Part 1: Introduction to the MELTS family of algorithms; modeling crystallization and liquid lines of descent

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If you don’t understand, PLEASE ASK!

- The point of this workshop is to make these methods practical and useful to each and every one of you,
- Not to get through a certain amount of material on a certain schedule!
- Therefore: *please* feel free to use the question, raise hand, chat box, and Slack channel!
  - In this format, you can easily ask questions without interrupting, so don’t be shy!
  - If you miss something or fall behind, probably so did lots of others...
What’s this all about?

- Petrology is complicated
- Understanding results from the interplay of observations, experiments, and models
  - Most petrologic observations can only be interpreted in the context of a protracted series of processes that cannot be entirely reproduced in a single experiment
  - Models are necessary to synthesize the results of many experiments, to test complex (or even simple) hypotheses, to generalize results, etc.
  - Frequently, a model can be used to reject unsuccessful or impossible hypotheses.
What’s this all about?

- Models can be (and often are) constructed empirically, e.g. by fitting experimental or natural data
  - For example, estimating fractionating phase proportions in a magmatic series by simple mass balance
  - Or parameterizing $K_{D}^{Fe/Mg}$ or $F(P,T,X_{H2O})$ directly from experiments

- But the governing principles of thermodynamic equilibrium offer at least the possibility of deriving general models that apply beyond the calibration set
  - If one can expect that equilibrium was achieved (more or less) and if your thermodynamic model is “good enough”
  - The MELTS family of models is an attempt to pursue this philosophy
Thermodynamic Potentials and Constraints

- 1\textsuperscript{st} and 2\textsuperscript{nd} laws of thermodynamics directly give
  \[ dE \leq TdS - PdV + \sum \mu_i d n_i \quad (\mu_i \equiv \left( \frac{\partial E}{\partial n_i} \right)_{S,V,n_j \neq i} ) \]

  ◦ Interpretation: If \( S, V, \) and \( n_i \) are held constant then the equilibrium state is the state of minimum \( E \)

- But these constraints are rare in nature and experiment, so we change variables to impose more relevant constraints:
  \[ H \equiv E + PV \rightarrow dH \leq TdS + VdP + \sum \mu_i d n_i \]
  \[ F \equiv E - TS \rightarrow dF \leq -SdT - PdV + \sum \mu_i d n_i \]
  \[ G \equiv E + PV - TS \rightarrow dG \leq -SdT + VdP + \sum \mu_i d n_i \]
  \[ L \equiv G - n_{O_2} \mu_{O_2} \rightarrow dL \leq \cdots - \sum n_{O_2} d \mu_{O_2} \]
Thermodynamic Potentials and Constraints

- Note: to express and minimize any of these functions and therefore find equilibrium subject to any of these constraints, it is sufficient to know Gibbs free energy $\bar{G}(P, T, X)$ and its derivatives:

  - $\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_j \neq i}$
  - $\bar{S} = -\left( \frac{\partial G}{\partial T} \right)_{P, X}$
  - $\bar{V} \equiv -\left( \frac{\partial G}{\partial P} \right)_{T, X}$
  - $\bar{H} \equiv \bar{G} + T\bar{S}$
  - $\bar{F} \equiv \bar{G} - P\bar{V}$
  - $\bar{E} \equiv \bar{G} + T\bar{S} - P\bar{V}$

  - $C_P = \left( \frac{\partial \bar{H}}{\partial T} \right)_{P, X}$
  - $\rho = \frac{mw}{\bar{V}}$
  - $fO_2 = \frac{[\mu_{O_2} - \mu_{O_2}^0 (1\text{bar}, T)]}{RT}$
Statement of General Problem

*Given*

- Bulk composition
- Two independent intensive parameters \([P \text{ or } V; T, S, \text{ or } H]\)
- and (optionally) \(fO_2\) and/or \(a_{H2O}\)

*Calculate equilibrium by finding the distribution of the masses of each component among all known phases that minimizes the appropriate thermodynamic potential*

