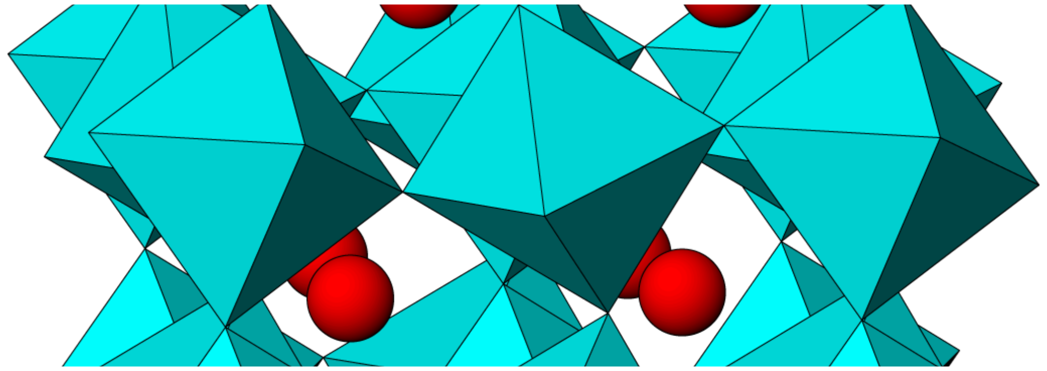
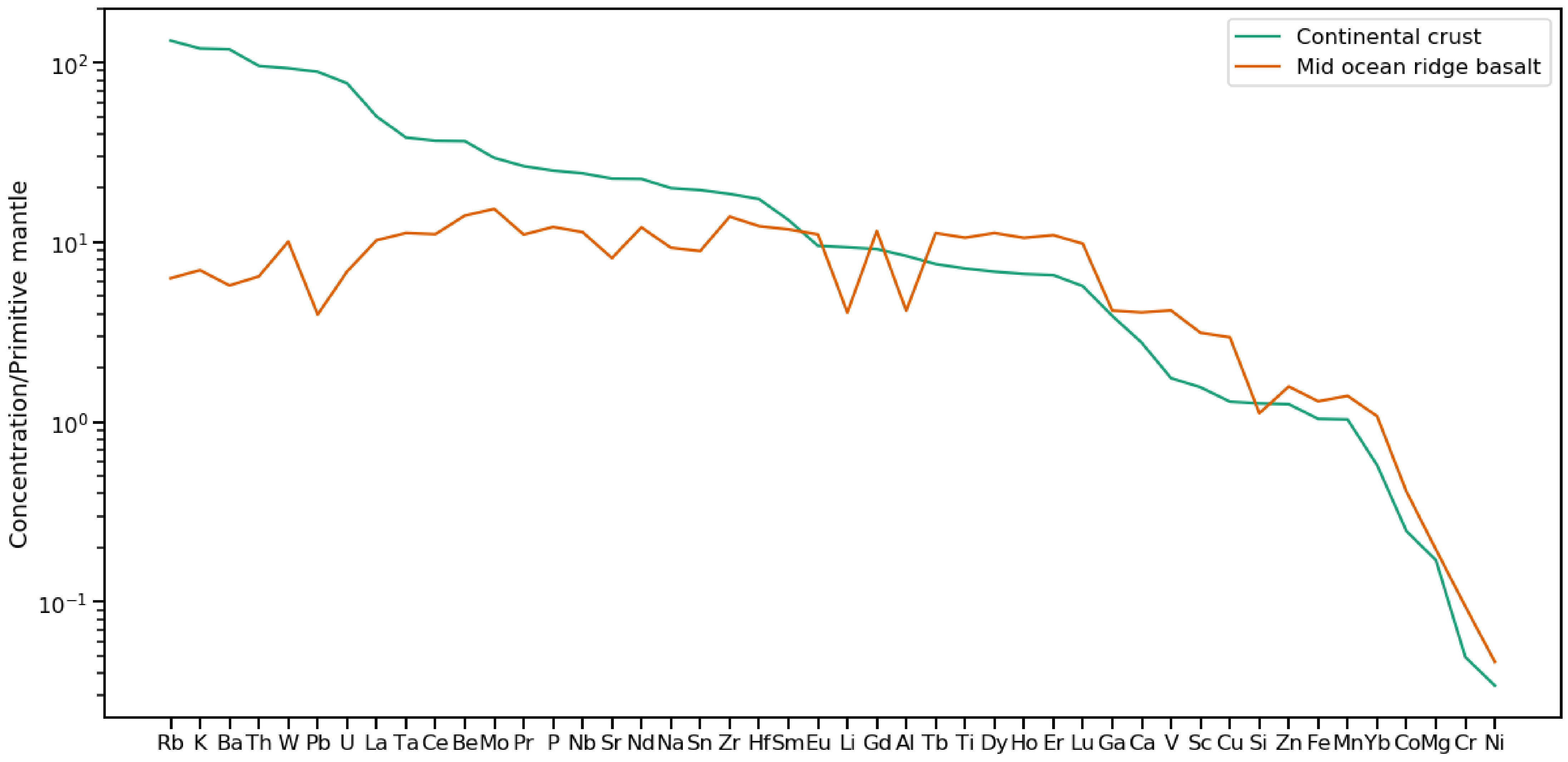


Lecture 6-10: trace element geochemistry

1. Review of equilibrium constant
    - A. Gibb's free energy of reaction
2. Trace element definitions
    - A. Compatibility and partition coefficients
    - B. General trends in compatibility
    - C. The relationship between partition coefficients and equilibrium constants
3. Thermodynamic basis for compatibility
4. Crystallization/melting models and trace elements
    - A. Batch crystallization: trace elements
    - B. Fractional crystallization
    - C. Bulk partitioning
    - D. Muskox Intrusion
    - E. Fractional melting

We acknowledge and respect the lək̓ʷəŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.

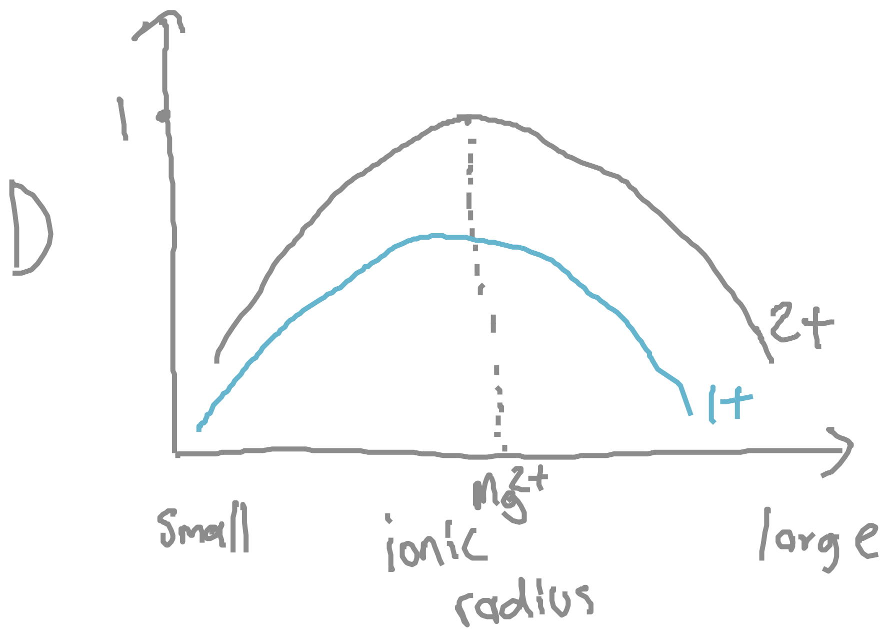


Continental crust
Mid ocean ridge basalt
Concentration/Primitive mantle
10^2
10^1
10^0
10^{-1}
Rb K Ba Th W Pb U La Ta Ce Be Mo Pr P Nb Sr Nd Na Sn Zr Hf Sm Eu Li Gd Al Tb Ti Dy Ho Er Lu Ga Ca V Sc Cu Si Zn Fe Mn Yb Co Mg Cr Ni

Trace elements, compatibility, and general trends.

Trace elements are < 0.1 wt% of a rock/mineral

- concentrations are too low to dictate phase
- trace elements passively substitute into phases



The partition coefficient: D

a trace element i

$$D_i = \frac{C_i^{solid}}{C_i^{liquid}} \text{ at equilibrium}$$

$D > 1$ compatible, trace element prefers solid phase

$D < 1$ incompatible, trace element prefer liquid phase

$0.1 - 1$: moderately incompatible

Equilibrium constants and partition coefficients. Ni exchange in olivine.

