

"Phase diagrams are the beginning of wisdom..."

-- Sir William Hume-Rothery

"It is unworthy of great (wo)men to lose hours like slaves in the labor of calculation."

-- Baron Gottfried Wilhelm von Leibniz

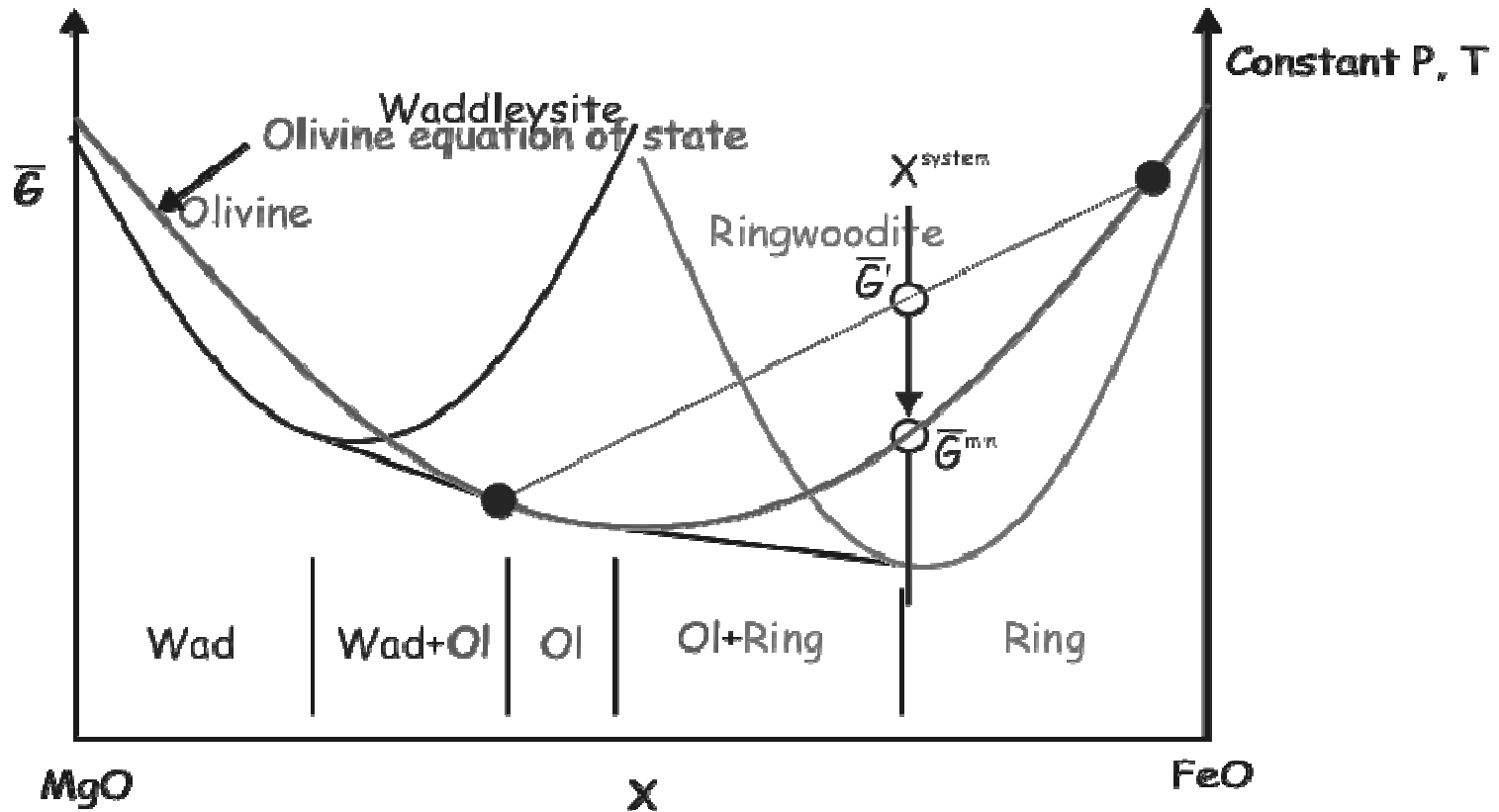
A Fast and Robust Method for the Calculation of Phase Equilibria

and

Application to Geophysical Inversions for Planetary Composition and Temperature

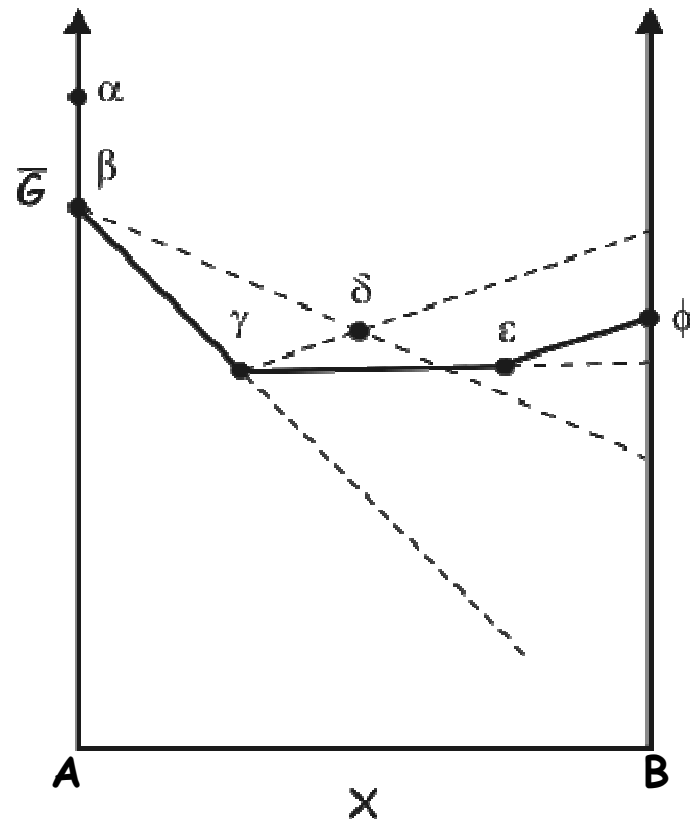
The Non-Linear Phase Equilibrium Problem

The stable state of a system minimizes its Gibbs Energy (G)

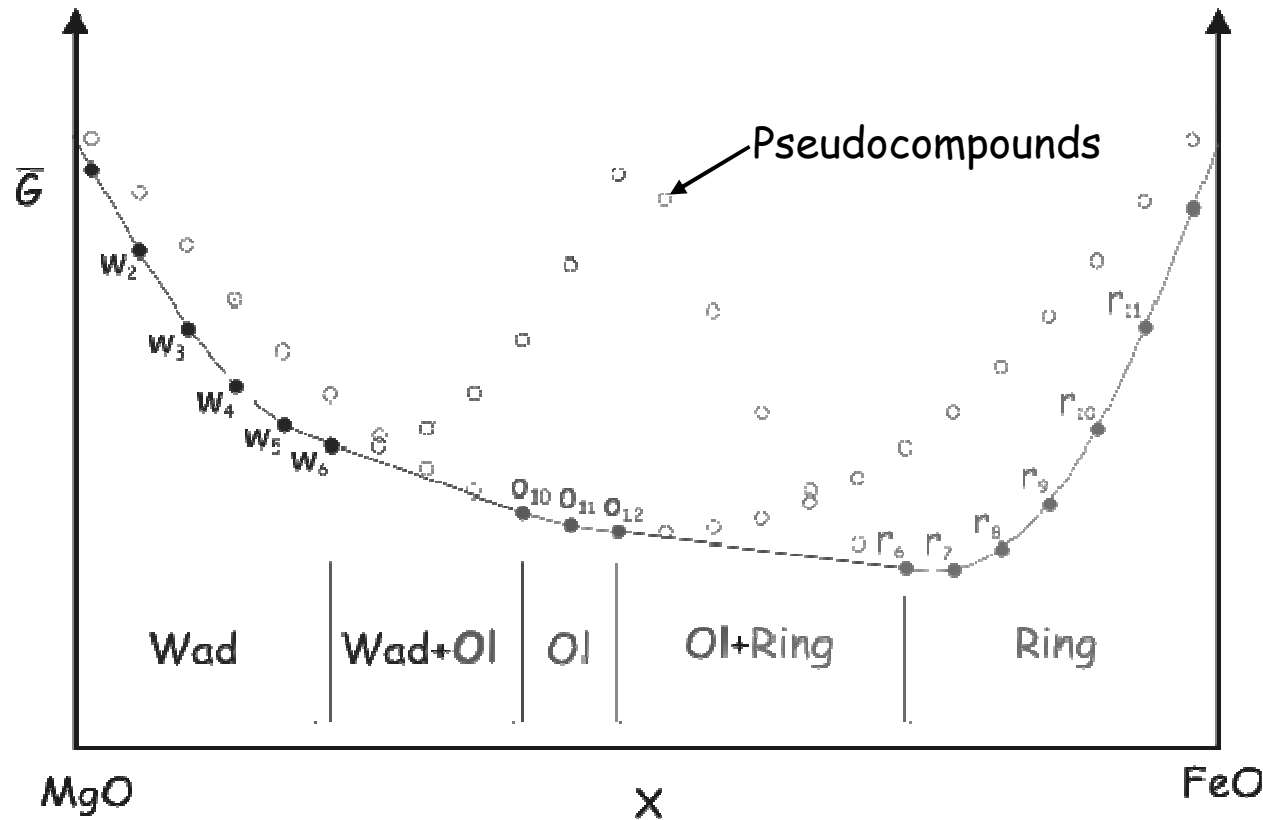


Brown & Skinner 1974, Saxena & Eriksson 1983, Wood & Holloway 1984, deCapitani & Brown 1987, Bina 1998, etc. etc.

The Linear Phase Equilibrium Problem



The Linearized Phase Equilibrium Problem: "Pseudocompound" Approximation



For a given X , reduces to the LP problem:

$$\min \left(G^{sys} = \sum_{i=1}^{\Pi} \alpha^i G^i \right)$$

$$\alpha^i \geq 0$$

$$n_j^{sys} = \sum_{i=1}^{\Pi} \alpha^i n_j^i, \quad j = 1 \dots c$$

solved by Danzig (1947) by the Simplex algorithm.

