Geophysics, Mineral Physics, and QMC

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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

<table>
<thead>
<tr>
<th>Depth</th>
<th>0</th>
<th>660</th>
<th>2890</th>
<th>5150</th>
<th>6371</th>
<th>km</th>
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<tbody>
<tr>
<td>Pressure</td>
<td>0</td>
<td>24</td>
<td>136</td>
<td>329</td>
<td>363</td>
<td>GPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>300</td>
<td>1800</td>
<td>3000</td>
<td>5500</td>
<td>6000</td>
<td>K</td>
</tr>
</tbody>
</table>
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

Earthquake: Jan Mayen Island (71.84N 1.49W), June 15, 1995, M=5.0

Recording: NARS station Naroch, Belarus, at 2300 km distance
Seismic networks

USArray

Global Seismic Network
Earthquake

Seismic phases

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

Radial
$S_r$ - 20.5 min
Breathing

Spheroidal
$S_r$ - 53.9 min
Football

Toroidal
$T_r$ - 43.8 min
Geoid

equipotential surface of the gravity field

Radial inhomogeneity

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

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

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

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

• 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 (1968) 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
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

Near surface
Old oceans fast
Young oceans slow
Cratons (old parts of continents) fast

Core-mantle boundary
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)

Explanation
- Elastic anisotropy of olivine
- Alignment of olivine crystals

\[ V_{avg} = 5.5 \text{ cm/yr} \]

Christensen & Salisbury (1979) JGR

Conrad & Lithgow-Bertelloni (2002) Science
Polarization anisotropy aka shear-wave splitting

Calcite: CaCO₃

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)

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...

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

Mantle xenoliths from San Carlos, Arizona

Eruption of Mt. Etna, October 28, 2002
Upper mantle xenolith: depth ~ 100 km

- yellow-green: olivine (ol) \( \text{Mg}_2\text{SiO}_4 \)
- black: orthopyroxene (opx) \( \text{Mg}_2\text{Si}_2\text{O}_6 \)
- green: clinopyroxene (cpx) \( \text{CaMgSi}_2\text{O}_6 \)
- red: garnet (gt) \( \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \) + 10 %Fe for Mg
Olivine, $\text{Mg}_2\text{SiO}_4$

- 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
Earth structure

Phase transformations
• Produce discontinuities
• Thermometers
• Influence dynamics

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

Stixrude & Lithgow-Bertelloni (2005) GJI
Phase equilibria

- Invert phase equilibria data for reference free energy, characteristic vibrational frequency
- Experimental Data
  - N~1000
  - CaO-FeO-MgO-Al$_2$O$_3$-SiO$_2$
  - One-component, two-component phase equilibria
  - Element partitioning

Stixrude and Lithgow-Bertelloni (2007)

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

Influence of phase transitions on mantle dynamics

Christensen (1995) Annual Reviews
Influence of phase transitions on mantle dynamics

Temperature  Composition

Nakagawa & Buffett (2005)
Upper mantle ~ Geology + half-space cooling
Lower mantle ~ Subduction history
Transition zone?

Ritsema et al. (2004)
Origin of lateral heterogeneity

Temperature

Composition

Radioactivity

Differentiation

Entropy

Latent Heat

Differentiation

Chemical Potential

Phase
Velocity-temperature scaling

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

Metamorphic term

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

\[
\begin{align*}
\nabla^2 + V_{KS}[\rho(\vec{r})]\psi_i(\vec{r}) &= \varepsilon_i \psi_i(\vec{r}) \\
V_{KS}[\rho(\vec{r})] &= V_N(\vec{r}) + \int \frac{\rho(\vec{r}')}{\vec{r} - \vec{r}'} d\vec{r}' + V_{xc}[\rho(\vec{r})]
\end{align*}
\]

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

\[ c_{ijkl} = \left( \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \right)_{T, \varepsilon'} = \frac{1}{V} \left( \frac{\partial^2 F}{\partial s_{ij} \partial s_{kl}} \right)_{s_{ij}', T} \]

Vanishes for isochoric \( \varepsilon \)

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

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

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

Steinle-Neumann et al. (1999) PRB
Stixrude & Lithgow-Bertelloni (2005) GJI
Methods: elastic constants 2

Variation of stress with strain

\[ \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \]

Density functional perturbation theory (linear response)

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

CaSiO$_3$ Perovskite

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 $\text{MgSiO}_3$

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

*Murakami et al. (2004) Science*
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
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

• 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?

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?

Ohtani (2005) Elements
Nominally anhydrous phases

- Stishovite
- Charge balance: $\text{Si}^{4+} \rightarrow \text{Al}^{3+} + \text{H}^+$
- 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

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

Garnero, 2006
Spin pairing transition

(Mg,Fe)O

Transition in Fe$^{2+}$ from

- high spin (4 unpaired electrons)
- 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$^{2+}$)

\[
C_{ijkl} = \frac{1}{4} \left[ \sum_{s=1}^{4} R_{im}^s R_{jn}^s R_{ko}^s R_{lp}^s \tilde{c}_{mnop} \right]
\]

Kiefer et al. (2002) GRL
Other planets

2M1207b

Chauvin et al. (2006)

Pressure-temperature regime of planets

Most Planets?
