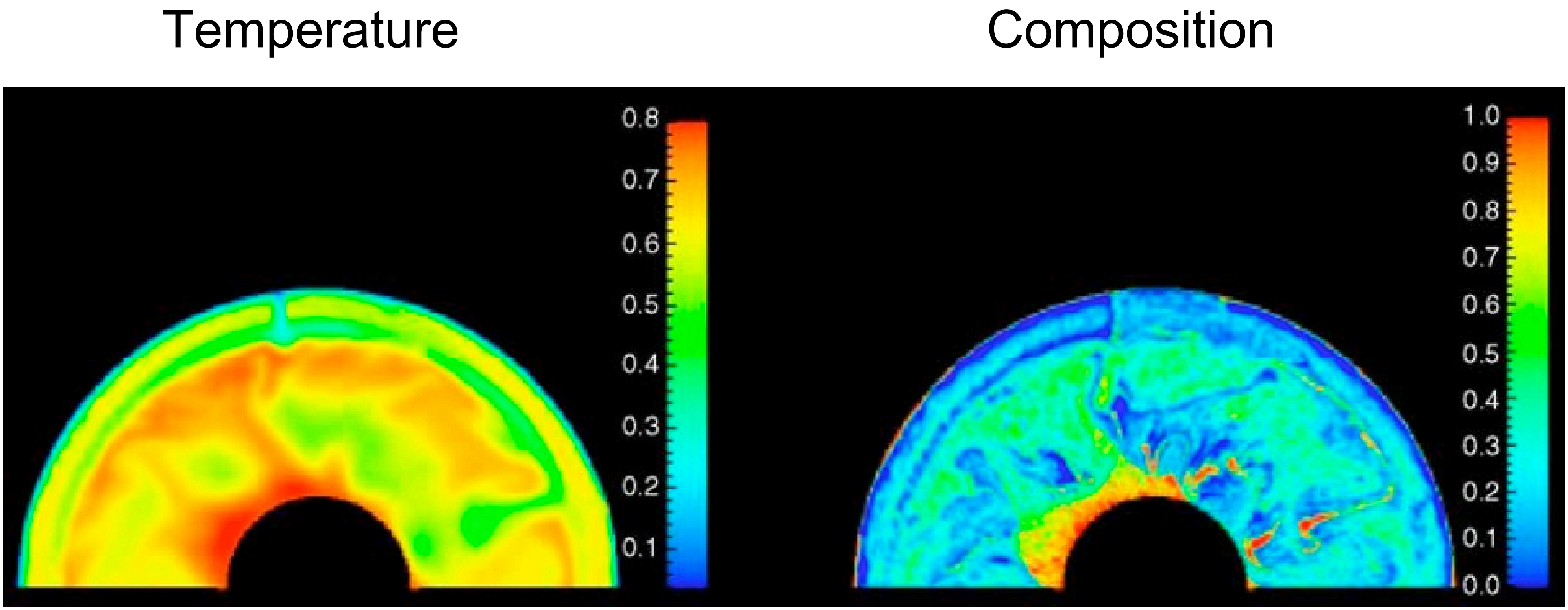

*Steinle-Neumann (2001) Nature*

# Influence of phase transitions on mantle dynamics



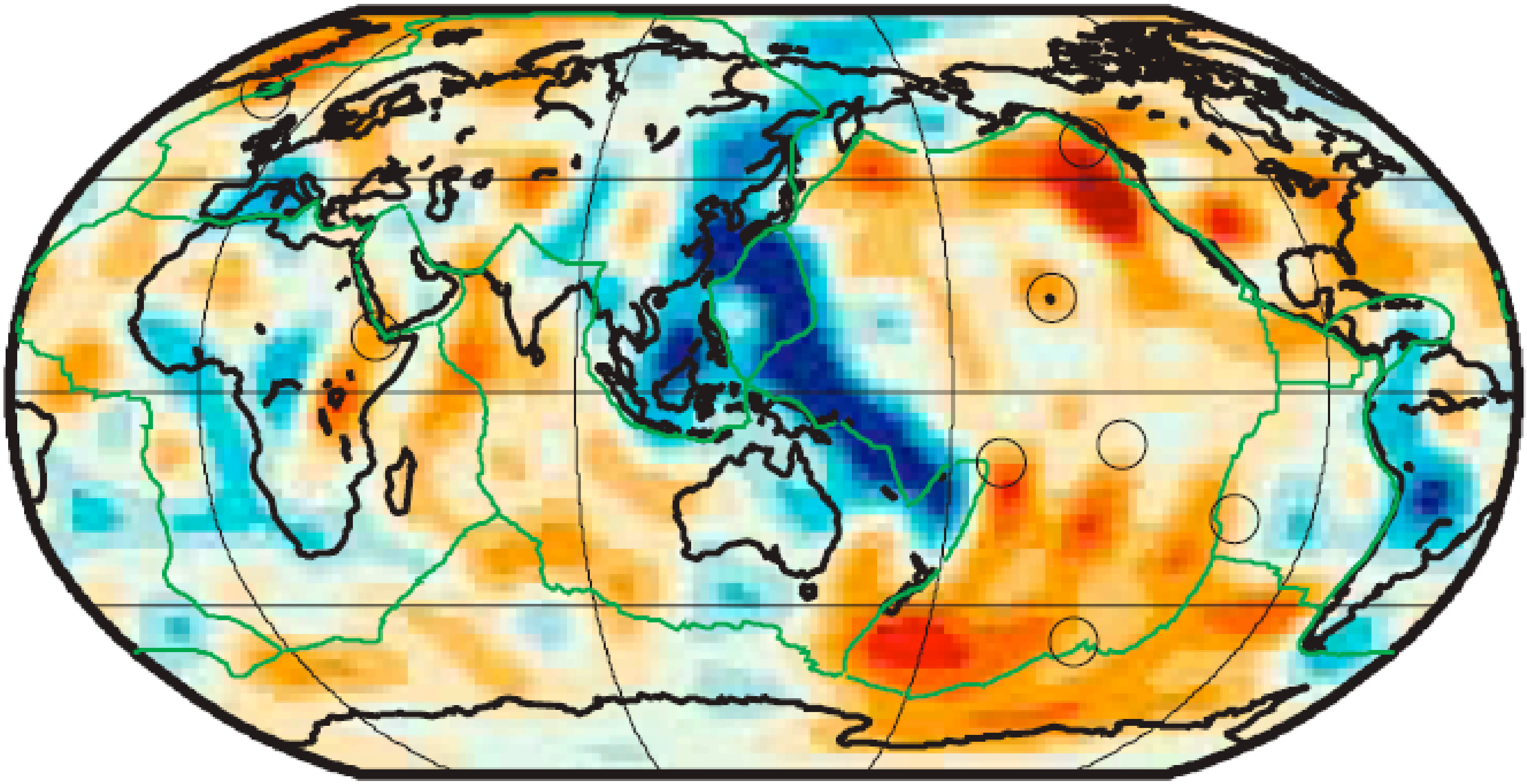

*Christensen (1995) Annual Reviews*

# Influence of phase transitions on mantle dynamics




*Nakagawa & Buffett (2005)*

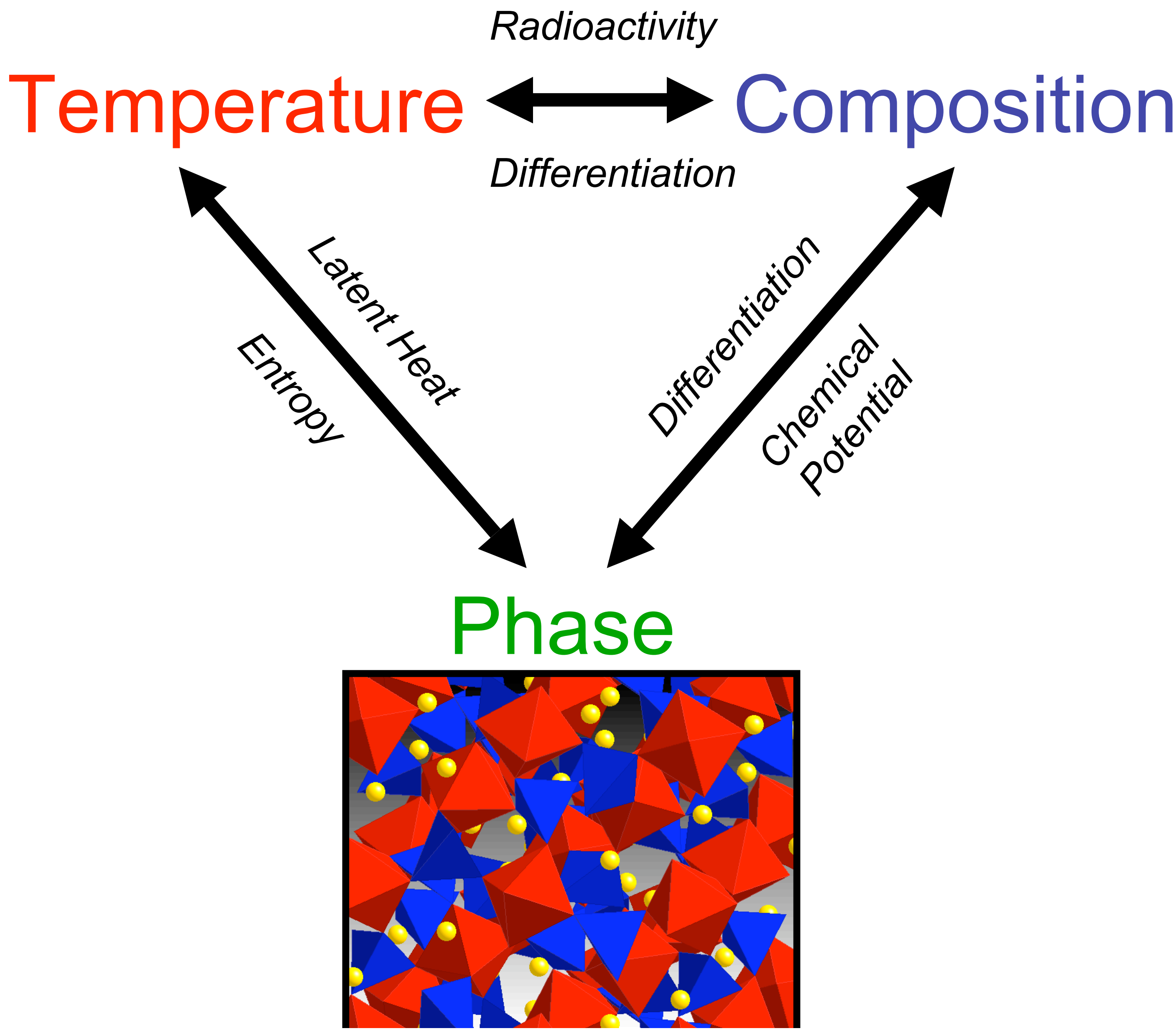
# 575 km (4.0%)



Upper mantle ~ Geology + half-space cooling
Lower mantle ~ Subduction history
Transition zone?