White et al. 1958, Connolly & Kerrick 1987

Optimize what when? And an Unexpected Virtue of the Linearized Solution

Thermodynamics provides stability criterion (i.e., an extremal function) for any choice of variables among the conjugate pairs P - V , T - S , μ - n

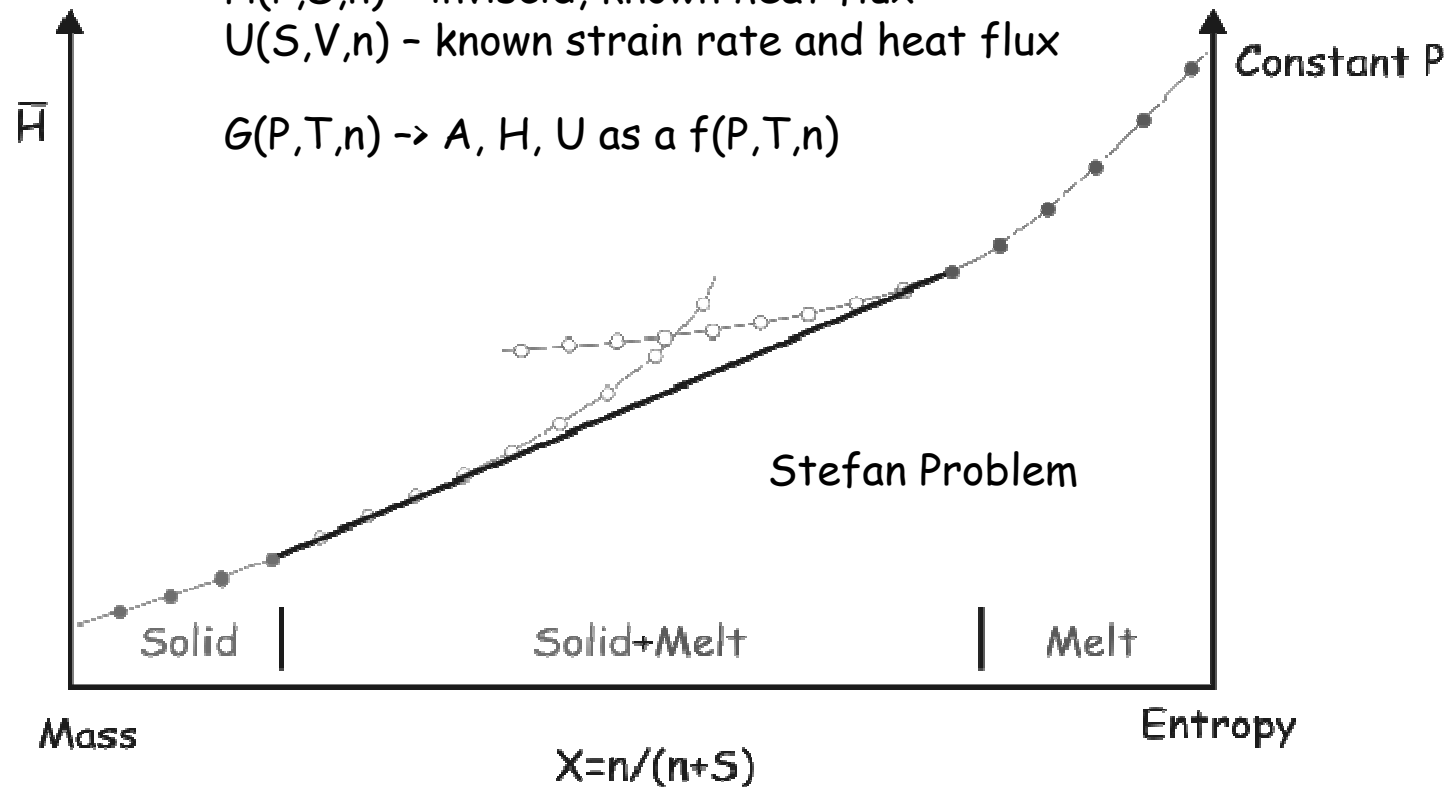
$G(P, T, n)$ - inviscid, known temperature

$A(V, T, n)$ - known strain rate, temperature

$H(P, S, n)$ - inviscid, known heat flux

$U(S, V, n)$ - known strain rate and heat flux

$G(P, T, n) \rightarrow A, H, U$ as a $f(P, T, n)$



Some thoughts about cultural differences and data

Geophysics/Mineral physics

- Limited data, lots of theory
- Individual minerals and phase transitions
- "A good experiment ****s any computation" D. Yuen, 2005

Pro: Amenable to simple parameterization for geodynamic models

Con: Ignores strong autocorrelation of thermodynamic parameters

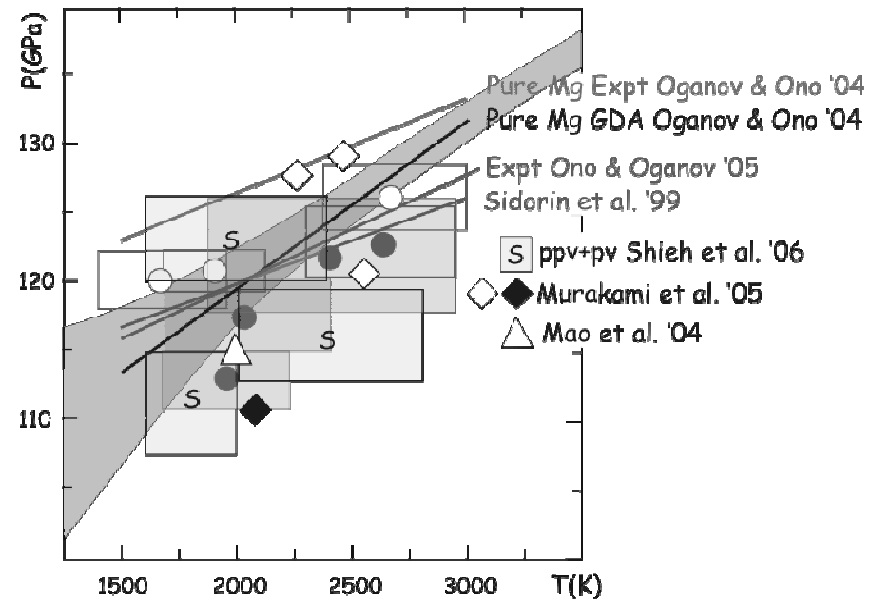
Petrology

- Lots of data, little theory
- Global average

Pro: Objectivity, single mega-parameter

Con: Difficult to: assess uncertainty; separate first and second order affects; modify without access to primary data

D'' and the Fe-Mg-Al Post-perovskite transition



Equation of State, Stixrude & Bukowinski 1990

Gruneisen model for Helmholtz Energy: $A(V, T) = A_0 + A_c(V, T_0) + \{A_{th}(V, T) - A_{th}(V, T_0)\}$

Birch-Murnaghan "cold" part:

$$A_c = \frac{9}{2} K_0 V_0 [f^2 + (K'_0 - 4) f^3]$$
$$f = \frac{1}{2} \left[\left(V_0/V \right)^{2/3} - 1 \right]$$

Debye "thermal" part:

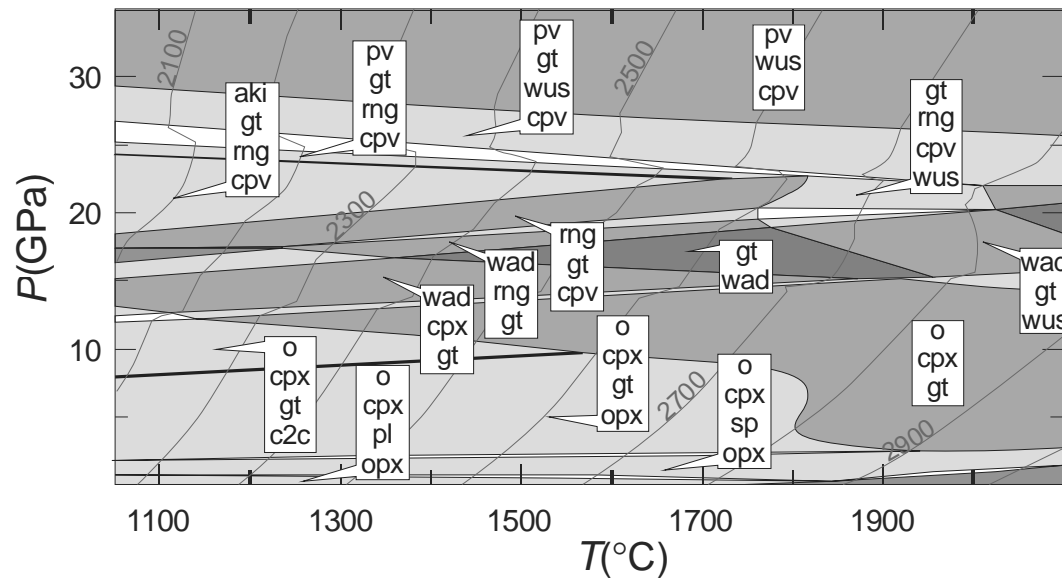
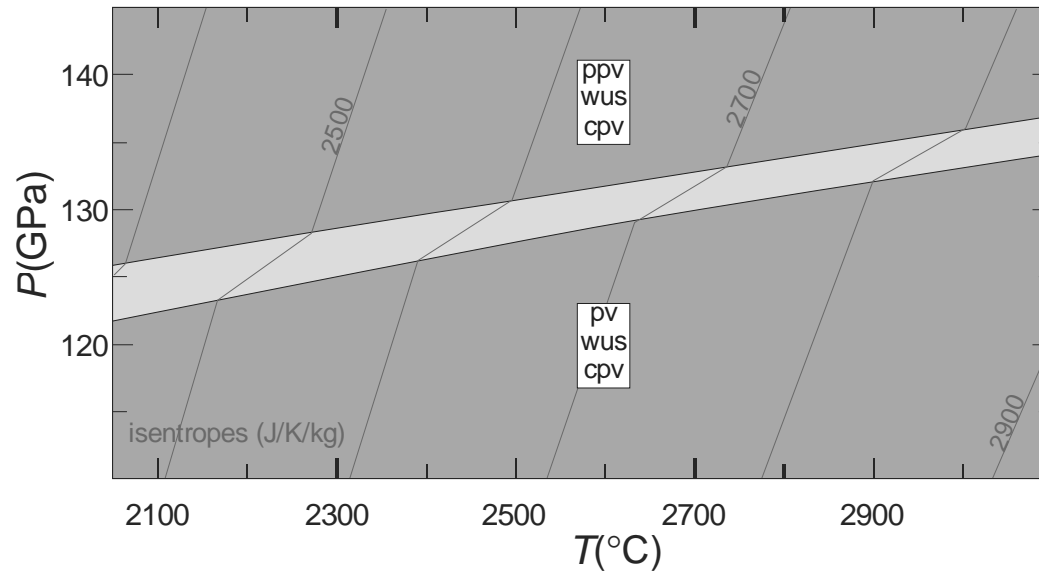
$$A_{th} = 9nRT (T/\theta)^3 \int_0^{\theta/T} \ln(1 - e^{-t}) t^2 dt$$
$$\theta = \theta_0 \exp \left[\gamma_0 \left(1 - (V/V_0)^q \right) / q \right]$$

Six parameters ($A_0, K_0, K'_0, V_0, \gamma_0, \theta_0, q$) + 3 parameters for seismic velocities

