Thermodynamics

Lars Stixrude

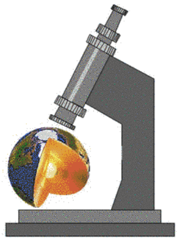
Mineral Physics Program

Lectures

- Lecture 1. Introduction to Thermodynamics (Lars)
- Lecture 2. Mineralogy and Crystal Chemistry (Lars)
- Lecture 3. Lattice dynamics and Statistical Mechanics (Tom)
- Lecture 4. Phase Equilibria (Marc)
- Lecture 5. Elasticity (Tom)
- Lecture 6. Fluids and Melts (Marc)

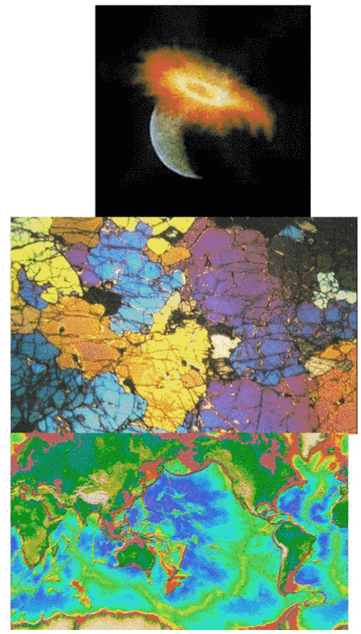
Tutorials

- 1. Constructing Earth Models (Lars)
- 2. MELTS (Marc)
- 3. Experimental Data (Tom)

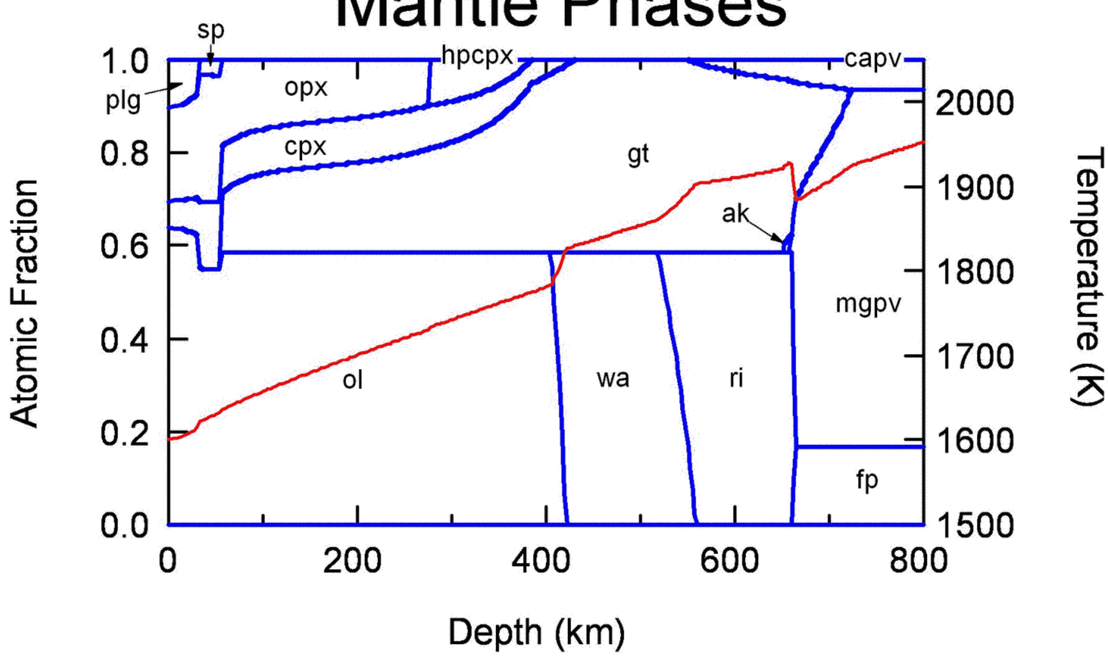


How does Earth respond?

