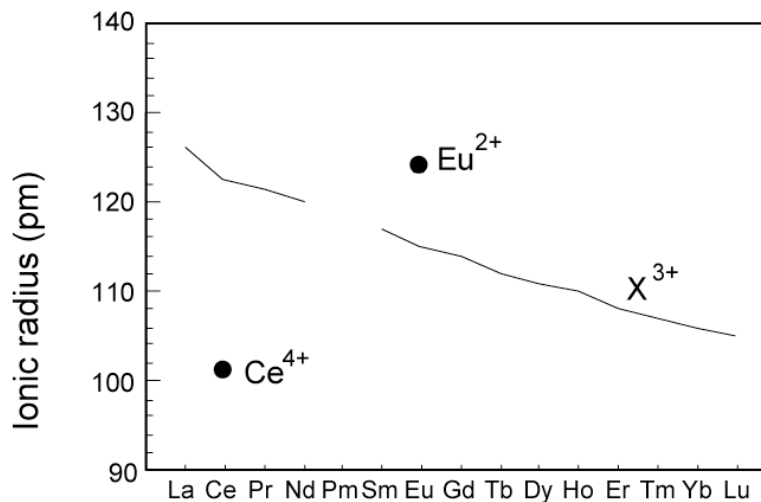


Using Rare Earth Elements to Model Silicate Melting and Crystallization

The Rare Earth Elements (REE)

The lanthanide series is formed by filling of 4f orbitals, and its constituents are commonly termed the rare earth elements (REE). The common valence state is +3 for all REE over a wide range of oxygen fugacity; Ce^{+4} can occur in highly oxidized environments at the earth's surface, and Eu^{+2} in reducing environments in the crust and mantle. The rare earth elements are lithophile elements (low electronegativities lead to the formation of highly ionic bonds), which substitute into many silicates and phosphates.

Ionic radii of the lanthanides decreases with increasing atomic number from La to Lu, the **lanthanide contraction...**



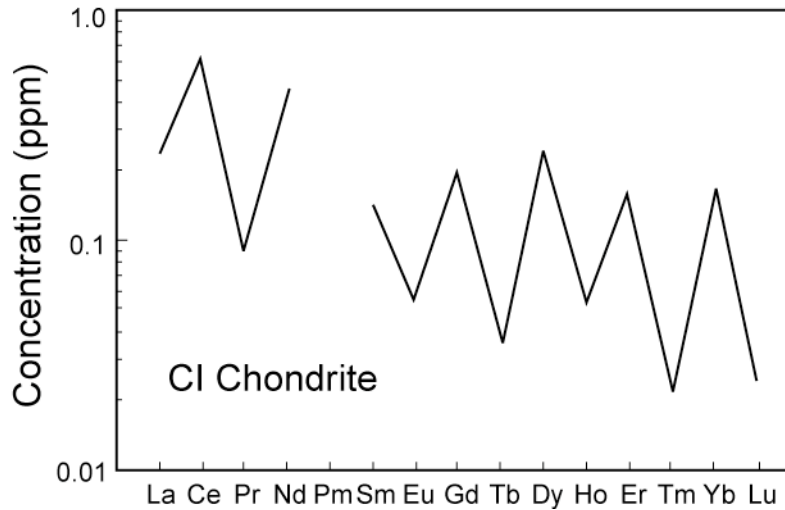
Because of their high charge and large radii, the rare earth elements are usually relatively **incompatible** in silicate minerals. However, due to the lanthanide contraction, the heavier rare earths are smaller and thus can "fit" within some lattice sites (although there must be charge compensation for the 3+ valence), so incompatibility decreases with increasing Z.

Class Discussion #1: What mineral lattice sites could host the heavy rare earth elements? What about Eu^{2+} ?

REE diagrams

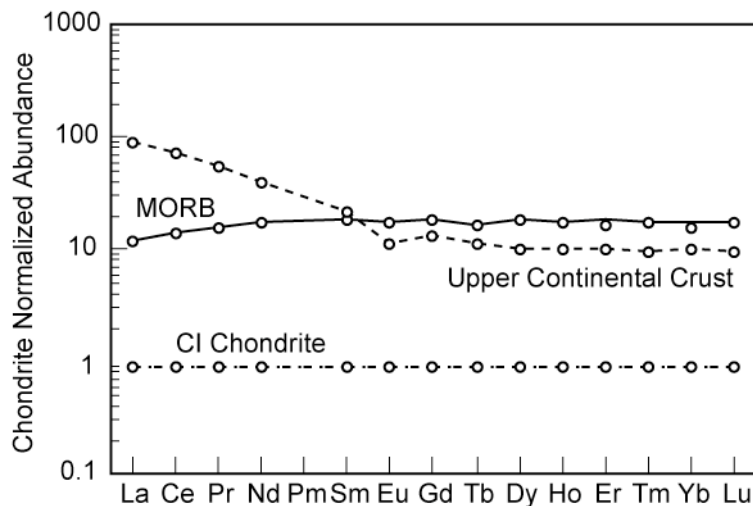
If we plot the concentrations of the rare earth elements as a group on a diagram of abundance versus atomic number, we observe two cosmochemical phenomena:

- 1) the decrease in absolute abundance with increasing atomic number;
- 2) the "even-odd effect" in relative abundances (higher abundances of even atomic number elements).