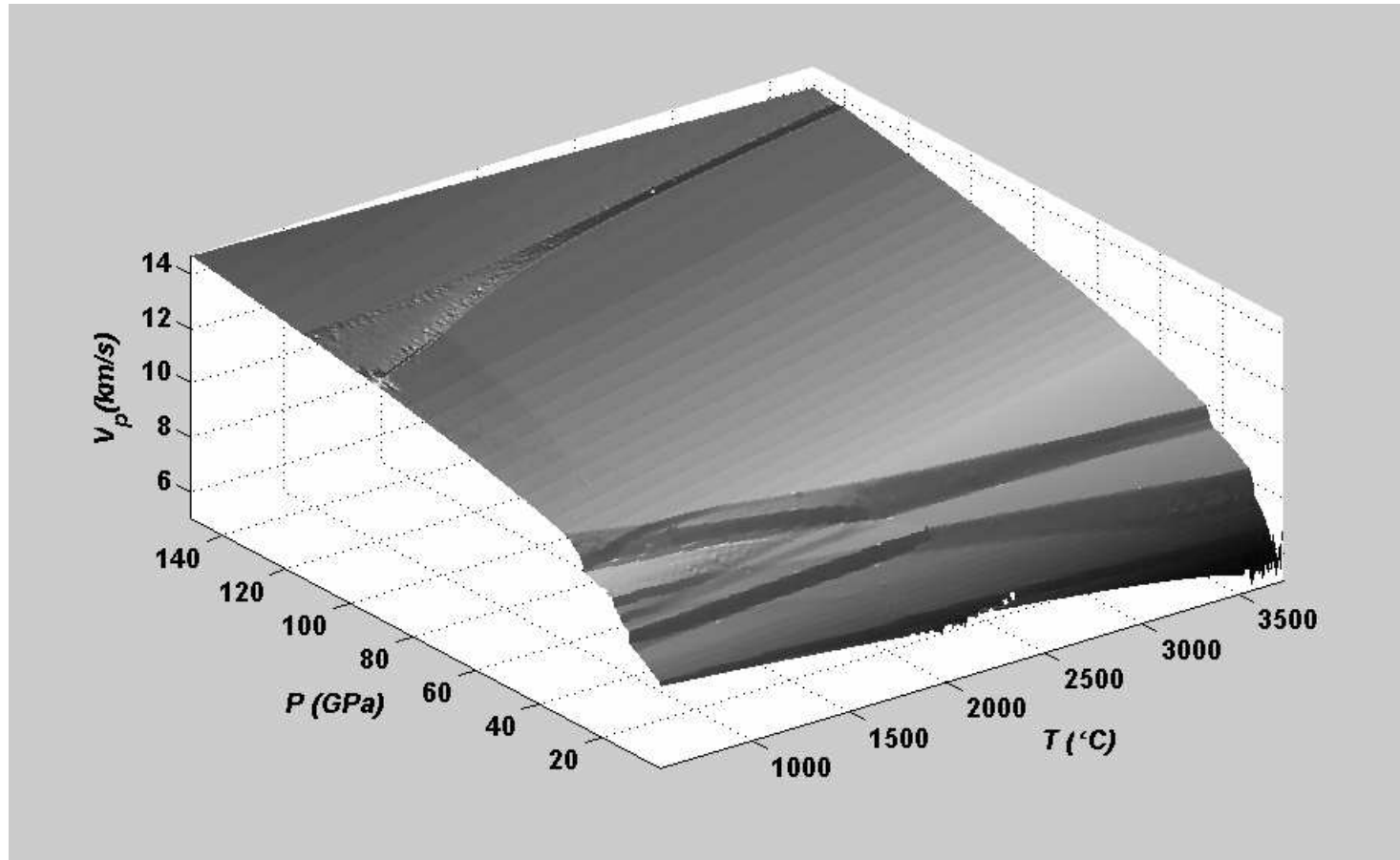
Data from Stixrude & Lithgow-Bertelloni (2005) augmented by

- Post-perovskite from Oganov & Ono (2004), Ono & Oganov (2005)
- Ca-perovskite from Akaogi et al. (2004), Karki & Crain (1998)
- Wuestite, perovskite from Fabrichnaya (1999), Irfune (1994)

Computed Pyrolite (CaO-FeO-MgO-Al₂O₃-SiO₂) Phase Relations



Pyrolite P-wave velocity



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Seismic Velocities and Thermodynamic Consistency

$$\rho = N / \frac{\partial G}{\partial P}, \quad K_S = -\frac{\partial G}{\partial P} \left[\frac{\partial^2 G}{\partial P^2} + \left(\frac{\partial}{\partial P} \frac{\partial G}{\partial T} \right)^2 / \frac{\partial^2 G}{\partial T^2} \right]^{-1}, \quad \mu_S = ?$$

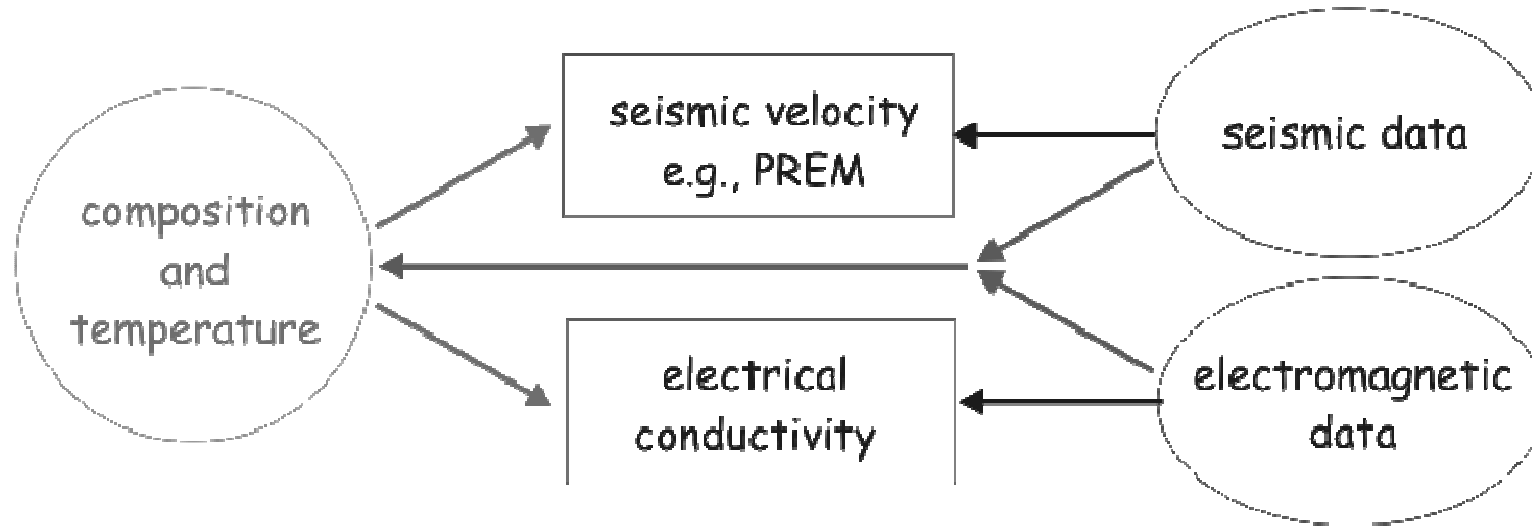
Stixrude & Lithgow-Bertelloni '05a,b → finite strain model EoS → $\mu_S = f(G[\rho, T])$

	ρ	K_S	μ_S
Sobolev & Babeyko '94	no	no	no
Connolly & Kerrick '02	yes	yes	no
Stixrude & Lithgow-Bertelloni '05	yes	yes	yes

Does it really matter? Probably not, phase relations are most sensitive to integration constants and low-order derivatives, seismic velocities are most sensitive to high-order derivatives.

Non-thermodynamic issues: anelasticity, aggregate moduli

Enter Amir Khan: Application to Geophysical Inversions for Planetary Composition, Temperature and Structure



- i) Inversion for secondary model parameters
- ii) Precludes joint inversion of unrelated geophysical data

P-wave velocities of cheese are 1.2 (Muenster)
- 2.1 (Swiss) km/s, velocities in the lunar regolith are 1.2-1.8 km/s

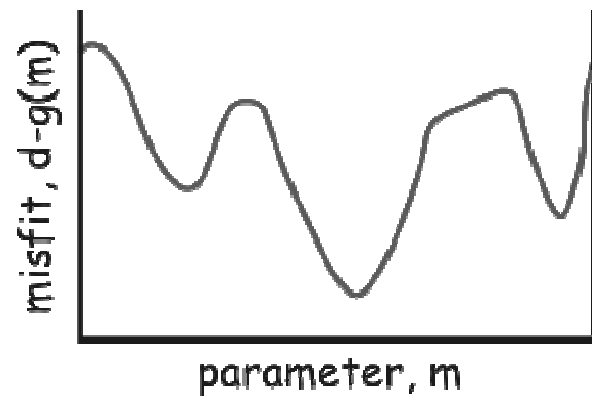
Ergo the moon is a mixture of Muenster and Swiss cheese

Inversion Strategy

- i) *Guess a physical configuration (T, c, d, ...)*
- ii) *Construct a forward model for the observed data*
- iii) *Test against observations, go to i)*

Sampling the Posterior Distribution (Tarantola & Valette, '82)

The forward model, $d' = g(m)$



Likelihood:

$$\mathcal{L} = \exp\left[-\frac{|d - g(m)|}{\sigma_{m_0}}\right]$$

i) Exhaustive search, e.g., 20 parameters, 10^6 samples? 2 points per dimension

If the mantle is pyrolite, then it is superadiabatic (Cammarano et al., 2005)

ii) Linearized least squares, e.g.,

$$\min \left[\frac{(d - g(m))^2}{\sigma_d^2} + \frac{(m - m_0)^2}{\sigma_{m_0}^2} \right]$$

If the mantle is pyrolitic, then it is subadiabatic (Mattern et al., 2005)

iii) General non-linear, drop 2nd term, Markov chain Monte Carlo algorithm to escape local minima; accepts candidates if $\mathcal{U}[0,1] \leq \min(1, \mathcal{L}^{\text{candidate}} / \mathcal{L}^{\text{current}})$

The mantle is superadiabatic and not pyrolite (Khan et al., 2006)

What's good about an EM inversion?

Test of ability to predict phase relations without requiring accuracy in high order derivatives necessary to calculate elastic properties

EM inversions are in principle a vastly superior method of probing planetary composition

Sensitivity of seismic (v_p) vs EM (σ) signals

	P-T	mineral composition	mineralogy
Perovskite	1.18	1.01	1.36
	2	11	
Wuestite	1.26	1.02	
	6	10	400

P-T: from 1880K - 23GPa to 2750K - 100GPa

Mineral composition: 10 mol % change in Fe- or Al-content

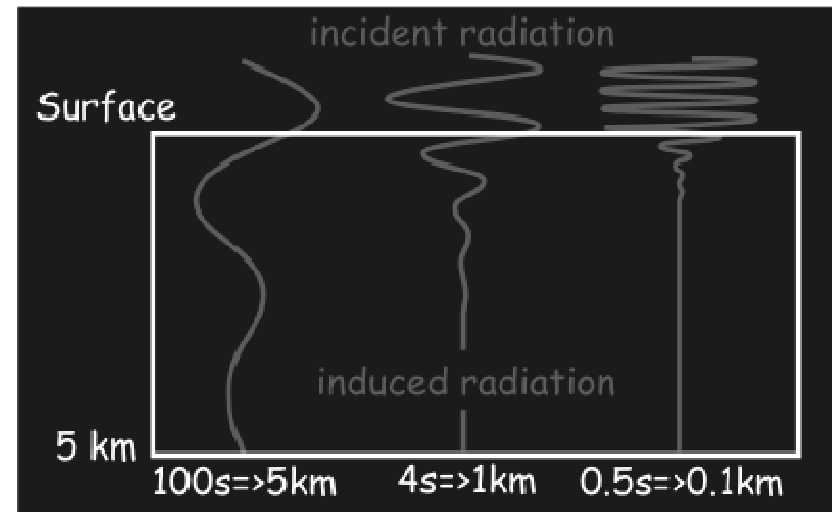
The Observations

Periodic ionospheric and magnetospheric fields induce secondary magnetic fields within the earth

Transfer function between external and induced fields is a function of earth's conductivity

Sub-European soundings (Olsen 1999) for periods of 3 h to 1 year (depths of 200-1500 km)

Earth's mass and moment of inertia



What's bad about EM inversion? The forward model.