(The existence of a unique answer to this problem is guaranteed by Duhem’s Theorem)
Solution of General Problem

- There are two distinct computational strategies to solve this problem:
  1. Simultaneous solution of lots of non-linear equations of the form
     \[ \mu_{\text{component}}^{\text{phase}} = \mu_{\text{component}}^{\text{another phase}} \]
  2. Constrained minimization of potential function such as \( G, F, H, -S, \) or \( L \)

- All MELTS programs use the second approach, which we consider numerically more tractable and scalable
Applications of General Problem

The equilibrium closed-system calculation forms the kernel of an approach that can approximate many natural processes, including open-system and fractional processes.

- Repeated application of the equilibrium engine along prescribed \((P, T)\) {or other constraints} paths, perhaps with intermediate open system operations (e.g., assimilation and/or fractionation steps), converges in the limit of small steps towards a model of a continuous or dynamic process.

Note: some people want their thermodynamic models expressed as phase diagrams, others want them as inverse models that fit data, others want them as forward models of a process … MELTS can do all of these, sort of, but it is primarily built to do the latter.
Solution of General Problem

• To perform such a calculation, we need...

• **Models** of $G(P,T,X)$ and all its derivatives for every possible phase of interest

• **Algorithms:** constrained minimization of nonlinear function, detection of phase saturation, recognition of metastability, and modifications of constraints according to specified rules

• An **Interface** to make input and output of such calculations convenient and accessible.

• There are four active variants of the **Model** and at least five supported **Interfaces**, all of which share basically the same **Algorithms**
Explaining the alphabet soup

Model variants:
- MELTS (1995) original calibration, obsolete
- pMELTS (2002) optimized for 1-3 GPa
  - pHMELETS (2004) treats H₂O in nominally anhydrous minerals
- Rhyolite-MELTS 1.0.2 (2012) tweaked for granite minimum
  - Rhyolite-MELTS 1.1.0 (2015) H₂O-CO₂ for granite minimum
  - Rhyolite-MELTS 1.2.0 (2015) H₂O-CO₂ all other cases
  (see http://melts.ofm-research.org/MELTS-decision-tree.html)
- xMELTS (?) full model never released

Interface variants:
- The graphical user interface (GUI) (MacOS or Linux, including VM and WSL)
- easyMELTS (all platforms)
- alphaMELTS 1.9 and 2.0 (all platforms)
- MELTS for Excel (Windows only & requires internet; plotting tools work on MacOS)
- MATLAB and Python wrappers to libalphaMELTS (all platforms)
- ENKI Jupyter ThermoEngine (Web interface)
- PhasePlot (MacOS only)
The Model: silicate liquid phase

- There is no precise general framework for thermodynamics of multicomponent silicate liquids. All existing models are basically heuristic at some level. MELTS, e.g., uses the basic formulation of mixing relations in the liquid proposed by Ghiorso and Carmichael (1983):
  - Liquid is treated as a stoichiometric solution of simple mineral-like molecules. Liquid must remain in the space spanned by positive quantities of these species:
    - $\text{SiO}_2, \text{TiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{MgCr}_2\text{O}_4, \text{Fe}_2\text{SiO}_4, \text{Mn}_2\text{SiO}_4, \text{Mg}_2\text{SiO}_4, \text{Co}_2\text{SiO}_4, \text{Ni}_2\text{SiO}_4, \text{CaSiO}_3, \text{Na}_2\text{SiO}_3, \text{KAlSiO}_4, \text{Ca}_3(\text{PO}_4)_2, \text{H}_2\text{O}$
  - ideal Entropy of mixing between these melt species
  - Volume and heat capacity of mixing are strictly zero
  - Enthalpy of mixing is treated as expanded regular solution using symmetric binary interaction parameters, independent of $P$ and $T$
MELTS liquid model: Details

- $G^{\text{excess}}$ is described by the simplest form likely to work, an expanded binary symmetric regular solution:

$$G^{\text{excess}} = \frac{N}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} W_{ij} X_i X_j$$

where $W_{ij}$ are calibrated interaction parameters that are

- independent of $P$ and $T$ (i.e., no $V$ or $C_p$ of mixing)
- symmetric ($W_{ij} = W_{ji}$)
- describe pairwise interactions between unlike molecules ($W_{ii}=0$)

- This term describes the enthalpy of mixing.
- No ternary or asymmetric terms are used. This limits the utility of the model to systems with many components. Simple systems like binaries need higher-order interaction terms.

