Taxonomy Of Magma Mixing I:
Magma Mixing Metrics And The Thermochemistry Of Magma Hybridization Illuminated With A Toy Model

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I: Introduction

The mixing of two thermally and compositionally distinct magmas (resident magma, **M** and Recharge magma, **R**) each containing distinctive crystal and melt populations plays a major role in modern petrogenetic theory. The study of the compositional diversity of igneous rocks observed on spatial scales from micrometers to kilometers and on time scales from seconds to millions of years has a long history dating back over 160 years. Abundant evidence of magma mixing includes mafic enclaves in plutonic rocks, syn-plutonic mafic or silicic dikes, and from cumulate rocks in layered intrusions and other intrusive bodies. Mixed-pumice eruptions and crystal-scale heterogeneity of phenocrysts and cumulate minerals provide *prima facie* evidence for magma mixing. It is not surprising that this evidence has lead to the view that magma mixing along with fractional crystallization is a first-order petrogenetic process active in all petrotectonic environments throughout geologic time.

When two magmas mix, there are a wide variety of potential end states depending on myriad details. Indeed the fluid dynamics of mixing of magmas (a heterogeneous suspensions of crystals, supercritical fluid bubbles and silicate or carbonatitic melt) is complex due to the influence of often ill-defined boundary and initial conditions and the relevant multi-level scales of heat, momentum and material transport. At zeroth–order, one can consider that magma mixing occurs by two end-member processes: hybridization and mingling. *Magma mingling* produces a heterogeneous mixture containing discrete portions of the end-member magmas, (e.g., **M** and **R**), due to the incomplete blending of the different magmas. In this case, the final product comprises spatially discrete portions of each lithic type and is very spatially heterogeneous. The 'goodness' of mixing has previously been defined in terms of a length scale (L) and an intensity (I) of mixing (Oldenburg and Spera, 1989, JGR, 94, p.9215) and depends on both the space correlation (L) and the second moment (I) of the composition field. The space correlation gives information on the probability that a positive (negative) composition fluctuation at one point is correlated with a positive (negative) anomaly a distance r away. In any flow with nonzero diffusion effects, I→0 as t→∞ since normal and shear strains associated with mixing diffusively reduce a compositional anomaly to a length of order $\ell \sim \sqrt{Dt}$; anomalies are essentially erased at macroscopic scales. As t→∞, L→0 as well; however, the timescale for reduction of L only weakly relates to molecular diffusivity and depends, instead, on flow dynamics, specifically the temporal and spatial evolution of the velocity field, a complicated issue not subject to soporific generalizations on an AGU poster. *Magma hybridization* involves the homogeneous mixing of two unlike magmas (**M** and **R**) to form a chemically and physically homogeneous mixture of intermediate bulk composition and enthalpy (but NOT necessarily temperature!). Unlike the case of magma mingling the end-member process of *magma hybridization* can be studied thermodynamically since initial and final states are uniquely defined according to thermodynamic dictates. In *magma hybridization*, two initially disparate magmas, each in internal equilibrium, thoroughly mix (hybridize) to form a new magma at thermodynamic (chemical potential, temperature, pressure) equilibrium. The hybrid magma is a multiphase mixture of homogeneous melt, unzoned crystals and possibly bubbles of a supercritical fluid; all coexisting phases are at a unique and identical temperature and pressure.

The goal of this study is to examine the thermodynamics of *magma hybridization* by studying a model binary eutectic system (ideal mixing, no crystalline solution) and then apply the principles gleaned to multicomponent-multiphase systems using the Magma Chamber Simulator (See adjacent POSTER). The thermodynamics of the toy model are transparent and hence the sensibility of hybridization outcome on the composition, phase state, temperature and mixing proportions of the mixing magmas is easy to grasp. The toy model enables rapid development of intuitive basis for understanding magma hybridization in natural systems.

Magma mixing is very different than **melt** mixing to form a third blended liquid. When two melts mix to form a third, the final temperature and composition of the hybrid liquid is the mass-weighted average of the mixing melts. This trivial case in which two superheated magmas are rare.