Dependent on a poorly known transport property rather than thermodynamic properties (i.e., more difficult to measure), more sensitive to contaminants and possibly texture.

$$\sigma = \sigma_0(x) T^m \exp\left[-H(P)/kT\right], \quad \sigma_0(x) = a + bx$$

Upper mantle: conductivities after Xu et al. 2000a,b (Cpx as a proxy for C2/c & akimotoite), no correction for mineral composition or oxygen fugacity (Mo-MoO₂)

Lower mantle: Wuestite $\sigma_0(x_{Mg})$ after Dobson & Brodholt (2000a); Perovskite $\sigma_0(x_{Al})$ after Xu & McCammon (2002, Goddat et al. 1999, Katsura et al. 1998); Al-free perovskite as a proxy Ca-perovskite

Aggregate conductivity computed as the volumetrically weighted geometric mean (Duba & Shankland 1990):

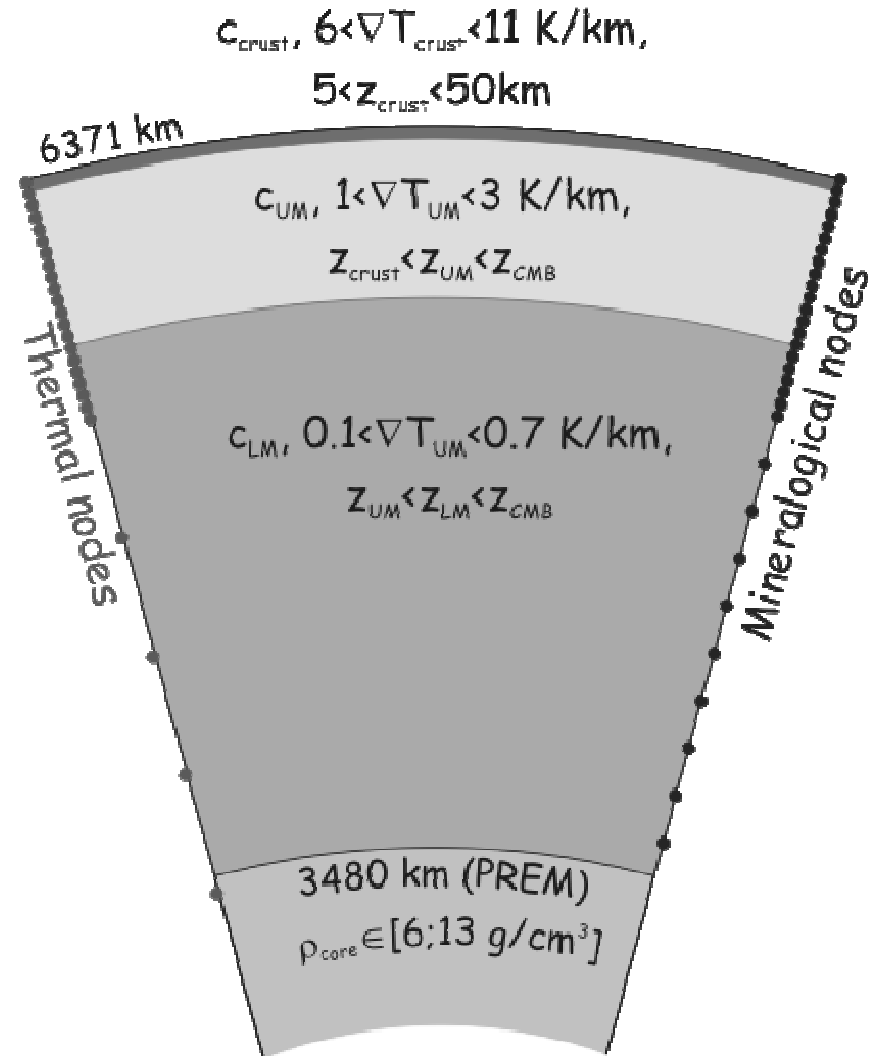
$$\sigma^{aggregate} = \prod_i \sigma_i^{f_i}, \quad f_i = \text{volume fraction mineral } i$$

Parameterization of the Physical Model

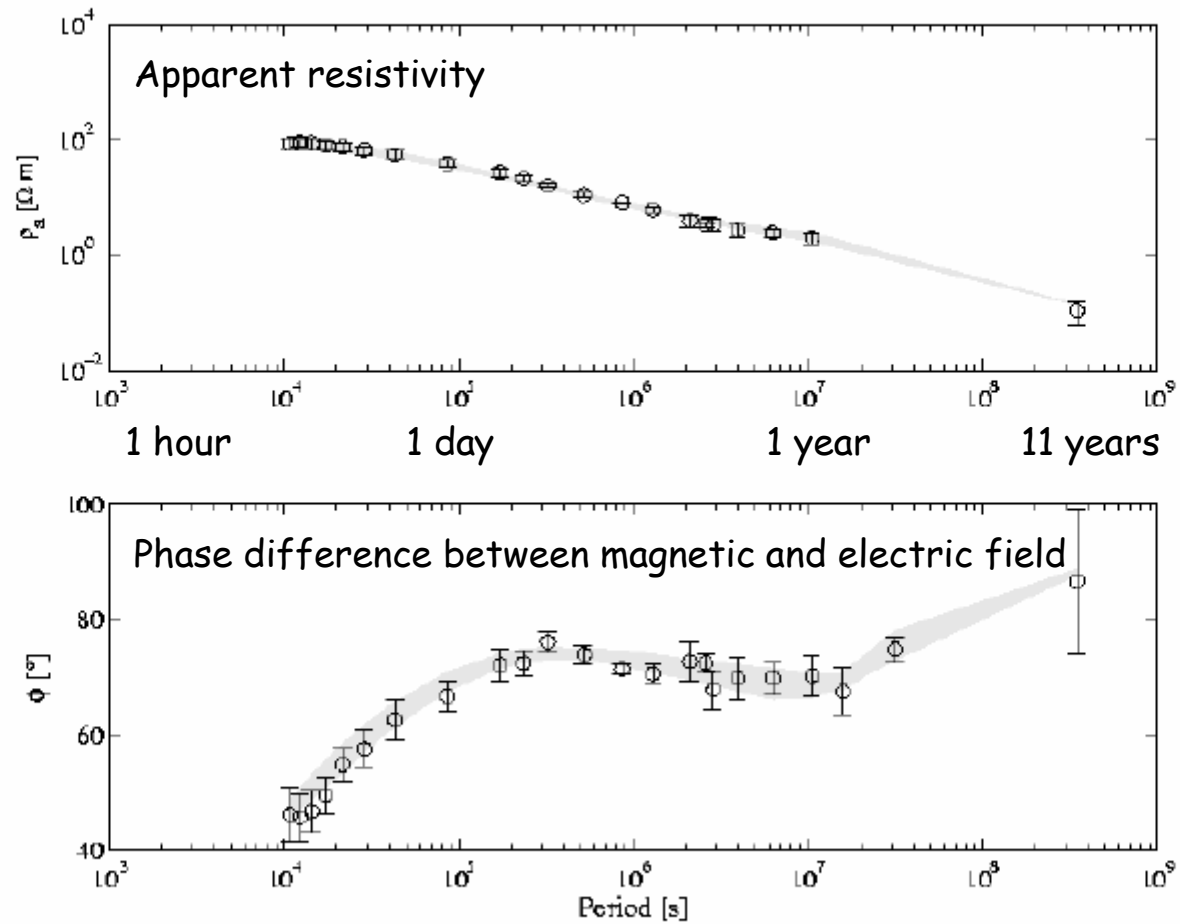
- Spherically symmetric 1-D model
- 3 silicate layers (crust, upper mantle and lower mantle)
- Parameterized by a composition thermal gradient and thickness
- Core parameterized by density

Compositional bounds (wt %)

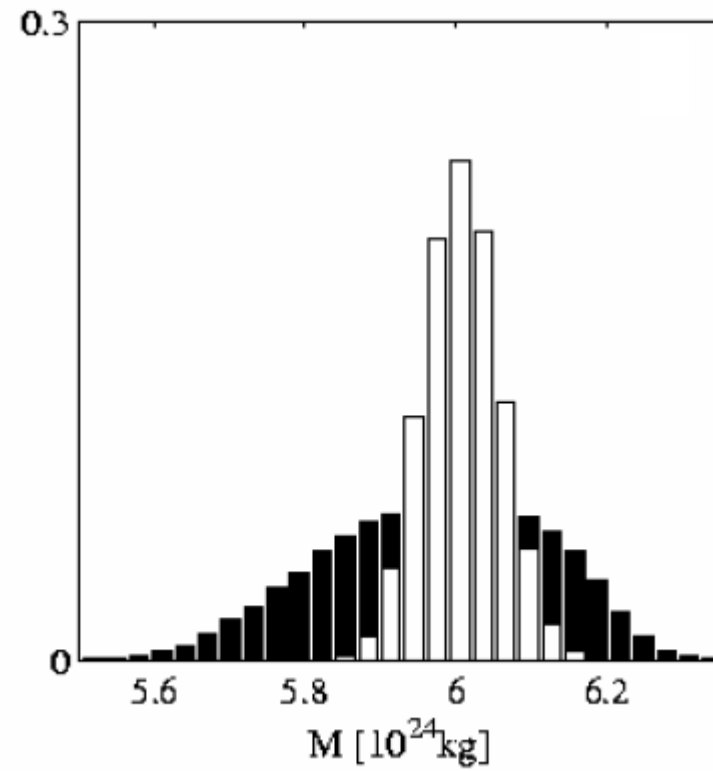
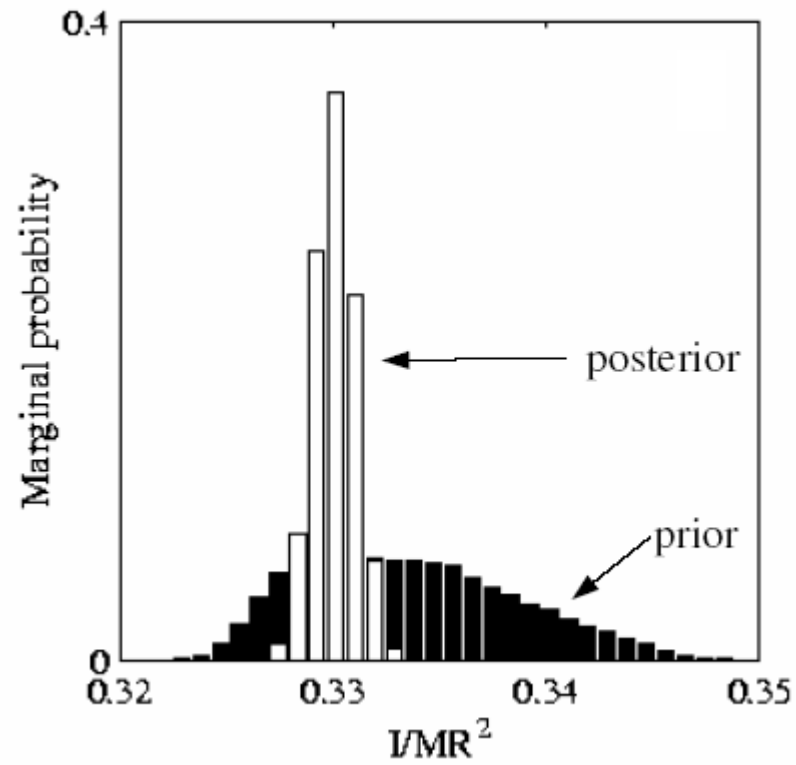
- $\text{CaO} \in [1;8]$
- $\text{FeO} \in [5;20]$
- $\text{MgO} \in [30;55]$
- $\text{Al}_2\text{O}_3 \in [1;8]$
- $\text{SiO}_2 \in [20;55]$