- For some users and critics this is a serious shortcoming!!
MELTS liquid model: Details

• H$_2$O is treated specially, because at low water contents it is presumed to speciate entirely into OH groups. So in this case (only) the liquid component is not also the liquid species
• This is handled by tacking on an extra term in the ideal and excess parts of the solution that accounts for the presence of two hydrous species for every H$_2$O in the composition
• This is only valid at relatively total water contents ≤4% for basalts and ≤6% for rhyolites, yet MELTS seems to work OK for higher water contents

• As of rhyoliteMELTS 1.1 and 1.2, CO$_2$ is added with freedom to speciate between CO$_2$ and CaCO$_3$ molecules
Minerals included in MELTS

- **pyroxene**: $(\text{Na, Ca, Mg, Fe}^{2+})^2\text{(Mg, Fe}^{2+, Ti, Fe}^{3+, Al})^\text{M}M\text{(Fe}^{3+, Al, Si)}^\text{TETO}_6$
- **olivine**: $(\text{Mg, Fe}^{2+}, \text{Ca, Mn, Ni, Co})_2\text{SiO}_4$
- **spinel**: $(\text{Mg, Fe}^{2+})(\text{Fe}^{3+, Al, Cr})\text{O}_4 - (\text{Mg, Fe}^{2+})_2\text{TiO}_4$
- **rhombohedral oxide**: $(\text{Mg, Fe}^{2+}, \text{Mn})\text{TiO}_3 - \text{Fe}_2\text{O}_3$
- **nepheline**: $(\text{K, Na, Ca, } □_x)\text{AlSi}_{(1+x)}\text{O}_4$ (also kalsilite)
- **melilite**: $(\text{Na, Ca})_2[(\text{Mg, Fe}^{2+, Al, Si})_3\text{O}_7]$
- **garnet**: $(\text{Mg, Fe, Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12}$
- **orthorhombic oxide**: $(\text{Mg, Fe}^{2+})\text{Ti}_2\text{O}_5 - \text{Fe}^{3+}_2\text{TiO}_5$
- **feldspar**: $(\text{K, Na})\text{AlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$
- **leucite**: $(\text{K, Na})\text{AlSi}_2\text{O}_{6-x}(\text{OH})_{2x}$
- **biotite**: $\text{K}(\text{Mg, Fe}^{2+})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$
- **hornblende**: $\text{NaCa}_2(\text{Mg, Fe}^{2+})_4(\text{Al, Fe}^{3+})\text{Al}_2\text{Si}_6\text{O}_{22}(\text{OH})_2$

Plus Fe-Ni alloy solid or liquid, ternary chlorite, $\text{H}_2\text{O- CO}_2$ fluid, quadrilateral ortho- and clinoamphibole, epidote

Plus one-component solids: sphene, aenigmatite, muscovite, quartz, tridymite, cristobalite, coesite, corundum, rutile, perovskite, whitlockite, hydroxyapatite, andalusite, sillimanite, kyanite, talc, anthophyllite, cordierite, lawsonite, carbonates…
What’s missing from the Minerals?

