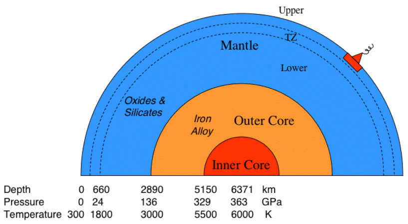
Mineral Physics

Questions…

7/25/04 CIDER/ITP Short Course

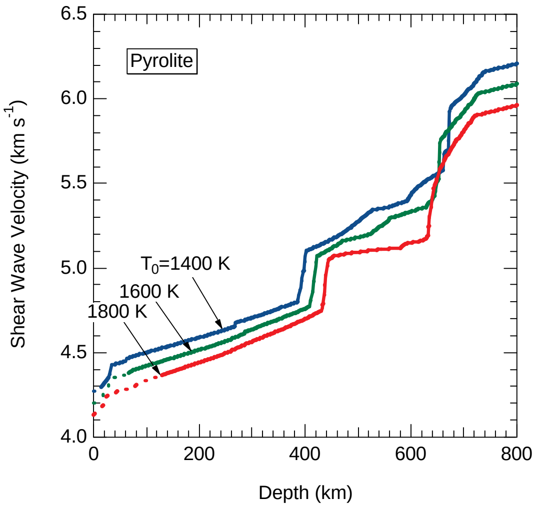
Boundaries

- Transition zone
- Core-Mantle
- Hydrosphere-Solid Earth
- Asthenosphere
- Defined by
  - Phase
  - Composition
  - Rheology
- Barriers?
  - Mass
  - Heat
  - Momentum



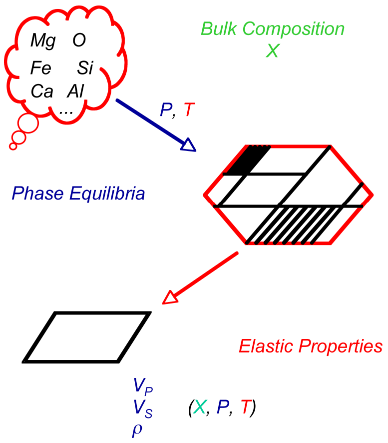
Transition Zone

- Velocity variations
  - Phase
  - Pressure
  - Temperature
  - Composition
- Discontinuities
  - Sharpness
  - Amplitude
  - Fine structure



Equilibrium Problem

- Bulk composition
- Pressure
- Temperature
- →
- Phase Equilibria
- Physical Properties



Bulk Composition
X

Phase Equilibria

Elastic Properties

V_P
V_S (*X*, *P*, *T*)
ρ

Fundamental Thermodynamic Relation

$$G(P,T,n_i) = \sum_{i=1}^{s} n_i G_i(P,T) + n_i RT \ln a_i$$

$$G_i(P,T) = F_i(V,T) + PV$$

$$F(V,T) = F_0 + af^2 + bf^3 + 9nRT(T/\theta)^3 \int_0^{\theta/T} \ln(1-e^t)\, t^2\, dt$$

$$\theta = \theta_0 \exp\left(\frac{\gamma_0 - \gamma}{q_0}\right)$$

Compute all equilibrium properties from strain/temperature derivatives, e.g.

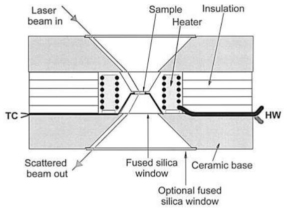
$$c_{ijkl}(V,T) = (1+2f)^{5/2}\left(c_{ijkl0} + (3K_0 c'_{ijkl0} - 5c_{ijkl0})\, f + \ldots\right)$$

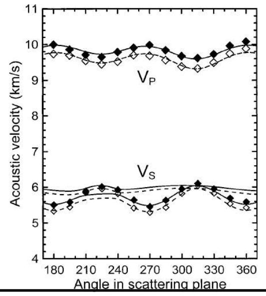
$$+(\gamma\delta_{ij}\delta_{kl} + \gamma_{ij}\gamma_{kl} - \eta_{ijkl})\frac{\Delta U_{TH}(V,T)}{V}$$

$$\eta_{ijkl} \approx \gamma q \delta_{ij}\delta_{kl} + \eta_S\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right)$$