Data fit I: Predicted transfer function components

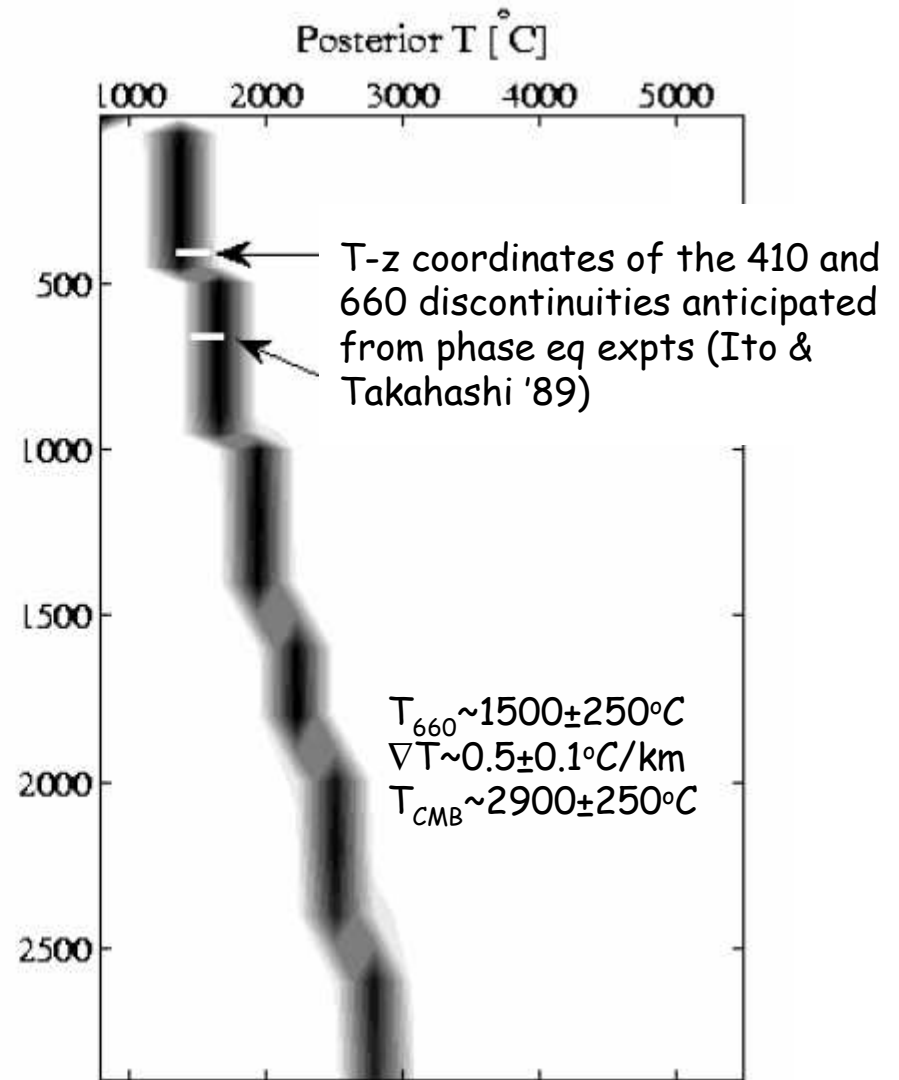
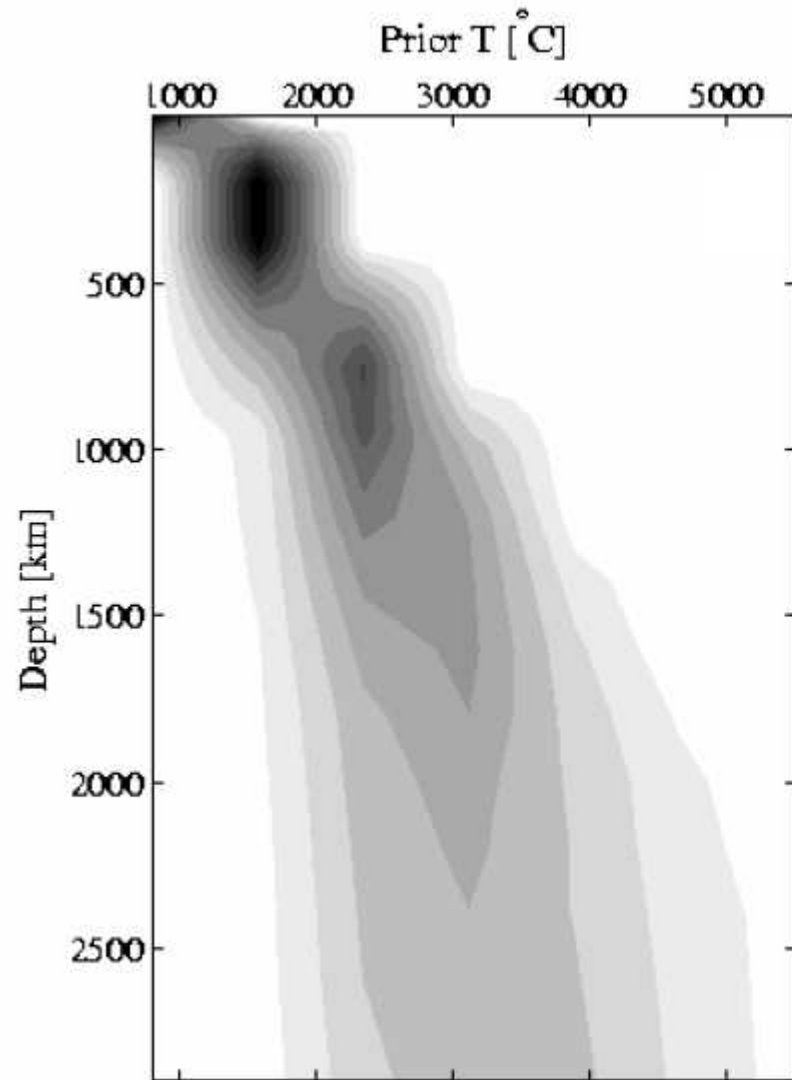


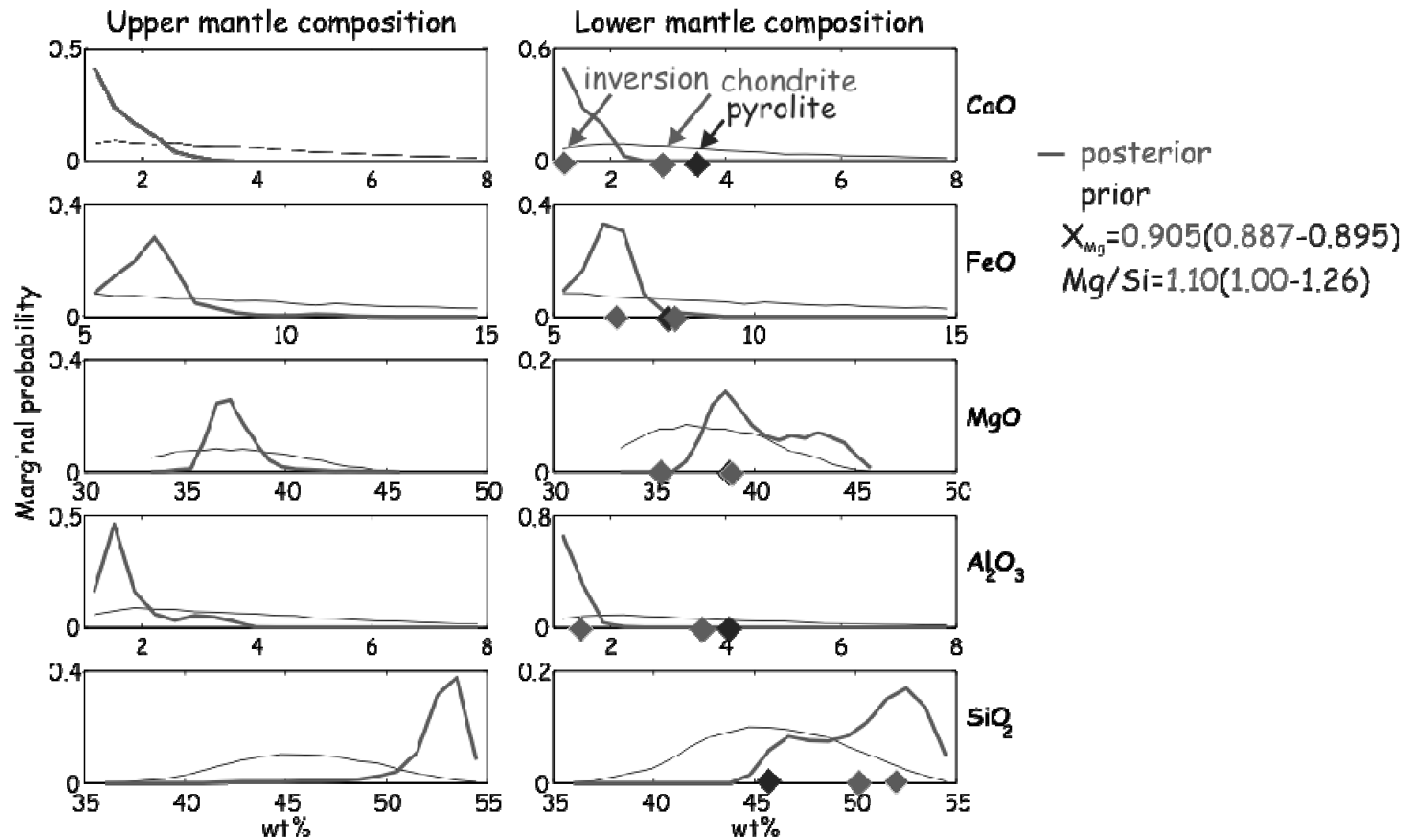
Data fit II: Mass (M) and Moment of Inertia (I)