X_{Ni} = molar fraction of nickel

$$wA + xB \overset{K}{\rightleftharpoons} yC + zD$$

$$K_{eq} \approx \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

recall:

$$\Delta G = -RT \ln K$$

R: gas constant

T in Kelvin

$$\Delta G \approx -RT \ln D_i$$

$$\underset{\text{olivine}}{Mg_2SiO_4} + \underset{\text{melt}}{Ni_2SiO_4} \longleftrightarrow \underset{\text{olivine}}{Ni_2SiO_4} + \underset{\text{melt}}{Mg_2SiO_4}$$

red = melt

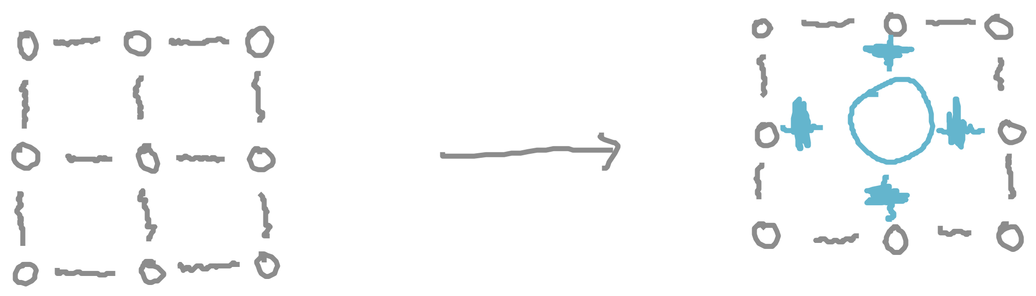
$$K = \frac{X_{Ni}^2 \cancel{\underline{X_{Mg}^2}}}{\cancel{X_{Mg}^2} \underline{X_{Ni}^2}}$$

$$1 \approx \frac{X_{Mg}^2 \text{ melt}}{X_{Mg}^2 \text{ solid}}$$

$$K = \frac{X_{Ni}^2}{\underline{X_{Ni}^2}}$$

$$D \approx \frac{C_S}{C_L}$$

Thermodynamic model for compatibility. Energy to displace lattice:



$W = f \cdot d$

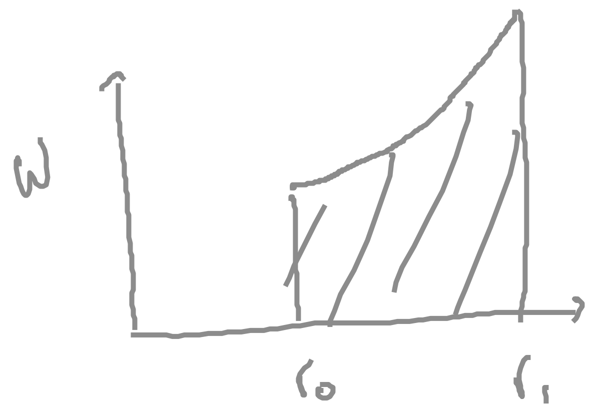
$\dot{\varepsilon}$ = strain = relative deformation $= \frac{r_1 - r_0}{r} = \frac{dr}{r}$

E = Young's modulus $= \frac{\sigma}{\dot{\varepsilon}}$ = resisting change

$\sigma = F/A$ = stress

$$W = F \cdot d = \frac{F}{A} \cdot A \cdot d = \sigma \cdot A \cdot d$$
$$= \frac{\sigma}{\dot{\varepsilon}} \dot{\varepsilon} A d$$
$$W = E \cdot \dot{\varepsilon} A d$$
$$W = E \frac{dr}{r} A d$$
$$W = E 4\pi r^2 \frac{dr}{r} \cdot d$$
$$w = E 4\pi r^2 \frac{dr}{r} (r - r_0)$$

$A = 4\pi r^2$ suface area of a sphere



Integral.

$$W = E\, 4\pi r\, (r - r_0)\, dr$$

$$W = E\, 4\pi r \int_{r_0}^{r} r(r - r_0)\, dr$$

$$W = E\, 4\pi \int_{r_0}^{r} (r^2 - r r_0)\, dr$$

$$W = E\, 4\pi \left(\frac{r^3}{3} - \frac{r_0 r^2}{2} \right) \Bigg|_{r_0}^{r}$$

$$W = E\, 4\pi \left(\frac{1}{3}(r - r_0)^3 - \frac{r_0}{2}(r - r_0)^2 \right) = \Delta G_{\text{strain lattice}}$$

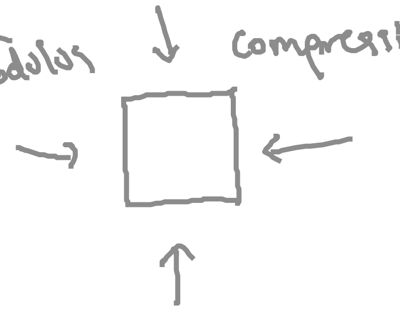
$$E = \text{Young's modulus} \simeq \frac{3K}{1 - 2\nu}$$

K ← Bulk modulus

ν ← poisson ratio

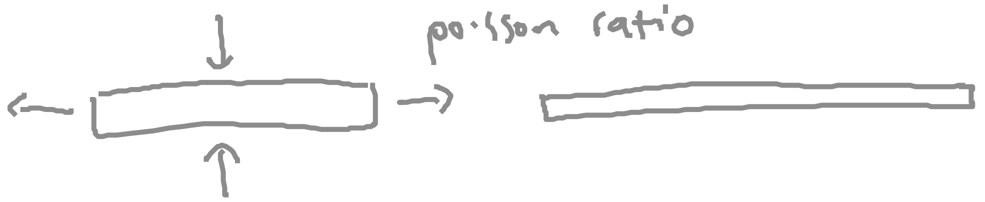
Bulk modulus

compression



$$K \simeq \frac{z_a z_c e^2 (n - 1)}{V_0}$$

poisson ratio



Thermodynamic model for compatibility. Ion exchange with Ca.

$$\underset{\text{melt}}{CaMgSi_2O_6} \longleftrightarrow \underset{\text{clinopyroxene}}{CaMgSi_2O_6}$$

$$K \approx D_{Ca} \approx \frac{cpx}{melt}$$

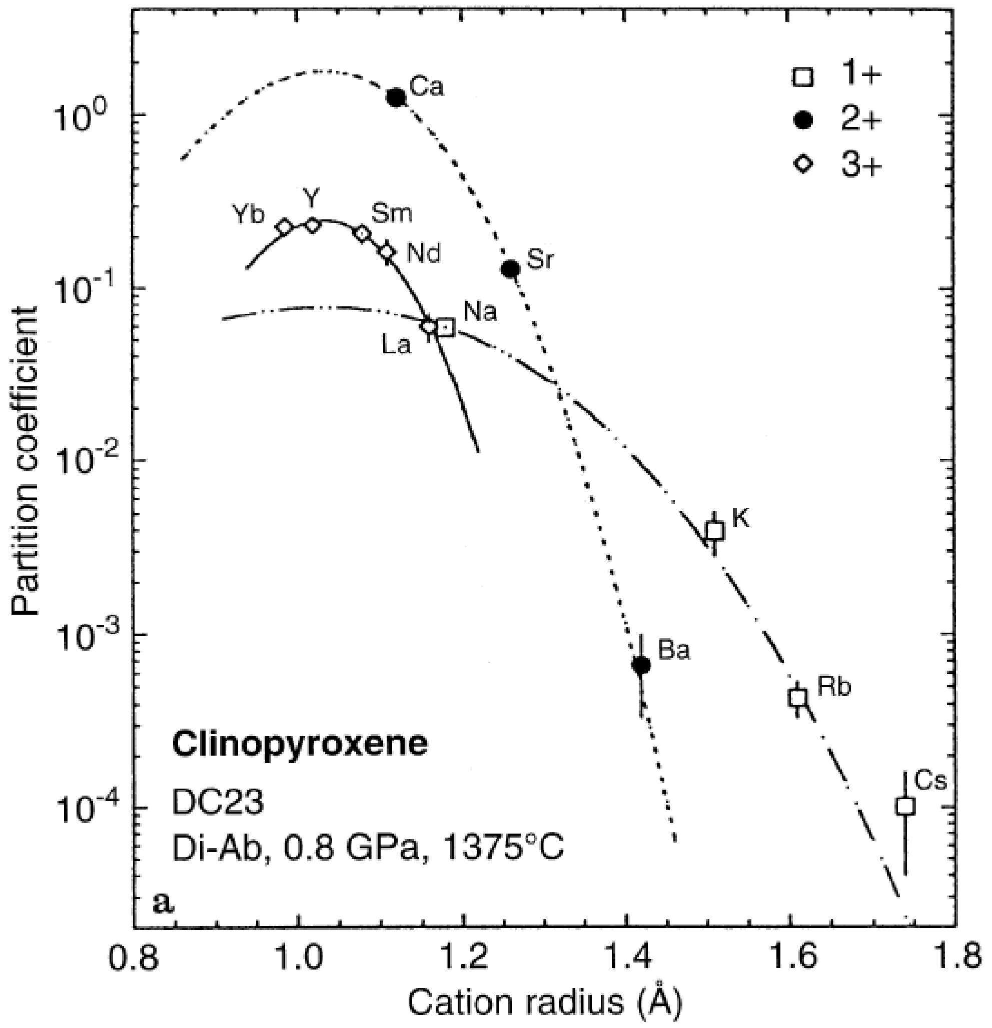
$$\underset{\text{melt}}{M^{2+}} + \underset{\text{cpx}}{CaMgSi_2O_6} \longleftrightarrow \underset{\text{melt}}{Ca^{2+}} + \underset{\text{cpx}}{M^{2+}_{Mg}MgSi_2O_6}$$

