

Thermodynamics of mantle systems

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Why use thermodynamics?

- Alternatives are simple forcing functions, simple parameterisations, phase diagrams
- Comparison with real samples and / or experimental data (natural or synthetic)
 - Major elements
 - Function of flow fields, thermal structure
 - Sensitivity to and memory of depth of melting
 - Trace elements
 - D(P,T,X)
 - Aluminous phases and minor phases
- Test transport regimes (majors and traces)
 - Equilibrium, reactive flow
 - Disequilibrium, fractional melting



Why use thermodynamics?

- Ability to model wide range of bulk compositions for major elements
 - Variety of rock types including peridotite, slab lithologies, pyroxenite
 - Progressive depletion of residue
 - Flux melting
- Energy budget
 - Including heterogeneous sources
- Density intrinsically known



The thermodynamic problem End-member properties and solution models functions of *PT* Experimental data at *PT*

- Free energy surfaces complicated for realistic phases
- Minimisation of total free energy (for *PT*) or solve for coincident tangent planes
- Need to know stable phase assemblage, either *a priori* or as part of algorithm



From Ghiorso 1994, GCA 58, 5489-5501



The thermodynamic problem

- Adiabatic reversible
 - Entropy conserved
 - Enthalpy minimisation
 - Mantle melting near isentropic?
- Adiabatic irreversible
 - Enthalpy conserved (particular case)
 - Entropy maximisation
 - Account for potential energy
 - Migration of melt in cracks?
- Similar levels of complexity compared to each other (more than isothermal)





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Available calibrations

- Thermodynamic database, solution models, algorithms:
 - Holland & Powell
 - THERMOCALC software
 - Phase diagram, metamorphic petrology oriented
 - User provided solution models
 - MELTS, pMELTS Ghiorso (Berman)
 - MELTS software
 - Includes isentropic, isenthalpic, isochoric calculations
 - Addition / removal of phases
 - Liquid calibrated for natural mantle compositions
 - Known issues e.g. minor components
 - xMELTS will treat these and extend to high P
 - Both good to ~ 4 GPa (subduction, MOR)
 - Not open source but data and models published
 - Should not be mixed... (in same calculation)







Coupling with flow models

- Major element composition function of flow fields as well as thermal structure
- Melting and / or (de)hydration reactions affect solid flow field and temperature structure
 - Water weakening
 - Latent heat
- Melt and solid viscosity are functions of composition and T
- Buoyancy is function of composition and T

- Use available code or algorithms
- Use available databases and / or solution models
 - May simplify solution models
 - May reduce number of components (though less experimental data available)
- Pre-calculate phase diagrams or parameterise results of fully thermodynamic model





Why use entropy?



- Realistic melt function
 - Latent heat of melting (also dehydration, other reactions)



Why use entropy / enthalpy?





- Energy budget of migrating melt
- Modelling of heterogeneous sources
 - Role of excess temperature vs. source 0

Geodynamic and Petrological Synthesis Model (GyPSM)

T = 273 K constant temperature rigid lithosphere, u = v = 0 velocities free velocities kinematically imposed figure 1b.

- Couples pHMELTS and ConMan
- Subduction (GyPSM-S), MOR (GyPSM-R)
 - Entropy as independent variable, latent heat (-R)
 - Water as trace element; effect on viscosity (-S)
 - Also hydrous phases, such as chlorite
 - Full coupling particularly important at slab wedge interface





- Lagrangian particles
 - Particle-node-particle interpolation of T, S, V, water
 - Convenient for evolving bulk composition
 - First equilibribrium step is always slowest
 - Other advection schemes require interpolation of bulk / phase compositions and modes
 - In GyPSM liquid is removed from system but adding incoming liquid to assemblage is easy, compared to solids
- Modified energy equation
 - Self-consistent thermal boundary conditions pHMELTS
- pHMELTS calculated density for buoyancy force







Alternatives

- pHMELTS occasionally fails and requires workaround
 - Use closest equilibrium state in *PT* space
 - Extrapolate using polynomial formulation for Cp and EOS (Berman)
- Outside calibrated range (includes slab)
 - As above
 - Peridotite outside PT range
 - Scaled-down version of pHMELTS algorithm does not fully re-equilibrate system
 - Water partitioned between existing phases but only fluid can join assemblage
- Extension to high P (> 4 GPa)
 - As above but approx. Birch-Murnaghan EOS
 - Ensure V, $\partial V / \partial P$, $\partial V / \partial T$ smooth at 4 GPa