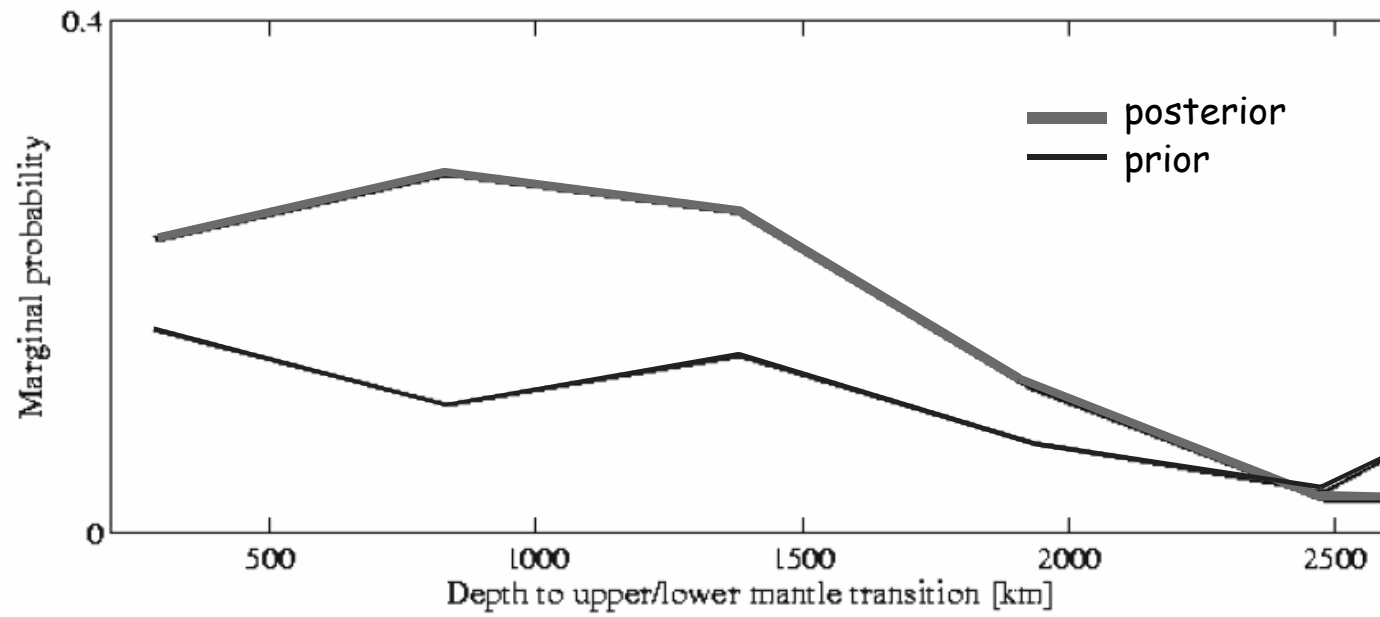
$\sim 10^6$ models

Thermal models

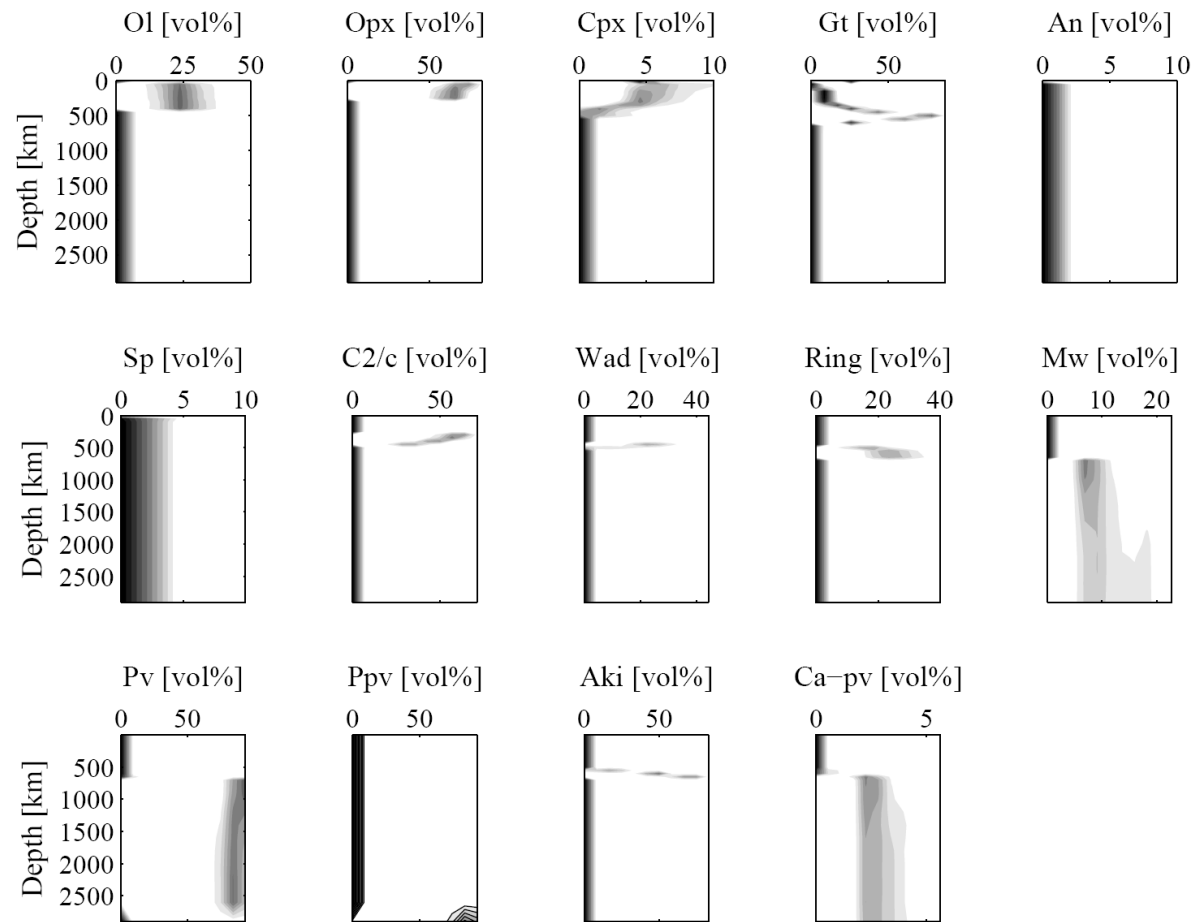




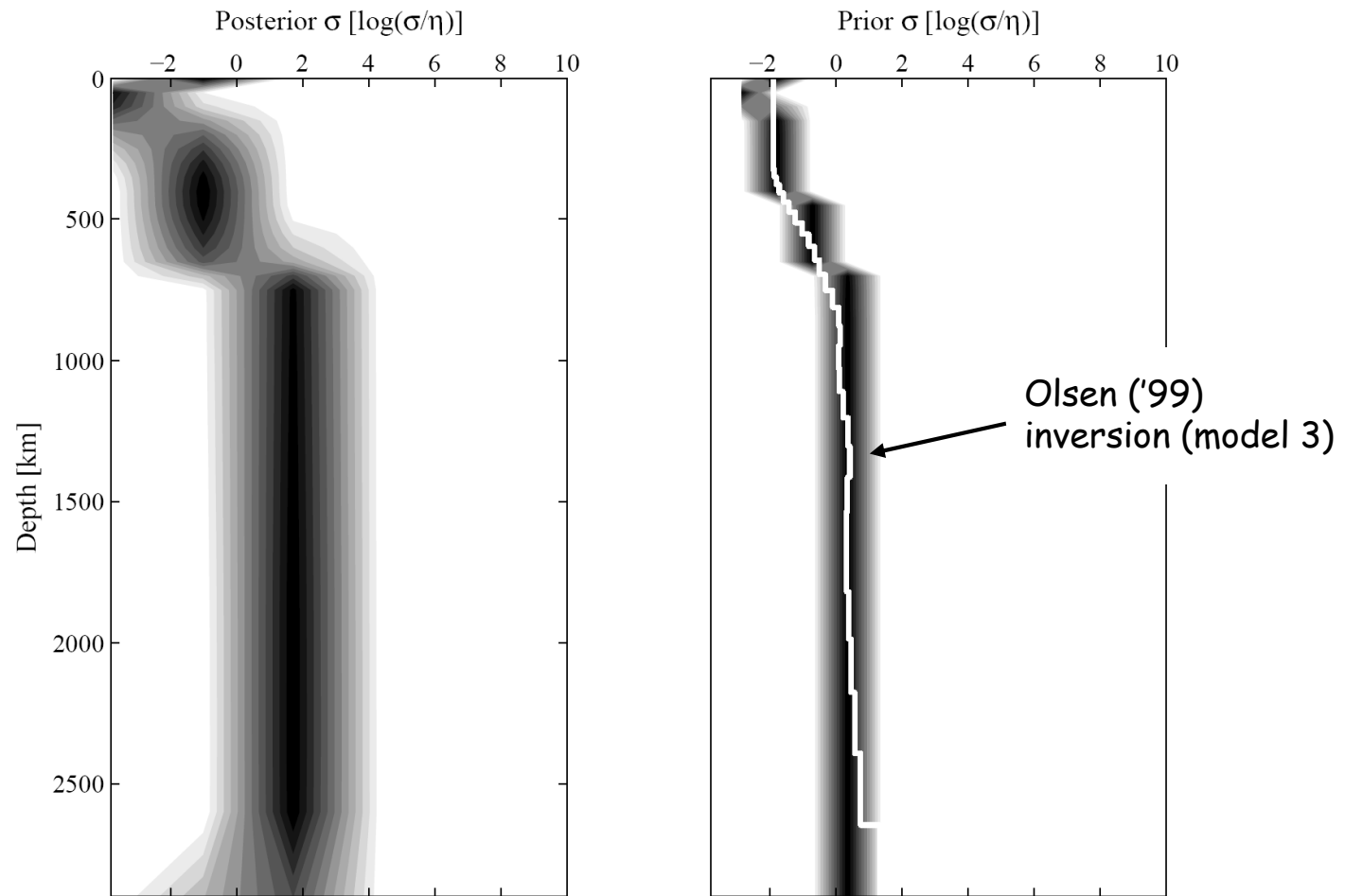
Is there a 660 layer?