II: Thermodynamics of Hybridization Illustrated *via* Toy Model

The phase diagram of the toy system is depicted in Figure 1. Pressure is constant. Table 1 gives the variable identifications. The toy system topology is that of a binary component eutectic phase diagram not unlike CaMgSi₂O₆ - CaAl₂Si₂O₈, with no crystalline solution. There are three phases in this system: crystals of phase α, crystals of phase β or a liquid phase. The two components of this system are A and B with α phase solely constituted by component A and phase β solely constituted by component B. For the ease of explanation, and without loss of any generality, liquidii are rendered as straight lines in Figure 1. There are eight thermodynamic parameters needed to define the topology of the toy system: the eutectic composition, X_e, eutectic temperature, T_e, melting temperature of α and β ($T^\alpha_{m.p}$ and $T^\beta_{m.p}$) and the specific fusion enthalpies of α and β (Δh^α, Δh^β). In the toy model, two isobaric specific heats are also introduced: one for all solid phases, C_s and one for the liquid, C_L. These isobaric specific heats are taken as constants independent of temperature and composition. At igneous temperatures, C_p varies remarkably little with temperature composition to first order. In the toy model, heats of mixing associated with non-ideality are neglected. Although excess enthalpies are generally not identically zero, they are relatively small compared to fusion enthalpies and, when translated into temperature differences, are of order 10-40 K. For example, in the system CaMgSi₂O₆ - CaAl₂Si₂O₈ the *maximum* excess enthalpy associated with mixing is ~60 kJ/kg. In comparison, the fusion enthalpies of diopside and anorthite are 636 kJ/kg and 478 kJ/kg, respectively, about 10 times larger. Similarly, if the excess enthalpy (heat of mixing) is couched in terms of a temperature difference then ΔT ~ 35 K. In addition to the aforementioned thermodynamic parameters, five additional parameters are needed. These parameters are: the initial temperatures (T^M_0, T^R_0) and bulk compositions (X^M_0, X^R_0) of both **M** and **R** magmas and the mass fraction of **M** magma (f_0) of the M+R mixture. Because the process of magma mixing is closed and adiabatic, the final bulk composition and specific enthalpy (h^H) of the hybrid magma are known. That is, the T, bulk composition and phase assemblage (proportions and liquid composition) of the final hybridized magma are uniquely determined. In Figure 3, an example of a hybridization solution is given along with the initial conditions for a toy system with thermodynamics very similar to the 1-bar system CaMgSi₂O₆ - CaAl₂Si₂O₈. A downloadable spreadsheet is available at http://magma.geol.ucsb.edu/index.html. Insights gained from analysis of the toy model pertaining to the thermodynamics of magma hybridization are discussed in the adjacent poster.

TABLE 1: Nomenclature

QUANTITY	DEFINITION
X	Mass fraction component B
Y	Mass fraction component A
X_e	Eutectic composition
T_e	Eutectic temperature
$T^\alpha_{m.p}$	Melting point phase α
$T^\beta_{m.p}$	Melting point phase β
Δh^α	Fusion enthalpy phase α
Δh^β	Fusion enthalpy phase β
C_s	Isobaric specific heat of solid
C_L	Isobaric specific heat of liquid
ΔC	$C_L - C_s$
X^M_0	Mass fraction of component B in M magma
X^{Ml}_0	Mass fraction of component B in M magma liquid
X^R_0	Mass fraction of component B in R magma
X^{Rl}_0	Mass fraction of component B in R magma liquid
T^M_0	Initial T of M magma
T^R_0	Initial T of R magma
$h^M_{\alpha s}$	Specific enthalpy M magma contributes to hybrid magma when M magma is single phase liquid of bulk composition X^M_0
h^M_{sp}	Specific enthalpy M magma contributes to hybrid magma when M magma is single phase liquid of bulk composition $X^M_0 > X_e$
h^M_{s-L}	Specific enthalpy M magma contributes to hybrid magma when M magma is L+β mixture of bulk composition $X^M_0 > X_e$
$h^M_{\alpha\beta}$	Specific enthalpy M magma contributes to hybrid magma when M magma is α+β crystal mixture
$h^R_{\alpha s}$	Specific enthalpy R magma contributes to hybrid magma when R magma is single phase liquid of bulk composition $X^R_0 < X_e$
h^R_{sp}	Specific enthalpy R magma contributes to hybrid magma when R magma is single phase liquid of bulk composition $X^R_0 > X_e$
h^R_{s-L}	Specific enthalpy R magma contributes to hybrid magma when R magma is L+β mixture of bulk composition $X^R_0 > X_e$
$h^R_{\alpha\beta}$	Specific enthalpy R magma contributes to hybrid magma when R magma is α+β crystal mixture