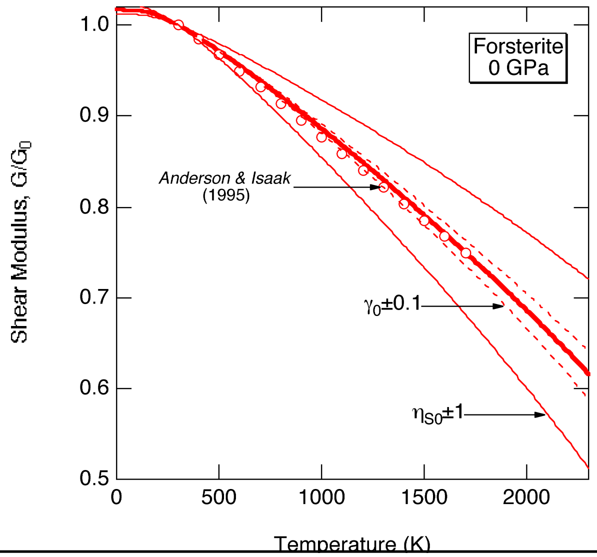
Elastic constants at elevated P/T

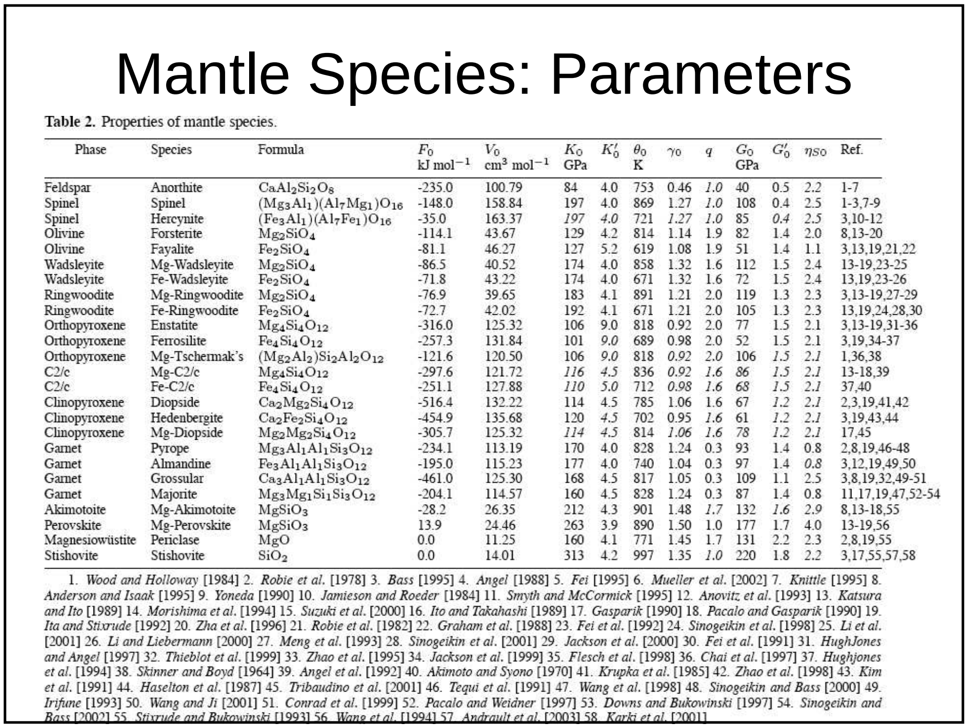
- Static compression
  - ω~0
- Dynamic compression
  - ω~MHz-GHz
- Brillouin spectroscopy
  - ω~THz, λ=500 nm, $k \rightarrow 0$
- Ultrasonic
  - ω~MHz-GHz





Shear modulus





Mantle Species: Parameters

Table 2. Properties of mantle species.