- pyroxene: Cr, Mn, and K; proto structure; hi-P clinoenstatite
- garnet: Cr, Mn, majorite component – *in progress*
- biotite: Phengite component
- amphiboles: Lots of components! (aside: why this matters)
- vapor: Everything except H$_2$O and CO$_2$

Many accessory phases (zircon, allanite, etc.)
Things that show up in peraluminous rocks (cordierite, tourmaline, topaz, sodic amphiboles, chloritoid, sapphirine)
Sulfides and sulfates
Low-T minerals (clays and zeolites)

More? (Ask about *your* favorite mineral now…)
Solid solution models

• The most complex of such models so far developed is the 7-component pyroxene model:

$$(\text{Ca, Fe}^{2+}, \text{Mg, Na})^{\text{M}_2} (\text{Mg, Fe}^{2+}, \text{Fe}^{3+}, \text{Ti, Al})^{\text{M}_1} (\text{Si, Al, Fe}^{3+})^{\text{T}_2} \text{O}_6$$

• 7 end members (6 independent $r$ variables) & 2 order parameters:

- CaMgSi$_2$O$_6$ (diopside)
- CaFeSi$_2$O$_6$ (hedenbergite)
- Mg$_2$Si$_2$O$_6$ (enstatite)
- NaAlSi$_2$O$_6$ (jadeite)
- CaFe$^{3+}$AlSiO$_6$ (essenite)
- CaMg$_{0.5}$Ti$_{0.5}$Fe$^{3+}$SiO$_6$ (buffonite)
- CaMg$_{0.5}$Ti$_{0.5}$AlSiO$_6$ (aluminobuffonite)

• Efficient numerical computations require analytical expressions for all 3rd derivatives of $G$ with respect to $X, s, P, T$: 1000 different derivatives are explicitly written into the code!
MELTS algorithms

Initial Guess

Detect Saturation?

Minimize Thermodynamic Potential (G, H, A, -S, or Korzhinskii)

Phase Trying to Disappear?

Check for Metastability?

Detect Saturation?

Equilibrium

Add Phase

Drop Phase

GUI Interface (Ghiorso)

Calling Program (Asimow)

* = Assert fO2 Buffer

(Ghiorso 1994, Asimow & Ghiorso, 1998)

(Ghiorso 1985)

(Asimow & Ghiorso, 1998)

(Asimow & Ghiorso, 1998)

(Asimow & Ghiorso, 1998)

(Ghiorso 1994, Asimow & Ghiorso, 1998)
Modeling fractionation

- One of the main classes of applications of MELTS is to understanding the differentiation of magma
  - Usually at low pressure, hence with rhyoliteMELTS, not pMELTS
  - Usually fractional crystallization during isobaric cooling, but not always...
  - Usually as a forward model from primitive melt towards more evolved melts, but not always...
  - Usually as a closed system (except for oxygen), but can be extended to AFC, RAFC, etc.
Hydrous basalt fractionation

Olivine+plagioclase fractionation

Ol+Pl+cpx fractionation

Troctolite: 24% Al₂O₃, 13% MgO

Gabbro: 17% Al₂O₃, 11% MgO

Dunite: 0% Al₂O₃, 50% MgO

Primary Liquid + titanolamagnetite or ilmenite
Hydrous basalt fractionation
Hydrous basalt fractionation

- +titanomagnetite or ilmenite

- 8% MgO

- EPR
- MAR
- Galapagos
- Lau Basin
- Dry fractionation
- 0.2% H2O
- 0.5% H2O
- 0.8% H2O (Lau)

- Olivine fractionation
- OI+PI+Cpx fractionation
- Primary Liquid

- MgO
- FeO*
Hydrous basalt fractionation

Azores data
Klein and Langmuir (dry) correction to 8% MgO
MELTS (H2O-aware) correction to 8% MgO
Reverse fractionation

• This is an inverse problem: given a sampled whole rock or glass, what was the parental or primary liquid from which it was derived?
  ◦ An ill-posed problem in two ways:
    • Any multiply saturated liquid has lost information about where it came from
    • A mono-saturated liquid sits at the end of a liquid line of descent, but one still must make an arbitrary choice how far up the line to go
  
• Solutions: freedom to specify Mg# or MgO target and the *amoeba* algorithm
Reverse fractionation