Phase diagram treatment



- THERMOCALC based
- No solid solution
 vunivarients
- Water in excess
- $dP/dT = \Delta S/\Delta V \Rightarrow$ consistent
 - Polynomial formulation for solids
 - Pitzer & Sterner 1994 EOS for water
- Dehydration over finite P interval







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Slab age and dip

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A CCR; B SCR; C NIB; D NMAR

Baker Hebert et al., submitted to EPSL

Melt and fluid release

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A CCR; B NIB; C ADD2; D NMAR; E SCR

Supplementary modelling

0.3

0.2

0.

0.0

50.0

100.0

150.0

Ba/La

200.0

250.0

300.0

F.

400.0

200.0

0.0

0.0

50.0

100.0 150.0 200.0 250.0 300.0

Ba/La

E.

Problems

- pHMELTS is slow!
 - Thermodynamic problem is difficult, tractable, but expensive
 - Treating water as trace element requires extra iteration (could be improved?)
- Limited to equilibrium case
- Removing melt from system
 - Crystallisation of pooled melts not implemented yet; affects heat budget, especially MOR
 - No information about melt transport
- Pressure is lithostatic
- Using incompressible version of ConMan
 - Makes conservation of composition tricky
 - Not clear how to implement in melting region

Problems

- Parallel scheme crude
 - Limits information, such as derivatives, that can be passed
 - Prevents interpolation of melt composition
- Timestep size determined by flow code
 - Rather small by pHMELTS standards
 - Too large for equilibrium Darcy flow of water

Can we take a step towards equilibrium?

Affinity and composition estimate:

$$\overline{G}_{S}^{0} = \overline{G}_{S}^{0} + \left(\frac{\partial \overline{G}_{L}}{\partial X}\right)_{X_{L}^{0}} \left(X_{S}^{0} - X_{L}^{0}\right) + A$$
$$\left(\frac{\partial \overline{G}_{S}}{\partial X}\right)_{X_{S}^{0}} = \left(\frac{\partial \overline{G}_{L}}{\partial X}\right)_{X_{L}^{0}}$$

Affinity is a measure of the chemical force driving a reaction

Can we take a step towards equilibrium?

Affinity and composition estimate:

$$\begin{split} \overline{G}_{S}^{0} &= \overline{G}_{S}^{0} + \left(\frac{\partial \overline{G}_{L}}{\partial X}\right)_{X_{L}^{0}} \left(X_{S}^{0} - X_{L}^{0}\right) + A \\ &\left(\frac{\partial \overline{G}_{S}}{\partial X}\right)_{X_{S}^{0}} = \left(\frac{\partial \overline{G}_{L}}{\partial X}\right)_{X_{L}^{0}} \end{split}$$

Solve for equilibrium i.e.:

$$\overline{G}_{S}^{1} = \overline{G}_{L}^{1} + \left(\frac{\partial \overline{G}_{L}}{\partial X}\right)_{X_{L}^{1}} \left(X_{S}^{1} - X_{L}^{1}\right)_{X_{L}^{1}} \left(\frac{\partial \overline{G}_{S}}{\partial X}\right)_{X_{S}^{1}} = \left(\frac{\partial \overline{G}_{L}}{\partial X}\right)_{X_{L}^{1}}$$

'Fast equilibrium method'

- Binary has an analytical solution with suitable approximation
- Method can be extended
 - General method for getting affinity and composition detailed in Ghiorso 1994
 - In MELTS only used before and after expensive full equilibrium step
 - Algorithm not restricted to MELTS model
 - Take one (or more) Newton's method steps towards equilibrium
 - Use extensive quantities, have derivatives
 - Can be generalised for realistic liquid and solid chemistry and arbitrary non-ideal solution models
 - Can, by considering energy as well as mass fluxes, use other 'potential' functions

'Fast equilibrium method'

- Investigation of partial disequilibrium possible?
- Speeds up calculation considerably
 - Preliminary test ~5X faster
- Requires good starting solution
- Requires a lot of interpolation (phase compositions, proportions etc.)
 - Approach to equilibrium may be very sensitive to interpolation...