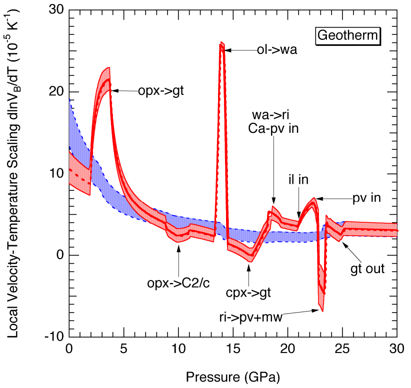
Phase	Species	Formula	F_0 kJ mol^{-1}	V_0 cm^3 mol^{-1}	K_0 GPa	K'_0	θ_0 K	γ_0	q	G_0 GPa	G'_0	η_{S0}	Ref.
Feldspar	Anorthite	$CaAl_2Si_2O_8$	-235.0	100.79	84	4.0	753	0.46	*1.0*	40	0.5	*2.2*	1-7
Spinel	Spinel	$(Mg_3Al_1)(Al_7Mg_1)O_{16}$	-148.0	158.84	197	4.0	869	1.27	*1.0*	108	0.4	2.5	1-3,7-9
Spinel	Hercynite	$(Fe_3Al_1)(Al_7Fe_1)O_{16}$	-35.0	163.37	*197*	*4.0*	721	*1.27*	*1.0*	85	*0.4*	2.5	3,10-12
Olivine	Forsterite	Mg_2SiO_4	-114.1	43.67	129	4.2	814	1.14	1.9	82	1.4	2.0	8,13-20
Olivine	Fayalite	Fe_2SiO_4	-81.1	46.27	127	5.2	619	1.08	1.9	51	1.4	1.1	3,13,19,21,22
Wadsleyite	Mg-Wadsleyite	Mg_2SiO_4	-86.5	40.52	174	4.0	858	1.32	1.6	112	1.5	2.4	13-19,23-25
Wadsleyite	Fe-Wadsleyite	Fe_2SiO_4	-71.8	43.22	174	4.0	671	1.32	1.6	72	1.5	2.4	13,19,23-26
Ringwoodite	Mg-Ringwoodite	Mg_2SiO_4	-76.9	39.65	183	4.1	891	1.21	2.0	119	1.3	2.3	3,13-19,27-29
Ringwoodite	Fe-Ringwoodite	Fe_2SiO_4	-72.7	42.02	192	4.1	671	1.21	2.0	105	1.3	2.3	13,19,24,28,30
Orthopyroxene	Enstatite	$Mg_4Si_4O_{12}$	-316.0	125.32	106	9.0	818	0.92	2.0	77	1.5	2.1	3,13-19,31-36
Orthopyroxene	Ferrosilite	$Fe_4Si_4O_{12}$	-257.3	131.84	101	*9.0*	689	0.98	2.0	52	1.5	2.1	3,19,34-37
Orthopyroxene	Mg-Tschermak's	$(Mg_2Al_2)Si_2Al_2O_{12}$	-121.6	120.50	106	*9.0*	818	*0.92*	*2.0*	106	*1.5*	*2.1*	1,36,38
C2/c	Mg-C2/c	$Mg_4Si_4O_{12}$	-297.6	121.72	*116*	*4.5*	836	*0.92*	*1.6*	*86*	*1.5*	*2.1*	13-18,39
C2/c	Fe-C2/c	$Fe_4Si_4O_{12}$	-251.1	127.88	*110*	*5.0*	712	*0.98*	*1.6*	*68*	*1.5*	*2.1*	37,40
Clinopyroxene	Diopside	$Ca_2Mg_2Si_4O_{12}$	-516.4	132.22	114	4.5	785	1.06	1.6	67	*1.2*	*2.1*	2,3,19,41,42
Clinopyroxene	Hedenbergite	$Ca_2Fe_2Si_4O_{12}$	-454.9	135.68	120	*4.5*	702	0.95	*1.6*	61	*1.2*	*2.1*	3,19,43,44
Clinopyroxene	Mg-Diopside	$Mg_2Mg_2Si_4O_{12}$	-305.7	125.32	*114*	*4.5*	814	*1.06*	*1.6*	*78*	*1.2*	*2.1*	17,45
Garnet	Pyrope	$Mg_3Al_1Al_1Si_3O_{12}$	-234.1	113.19	170	4.0	828	1.24	0.3	93	1.4	0.8	2,8,19,46-48
Garnet	Almandine	$Fe_3Al_1Al_1Si_3O_{12}$	-195.0	115.23	177	4.0	740	1.04	0.3	97	1.4	*0.8*	3,12,19,49,50
Garnet	Grossular	$Ca_3Al_1Al_1Si_3O_{12}$	-461.0	125.30	168	4.5	817	1.05	0.3	109	1.1	2.5	3,8,19,32,49-51
Garnet	Majorite	$Mg_3Mg_1Si_1Si_3O_{12}$	-204.1	114.57	160	4.5	828	1.24	0.3	87	1.4	0.8	11,17,19,47,52-54
Akimotoite	Mg-Akimotoite	$MgSiO_3$	-28.2	26.35	212	4.3	901	1.48	*1.7*	132	*1.6*	*2.9*	8,13-18,55
Perovskite	Mg-Perovskite	$MgSiO_3$	13.9	24.46	263	3.9	890	1.50	1.0	177	1.7	4.0	13-19,56
Magnesiowüstite	Periclase	MgO	0.0	11.25	160	4.1	771	1.45	1.7	131	2.2	2.3	2,8,19,55
Stishovite	Stishovite	SiO_2	0.0	14.01	313	4.2	997	1.35	*1.0*	220	1.8	*2.2*	3,17,55,57,58