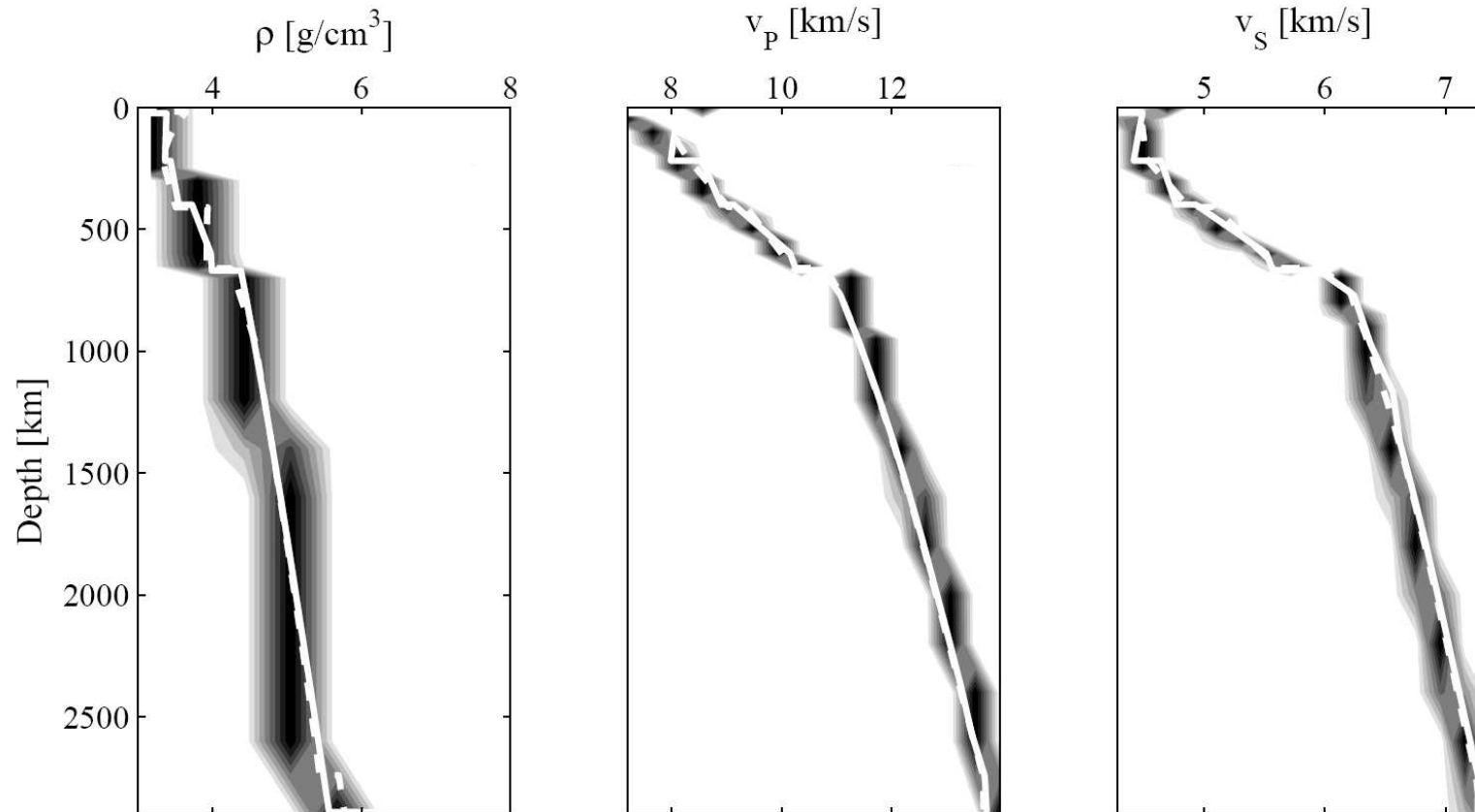
Mantle Mineralogy



Mantle Conductivity Profile



Density and Seismic Velocities

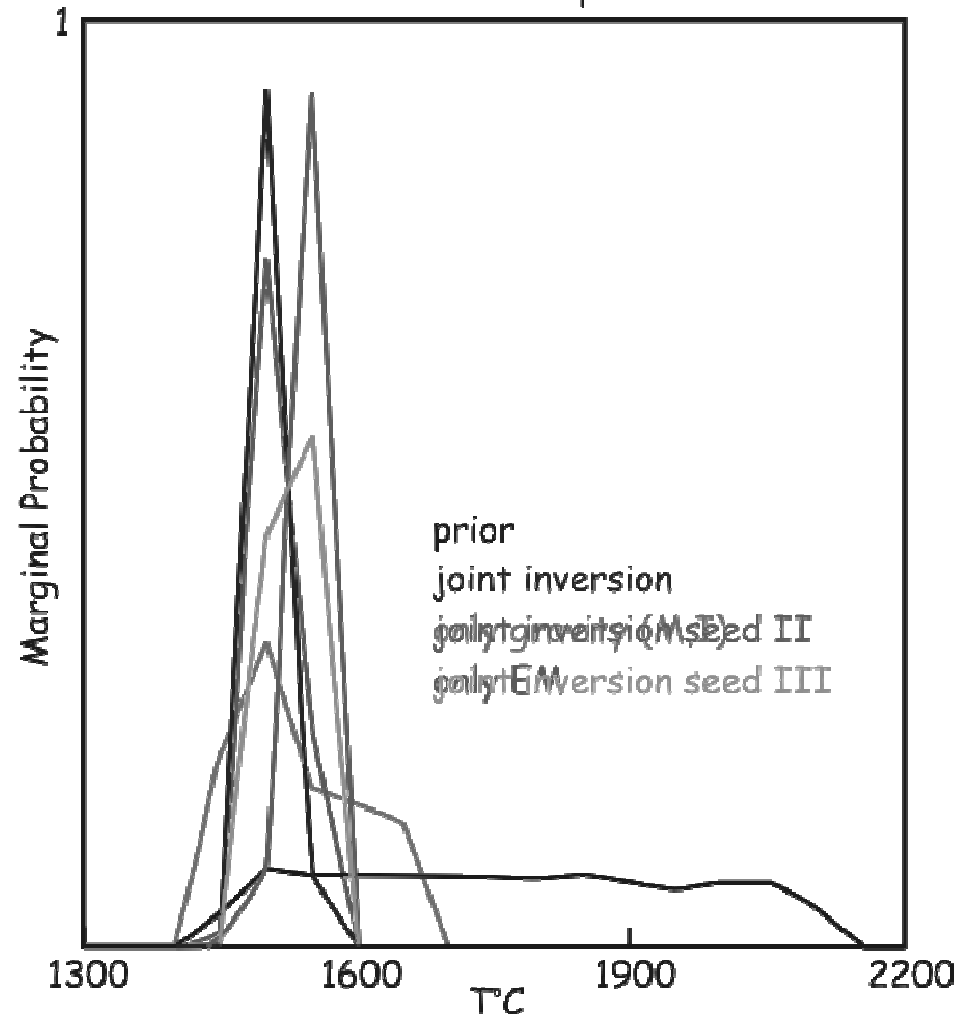


PREM (Dziewonski & Anderson '81) - solid white line

AK135 (Kennett et al. '95) - dashed white line

Resolution and Stability

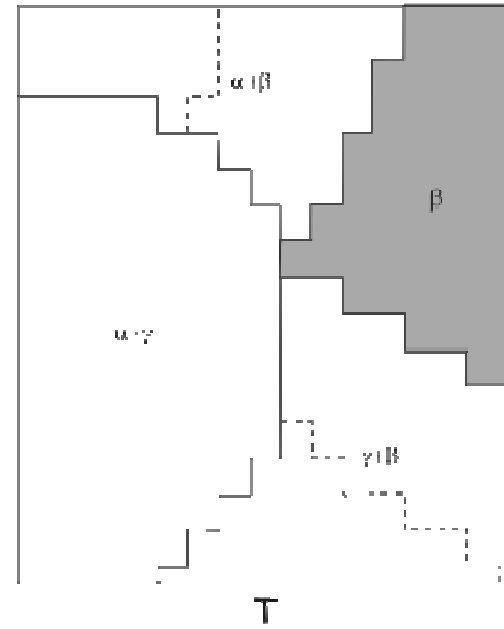
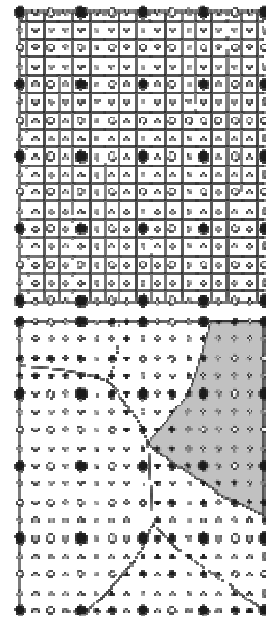
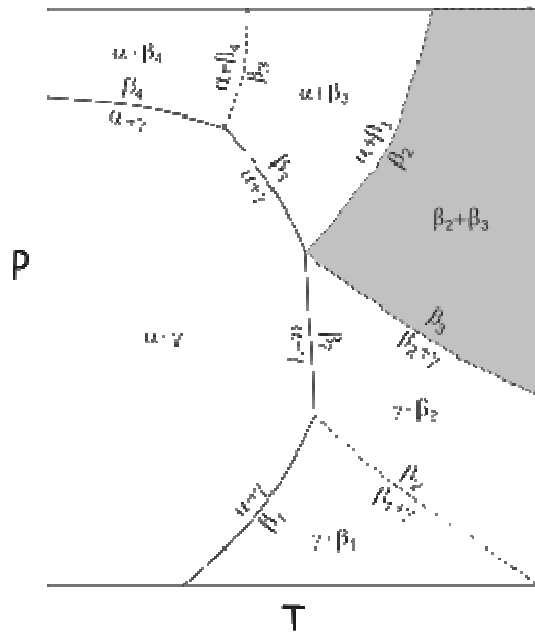
T at 450 km depth



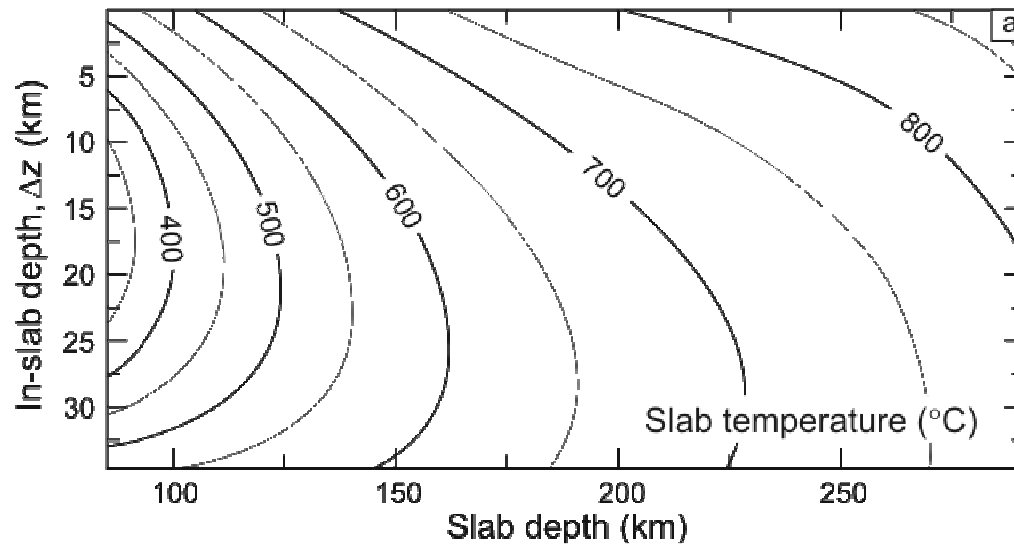
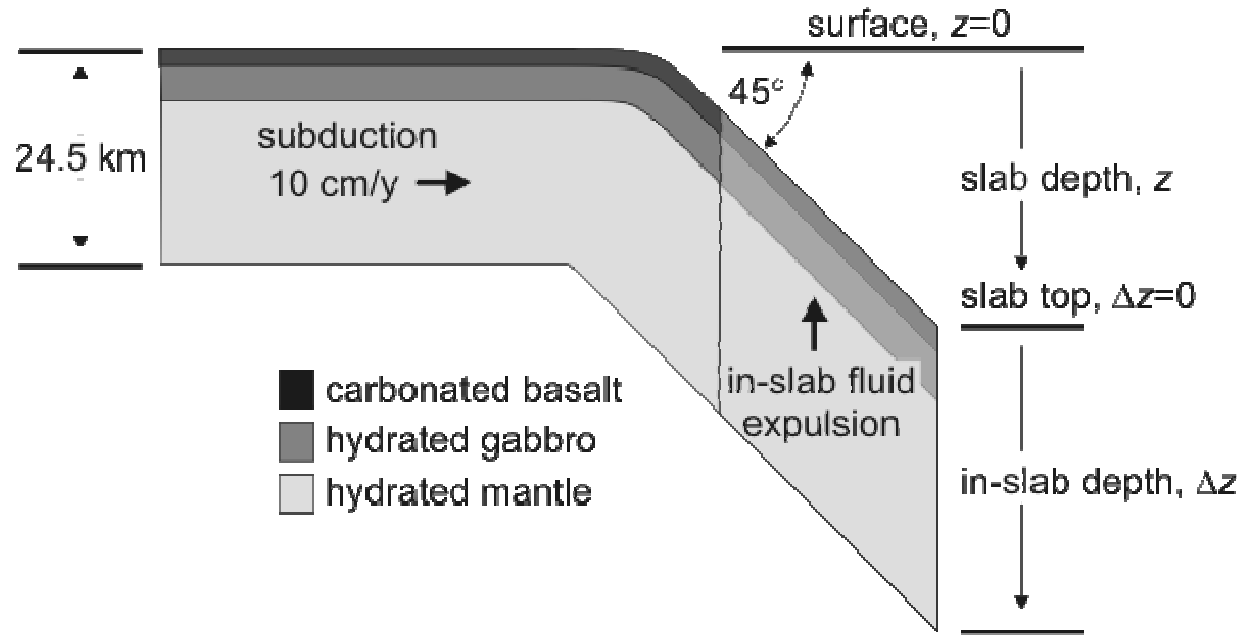
"This is not the end, this is not even the beginning of the end, perhaps it is the end of the beginning." -- Winston Churchill