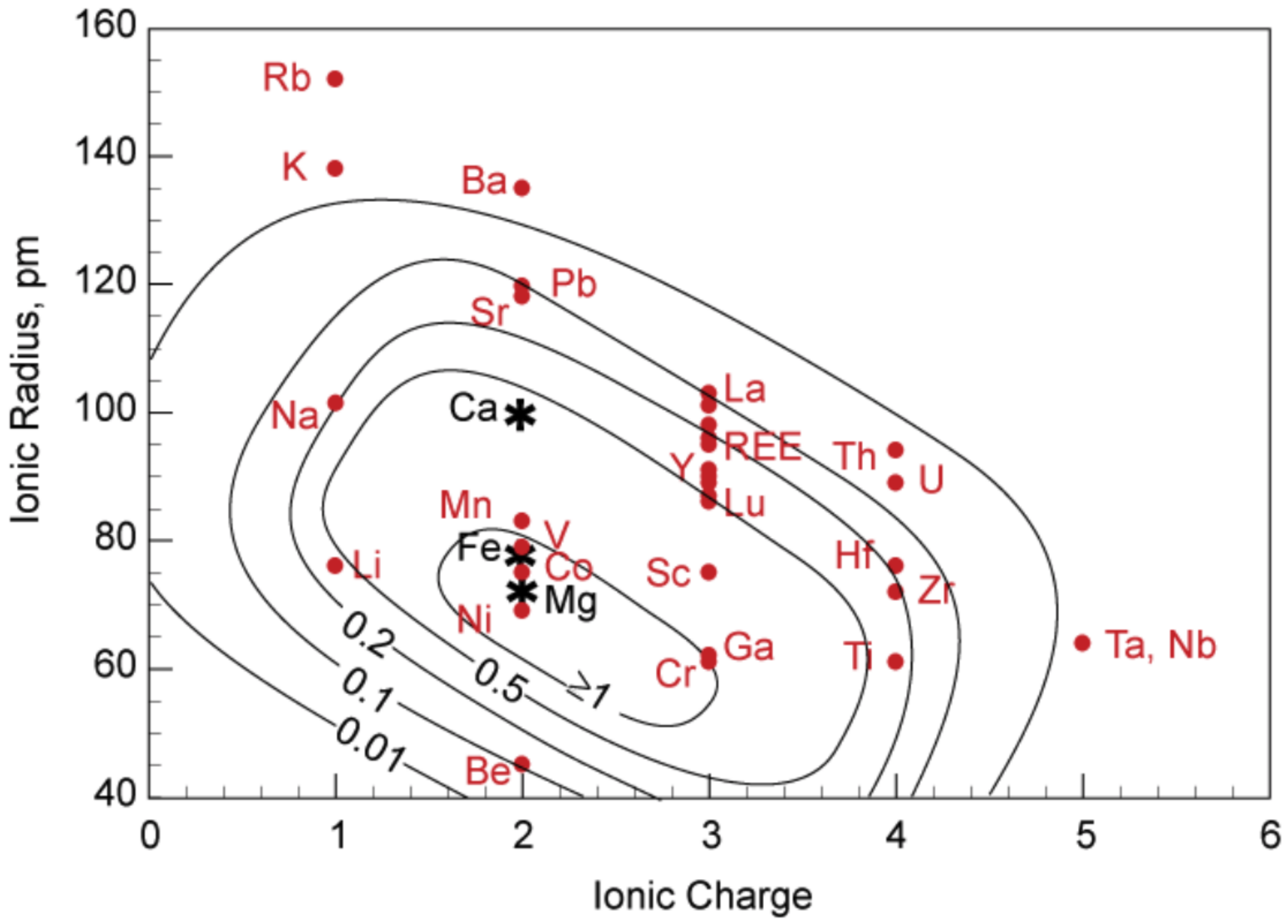
$$\Delta G = \Delta G_{products} - \Delta G_{reactants}$$

$$\Delta G = \cancelto{0}{\Delta G_{\substack{Ca^{2+}\\ melt}}} + \Delta G_{\substack{m^{2+}\\ cpx}} - \left(\cancelto{0}{\Delta G_{\substack{m^{2+}\\ melt}}} + \Delta G_{\substack{Ca^{2+}\\ cpx}} \right)$$

Thermodynamic model for compatibility. Returning to ΔG and partition coefficients.

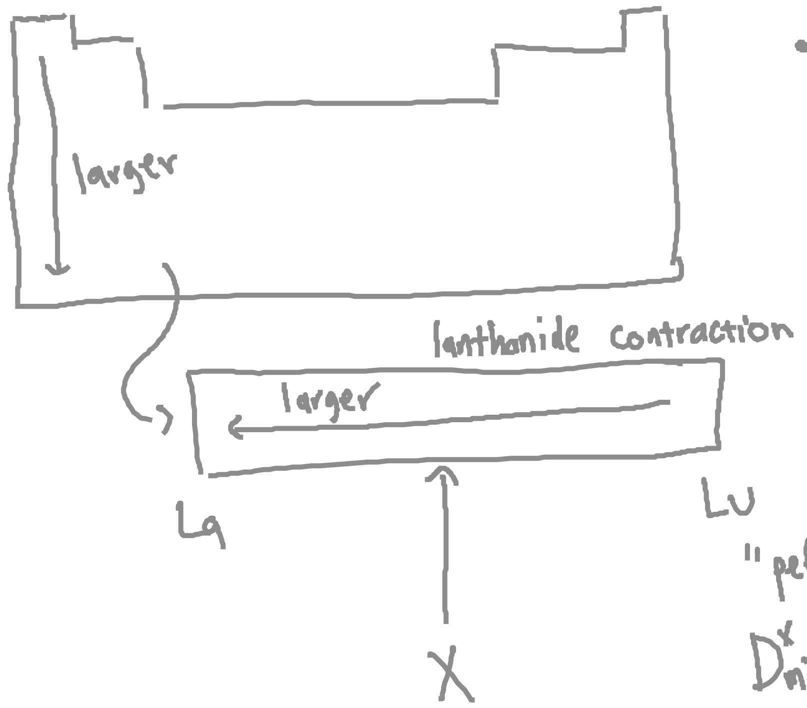
(equilibrium review hand notes, digitize for 2025)


1+
2+
3+
Ca
Sr
Ba
Yb
Y
Sm
Nd
La
Na
K
Rb
Cs
Clinopyroxene
DC23
Di-Ab, 0.8 GPa, 1375°C
a
Partition coefficient
Cation radius (Å)
0.8
1.0
1.2
1.4
1.6
1.8



Ionic Radius, pm
Ionic Charge
160
140
120
100
80
60
40
0
1
2
3
4
5
6
Rb
K
Ba
Pb
Sr
Na
Ca
La
REE
Y
Lu
Th
U
Mn
V
Fe
Co
Mg
Ni
Li
Sc
Hf
Zr
Ga
Cr
Ti
Ta, Nb
Be
0.2
0.1
0.01
0.5
≥1

Periodic table, general patterns in ion size



ionic radius

- more shells, generally large ion
- as Z, atomic number, increases along a row
  - ionic radius decreases
- $r_{cation} < r^{0+}_{neutral} < r_{anion}$

"perfect size"

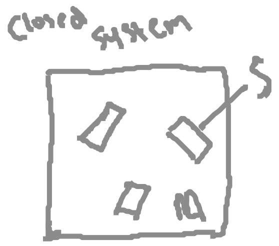
$D^{x}_{min} = 1$ $\quad D^{Lu}_{min} \nless D^{x}_{min}$

Batch melting or crystallization: conceptual *drawing...*

Batch melting or crystallization: derivation

$L = M$

liquid = melt



M = melt

S = solid

C = concentration of a trace element i

$D = \frac{C_s}{C_m}$

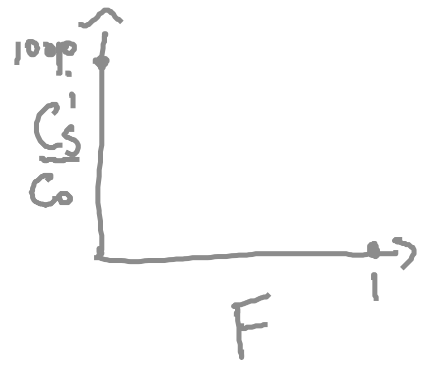
$D \cdot C_m = C_s$

$F = \%$ melt $= \frac{\text{mass of melt}}{\text{Mass in the box}} = \frac{M_m}{M_o}$

$F = 1$, all melt

total i = 1000 ppm, and S is 10 % of the mass, what is C_s^i?