1. *Wood and Holloway* [1984] 2. *Robie et al.* [1978] 3. *Bass* [1995] 4. *Angel* [1988] 5. *Fei* [1995] 6. *Mueller et al.* [2002] 7. *Knittle* [1995] 8. *Anderson and Isaak* [1995] 9. *Yoneda* [1990] 10. *Jamieson and Roeder* [1984] 11. *Smyth and McCormick* [1995] 12. *Anovitz et al.* [1993] 13. *Katsura and Ito* [1989] 14. *Morishima et al.* [1994] 15. *Suzuki et al.* [2000] 16. *Ito and Takahashi* [1989] 17. *Gasparik* [1990] 18. *Pacalo and Gasparik* [1990] 19. *Ita and Stixrude* [1992] 20. *Zha et al.* [1996] 21. *Robie et al.* [1982] 22. *Graham et al.* [1988] 23. *Fei et al.* [1992] 24. *Sinogeikin et al.* [1998] 25. *Li et al.* [2001] 26. *Li and Liebermann* [2000] 27. *Meng et al.* [1993] 28. *Sinogeikin et al.* [2001] 29. *Jackson et al.* [2000] 30. *Fei et al.* [1991] 31. *HughJones and Angel* [1997] 32. *Thieblot et al.* [1999] 33. *Zhao et al.* [1995] 34. *Jackson et al.* [1999] 35. *Flesch et al.* [1998] 36. *Chai et al.* [1997] 37. *Hughjones et al.* [1994] 38. *Skinner and Boyd* [1964] 39. *Angel et al.* [1992] 40. *Akimoto and Syono* [1970] 41. *Krupka et al.* [1985] 42. *Zhao et al.* [1998] 43. *Kim et al.* [1991] 44. *Haselton et al.* [1987] 45. *Tribaudino et al.* [2001] 46. *Tequi et al.* [1991] 47. *Wang et al.* [1998] 48. *Sinogeikin and Bass* [2000] 49. *Irifune* [1993] 50. *Wang and Ji* [2001] 51. *Conrad et al.* [1999] 52. *Pacalo and Weidner* [1997] 53. *Downs and Bukowinski* [1997] 54. *Sinogeikin and Bass* [2002] 55. *Stixrude and Bukowinski* [1993] 56. *Wang et al.* [1994] 57. *Andrault et al.* [2003] 58. *Karki et al.* [2001]