- To changes in energy
  - Change in temperature (Heat Capacity)
  - Change in Density (thermal expansivity)
  - Phase Transformations (Gibbs free energy)
- To hydrostatic stress
  - Compression (bulk modulus)
  - Adiabatic heating (Grüneisen parameter)
- To deviatoric stress
  - Elastic deformation (elastic constants)
  - Flow (viscosity)
  - Failure (state and rate dependent friction)
- Rates of Transport of
  - Mass (chemical diffusivity)
  - Energy (thermal diffusivity)
  - Momentum (viscosity, attenuation)
  - Charge (electrical conductivity)



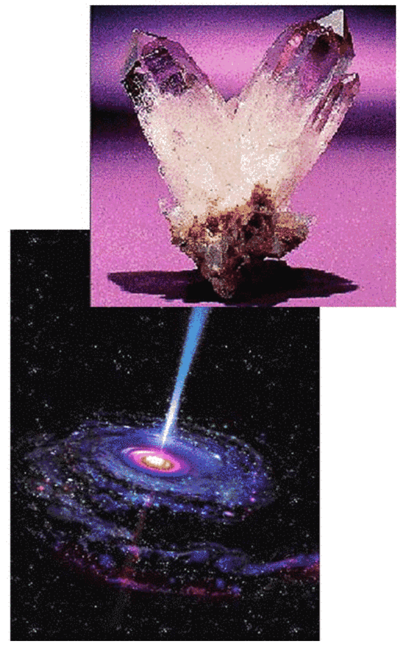
Mantle Phases



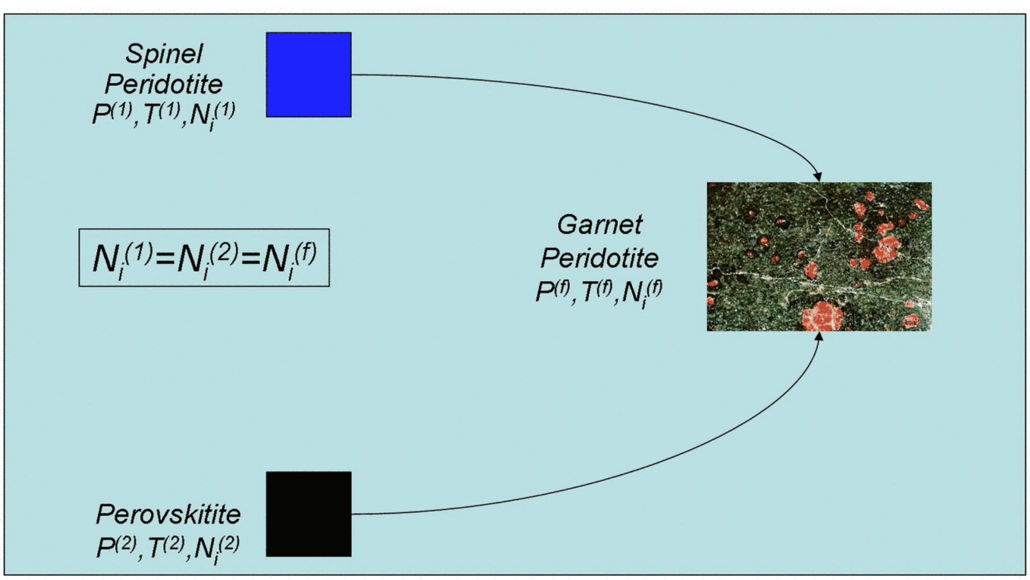
Wadsleyite (wa); Ringwoodite (ri); akimotoite (ak); Mg-perovskite (mgpv); Ca-perovskite (capv); Ferropericlase (fp)

Scope of Thermodynamics

- Applicable to any system
- Only to a certain set of states, called equlibrium states
- Only to certain properties of those states: macroscopic
- No specific, quantitative predictions, instead, limits and relationships

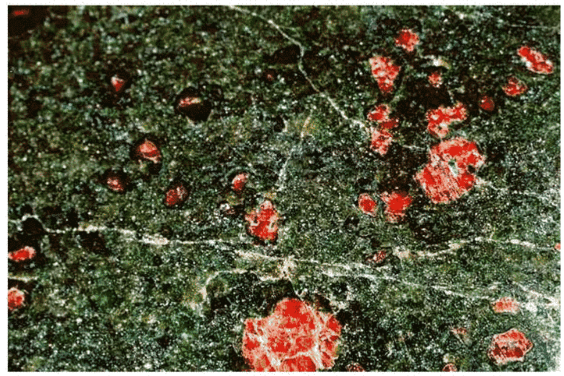


Equilibrium



Macroscopic Properties

- Volume (Density)
- Entropy
- Energy
- Proportions of Phases
- Composition of Phases
- …
- Not
  - Crystal size
  - Crystal shape
  - Details of arrangement