*Ritsema et al. (2004)*

# Origin of lateral heterogeneity



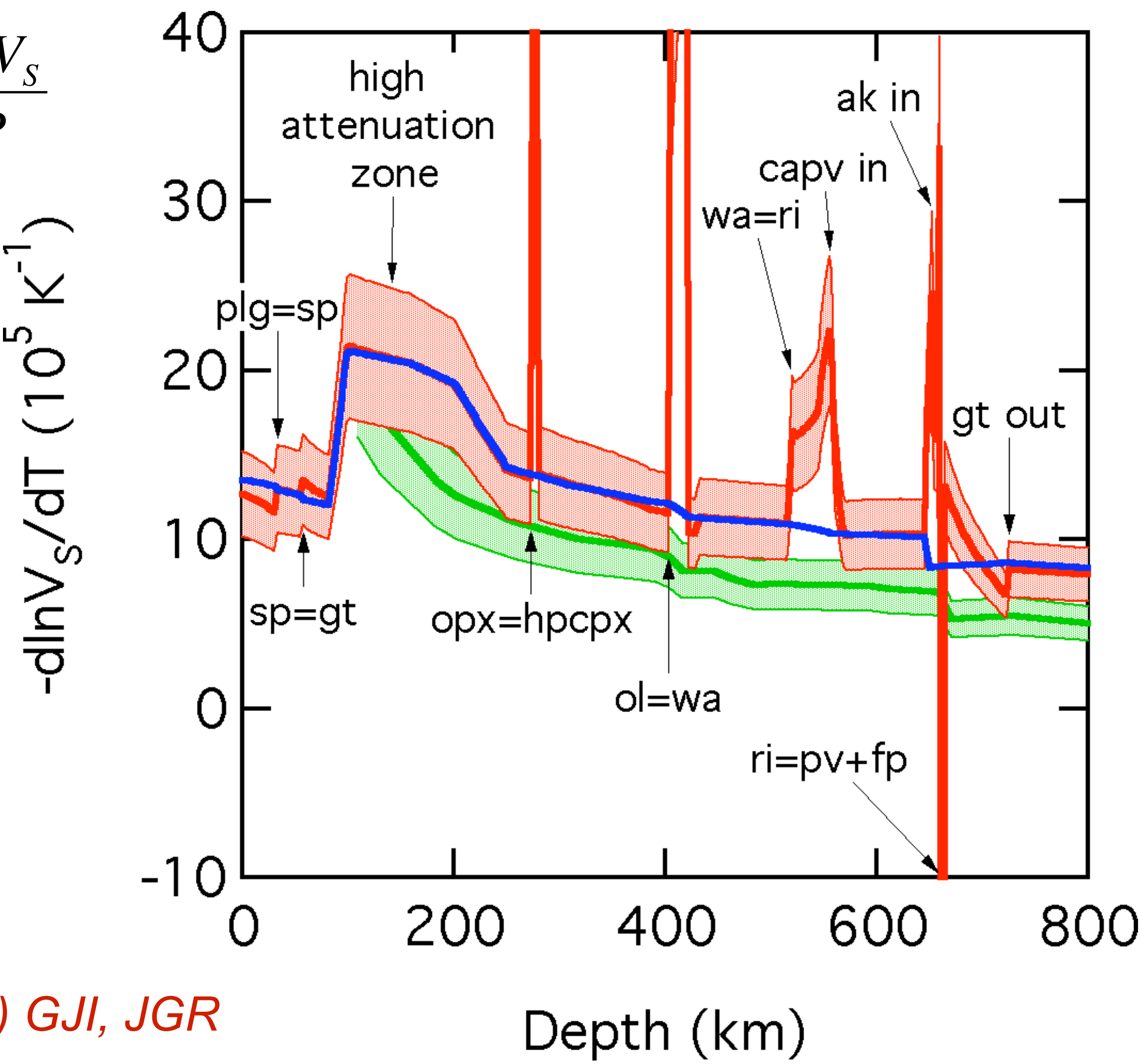
# Velocity-temperature scaling

Metamorphic term

$$\left(\frac{\partial \ln V_S}{\partial n_i}\right)_{P,T}\left(\frac{\partial n_i}{\partial T}\right)_P \approx f\left(\frac{\partial P}{\partial T}\right)_{eq}\frac{\Delta \ln V_S}{\Delta P}$$

Topography?

$$\left(\frac{\partial P}{\partial T}\right)_{eq}\delta T < \Delta P$$




*Stixrude & Lithgow-Bertelloni (2005) GJI, JGR*
*Cammarano et al. (2003) PEPI*

# African anomaly

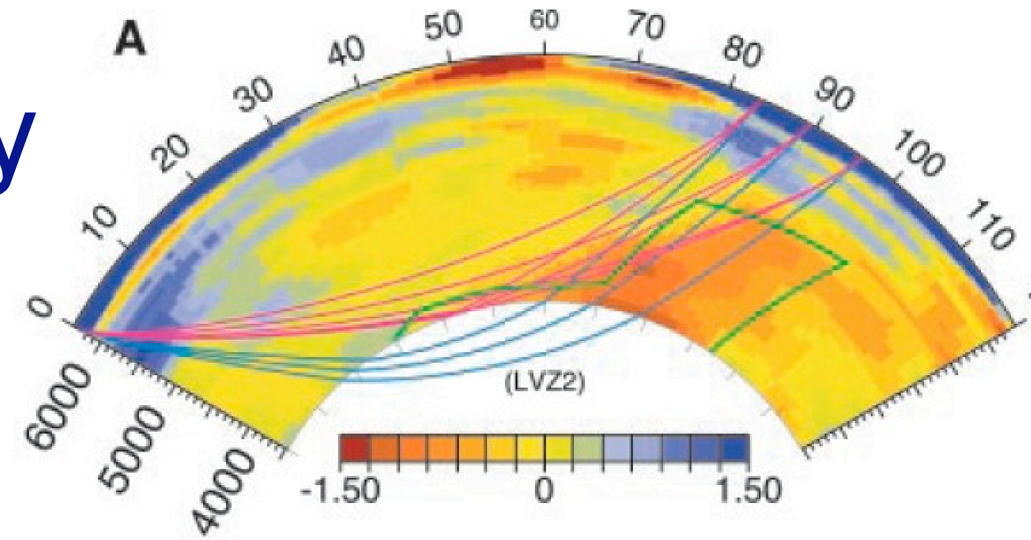
Large low velocity feature
Sharp sided!
Cannot be entirely thermal in origin
Composition?
Phase?

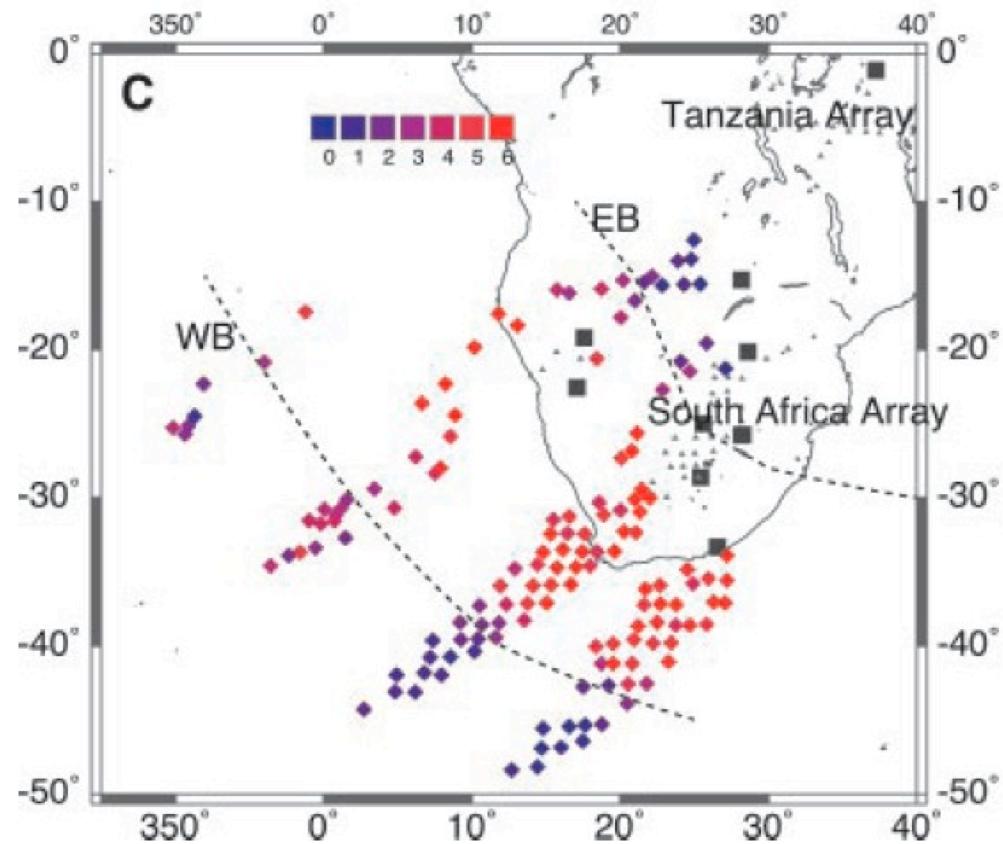
Limitations:

Elasticity of high pressure phases

Phase equilibria at high pressure

*Ni et al. (2002) Science*



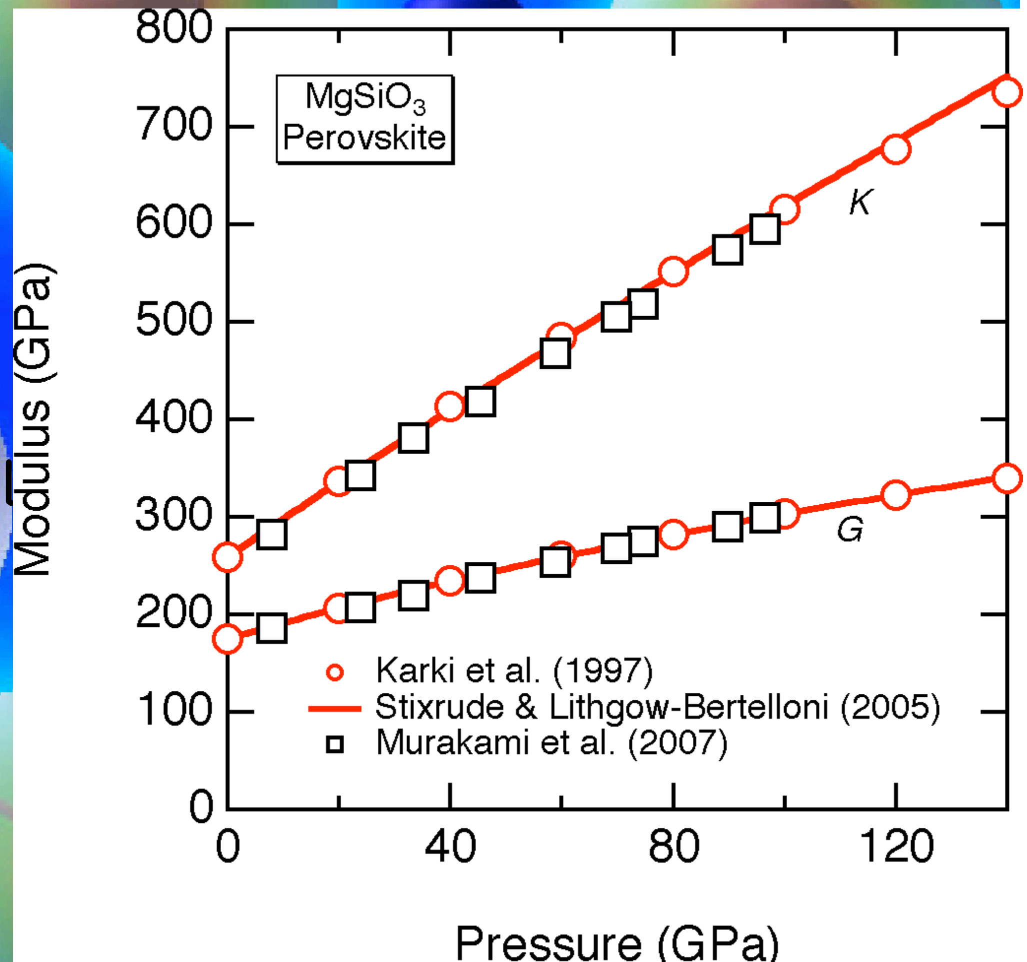



# Density functional theory

- Density Functional Theory
  - *Kohn, Sham, Hohenberg*
- Local Density and Generalized Gradient approximation to $V_{xc}$
- Plane-wave pseudopotential method
  - *Heine, Cohen*
- VASP
  - *Kresse, Hafner, Furthmüller*

$$\left\{-\nabla^2 + V_{KS}\left[\rho(\vec{r})\right]\right\}\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

$$V_{KS}\left[\rho(\vec{r})\right] = V_N(\vec{r}) + \int \frac{\rho(\vec{r}')}{\vec{r}-\vec{r}'}d\vec{r}' + V_{XC}\left[\rho(\vec{r})\right]$$