Origin of Lateral Heterogeneity

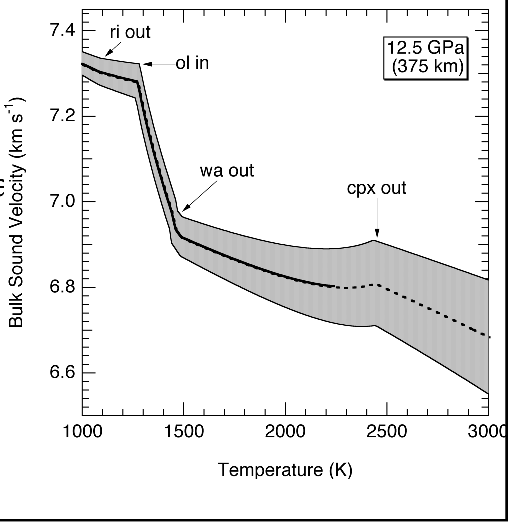
- How does velocity depend on temperature at constant depth (pressure)?
- Assume fixed composition
- Temperature influences
  - Properties of phases
  - Proportions of phases

$\boxed{f\Delta\ln V\Gamma_{eff}/\Delta P}$



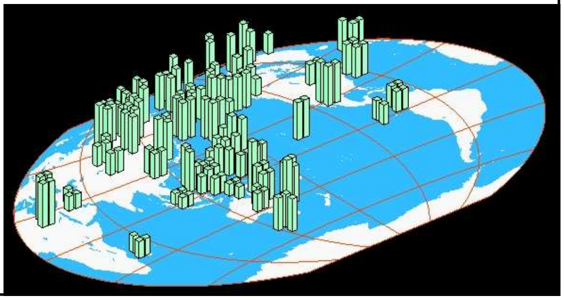
Velocity vs. Temperature

- Start with tomographic model
- Convert
  - Seismic wave velocity at a point to
  - Temperature



New phases?

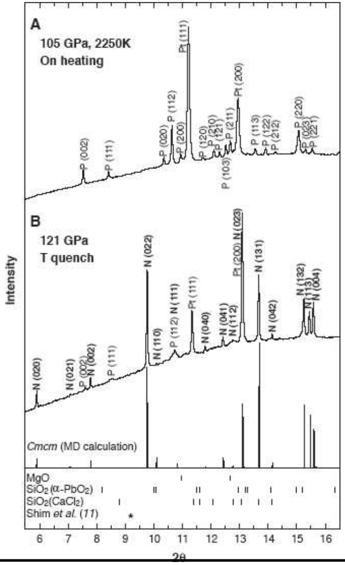
- Velocity contrast associated with phase changes are large compared with other sources of lateral heterogeneity
- Heat, volume of transformation may influence dynamics
- Are Mg-pv forming reactions the last?



Kendall & Shearer (1994) JGR

Post-perovskite phase

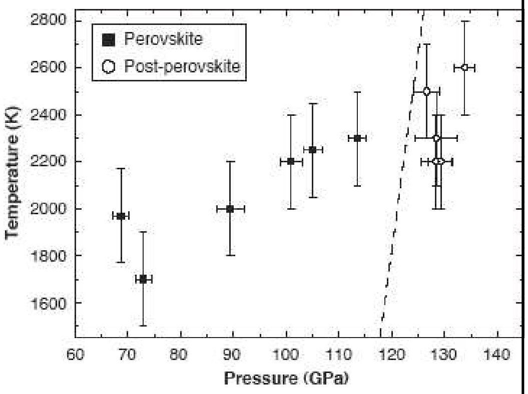
- Starting material
  - $MgSiO_3$+Pt
- Laser heated diamond anvil cell
  - Pressure: Pt equation of state
  - Temperature: spectroradiometry
- Probe
  - X-ray diffraction