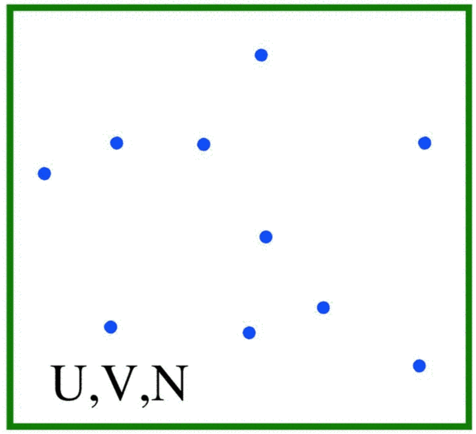
Thermodynamic Variables

- Second Order
  - Heat capacity $C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,Ni}$
  - Thermal expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,Ni}$
  - Bulk modulus $K_S = -V\left(\frac{\partial P}{\partial V}\right)_{S,Ni}$
  - Grüneisen parameter $\gamma = -\frac{V}{T}\left(\frac{\partial T}{\partial V}\right)_{S,Ni}$
- First Order
  - V: Volume,
  - S: Entropy
  - N_i: Amount of components
  - P: Pressure
  - T: Temperature
  - μ_i : Chemical Potential

Foundations 1

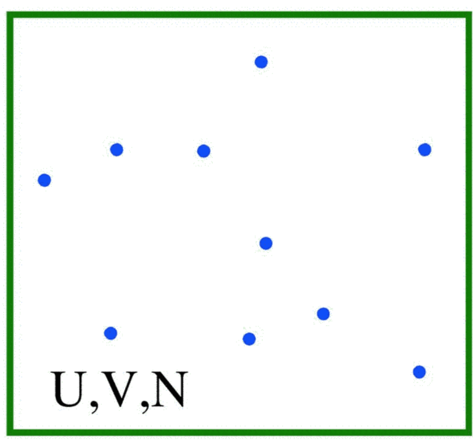
H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2ed, Wiley, 1985

- What defines the equilibrium state of our system?
  - Three quantities
    - N_i (Composition)
    - V (Geometry)
    - U (potential and kinetic)
- Ideal Gas
  - Energy is all kinetic so
  - $U = \Sigma_i m_i v_i^2$
  - Ω ways to redistribute KE among particles while leaving U unchanged



Foundations 2

- Entropy
  - $S = R\ln\Omega$
  - $S = S(U,V,N_i)$
- Relationship to U
  - As U decreases, S decreases
  - S monotonic, continuous, differentiable: invertible
- $U = U(S,V,N_i)$
- *Fundamental Thermodynamic Relation*



Properties of Internal Energy, U

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_i} dV + \left(\frac{\partial U}{\partial N_j}\right)_{V,S,N_{i\neq j}} dN_j$$

define

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N_i}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N_i}$$

$$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{V,S,N_{i\neq j}}$$

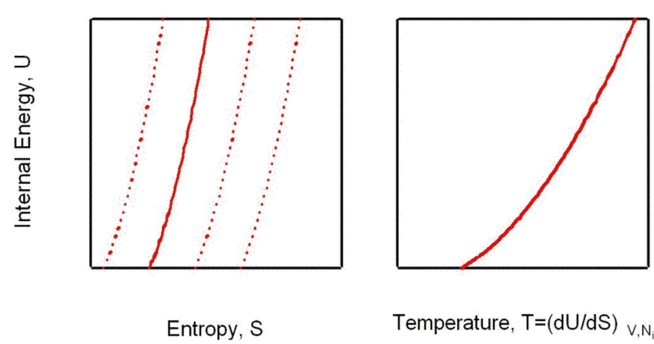
then

$$dU = TdS - PdV + \mu_j dN_j$$

- Complete First Law

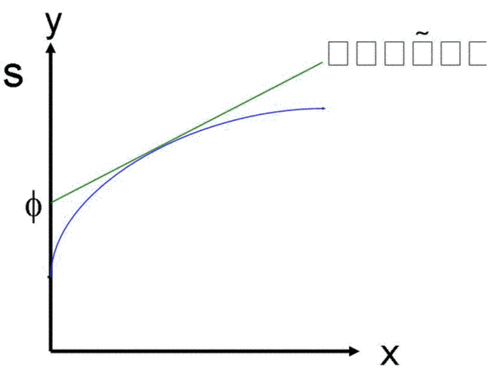
Fundamental Relation

- $U = U(S,V,N_i)$
- Complete information of all properties of all equilibrium states
- S,V,N_i are natural variables of U
- $U = U(T,V,N_i)$ not fundamental



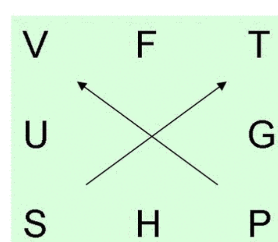
Legendre Transformations

- Two equivalent representations
  - $y=f(x)$
  - □ $\phi=y-px$
  - i.e. $\phi=g(p)$
- Identify
  - $y \to U$, $x \to V,S$, $p \to P,T$, $\phi \to G$
- G = U - dU/dV V - dU/dS S or
- $G(P,T,N_i) = U(V,S,N_i) + PV - TS$
- $G(P,T,N_i)$ is also fundamental!