*Circles: Karki et al., 1997, Am. Min.*
*Squares: Murakami et al., 2006, EPSL*

# Methods: elastic constants 1

Variation of the total energy with isochoric strain

Vanishes for isochoric ε

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}\right)_{T,\varepsilon'} = \frac{1}{V}\left(\frac{\partial^2 F}{\partial S_{ij}\partial S_{kl}}\right)_{S'_{ij},T} + P\left(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk} + \delta_{jl}\delta_{ik}\right)$$

Eulerian
(Lagrangian different)

$$\frac{c_{ijkl}\delta_{ij}\delta_{kl}}{9} = K = -V\left(\frac{\partial P}{\partial V}\right)_T = V\left(\frac{\partial^2 F}{\partial V^2}\right)$$

$$\varepsilon(\delta)\begin{pmatrix} 0 & 0 & \delta \\ 0 & \delta^2/(1-\delta^2) & 0 \\ \delta & 0 & 0 \end{pmatrix}$$

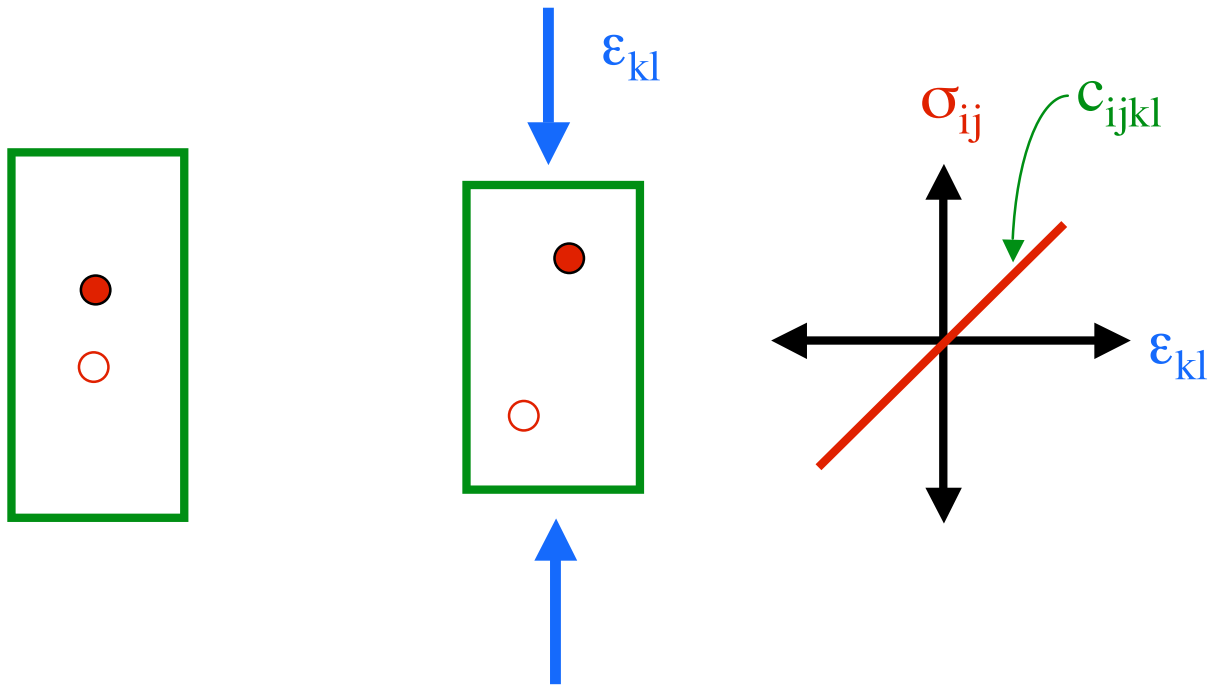
$$F(\delta) = F(0) + 2c_{44}\delta^2 + O(\delta^4)$$

*Stixrude & Cohen (1995) Science*
*Steinle-Neumann et al. (1999) PRB*
*Stixrude & Lithgow-Bertelloni (2005) GJI*

# Methods: elastic constants 2

Variation of stress with strain

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}$$



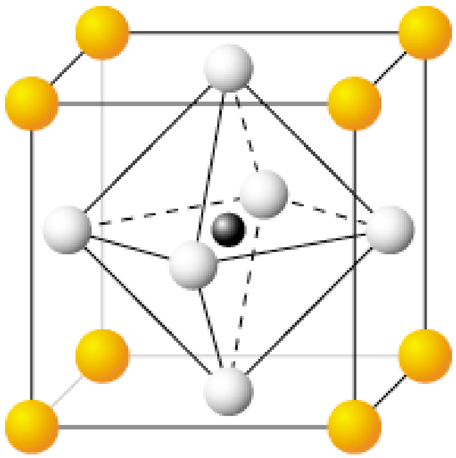

Optimize Structure

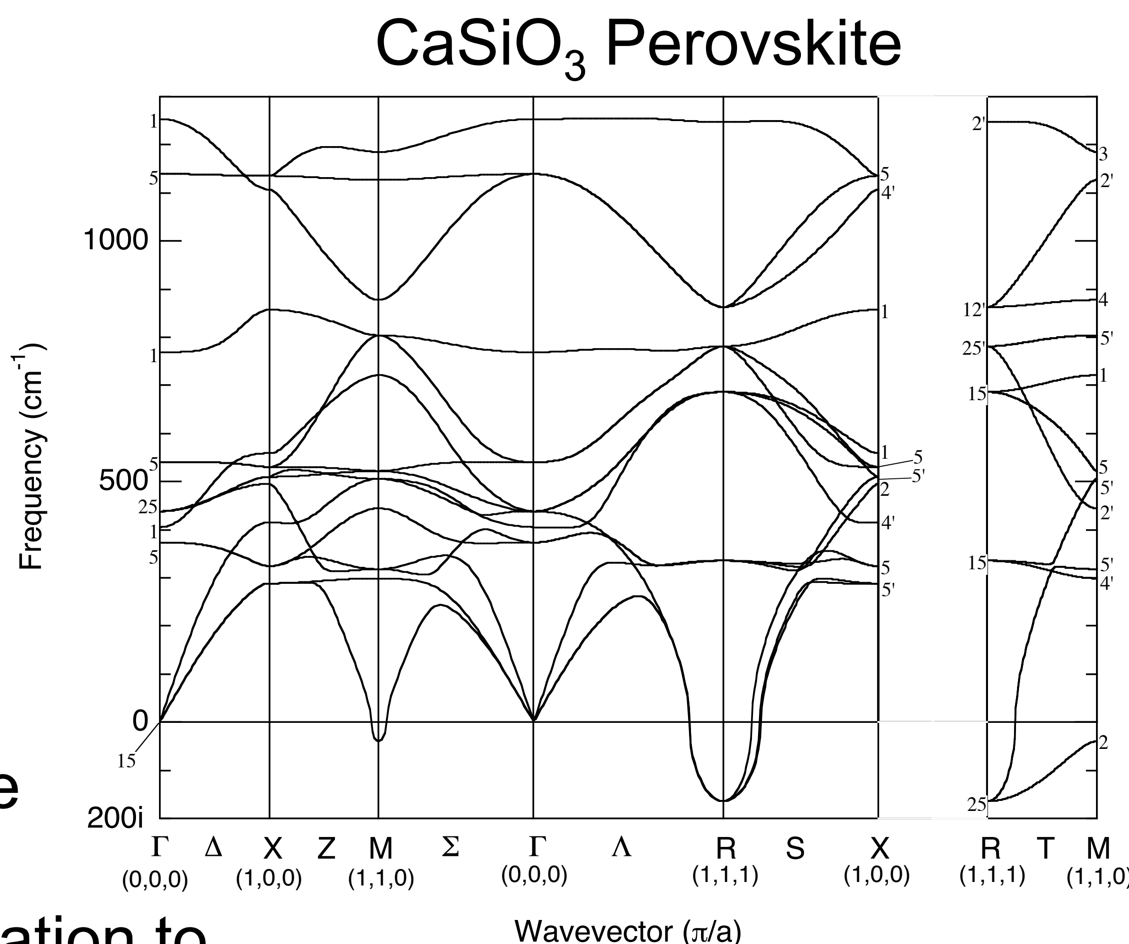
Apply Strain, Re-optimize

Calculate Stress

*Karki et al. (1997) Am. Min.; Karki et al., (2001) Rev. Geophys.*

# Density functional perturbation theory (linear response)

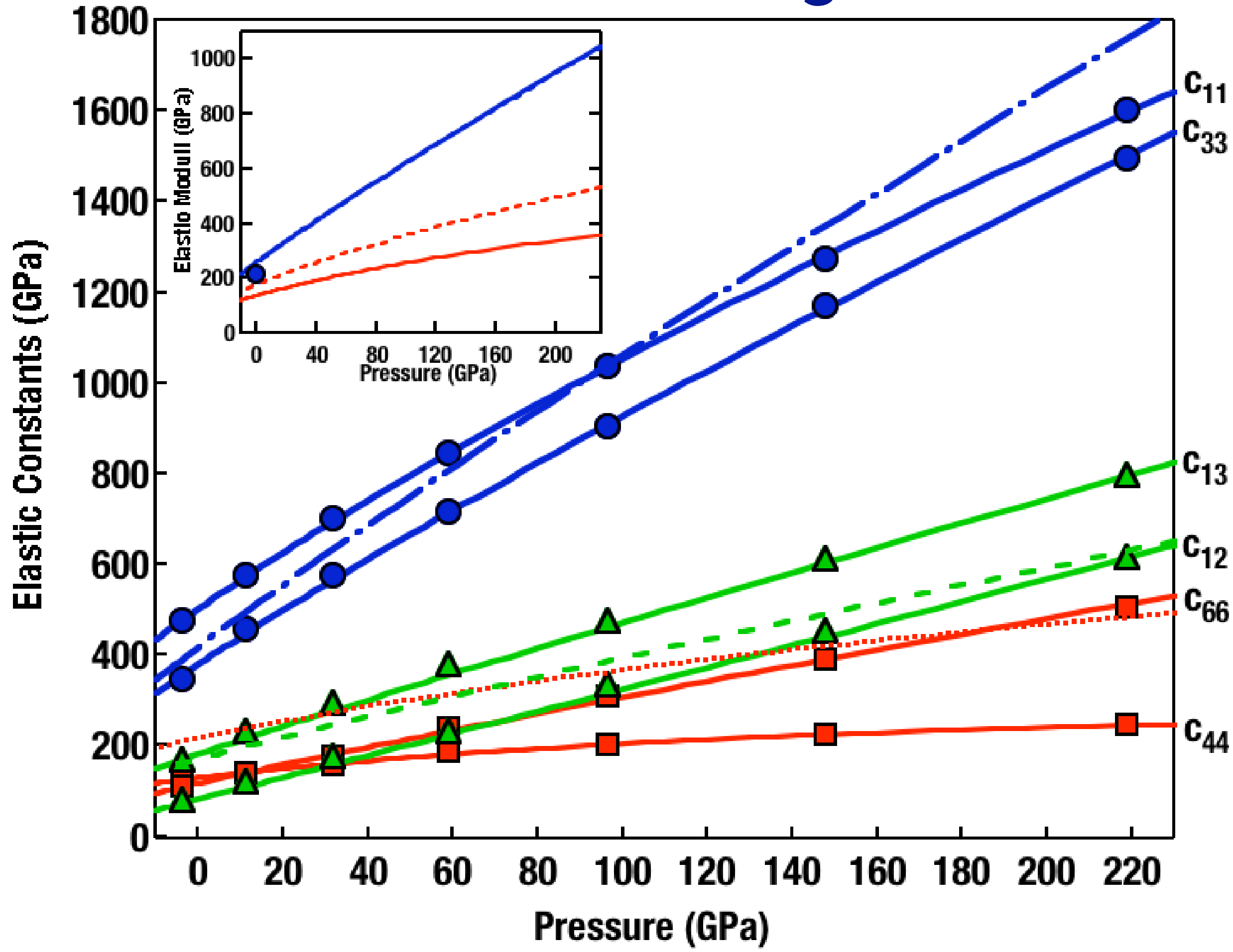





- Phonon spectrum
- Shows instability at zone boundary
- Predict phase transformation to tetragonal I4/mcm