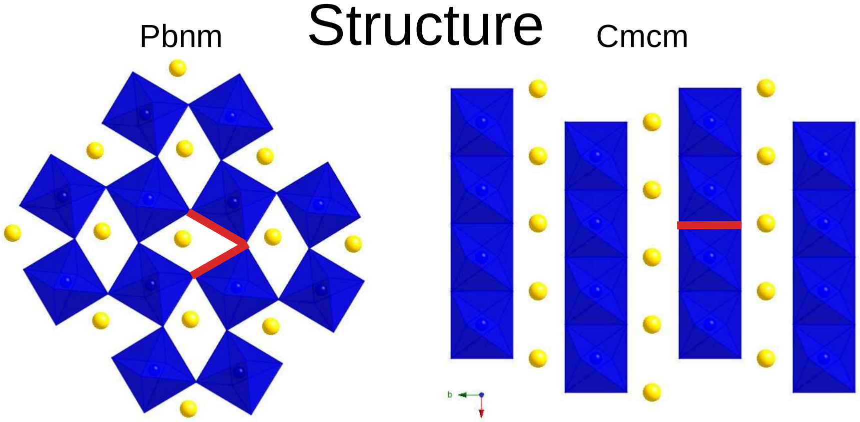
Murakami et al., Science, 304, 855, 2004

Phase transition

- Pressure ~ 120 Gpa
- Depth ~ 2600 km
- Density contrast=1 %
- Unconstrained by experiment
  - Clapeyron slope
  - Effect of other elements
  - Seismic wave velocities



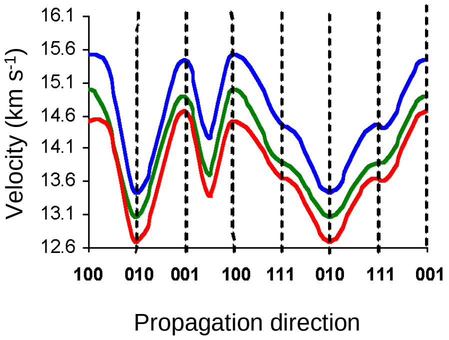
Structure



- Cmcm structure
- Layered
  - Anisotropic
  - Strongly preferred glide plane (010)
  - Flexible: Ca incorporation?
- Edge sharing octahedra
  - Lower entropy: positive Clapeyron slope

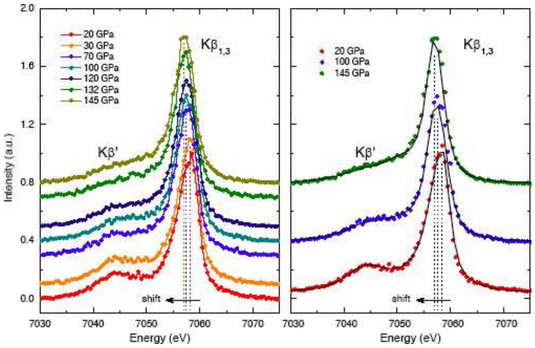
Elasticity

- Theory
- P,S azimuthal anisotropy ~ 20%
- Shear-wave splitting ~ 20%



Stackhouse et al., EPSL, submitted

New Physics



- High spin to low spin transition in (Mg,Fe)SiO$_3$ perovskite?