F=



- if $F = 0$, $C_s^i = 1000$ ppm
- if $F = 1$, $S_m^i = 1000$ ppm

mass balance

$$C_o M_o = C_m \cdot M_m + C_s \cdot M_s$$

$$\frac{C_o \cancel{M_o}}{\cancel{M_o}} = \frac{C_m M_m}{M_o} + \frac{D\, C_m \cdot M_m}{M_o} = \underset{\text{melt}}{C_o} = C_m \cdot \underbrace{\frac{M_m}{M_o}}_{F} + D\, C_m \underbrace{\frac{M_s}{M_o}}_{(1-F)}$$

$$C_o = C_m F + D\, C_m (1-F)$$

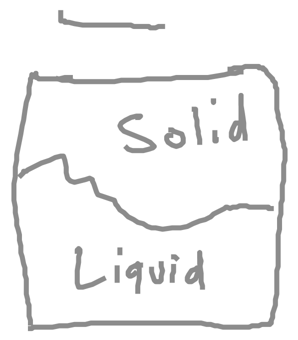
$$C_o = C_m (F + D(1-F))$$

$$\boxed{\frac{C_m}{C_o} = \frac{1}{F + D(1-F)}}$$

$$\boxed{\frac{C_s}{C_o} = \frac{D}{F + D(1-F)}}$$

Batch melting or crystallization: predictions

L = Melt
L = Liquid

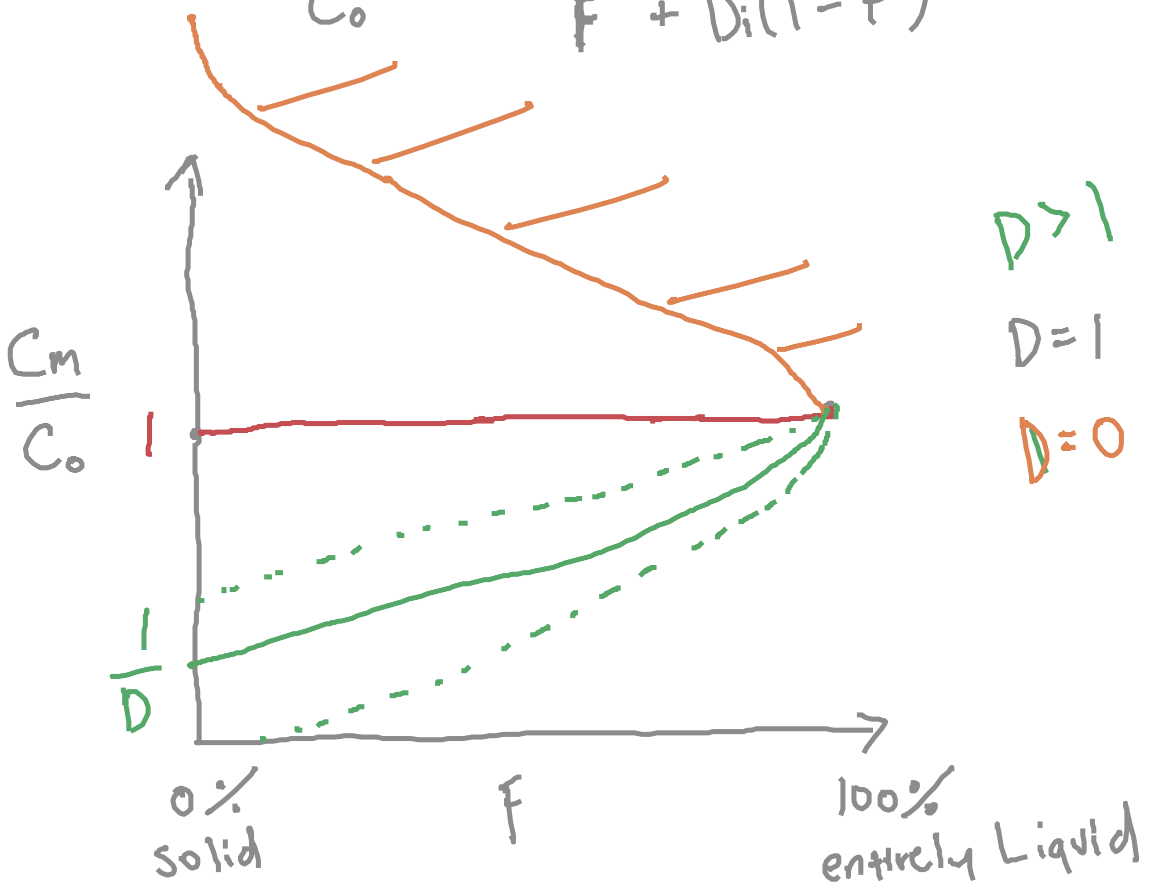


D_i = partition coefficient = $\frac{C_s}{C_L}$

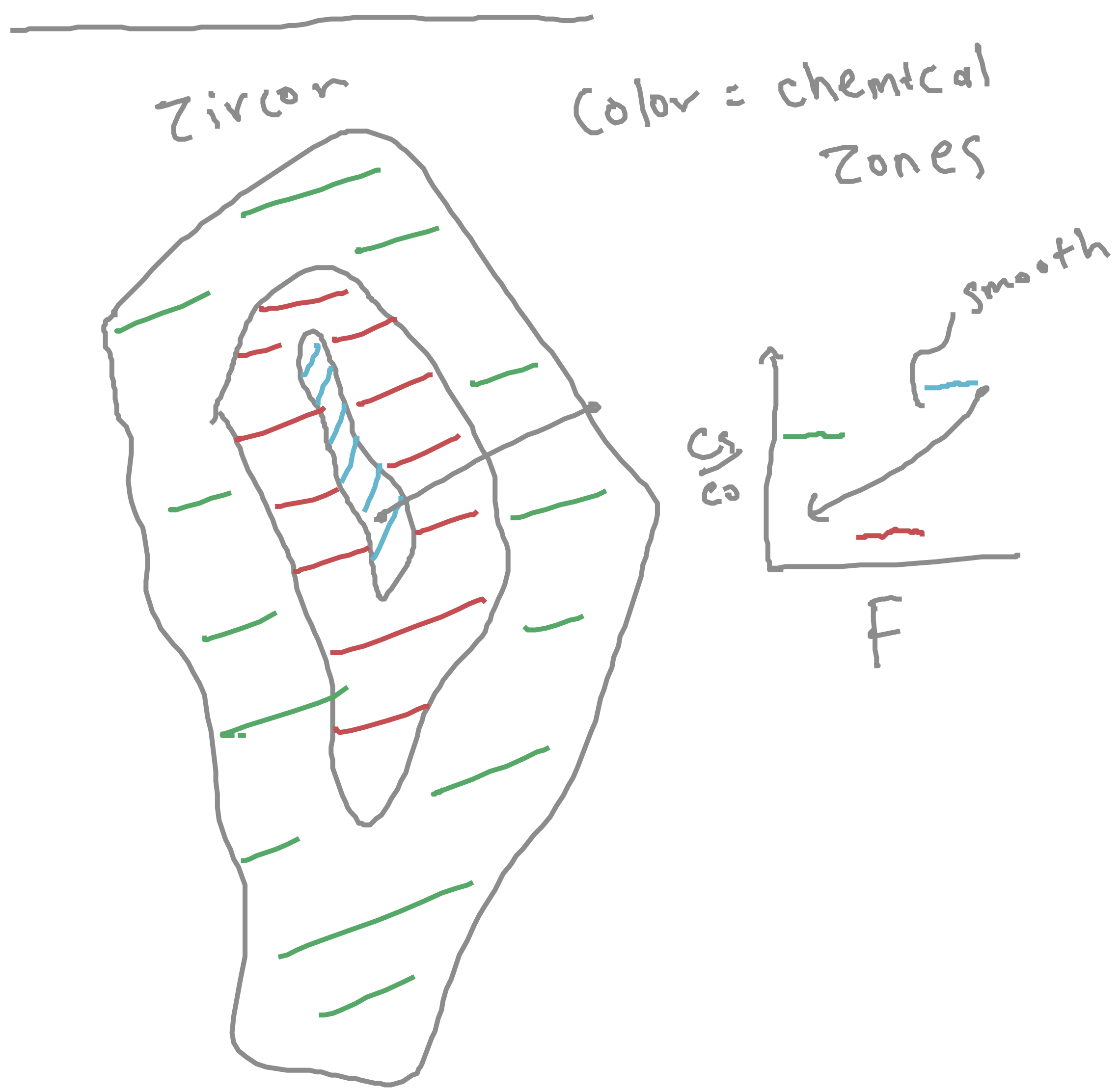
$F = \frac{M_L}{M_0}$ ← mass of system

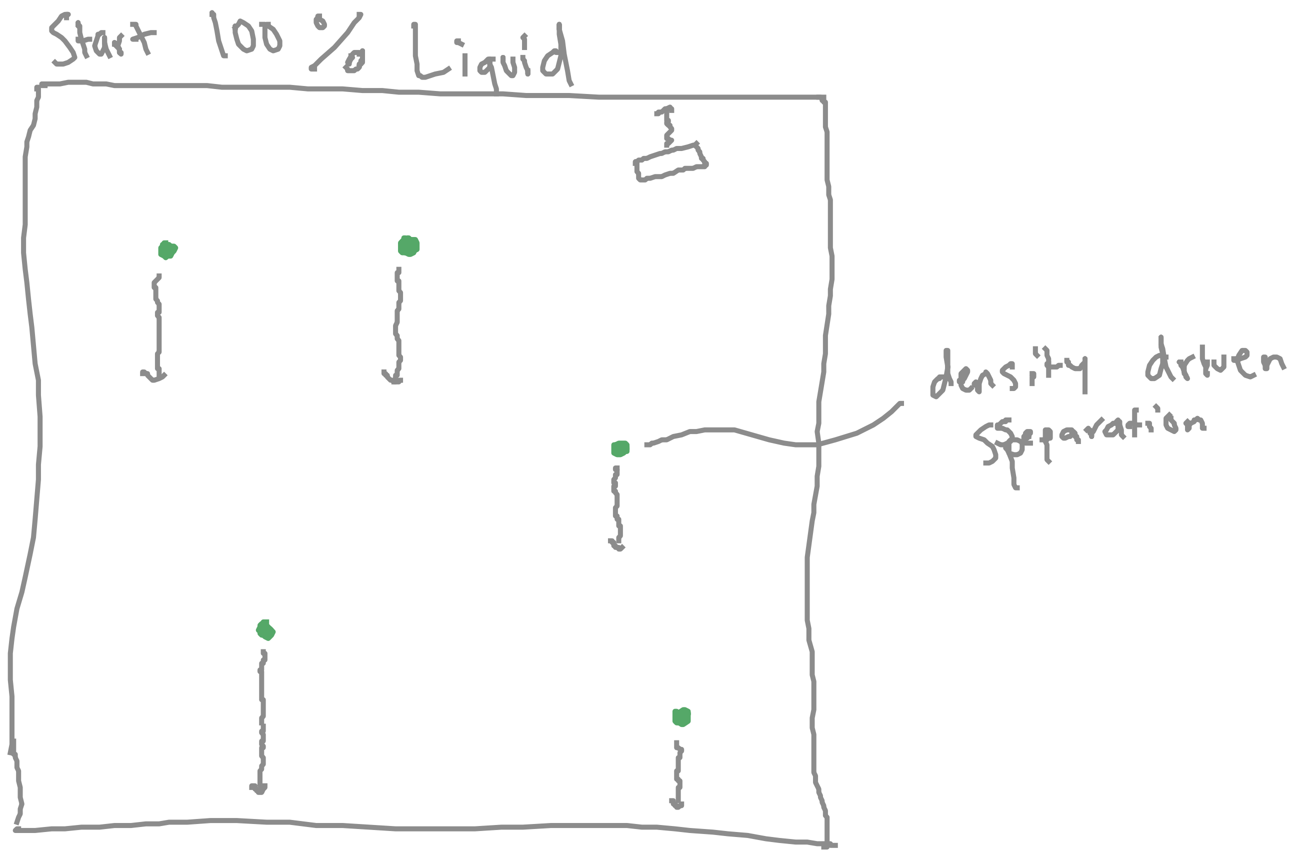
$$\frac{C_L}{C_0} = \frac{1}{F + D_i(1-F)}$$

$$\frac{C_s}{C_0} = \frac{D_i}{F + D_i(1-F)}$$



Fractional crystallization: conceptual





Fractional crystallization: derivation

Starting w/ 100 % melt

$M \cdot C = M_c$