*Stixrude et al. (1996) Am. Min.*

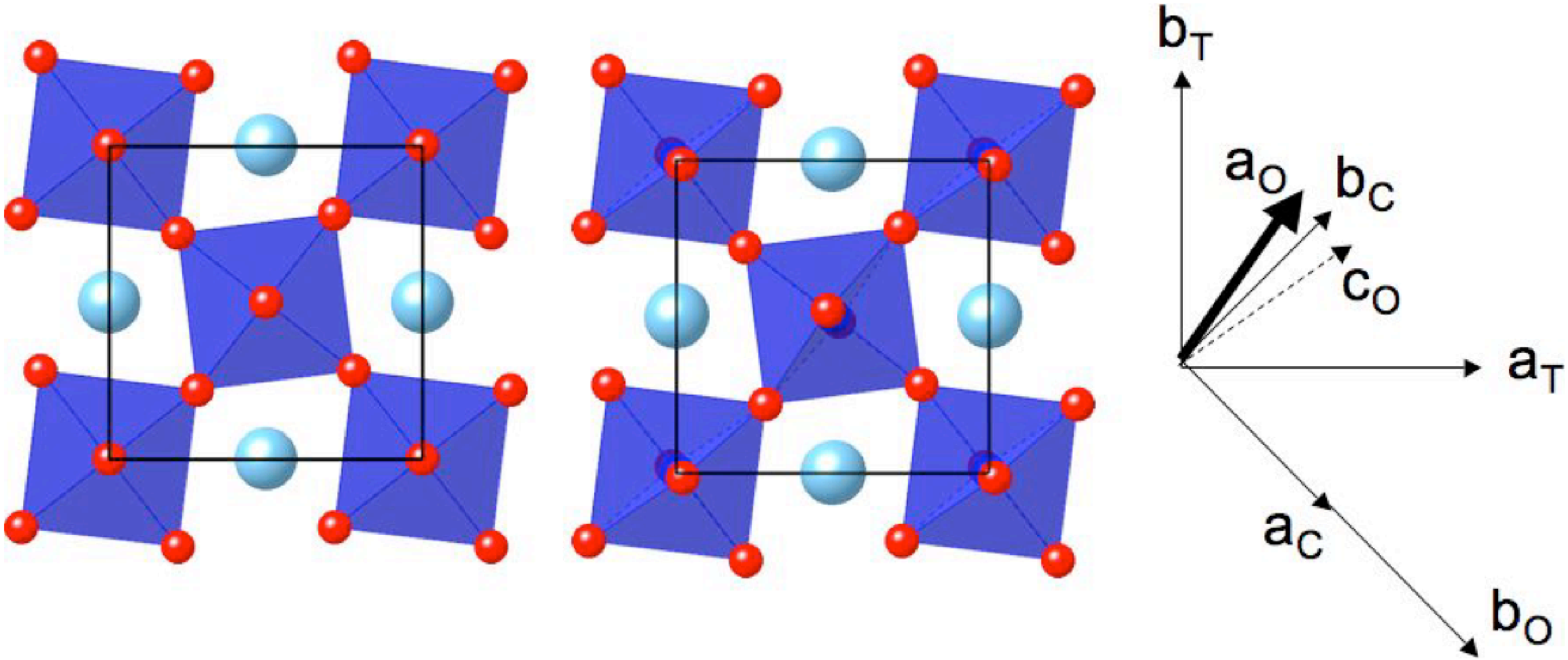
# Elasticity of $CaSiO_3$ perovskite




Tetragonal phase much softer than cubic!
Particularly $c_{44}$ (40 %)
VRH shear modulus 29 % smaller at 100 GPa

*Stixrude et al. (2007) PRB*

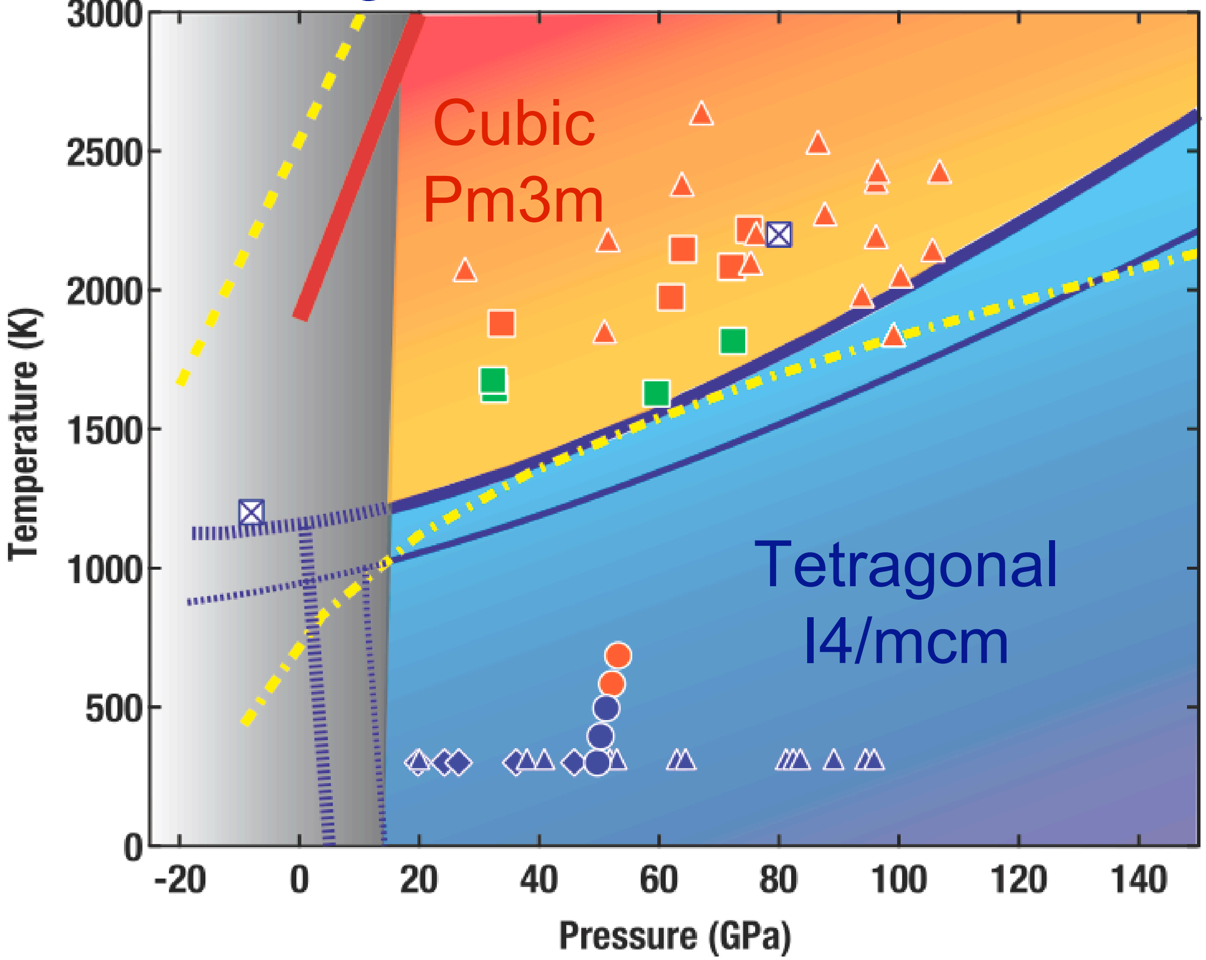
# Origin of shear softening




Strain-induced excitation of additional octahedral rotation

*Stixrude et al. (2007) PRB*

# $CaSiO_3$ phase diagram




Tetragonal to cubic phase transition
Lower mantle pressure-temperature conditions
Large elastic anomaly should be seismically detectable

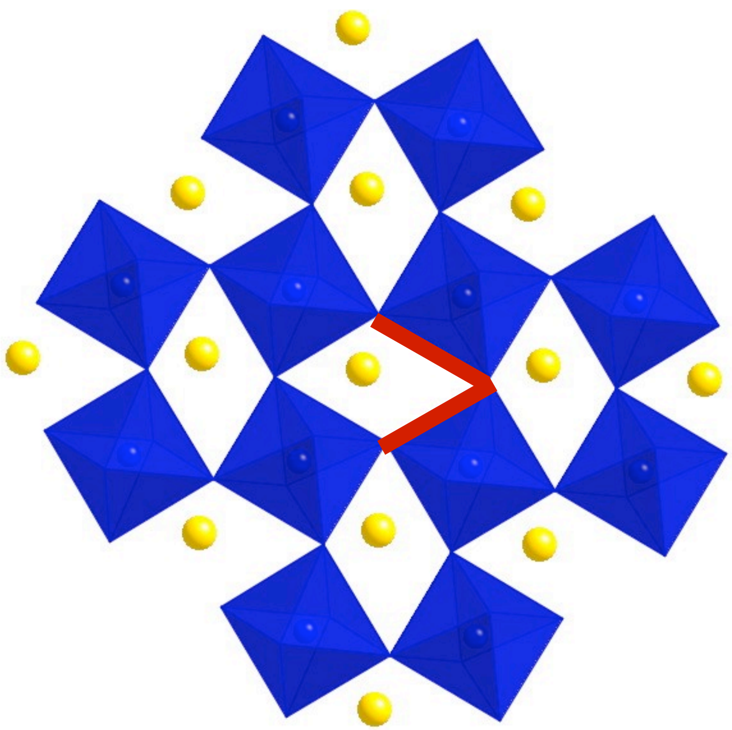
*Stixrude et al. (2007) PRB*

# Post-perovskite $MgSiO_3$

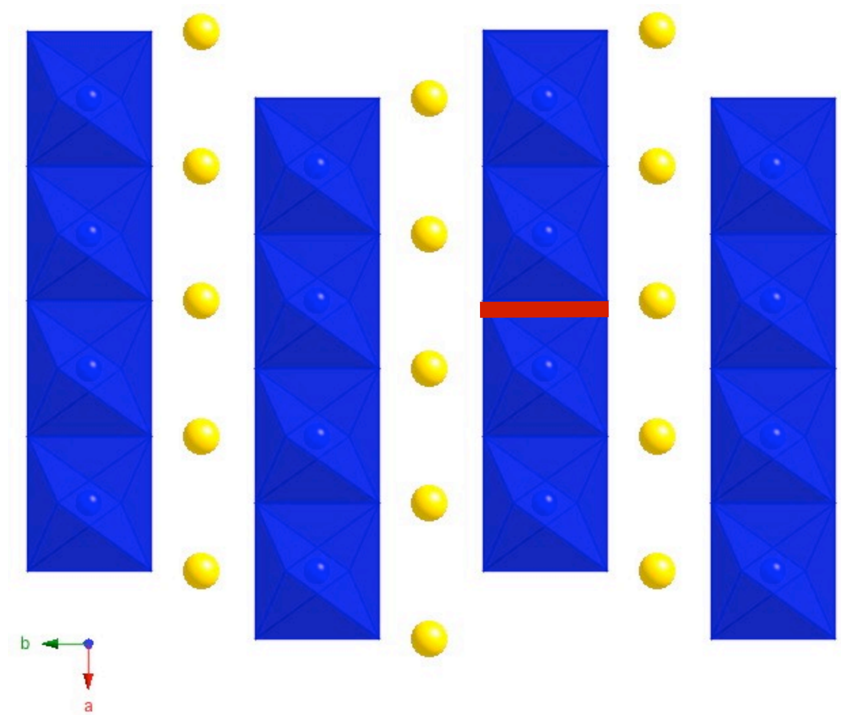
- Transition near base of mantle
- Layered, presumably strongly anisotropic
- Possible implications for D'' structure