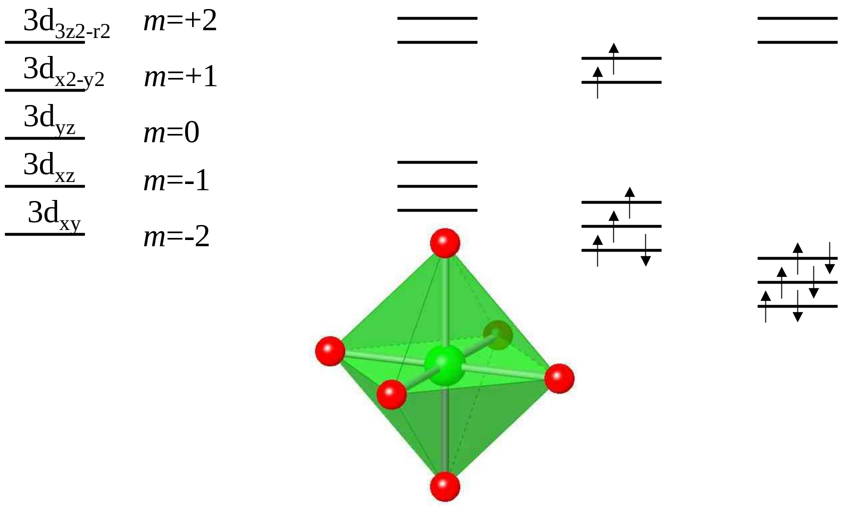
Badro et al., Science, 305, 383, 2004

Multi-electron atom
in a crystal field

Fe^{2+}

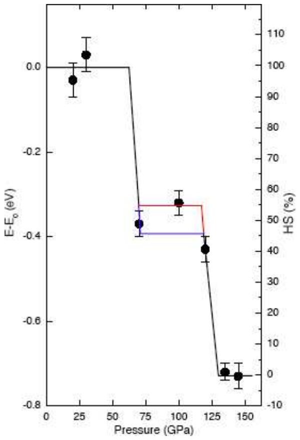
High Spin

Low Spin



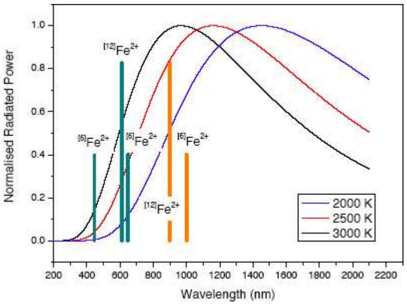
Spin transition in perovskite

- Energy of satellite changes with pressure
- Expect no change in absence of change in local electronic structure
- Compare energies with other high spin and low spin compounds
- Intermediate state?
  - Fe^{3+}?
  - A and B site occupancy?
- Cmcm?
  - Possibly at highest pressure



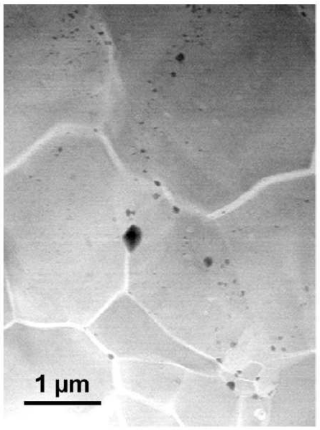
Heat transport

- Convection
  - Mass
- Conduction
  - Phonons
- Radiation
  - Photons
  - Black body radiation
  - Requires transparency, i.e. limited absorportion, scattering of light in BB spectrum



New Chemistry

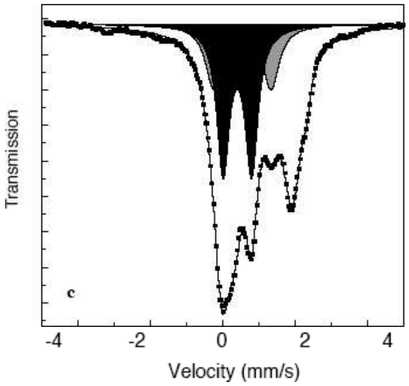
- Upper mantle minerals
  - Fe^{2+}
  - Olivine $(Mg,Fe)_2SiO_4$
- Lower mantle minerals?
- Fe^{2+}, Fe^{3+}, $Fe^{\pm x}$?
- Issues
  - Crystal chemistry
  - Mass balance
  - Chemical potential of oxygen (oxygen fugacity)
  - Meaning of valence at high pressure



Frost et al., Nature, 428, 409, 2004
Lauterbach et al., CMP, 138, 17, 2000

How to make Fe^{3+}?

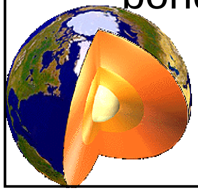
- Three possibilities
- Preferred by authors
  - $3Fe^{2+}O = Fe^{3+}{}_2O_3 + Fe^0$
  - May require vacancies
- Reaction with air
  - $2Fe^{2+}O + 1/2O_2 = Fe^{3+}{}_2O_3$
  - May not account for Fe metal
- Metallization?
  - $Fe^{2+}O = Fe^{3+}O + e^-$
  - What would this look like to Mossbauer?