$D = \frac{C_s}{C_m}$

$D \cdot C_m = C_s$

$\int_Y^Z \frac{dx}{x} = \ln x \Big]_Y^Z$

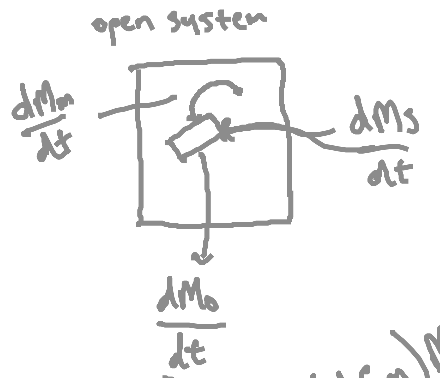
$\ln Z - \ln Y$

$\ln \frac{Z}{Y}$

$a \ln x = \ln x^a$

$\ln a = \ln b$

$a = b$



$$\frac{dM_m}{dt} = -\frac{dM_s}{dt} \quad (1)$$

Change in mass of melt over time

rate of crystal segregation

"product rule"

$d(C_m M_m) = (dC_m) M_m + (dM_m) C_m$

$$\frac{d(C_m M_m)}{\cancel{dt}} = -\frac{d(C_s M_s)}{\cancel{dt}} = -\frac{C_s \, dM_s}{\cancel{dt}}$$

$dC_m \cdot M_m + dM_m \cdot C_m = -D \cdot C_m \, dM_s$ ← using (1)

$dC_m \cdot M_m + dM_m \cdot C_m = -D \cdot C_m \cdot dM_m$

$dC_m \cdot M_m = D \cdot C_m \cdot dM_m - dM_m \cdot C_m$

$dC_m \cdot M_m = (D-1) \, C_m \cdot dM_m$

$$\int_{C_{m_0}}^{C_m} \frac{dC_m}{C_m} = \int_{M_o}^{M_m} (D-1) \frac{dM_m}{M_m}$$

$$(D-1)^{-1} \ln \frac{C_m}{C_{m_0}} = \ln \frac{M_m}{M_o}$$

$$= \ln F$$

$$\ln \frac{C_m}{C_{m_0}} = (D-1) \ln F$$

$$\ln \frac{C_m}{C_{m_0}} = \ln F^{(D-1)}$$

$$\boxed{\frac{C_m}{C_{m_0}} = F^{(D-1)} \qquad \frac{C_s}{C_{m_0}} = D \cdot F^{(D-1)}}$$