Thermodynamic Square

- Thermodynamic Potentials
  - F = Helmholtz free energy
  - G = Gibbs free energy
  - H = Enthalpy
  - U = Internal energy
- Surrounded by natural variables
- First derivatives
- Second derivatives (Maxwell Relations)



Summary of Properties

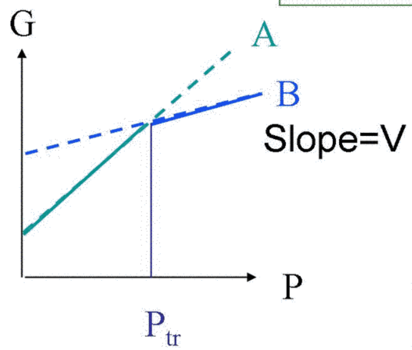
	1	$\left(\frac{\partial}{\partial P}\right)_T$	$\left(\frac{\partial}{\partial T}\right)_P$
1	G	V	$-S$
$\left(\frac{\partial}{\partial P}\right)_T$	V	$-\frac{V}{K_T}$	$V\alpha$
$\left(\frac{\partial}{\partial T}\right)_P$	$-S$	$-\left(\frac{\partial S}{\partial P}\right)_T$	$-\frac{C_P}{T}$

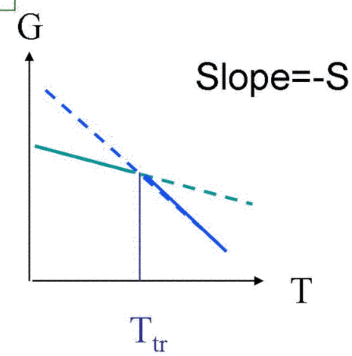
Phase Equilibria

- How does G change in a spontaneous process at constant P/T?
  - L1: dU = dQ - PdV
  - L2: dQ ≤ TdS
  - dG = dU + PdV + vdP - TdS - SdT
  - Substitute L1, take constant P,T
  - dG = dQ - TdS
  - This is always less than zero by L2.
- G is lowered by any spontaneous process
- State with the lowest G is stable

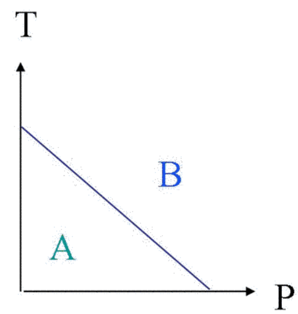
One Component Phase Equilibria

$$dG = VdP - SdT$$





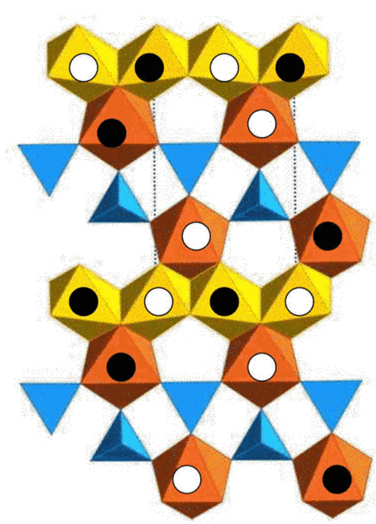
Phase Diagram



$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}$$

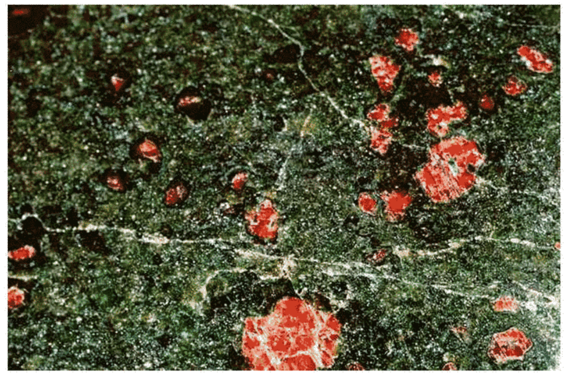
Two Component Phase Equilibria

- Phase: Homogeneous in chemical composition and physical state
- Component: Chemically independent constituent
- Example: $(Mg,Fe)_2SiO_4$
- Phases: olivine, wadsleyite, ringwoodite, …
- Components: Mg_2SiO_4,Fe_2SiO_4
- Why not Mg,Fe,Si,O?