TABLE 2: Enthalpy Expressions of M and R Magmas

TABLE 3: Specific Enthalpy Boundary Values Separating Phase Assemblages

Specific enthalpy	Fields Separated	Expressions for Specific enthalpy for $X^M < X_e$ and $X^M > X_e$ cases
h_{max}	L and α+L or β+L field	(expressions)
h_{mid}	α+L+β and L+α+β field	(expressions)
h_{min}	L+α+β and α+β field	(expressions)

TABLE 4: Hybrid magma bulk composition less enriched in component A than eutectic composition ($X^H < X_e$) NOTE: analogous tables exist for ($X^H > X_e$) and ($X^H = X_e$)

TABLE 5: Thermodynamics of Toy binary eutectic system. Parameters closely follow those in system CaMgSi₂O₆ - CaAl₂Si₂O₈ at 10^5 Pa.

Thermodynamic parameter	Symbol	Value	Units
Eutectic composition, mass fraction component A	X_e	0.42	
Eutectic temperature	T_e	1547	K
Melting point of α crystals	$T^\alpha_{m.p}$	1665	K
Enthalpy of fusion of α crystals at $T^\alpha_{m.p}$	Δh^α	636000	J/kg
Melting point of β crystals	$T^\beta_{m.p}$	1830	K
Enthalpy of fusion of β crystals at $T^\beta_{m.p}$	Δh^β	478000	J/kg
Crystal specific isobaric heat capacity	C_s	1400	J/kg-K
Liquid specific isobaric heat capacity	C_L	1600	J/kg-K

FIGURE 1: Binary Eutectic Phase Diagram

FIGURE 2a: Temperature vs. Enthalpy

FIGURE 2b: Temperature vs. Enthalpy

FIGURE 3: Generalized Toy Initial Conditions & Solution

III: Analysis

For fixed thermodynamic parameters, the five initial conditions of $X^M_0, X^R_0, T^M_0, T^R_0$, and f_0 determine the state of hybridized magma (**H**). There are five possible mutually exclusive *Phase Assemblage Outcomes* (**PAO**'s) (see Fig 1) for any set of initial conditions:

L only (PAO1), L + α (PAO2), L + β (PAO3), $L_{eutectic}$ + α + β (PAO4) or α + β (PAO5)

QUESTION: What is the *probability distribution* of *Phase Assemblage Outcomes* given a reasonable range for each of the five initial conditions?

SOLUTION: Apply a **Monte Carlo (MC)** method to study the statistics of the five possible outcomes given a realistic range of possible values for each of the five initial parameters X_0, X_0, T_0, T_0, f_0

- Table 6 provides the distribution (mean, one sigma, max and min) of the input parameters
- Use Monte Carlo (MC) approach to generate several million solutions (realizations)
- Perform statistical analysis of outcomes to seek preferred states
- By choosing a temperature range, an enthalpy range is implicitly defined
  - Enthalpy of M, R and H is a function of temperature, phase abundance and melt (if present) composition.
  - A global enthalpy maximum and minimum (h_{GMAX} and h_{GMIN}) are also defined (see Fig 2)
- Once IC's have been defined, PAO's can be determined explicitly (refer to Fig 2)
  - define Δh = h_{GMAX} - h_{GMIN}
  - The probability of a particular of Phase Assemblage Outcome is proportional to the fraction of hybrid system enthalpies that fall within a given increment based on Figure 2. Specifically,

PAO1 fraction = (h_{GMAX} - h_{max}) / Δh
∑(PAO2 + PAO3) fractions = (h_{max} - h_{mid}) / Δh
PAO4 fraction = (h_{mid} - h_{min}) / Δh
PAO5 fraction = (h_{min} - h_{GMIN}) / Δh

TABLE 6: Distribution of Initial Condition variables $X^M_0, X^R_0, T^M_0, T^R_0, f_0$