*Murakami et al. (2004) Science*

*Pbnm*

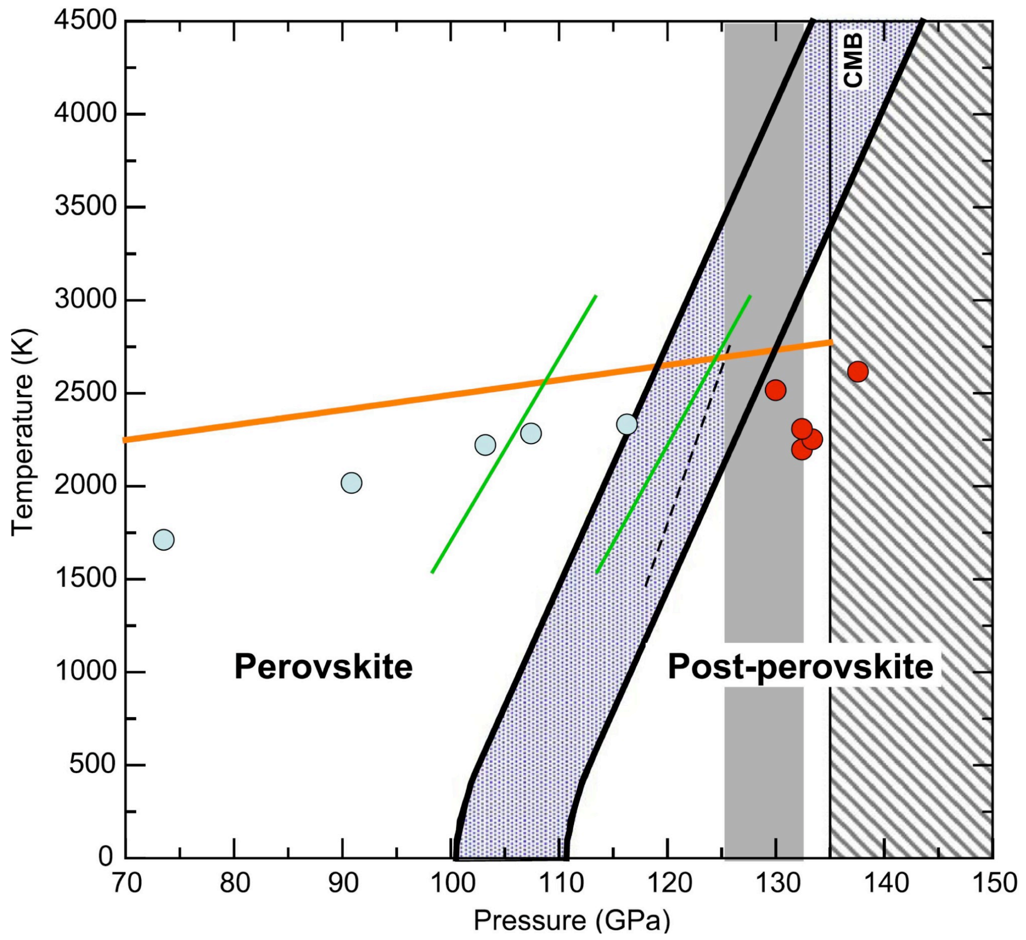


*Cmcm*



# Post-perovskite transition

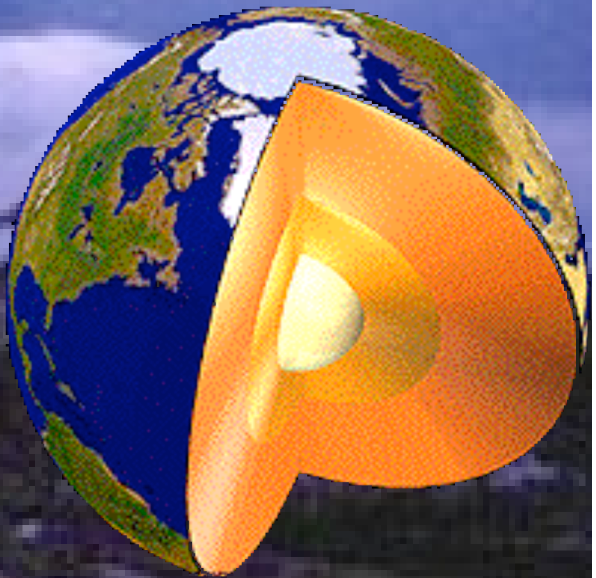
- Transition occurs near core-mantle boundary
- May explain discontinuity at the top of D''
- May explain anomalies in lateral heterogeneity
- "Double-crossing" seems possible




*Blue: Tsuchiya et al. (2004) EPSL*
*Green: Oganov & Ono (2004) Nature*
*Points: Murakami et al. (2004) Science*

# In search of the terrestrial hydrosphere

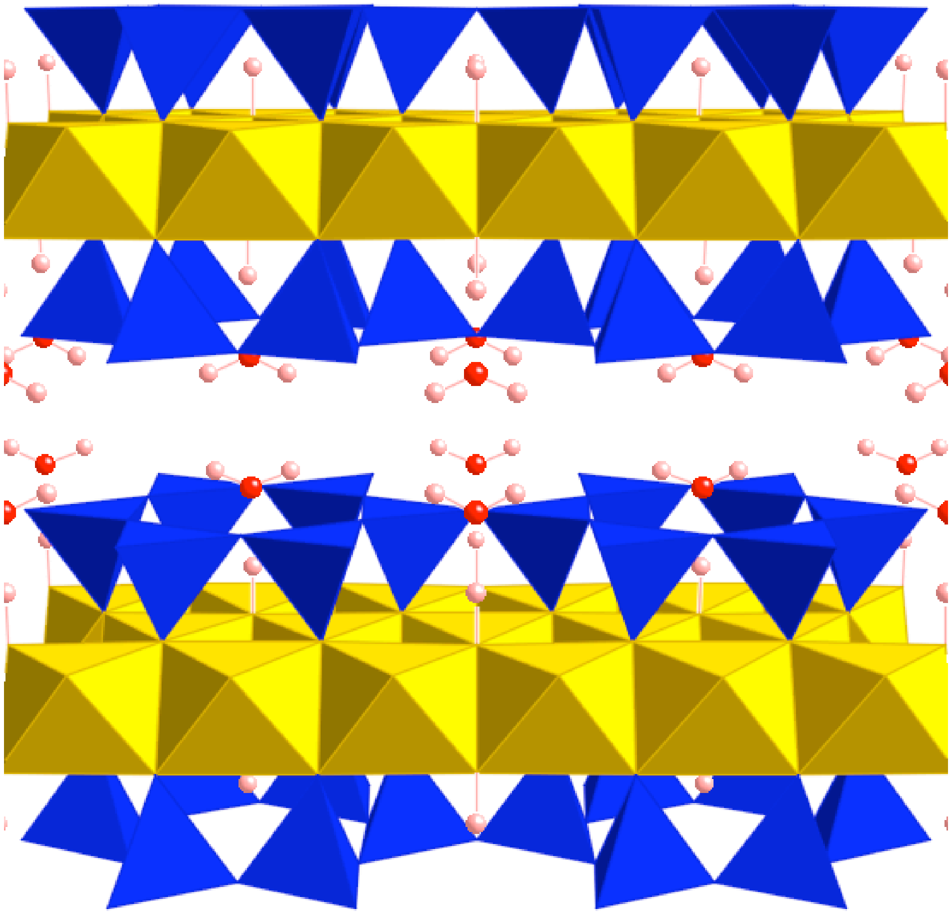
- How is water distributed?
  - Surface, crust, mantle, core
  - What is the solubility of water in mantle and core?
  - Can we detect water at depth?
  - Physics of the hydrogen bond at high pressure?
- Has the distribution changed with time?
  - Is the mantle (de)hydrating?
  - How is “freeboard” related to oceanic mass?
  - How does (de)hydration influence mantle dynamics?
- Where did the hydrosphere come from?
- What does the existence of a hydrosphere tell us about Earth’s origin?



# Hydrous phases

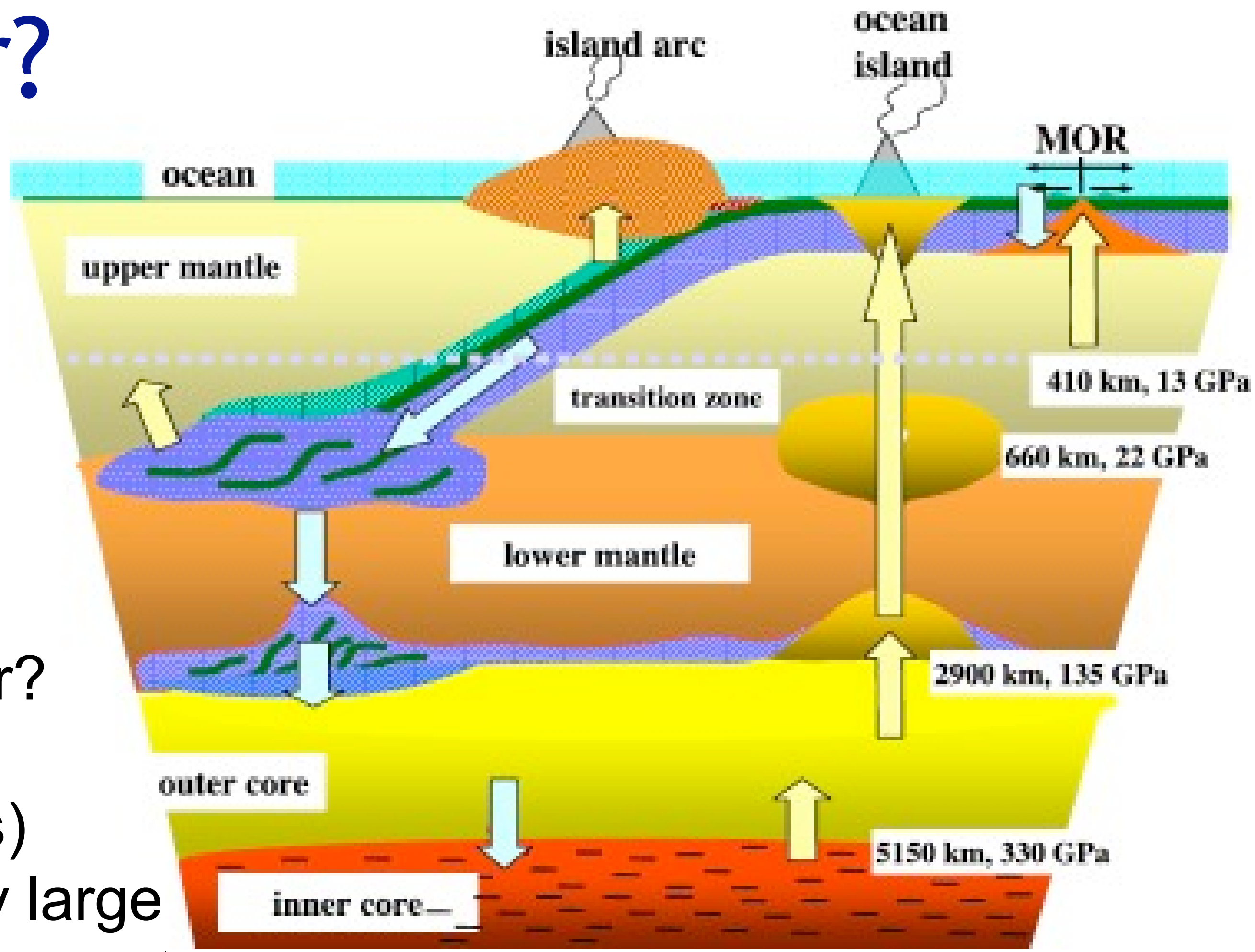
## 10 Å phase

- Important for carrying water from surface to deep interior
- Subduction zones
- Some water removed to melt
- How much is subducted?
- How much is retained in the slab?
- Phase stability