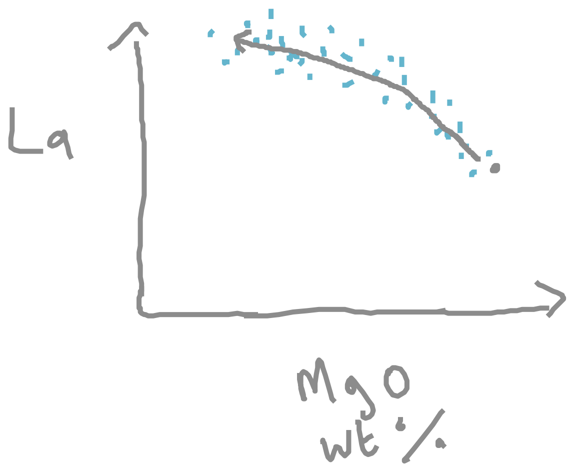
Fractional crystallization: examples

magma w/ olivine crystallizing

Starting composition of our magma

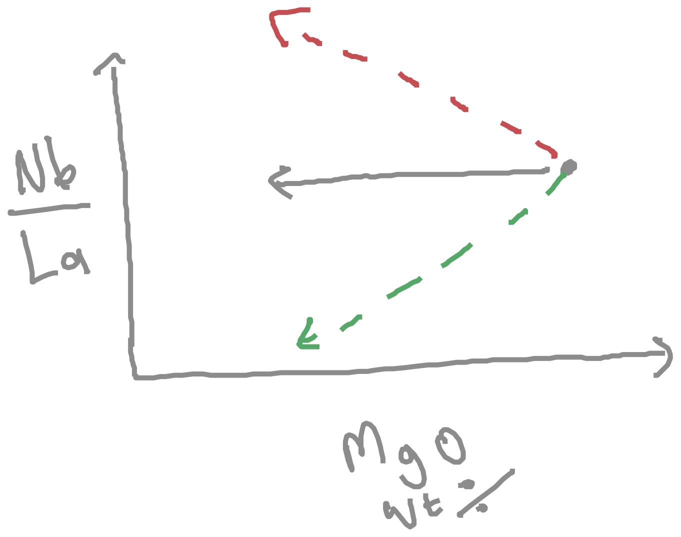
– Ni is compatible in olivine

$D_{Ni} > 1$



La is incompatible in olivine

$D_{La} < 1$



$D_{Nb} < D_{La}$

$D_{Nb} > D_{La}$

$D_{Nb} = D_{La}$

Let's consider Ti

new mineral starts crystallizing

D_{BULK} = partitioning into a real rock

Bulk Partitioning

peridotite
L = melt

$$D_{BULK} = \frac{C_s}{C_m} = D^{ol}\, X^{ol} + D^{opx}\, X^{opx} + D^{cpx} \cdot X^{cpx}$$

mass fraction of olivine

$$= \sum_i D^i X^i$$

Case 1: modal melting

Y = mass fraction at the end of melting

$$X^{ol} = X^{opx} = 0.5$$

$$Y^{ol} = Y^{opx} = 0.47$$

$$D^{ol} = 0.01$$

$$D^{opx} = 0.1$$

what is D_{BULK} before / after melt

Bulk Partitioning

X = mass fraction of some mineral

D_{BULK}?

$$\boxed{D_{BULK} = \frac{C_S}{C_m} = D^{ol}X^{ol} + D^{opx} \cdot X^{opx} + D^{cpx} \cdot X^{cpx}}$$

$X^{ol} + X^{cpx} + X^{opx} = 1$ initial

$Y^{ol} + Y^{cpx} + Y^{opx} = F$ t_1 (time of interest)

F = melt fraction

Case 1: $X^{cpx} = 0$

$X^{ol} = X^{opx} = 0.5$

$Y^{ol} = Y^{opx} = 0.03$

$D^{ol} = 0.01$ $D^{opx} = 0.1$

$D_{BULK} = 0.0517$

Case 2: $X^{ol} = X^{opx} = 0.5$

$Y^{opx} = 0.06$ $Y^{ol} = 0$

$D_{BULK} = 0.049$

Case 1 vs Case 2: similar bulk partitioning

→ trace element i behaves "the same"

→ major element evolution of melt could be very different

Bulk Partitioning

Case 3: introduce new mineral, $D^{min} = 10$

$D^{opx} = 0.1$

$D^{ol} = 0.01$

$X^{ol} = X^{opx} = 0.495$

$X^{min} = 0.01$ $\quad Y^{opx} = 0.06$

$Y^{ol} = Y^{min} = 0$ $\quad D_{BULK} = X^{ol} \cdot D^{ol} + X^{opx} \cdot D^{opx} + X^{min} \cdot D^{min}$

$= (X^{ol} - Y^{ol}) \cdot D^{ol} + (X^{opx} - Y^{opx}) \cdot D^{opx} + (X^{min} - Y^{min}) D^{min}$

troeee element highly compatible in this phase, $D^{min} = 10$

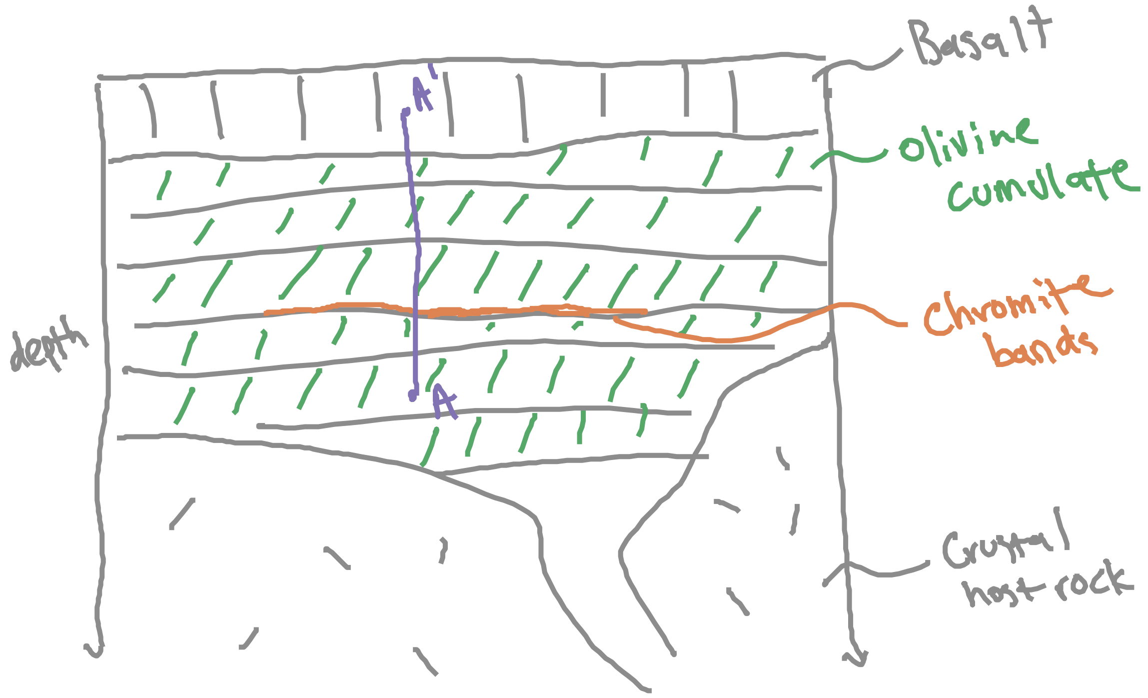
examples: garnet in mantle (high P)