Figure 1. (a) Illustration showing the method for computing parental magma compositions for basalts from the Ontong Java Plateau and the Siqueiros Fracture Zone (East Pacific Rise) and komatiites and picrites from Gorgona. Green lines are Fo contents of olivine (100 MgO/(MgO + FeO) molar) at 1 atm calculated from the $K_{D}$ model of Toplis [2005] at 1 atm. Arrays of small circles indicate liquid compositions produced by addition, i.e., of olivine into a representative lava composition. Crosses in circles indicate parental magma, which is defined by the coincidence of an olivine addition array with an olivine phenocryst composition having the maximum Fo content (target olivine). Black, red, and blue circles are whole rock and glass data for Gorgona komatiites, Ontong Java Plateau, and MORB from the Siqueiros FZ. Olivine was added to Gorgona sample 149 [Aitken and Echeverria, 1984], Ontong Java sample 1187 [Fitton and Godard, 2004], and Siqueiros sample ALV2384-007 [Perfit et al., 1996]. (b) Illustration showing the method for computing primary magma composition of the lavas in Figure 1a. Red lines indicate FeO and MgO contents of accumulated fractional melts of depleted peridotite at the melt fractions F shown [Herzberg and O'Hara, 2002]. Green arrows illustrate the approximate range of instantaneous fractional melts that, when mixed together, produce the accumulated fractional melts. Crosses in gray circles for MORB and Ontong Java Plateau are the parental magmas from Figure 1a. Crosses in white circles indicate primary magmas formed at the same melt fractions as those given in Figure 2. MgO contents do not change much with decompression because $dT/dP$ of isopleths of MgO in partial melts of peridotite approximately parallel the adiabatic gradient [Herzberg and O'Hara, 2002] (but see small changes in Appendix A for fertile peridotite). Black, red, and blue circles are whole rock and glass data from Figure 1a.

Herzberg et al. (2007)
Reverse fractionation

- The Amoeba
Mixed-volatile degassing

Typical fit of rhyoliteMELTS 1.2 to saturation isobars:

$T_{	ext{amic, N., Behrens, H., Holtz, F. (2001) - 1100 °C}}$

$P = 200$

$P = 500$

$\text{CO}_2$ wt% vs $\text{H}_2\text{O}$ wt%
Mixed-volatile degassing

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**Expected degassing behavior:**

- **Basalt (49 wt.% SiO$_2$)**
  - 1200°C
  - Closed-system with 2% exsolved vapor
  - Open System

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**Rhyolite**

- **ISOBARS 800°C**
  - 2000 Bars
  - 1000 Bars
  - 500 Bars

- **ISOPLETHS 800°C**
  - Wt.% H$_2$O dissolved in melt
  - PPM CO$_2$ dissolved in melt
  - 20 mol% H$_2$O
  - 50 mol% H$_2$O
  - 80 mol% H$_2$O

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Wyman and Lowenstern, 2002
The good, the bad and the ugly

- **Good:** Opportunity to hypothesis test, ability to surprise, able to simulate complex processes and track many properties
- **Bad:** Common errors with minor components; Missing (or inadequate) phases, e.g. complex amphiboles; Need to reality check results
- **Ugly:** Crashes, convergence failures and workarounds
Alternatives to MELTS

- MELTS does not have a monopoly on petrologic modeling. ...
- THERMOCALC (Holland and Powell) & Perple_X (Connolly) – both better for drawing phase diagrams and pseudosections, metamorphic petrology, and simple systems. Limited (until recent Jennings & Holland model) description of silicate liquids or mantle pressures, but rapidly advancing in this area.
- Thermo_Calc (commercial software) – not much geologic information, only for synthetic systems at 1 bar or less
- Empirical parameterizations of melting (Kinzler and Grove, Langmuir et al., Niu and Batiza, Walter and Presnall, Herzberg and O’Hara, etc.) – may accurately capture experimental trends, but no thermodynamic basis, no energy budget
- Empirical parameterizations of fractionation (Weaver and Langmuir, Ariskin et al., Danyushevsky, Yang et al., Bézos, Niu, Herzberg, etc., etc.) – all very accurate over certain ranges, but each has limitations