Phase Rule

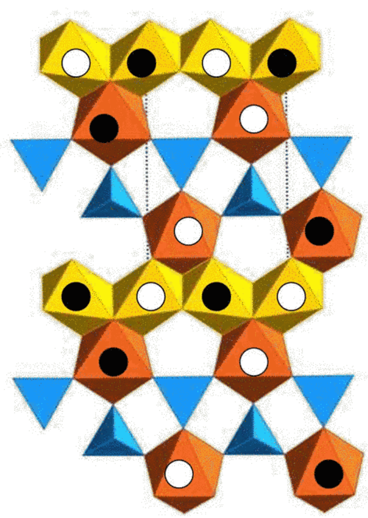
- p phases, c components
- Equilibrium: uniformity of intensive variables across coexisting phases:
- $P^{(a)}, T^{(a)}, \mu_i^{(a)}$
- Equations
  - 2(p-1)+c(p-1)
- Unknowns
  - 2p+p(c-1)
- Degrees of Freedom
  - f=c-p+2



c≈5,p≈4
f≈3

Properties of ideal solution 1

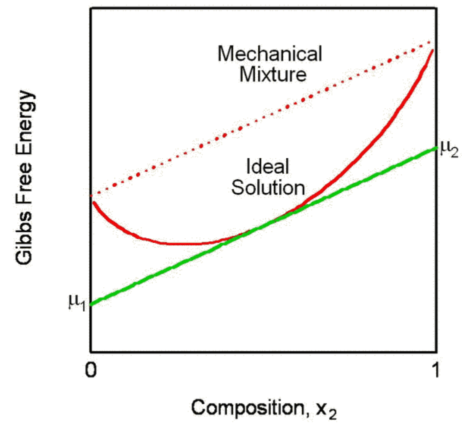
- N_1 type 1 atoms, N_2 type 2 atoms, N total atoms
- $x_1=N_1/N$, $x_2=N_2/N$
- Volume, Internal energy: linear
  - $V = x_1V_1 + x_2V_2$
- Entropy: non-linear
  - $S = x_1S_1 + x_2S_2 - R(x_1\ln x_1 + x_2\ln x_2)$
- $S_{conf} = R\ln\Omega$
  - Ω is number of possible of arrangements.