*Fumagalli et al. (2001) EPSL*
*Fumagalli & Stixrude (2007) EPSL*

# Where's the water?



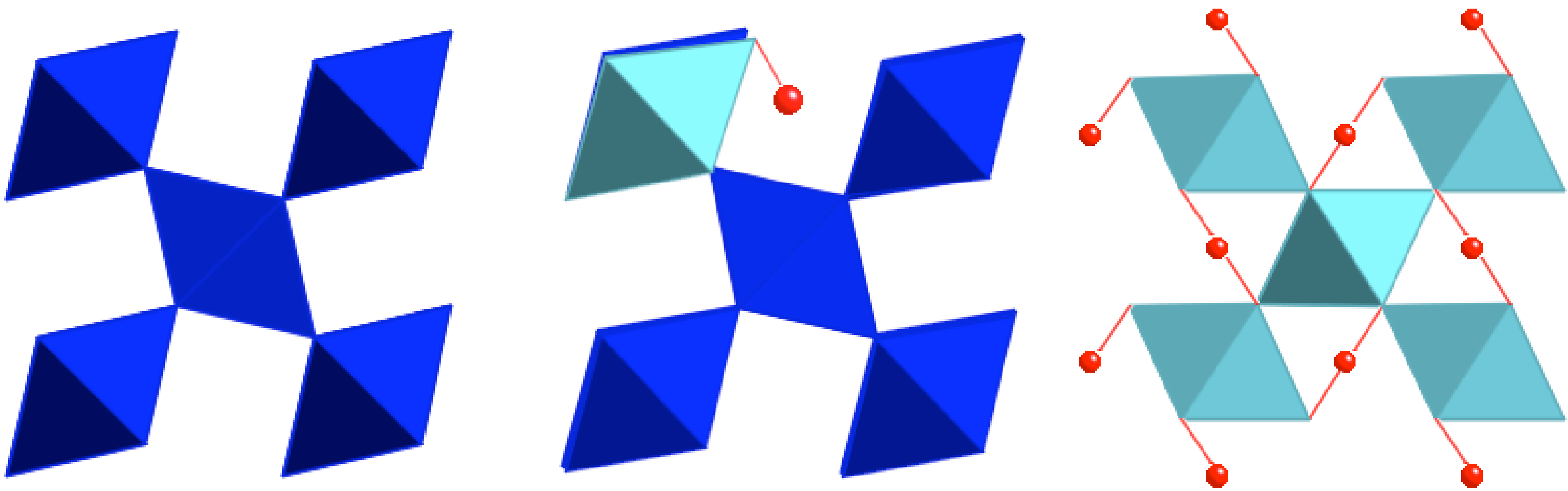

*Ohtani (2005) Elements*

Source of deep water?
Surface (subduction)
Accretion (chondrites)
Chondrites have very large water contents (much greater than Earth)
How much of this water could be retained on accretion?

# Nominally anhydrous phases

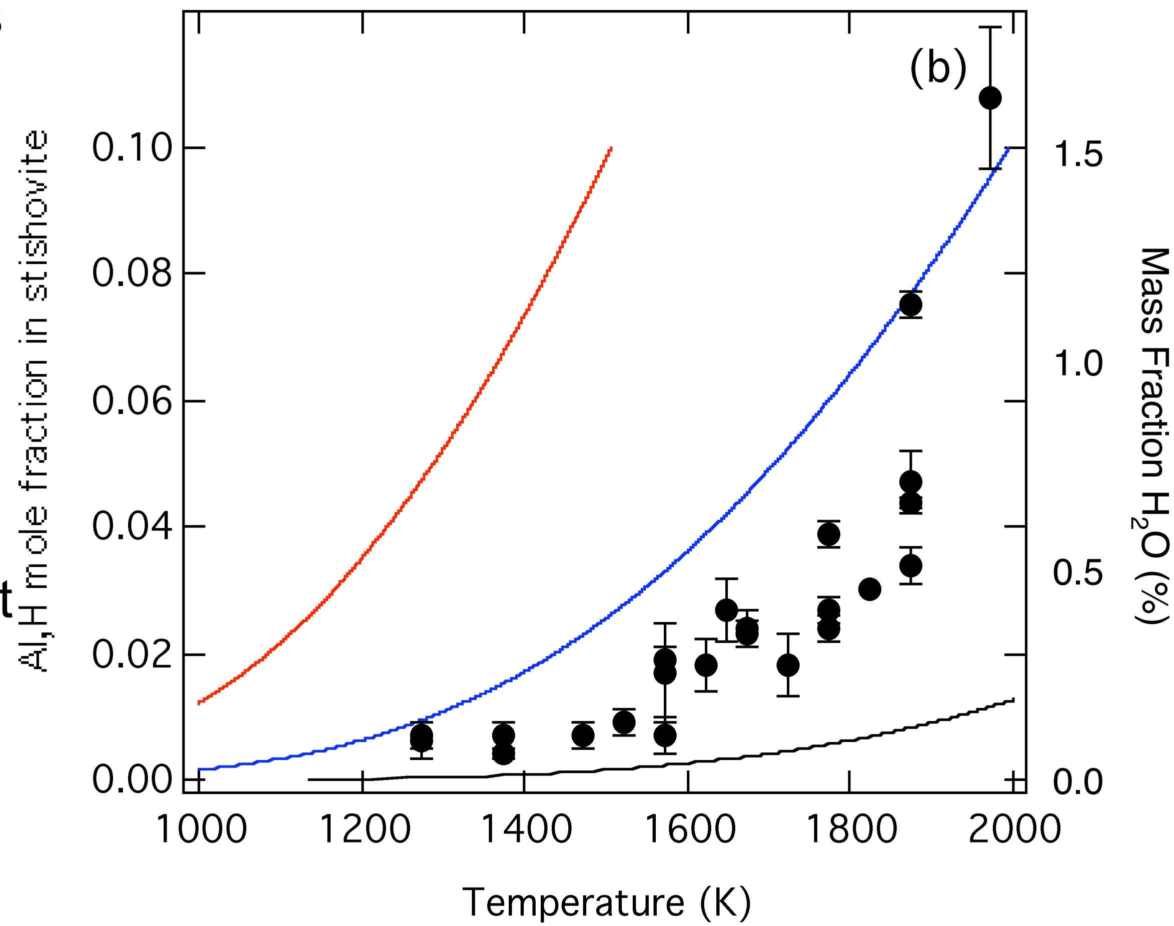
- Stishovite
- Charge balance: $Si^{4+}$ -> $Al^{3+}$ + $H^{+}$
- Low pressure asymmetric O-H…O
- High pressure symmetric O-H-O
- Implications for
  - Elasticity, transport, strength, melting

*Panero & Stixrude (2004) EPSL*



# $SiO_2$:AlOOH stishovite

- Primary reservoir of water in mantle?
- Incorporation of H requires charge balance
- Investigate Al+H for Si in stishovite
- End-member (AlOOH) is a stable isomorph
- Enthalpy and entropy of solution
- Solubility
- Consistent with experiment
- Large!




*Panero & Stixrude (2004) EPSL*

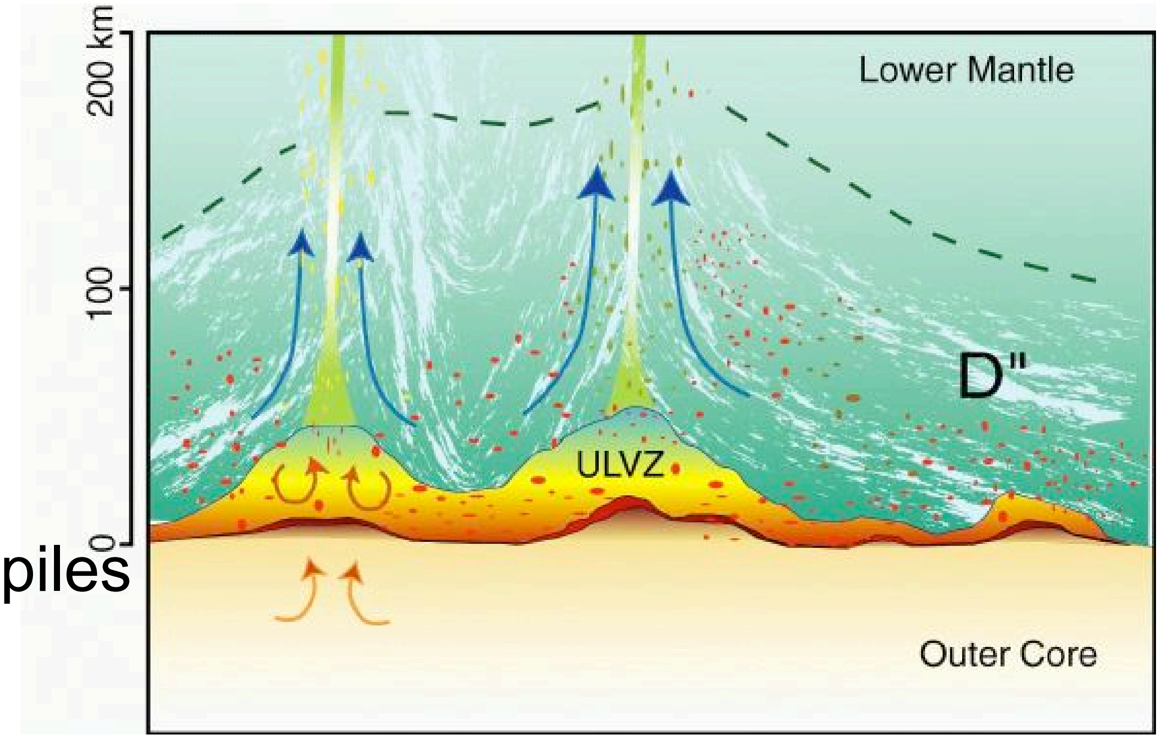
# The core mantle boundary

Largest contrast in physical properties in the planet

- Density
- Elasticity
- Conductivity
- Viscosity…

Structural features

- D''
- ULVZ
- Dense thermochemical piles
- Internal discontinuities




*Garnero, 2006*

Processes

- Melting
- Core-mantle chemical reaction
- Upward core-side sedimentation
- Phase transformation