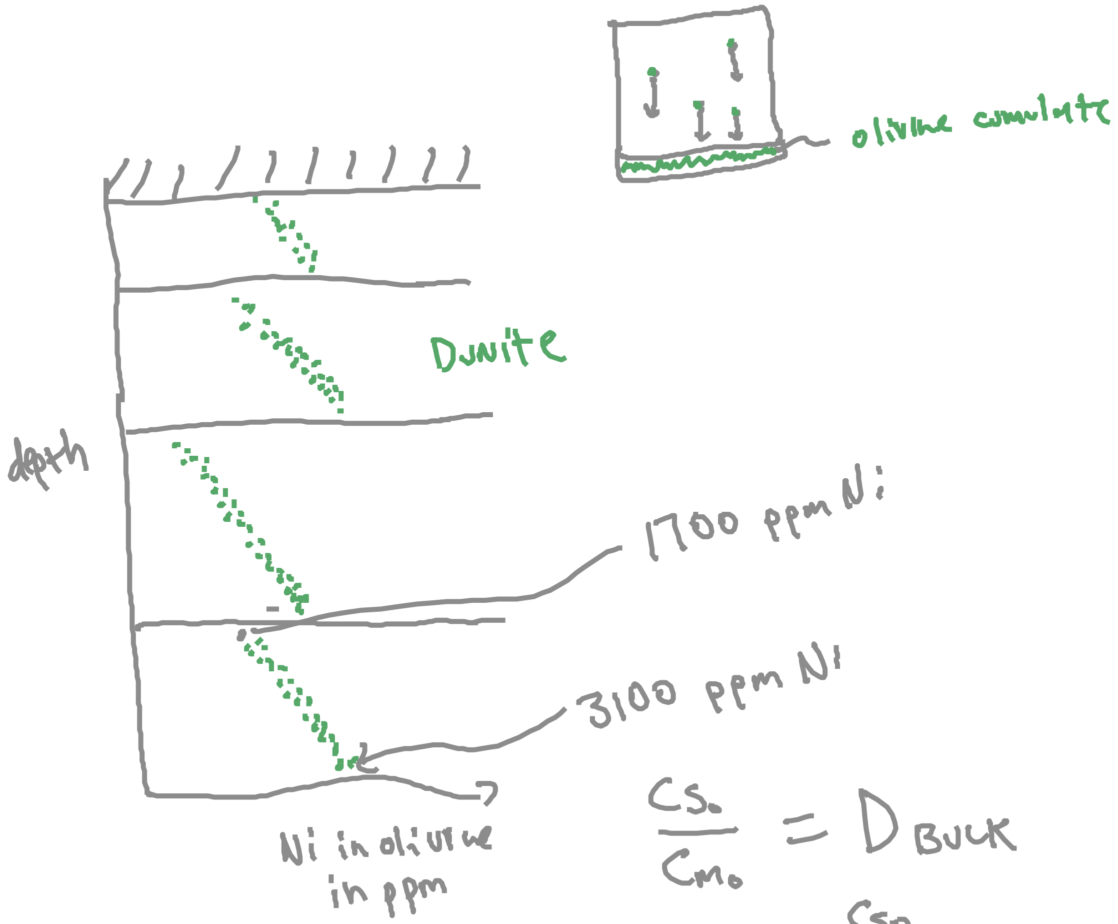
zircon in crustal rocks

$D_{BULK} = X^{ol} \cdot D^{ol} + 0.489 \cdot D^{opx} + X^{min} \cdot D^{min}$

$D_{BULK} = 0.148$

Muskox Layered Intrusion Example





$$\frac{C_{s_0}}{C_{m_0}} = D_{Bulk}$$

$$C_{m_0} = \frac{C_{s_0}}{D}$$

Assume $D^{Ni}_{Bulk} = 15$

From 3100 ppm to 1700 ppm, how much melt crystallized?

$$\frac{C_m}{C_{m_0}} = F^{D-1} \qquad \frac{C_s}{C_{m_0}} = D \cdot F^{D-1} \qquad \frac{1700}{\left(\frac{3100}{\cancel{15}}\right)} = \cancel{15} \cdot F^{15-1}$$

Solution.

$$\frac{1700}{3100} = F^{15-1}$$

$$\log x^y = y \cdot \log x$$

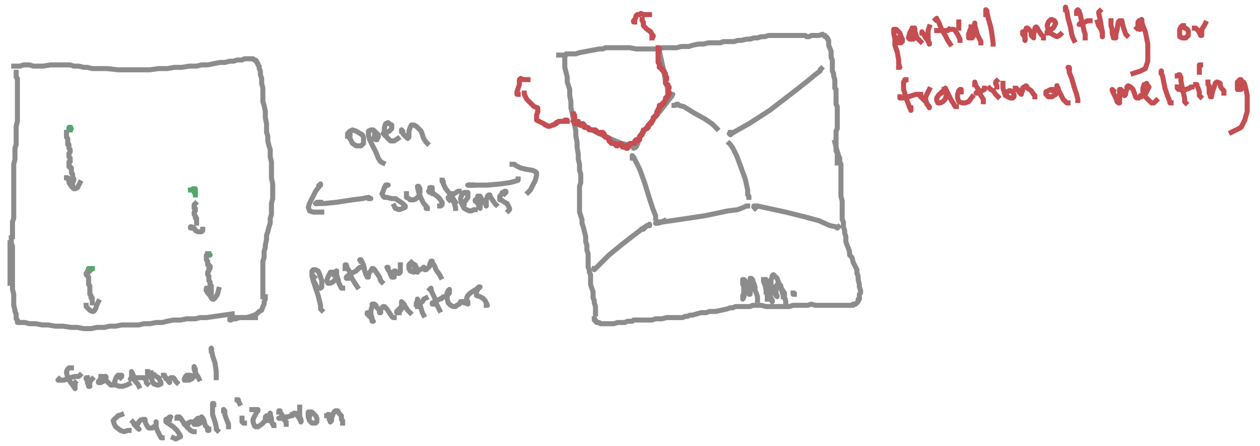
$$\log \frac{1700}{3100} = (15-1) \log F$$

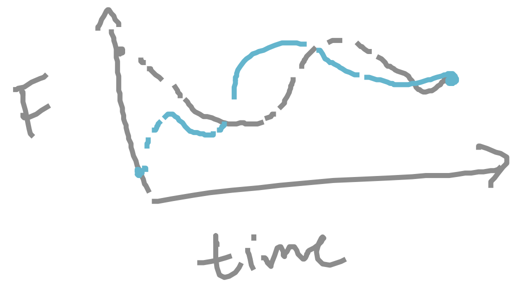
$$\frac{\log \frac{1700}{3100}}{(15-1)} = \log F$$

$F \approx 0.96$ 4% crystallized

$$e^{\frac{\log \frac{1700}{3100}}{(15-1)}} = F$$

Fractional melting: concept and derivation





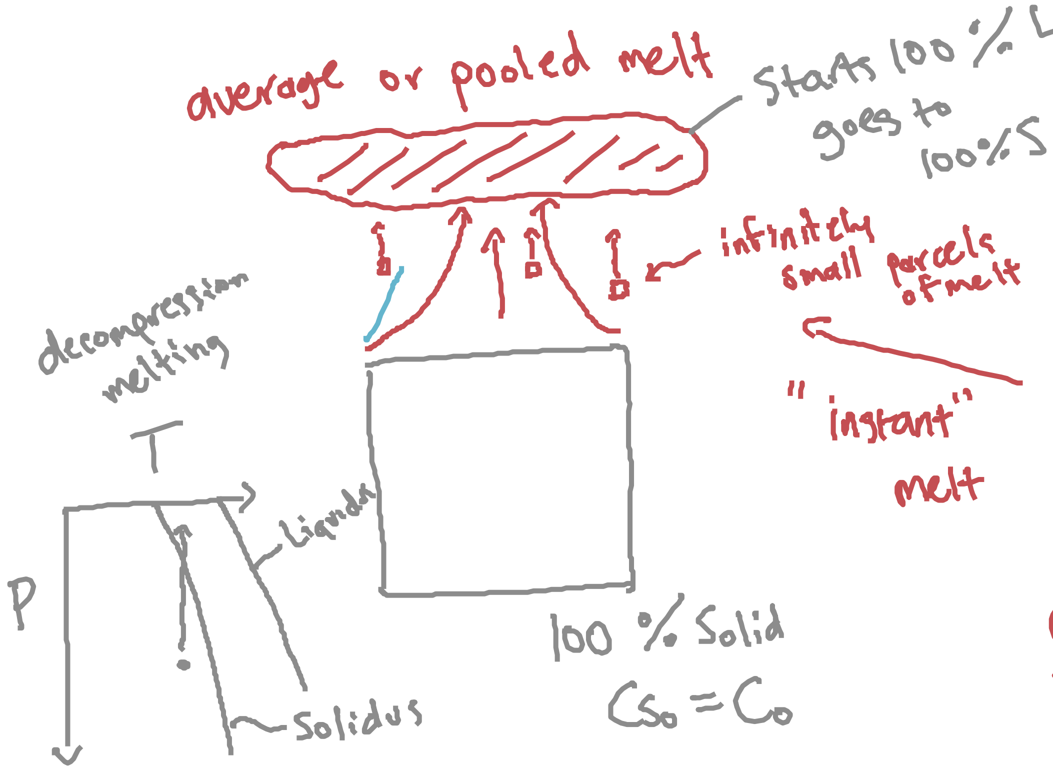
Change in the mass of the system = rate of melting