Mossbauer spectrum

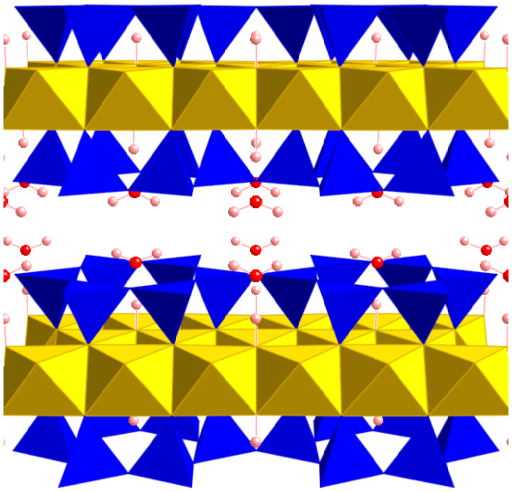
Water in the Earth’s Interior

- How much?
- What is the capacity (solubility)?
- How is it incorporated in crystal structures?
- Hydrous phases vs. nominally anhydrous phases
- High pressure physics of hydrogen bond



Hydrous phases

- Transport of water to deep mantle in subduction zones?
- 10 Å Phase
- Hydroxyl and water molecules
- Variable amounts of water

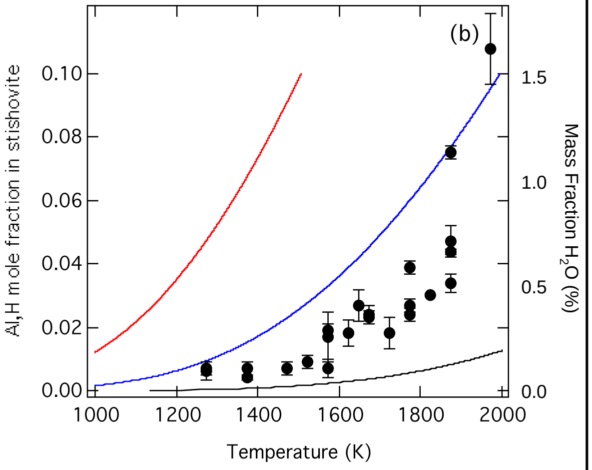


Fumagalli et al. (2002) EPSL

Nominally anhydrous phases

- 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

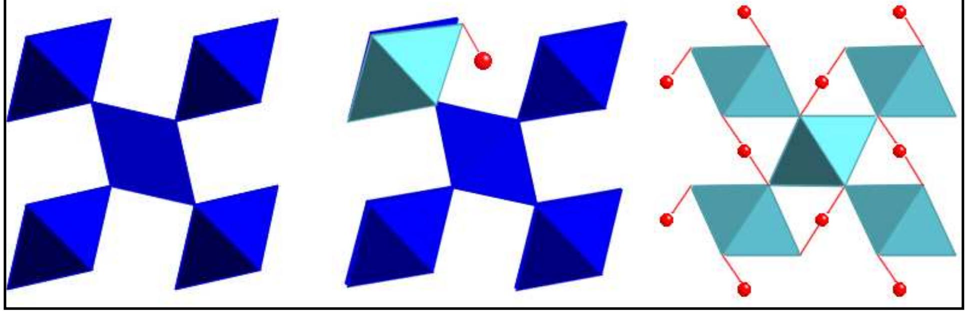


Panero & Stixrude (2004) EPSL

Physics of hydrogen bond at high pressure

- Low pressure asymmetric O-H…O
- High pressure symmetric O-H-O
- Implications for
  - Elasticity, transport, strength, melting

Panero & Stixrude (2004) EPSL



“Asthenosphere”

- Attenuation is an activated process
- Arrhenius relation
  - $Q=Q_0\exp[-(\Delta E+P\Delta V)/RT]$
- Weertman relation
  - $Q=Q_0\exp(-\beta T_m/T)$
- Homologous temperature
  - T/T_m