# Spin pairing transition

(Mg,Fe)O

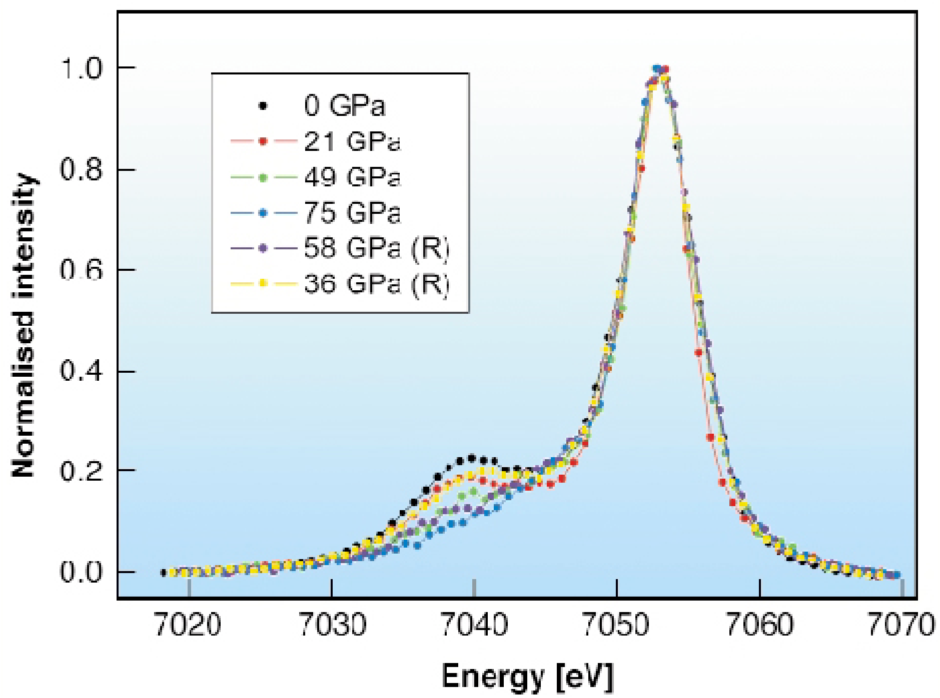
Transition in $Fe^{2+}$ from

high spin (4 unpaired electrons) to

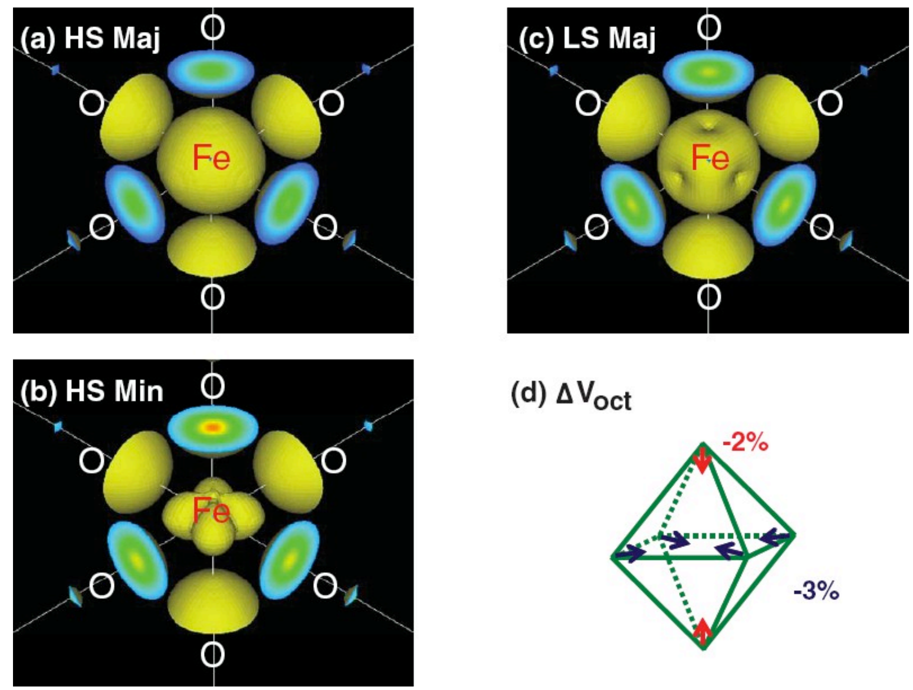
low spin (0 unpaired electrons)

Experiment: Kβ x-ray emission spectroscopy

Theory: DFT+U with U determined self-consistently



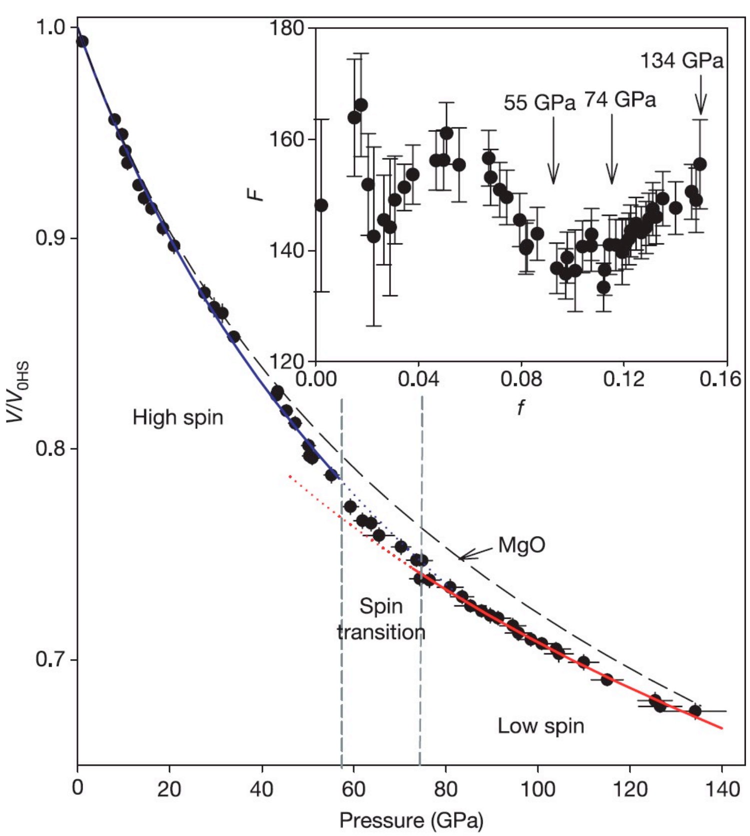

*Badro et al. (2003) Science*



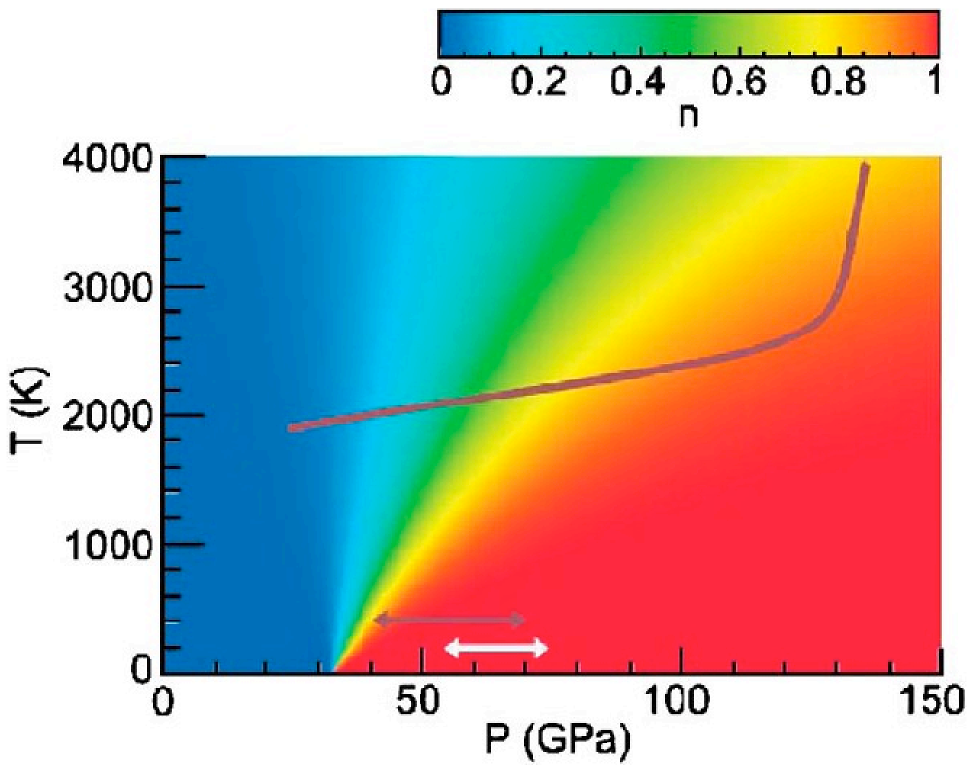

*Tsuchiya et al., (2006) PRL*

# Spin-pairing transition

Influences many physical properties
Transition likely spread out in pressure via entropic effects
Softening of elasticity within transition region




*Lin et al. (2005) Science*

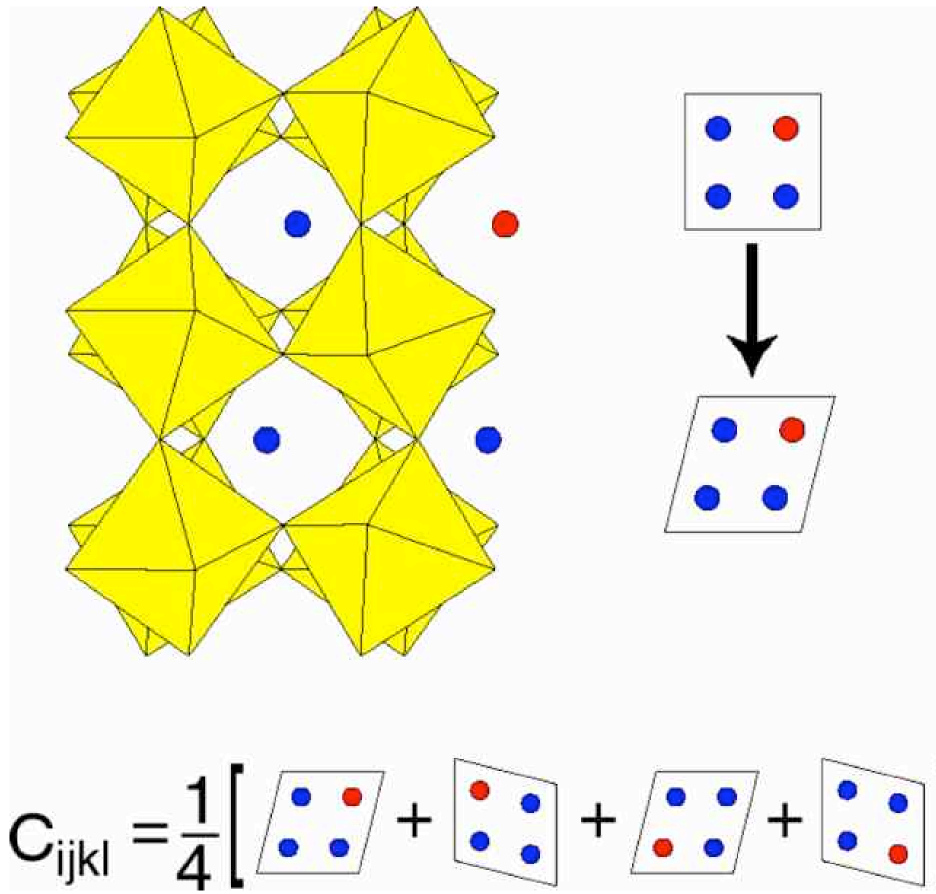



*Tsuchiya et al. (2006) PRL*

# (Mg,Fe)$SiO_3$ perovskite

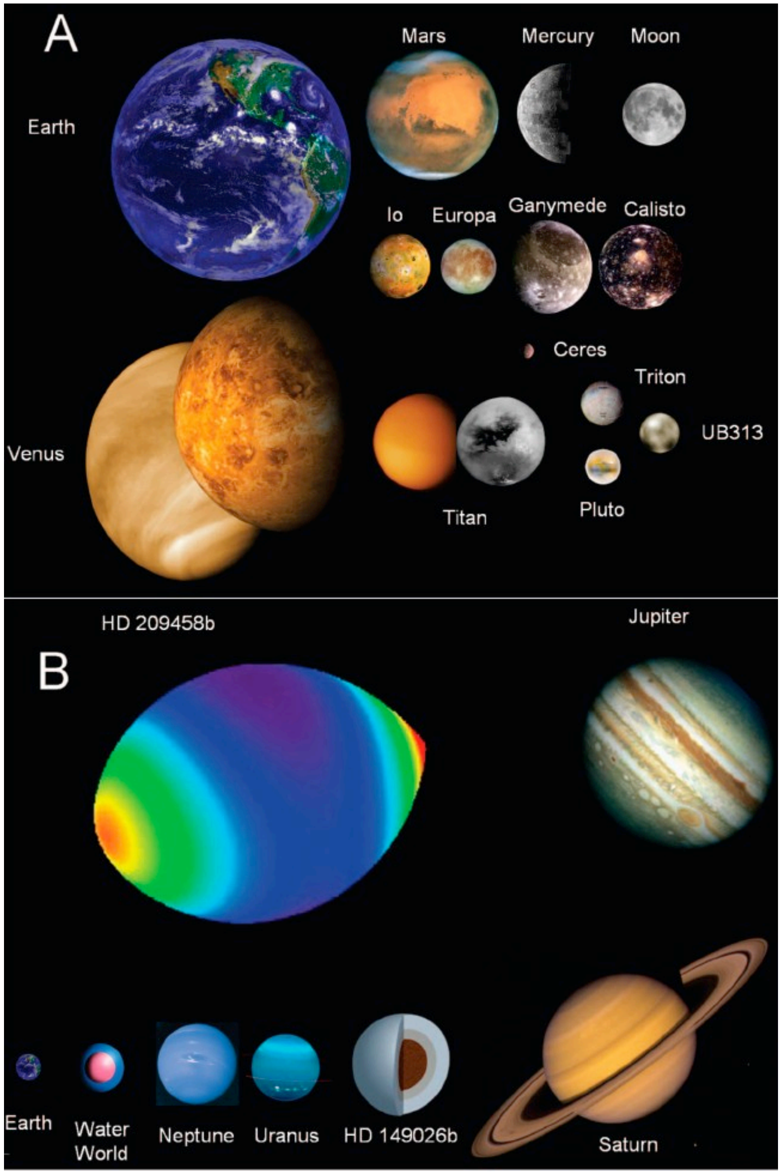
•Experimental evidence for spin-pairing transition
•Possibly an intermediate spin state
•Evidence for $Fe^{3+}$ even in samples initially synthesized with only $Fe^{2+}$
•Dilute solid solution!
•Method for computing elastic constants: (high spin $Fe^{2+}$)

$$c_{ijkl} = \frac{1}{4}\sum_{s=1}^{4} R^s_{im} R^s_{jn} R^s_{ko} R^s_{lp} \tilde{c}_{mnop}$$