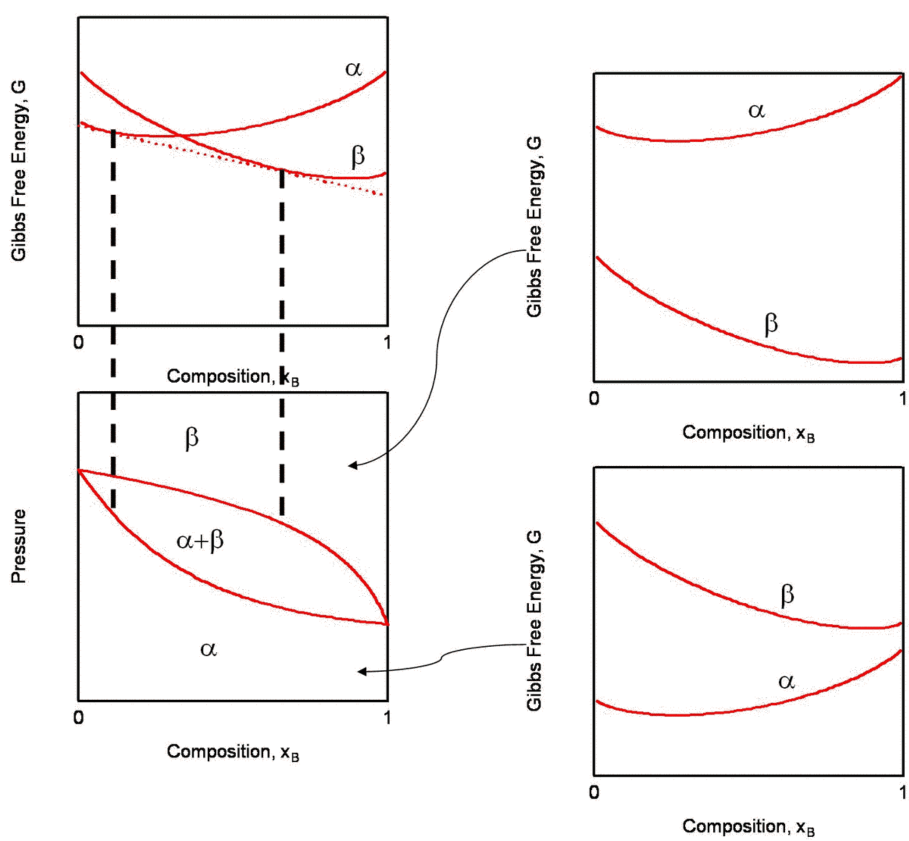


Properties of Ideal Solution 2

- Gibbs free energy
  - $G = x_1G_1 + x_2G_2 + RT(x_1\ln x_1 + x_2\ln x_2)$
- Re-arrange
  - $G = x_1(G_1 + RT\ln x_1) + x_2(G_2 + RT\ln x_2)$
- $G = x_1\mu_1 + x_2\mu_2$

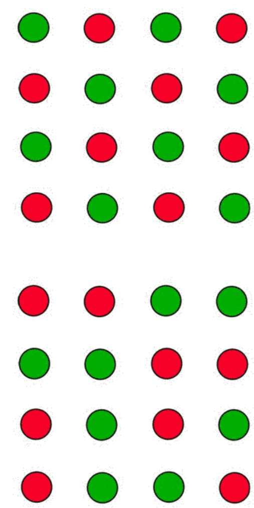
□ $\mu_i = G_i + RT\ln x_i$





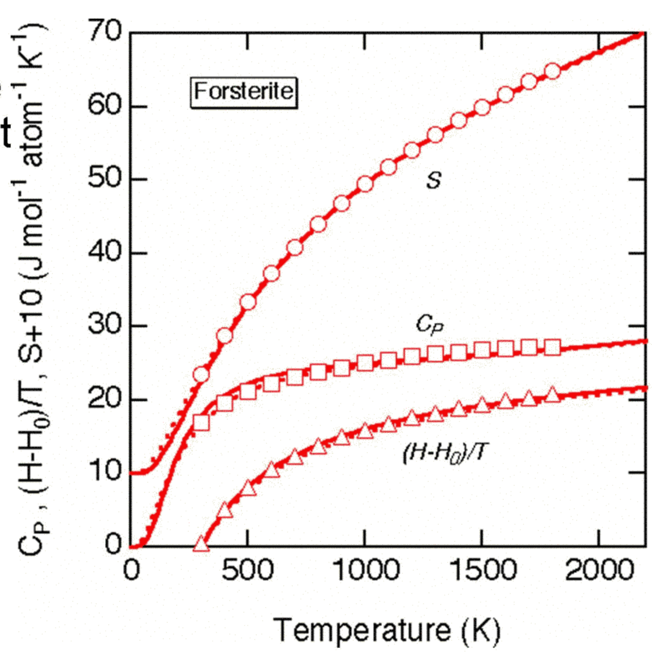
Non-ideal solutions

- Internal Energy a non-linear function of composition
  - Compare A-B bond energy to average of A-A, B-B
  - Tendency towards dispersal, clustering.
- Exsolution
  - cpx-opx,Mg-pv,Ca-pv
- Formally:
  - $\mu_i = G_i + RT\ln a_i$
  - a_i is the activity and may differ from the mole fraction



Example: Thermochemistry

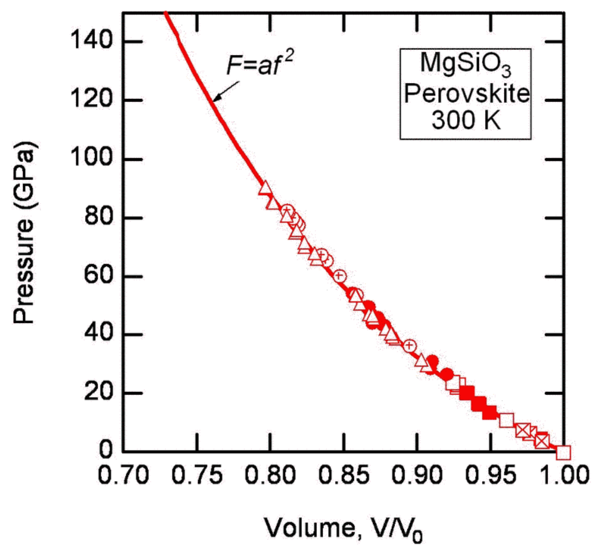
- Increase temperature slightly, measure heat evolved
- $C_P=(dH/dT)_P$
- $C_V \rightarrow 3R$
- Calculate S,H by integration
- $(dT/dP)_{eq}=\Delta V/\Delta S$
- Debye Model