$$dM_o = -dM_m = dM_s \qquad -C_m\, dM_m = d(C_s M_s)$$

$$\frac{C_s}{C_{so}} = (1-F)^{\frac{1}{D}-1}$$

$$\frac{C_m}{C_{so}} = \frac{1}{D}(1-F)^{\frac{1}{D}-1}$$

Fractional melting: concept and derivation



for some trace element i

$$F = \frac{M_m}{M_o}$$

$$\frac{C_s}{C_{s_0}} = (1-F)^{\left(\frac{1}{D}-1\right)}$$

$$\frac{C_m}{C_{s_0}} = \frac{1}{D}(1-F)^{\left(\frac{1}{D}-1\right)}$$

discrete

$$\frac{\bar{C}_m}{C_{s_0}} = \text{average} = \frac{\text{Sum}}{N}$$

$N \leftarrow F$

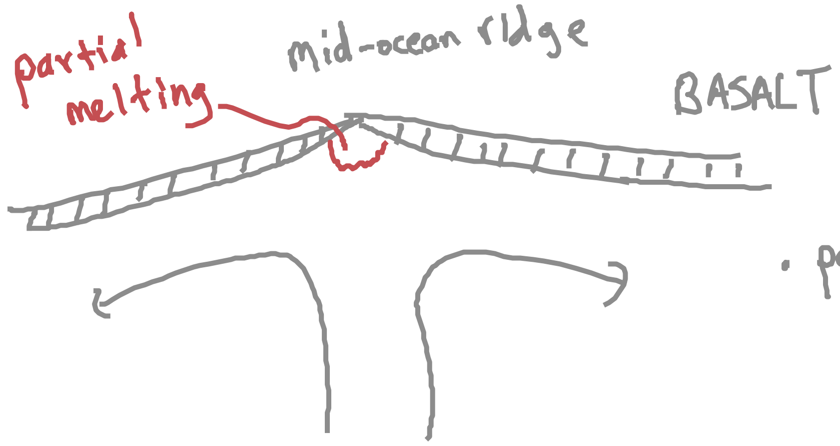
integral

continuous

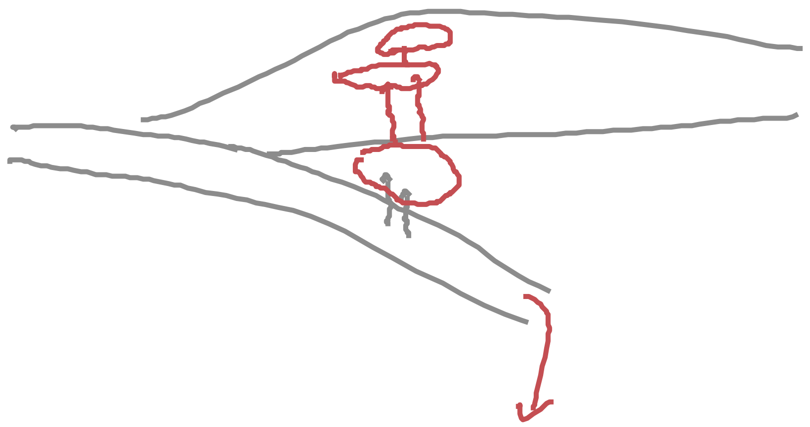
$$= \int_0^F \frac{C_m}{C_{s_0}}\, dF = \text{Lab 4}$$

hint:

$$dF = -d(1-F)$$

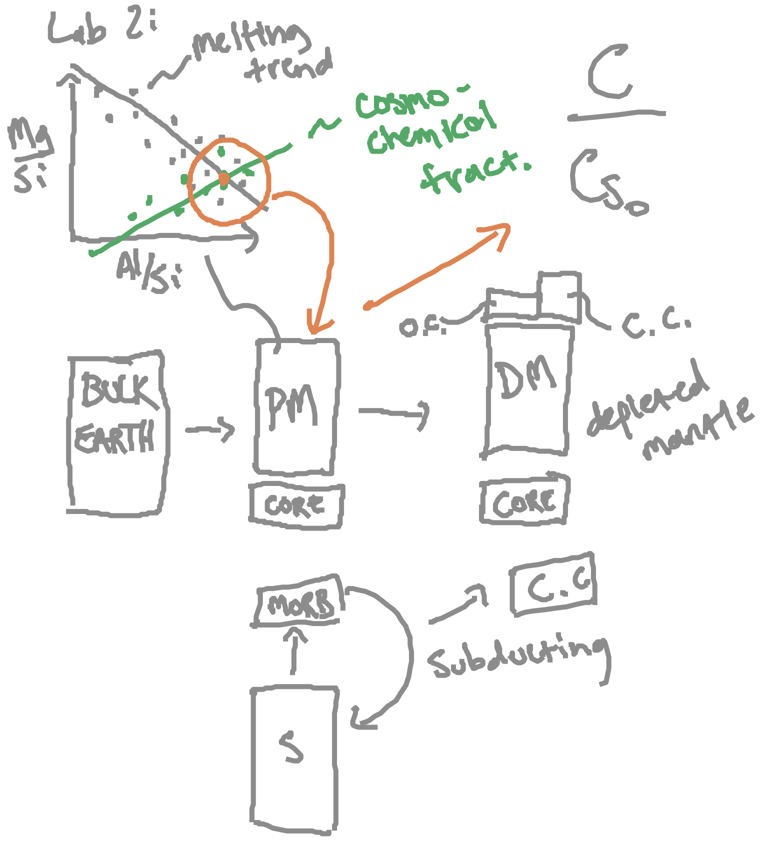


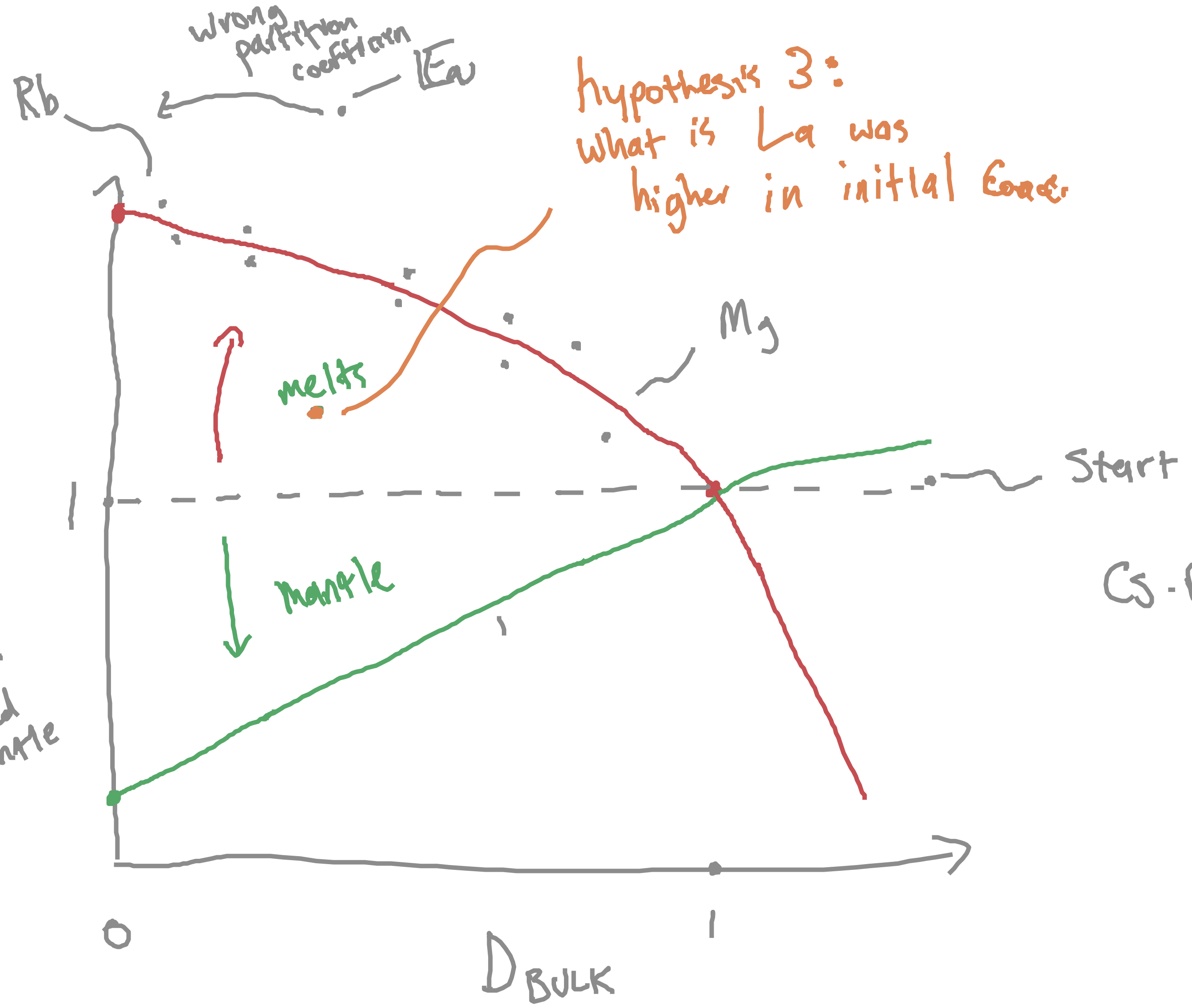
- partial melting extracts incompatible elements from the mantle



hypothesis 1: wrong D_{BULK}?

hypothesis 2: model too simple





hypothesis 3:
what is La was
higher in initial conc.

$D = 1 = \frac{C_S}{C_m}$

$C_S \cdot M_S$ "mass balance"