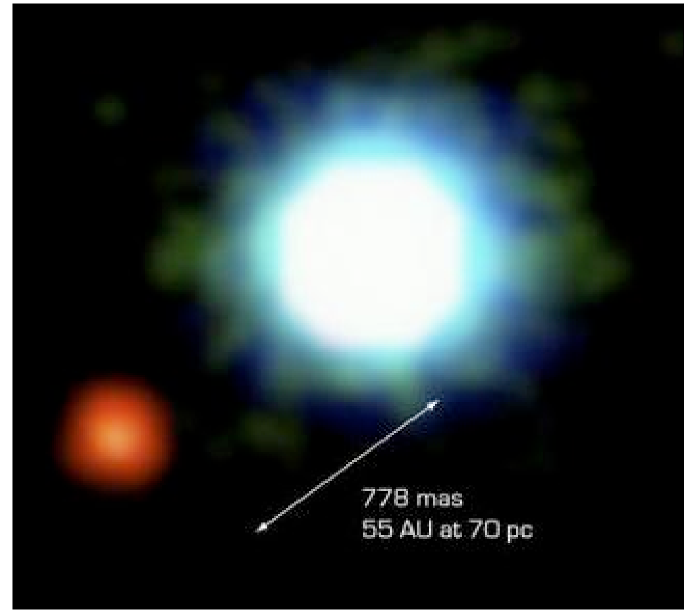

*Kiefer et al. (2002) GRL*

# Other planets

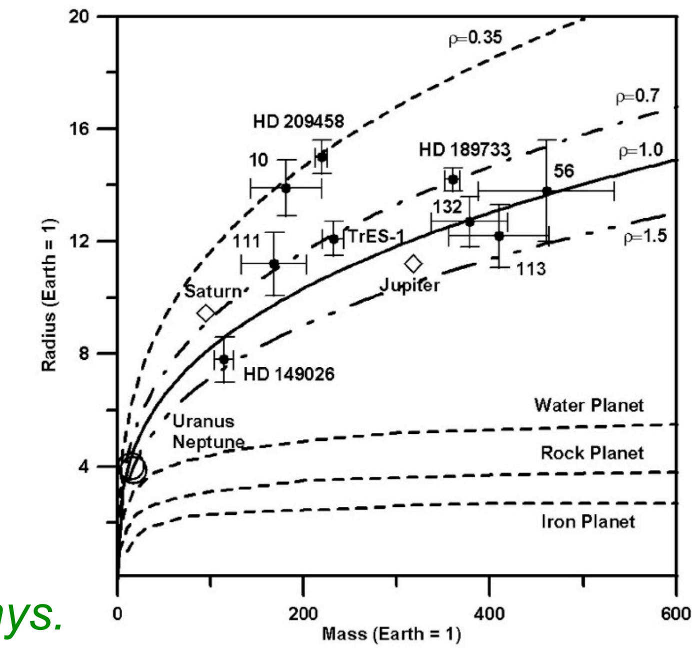



Sanchez-La Vega (2006) Cont. Phys.

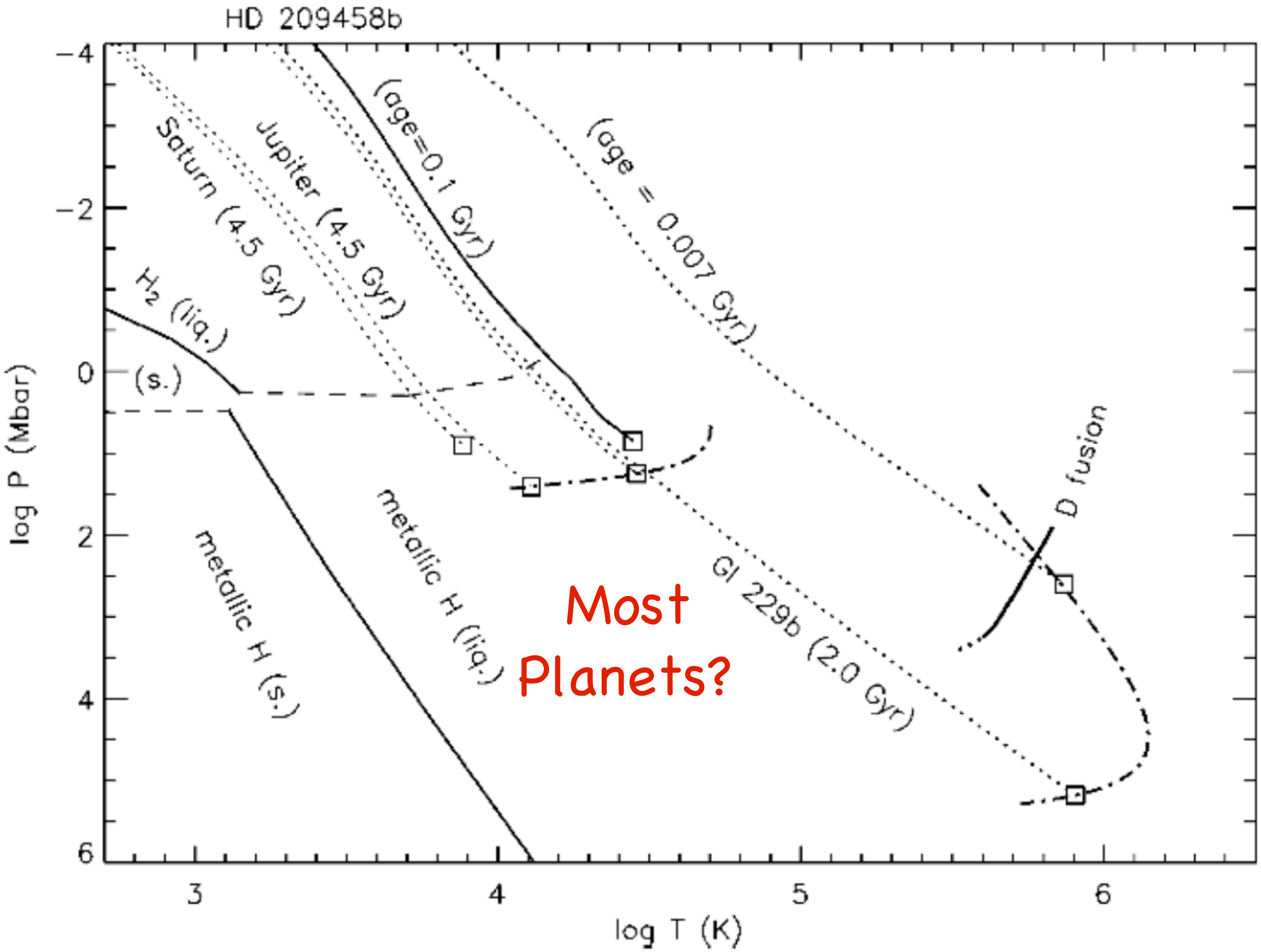
2M1207b



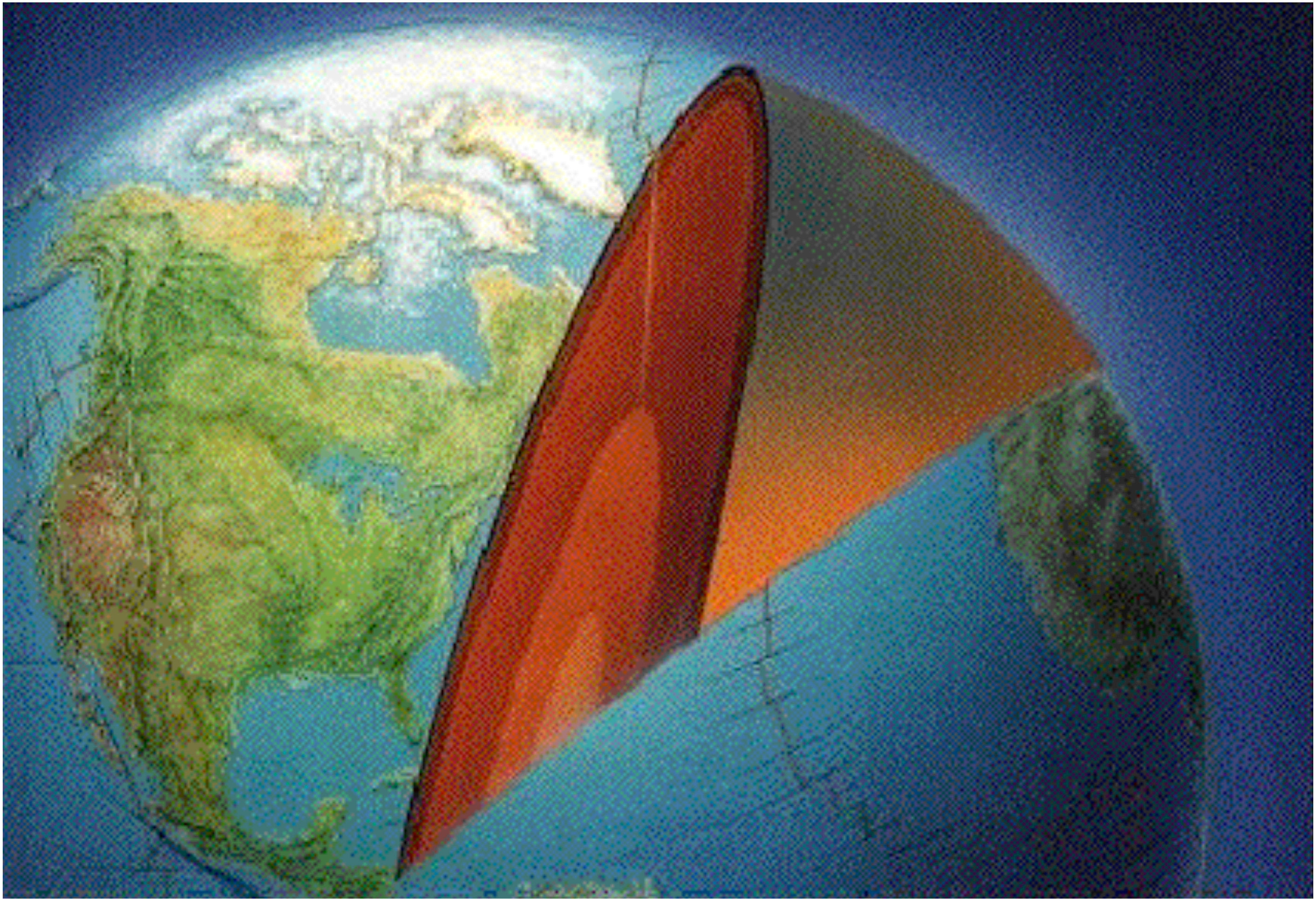

Chauvin et al. (2006)



# Pressure-temperature regime of planets




*Hubbard et al. (2002) Ann. Rev. Astro. Astro.*


*Press & Siever*