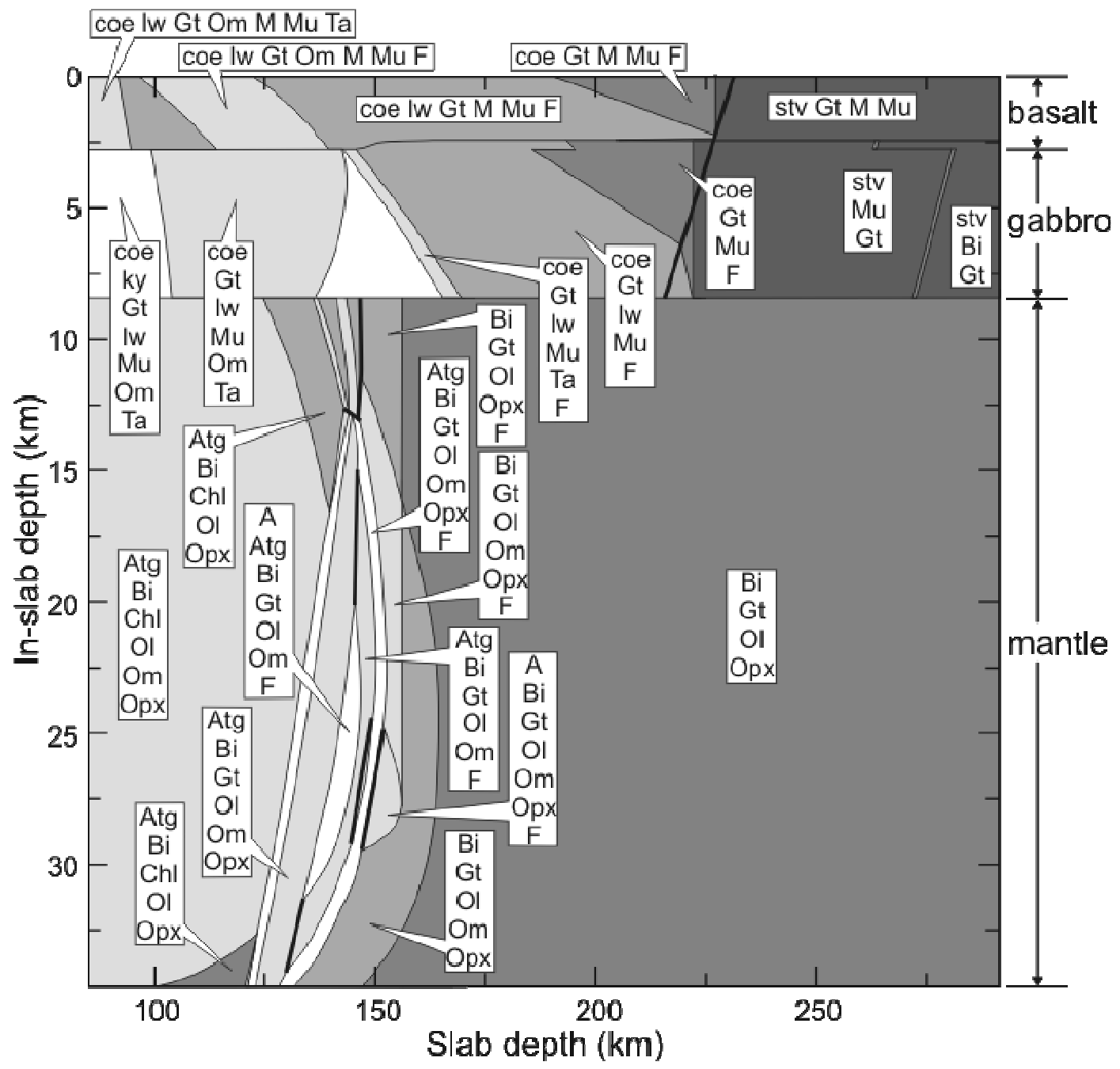
- Free energy minimization provides the basis for a general physical model that permits joint inversion of a priori unrelated geophysical data sets (seismic, gravity, electromagnetic)
- The EM inversion results suggest a relatively homogeneous, superadiabatic mantle of chondritic composition
- The results are surprisingly good given the limited experimental data used to construct the forward EM model and must be confirmed by inversion of seismic data

Mapping Strategy

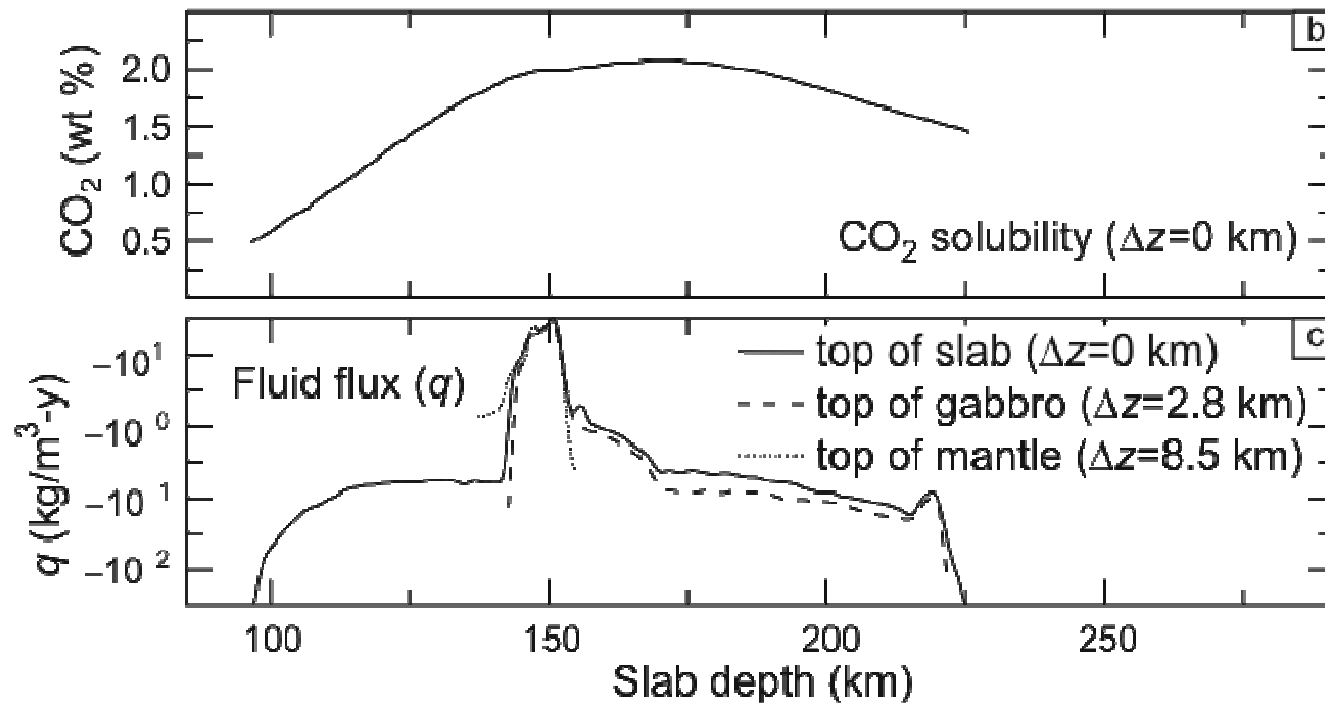


Slab Devolatilization Model Geometry

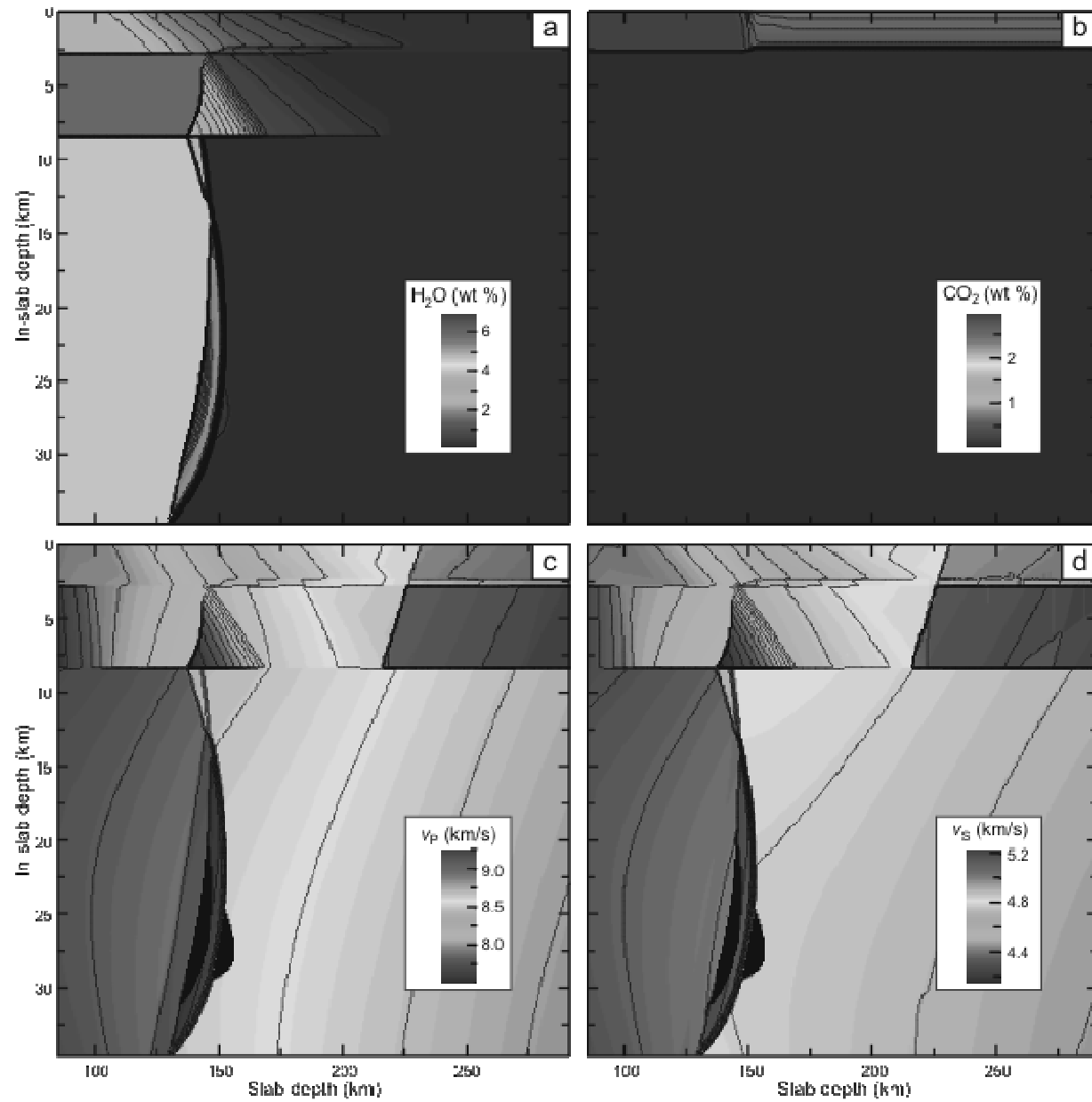




Slab fluid composition and production



Slab Properties



Free Energy Minimization by Linear Programming and Applications to Geophysical Inversion for Composition and Temperature

Free Energy Minimization - a method for predicting the thermodynamic (elastic) properties of rocks as a function of environmental variables (typically pressure and temperature)

→A forward model for rock properties: Geodynamic and Inversion calculations.

→A robust and efficient method.

→Some thoughts about cultural differences and data

→Two inversions for planetary composition and temperature

"Phase diagrams are the beginning of wisdom not the end of it."
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Inversion Strategy

- i) *Guess a physical configuration (T, c, d, ...)*
- ii) *Compute mineralogy and physical properties*
- iii) *Construct a forward model of the observed data*
- iv) *Test against observations*
- v) *Generate a new configuration, go to ii)*
- vi) *repeat 10^7 times*