Stixrude and Lithgow-Bertelloni (2005)

Equation of State

- Start from fundamental relation
- Helmholtz free energy
  - $F=F(V,T,N_i)$
- Isotherm, fixed composition
  - $F=F(V)$
- Taylor series expansion
- Expansion variable must be V or function of V
  - $F = af^2 + bf^3 + \dots$
- $f = f(V)$ Eulerian finite strain
- $a = 9K_0V_0$



Grüneisen Parameter

$$\gamma \equiv \frac{1}{\rho}\left(\frac{\partial P}{\partial U}\right)_\rho = \frac{\alpha K_T}{\rho C_\rho} = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S$$

- Thermal pressure
- Adiabatic Gradient
- Dimensionless
- 1-2 for most mantle phases
- Decreases on compression

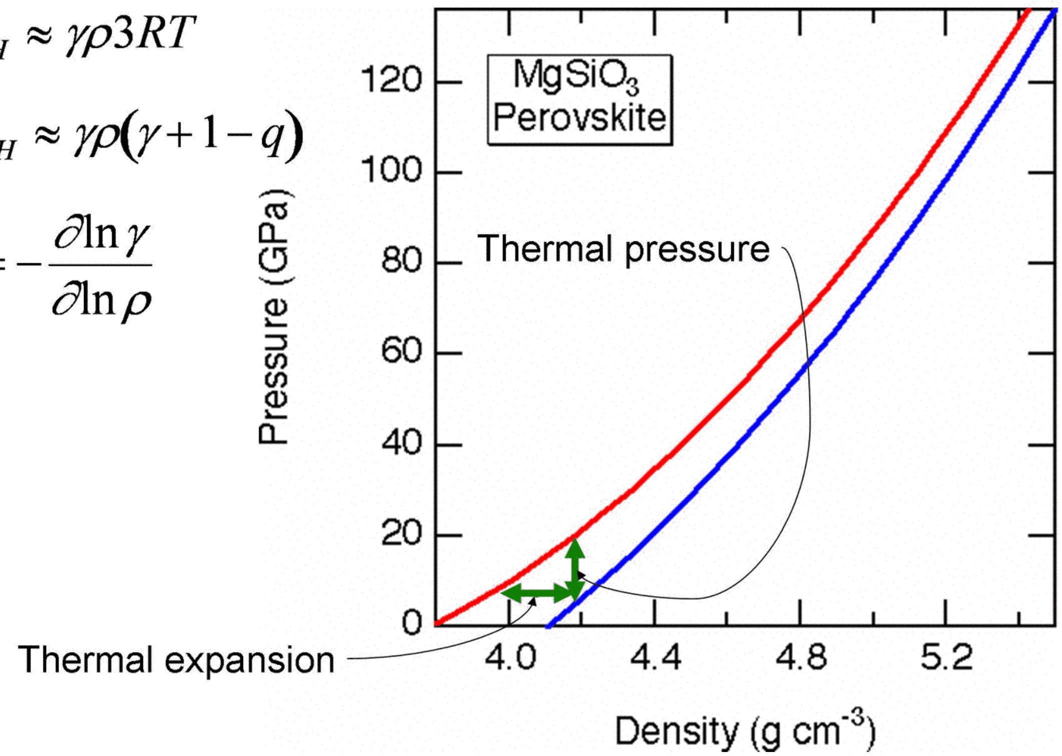
Note: $\rho=1/V$=density

$$U_{TH} \approx 3nRT$$

$$P_{TH} \approx \gamma\rho 3RT$$

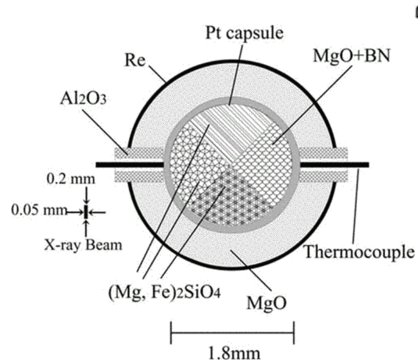
$$K_{TH} \approx \gamma\rho(\gamma + 1 - q)$$