Input	Mean Value	1σ	Minimum	Maximum
X^M_0	0.5	±0.3	> 0	< 1
X^R_0	0.5	±0.3	> 0	< 1
T^R_0	If $X^R_0 < X_e$, then mean = average of $T^\alpha_{m.p}$ and 0.98 T_e	±150	0.98 T_e	$T^\alpha_{m.p}$
T^R_0	If $X^R_0 > X_e$, then mean = average of $T^\beta_{m.p}$ and 0.98 T_e	±150	0.98 T_e	$T^\beta_{m.p}$
T^M_0	If $X^M_0 < X_e$, then mean = average of $T^\alpha_{m.p}$ and 0.98 T_e	±150	0.98 T_e	$T^\alpha_{m.p}$
T^M_0	If $X^M_0 > X_e$, then mean = average of $T^\beta_{m.p}$ and 0.98 T_e	±150	0.98 T_e	$T^\beta_{m.p}$
f_0	0.5	±0.3	$f_0 > 0$	$f_0 < 1$

IV: Results

- Statistical analyses were conducted on a population of over **5 million MC realizations** in which **M** was melt and **R** magma (crystal + liquid) or both **M** and **R** were magmas (i.e., both **M** and **R** were crystal + liquid, respectively). The statistical results were:

- melt (**M**) + magma (**R**) mixing:
  - L = 46.3%
  - L + α = 11.3%
  - L + β = 31.4%
  - $L_{eutectic}$ + α + β = 10.8%
  - α + β = 0.2%

- magma (**M**) + magma (**R**) mixing:
  - L = 6.5%
  - L + α = 8%
  - L + β = 18.5%
  - $L_{eutectic}$ + α + β = 44%
  - α + β = 23%

- Note proclivity toward the eutectic condition $L_{eutectic}$ + α + β in magma - magma mixing

Eutectic "Attractor" - the tendancy for the hybridized magma **H** to be at the invariant point

melt M + magma R mixing, $f_0 = 0.5$; magma M + magma R mixing, $f_0 = 0.5$

Magma Cooling Effect - T of **H** is *LESS* than initial T of both **M** and **R**

- Some realizations produce a thermal outcome of special interest when the temperature of the equilibrated **hybrid** (**H**) magma is lower than EITHER of the starting magmas (**M** and **R**). I.e., $T^H < T^M_0$ and $T^H < T^R_0$
  - This thermal condition occurs in 18% of the **M** (melt) + **R** (magma) realizations (~90,000 cases)
  - This thermal condition occurs in 9% of the **M** (magma) + **R** (magma) realizations (~405,000 cases)

melt M + magma R mixing, $f_0 = 0.65$; magma M + magma R mixing, $f_0 = 0.2$

Suppression of α Crystallization of Previously α-Saturated **M**

melt M + magma R mixing, $f_0 = 0.4$; magma M + magma R mixing, $f_0 = 0.4$

Crystal-laden Suspension **M** Converted to Superheated Liquid by Addition of Hot **R**

magma M + melt R mixing, $f_0 = 0.5$; magma M + magma R mixing, $f_0 = 0.5$

Loss of 'memory' of Liquidus Phase of **R** Magma Due to Mixing

melt M + magma R mixing, $f_0 = 0.6$; magma M + magma R mixing, $f_0 = 0.75$

Variable Effects of Stoping Cold Blocks of **R** into **M**

In order to bring a melt **M** below the solidus, a large stoped block (33% total system mass) is needed, whereas the same result is accomplished for a magma **M** with a much smaller stoped block (17% total system mass) even though the starting **M** temperatures only differ by < 20K and T^R_0 is the same in both cases

melt M + solid R mixing, $f_0 = 0.66$; magma M + solid R mixing, $f_0 = 0.83$

A cool **R** block dropped into a melt **M** promotes crystallization, but only of the α phase; crystallization of the β phase (50% of R) is suppressed

melt M + solid (α + β) R mixing, $f_0 = 0.75$

V: Conclusions

- In many magma mixing scenarios, the T of the hybrid magma (**H**) is **less than** the T of the magmas (**M** and **R**) that mix. This can lead to some interesting phenocryst compositional profiles.
- The tendency for hybrid magma (**H**) to be "attracted" to the invariant point is common, particularly in magma-magma mixing
- Expression of crystallization in **H** can be highly variable and is sensitive to the mixing conditions (i.e. $X^M_0, X^R_0, T^M_0, T^R_0$, and f_0)
- Experimentation with stoping blocks of different masses & T^R_0 into **M** suggests a sensitive dependence on mass, bulk composition and T of the stoped rocks
- Toy model provides valuable insights into complex multi-component, multi-phase systems (see next poster, MCS)