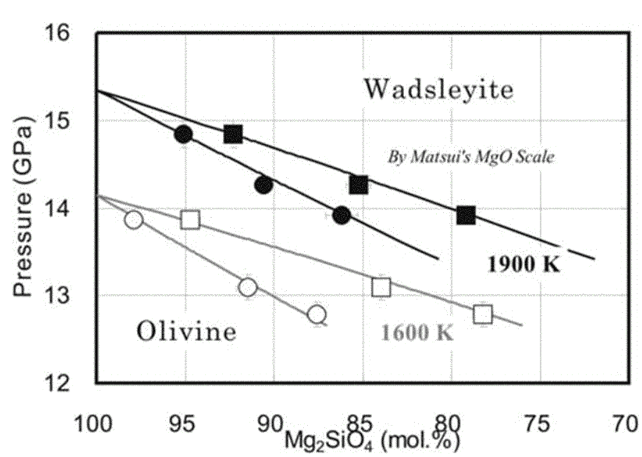
$$q = -\frac{\partial \ln \gamma}{\partial \ln \rho}$$



Example: Phase Equilibria

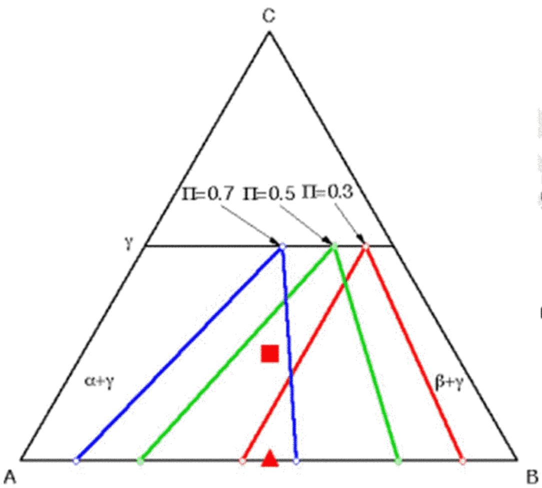
- Mg_2SiO_4-Fe_2SiO_4 System
- Olivine to wadsleyite phase transformation



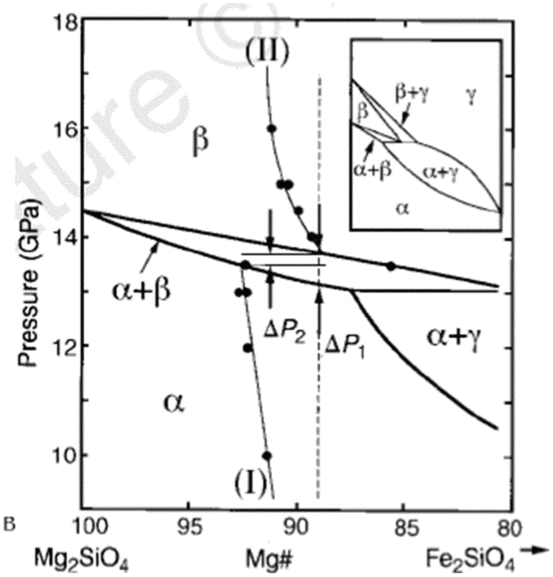


Katsura et al. (2004) GRL

Sharpness of the 410 km discontinuity



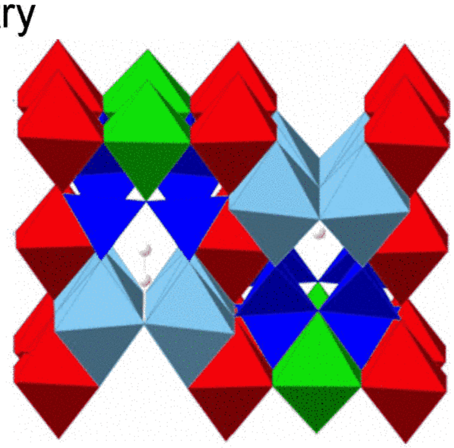
Stixrude (1997)



Irifune and Isshiki (1998)

Road Map

- Mineralogy and Crystal Chemistry
- Lattice Dynamics and Statistical Mechanics
  - Microscopic to Macroscopic
- Phase Equilibria
- Elasticity
  - $V \rightarrow \varepsilon_{ij}$
  - $P \rightarrow \sigma_{ij}$
- Fluids and Melts



Wadsleyite