Because these cosmochemical effects are common to all terrestrial rocks, we would rather ignore them in order to accentuate more subtle variations in absolute and relative concentrations of REE between samples.

To do this we normalize the REE concentrations in a sample to that of a reference, for example chondritic meteorites. We then present the concentrations of the rare earth elements as a group on eponymous diagrams of normalized abundance versus atomic number (represented by the element abbreviation):



This normalization creates a typically smoothly varying REE pattern (with possible anomalies at Ce and/or Eu due to valence effects) for most terrestrial materials.

Class Discussion #2: Why did we choose meteorites as the reference for normalizing sample REE concentrations?

Distribution Coefficient (or Partition Coefficient)

The distribution coefficient quantifies the partitioning of an element between two phases of a system, for example a mineral coexisting with a silicate melt:

$$D_i^{\alpha/\beta} = \frac{C_i^\alpha}{C_i^\beta} \quad \begin{array}{l} i = \text{element} \\ \alpha, \beta = \text{phases} \end{array}$$

$$D_i^{s/l} = \frac{C_i^s}{C_i^l} = \frac{C_i^{\text{mineral}}}{C_i^{\text{melt}}} \quad \begin{array}{l} D < 1, \text{ incompatible} \\ D \geq 1, \text{ compatible} \end{array}$$

We can use distribution coefficients to model how different trace elements fractionate between melt and solid phases during igneous processes of partial melting and crystallization.

Trace Element Distribution During Melting

Equilibrium Melting

In the process of equilibrium melting, the liquid and solid phases of a system undergo continuous equilibration during the melting process (through diffusion of constituents in the solid and liquid).

To derive a relationship between the degree of melting, and the trace element concentrations in the melt and solid phases, we start with a mass balance equation:

$$C_i^o = C_i^s(1 - F) + C_i^l F$$

C_i^o = starting concentration of element i in the system

C_i^s = concentration of element i in the solid phase

C_i^l = concentration of element i in the melt phase

F = melt fraction

Introducing the distribution coefficient,

$$D_i^{s/l} = \frac{C_i^s}{C_i^l} \quad \therefore \quad C_i^s = D_i^{s/l} C_i^l$$

We can make a substitution for one of the phase concentrations to simplify the mass balance equation:

$$\begin{aligned} C_i^o &= D_i^{s/l} C_i^l (1 - F) + C_i^l F \\ &= C_i^l (D_i^{s/l} (1 - F) + F) \end{aligned}$$

Rearranging...

$$\frac{C_i^l}{C_i^o} = \frac{1}{(D_i^{s/l} (1 - F) + F)}$$

Class Discussion #3a: What if $D \ll F$? (e.g. $D \rightarrow 0$)?

$$\frac{C_i^l}{C_i^o} = \frac{1}{F}$$

...highly incompatible element enrichment is inversely proportional to the degree of melting

Class Discussion #3b: What if $F \rightarrow 0$?

$$\frac{C_i^l}{C_i^o} = \frac{1}{D_i^{s/l}}$$

...maximum enrichment or depletion of elements in the melt is inversely proportional to D

Class Discussion #4: Derive the corresponding equation for the concentration of element i in the solid residue as a function of D and F .

$$\frac{C_i^s}{C_i^o} = \frac{1}{(1 - F) + \frac{F}{D_i^{s/l}}}$$

Fractional Melting

In the process of fractional melting, the liquid fraction is removed from the solid residue as soon as it is formed (the liquid and solid do not maintain equilibrium). The corresponding equations for melt and solid concentrations are given by:

$$\frac{C_i^l}{C_i^o} = \frac{1}{D} (1-F)^{\left(\frac{1}{D}-1\right)}$$

Instantaneous melt composition

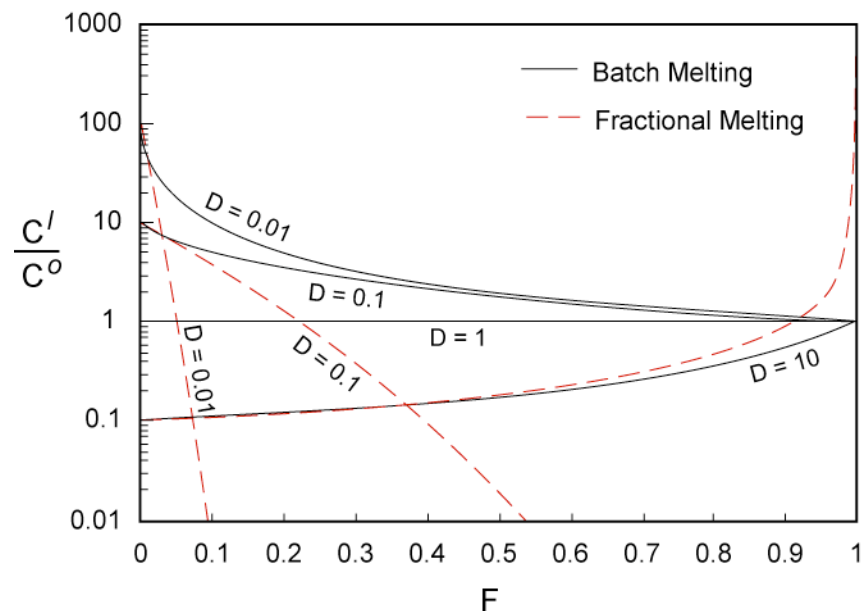
$$\frac{\overline{C_i^l}}{C_i^o} = \frac{1 - (1-F)^{\left(\frac{1}{D}-1\right)}}{F}$$

Aggregated melt composition

$$\frac{C_i^s}{C_i^o} = (1-F)^{\left(\frac{1}{D}-1\right)}$$

Instantaneous residue composition

Class Discussion #5: How do concentrations in the liquid and solid vary during batch versus fractional melting?



Trace Element Distribution During Crystallization

Equilibrium Crystallization

In the process of equilibrium crystallization, the liquid and solid phases of a system undergo continuous equilibration during the melting process (through diffusion of constituents in the solid and liquid).

The same equations for equilibrium melting apply to equilibrium crystallization, however sometimes it is convenient to recast the formulas as functions of the degree of crystallization, X , where $X = 1-F$ (and $F = 1-X$):

$$C_i^o = C_i^s X + C_i^l (1 - X) \quad X = \text{degree of crystallization}$$

$$D_i^{s/l} = \frac{C_i^s}{C_i^l} \quad \therefore C_i^s = D_i^{s/l} C_i^l$$

$$\begin{aligned} C_i^o &= D_i^{s/l} C_i^l X + C_i^l (1 - X) \\ &= C_i^l (D_i^{s/l} X + (1 - X)) \end{aligned}$$

$$\frac{C_i^l}{C_i^o} = \frac{1}{(D_i^{s/l} X + (1 - X))}$$

Class Discussion #6: What if $X \rightarrow 1$ (same as $F \rightarrow 0$)?

$$\frac{C_i^l}{C_i^o} = \frac{1}{D_i^{s/l}}$$

...maximum enrichment or depletion of an element in the melt is inversely proportional to D

Fractional Crystallization

In the process of fractional melting, the solid (crystal) fraction is removed from the liquid as soon as it is formed (the liquid and solid do not maintain equilibrium). The corresponding equations for melt and solid concentrations are given by:

$$\frac{C_i^l}{C_i^o} = (1 - X)^{(D-1)}$$

Instantaneous melt composition

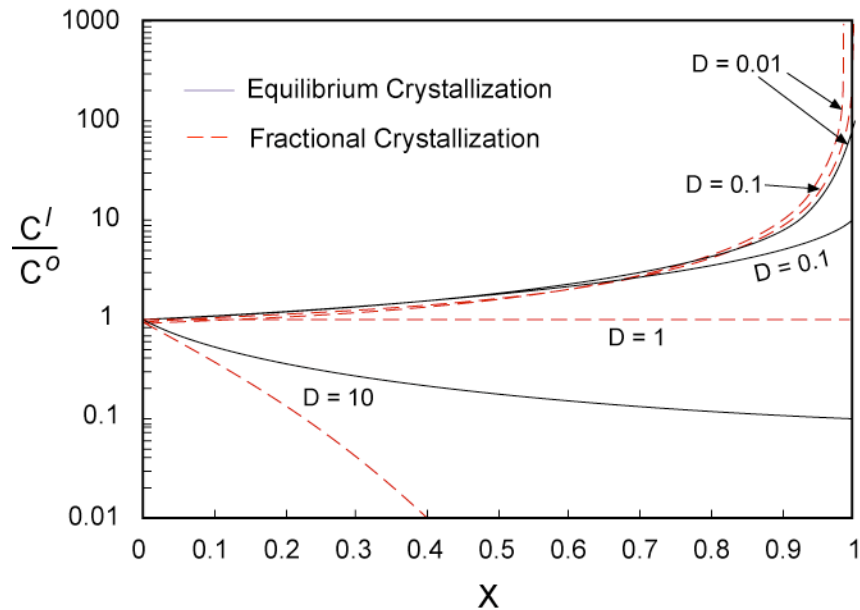
$$\frac{C_i^s}{C_i^o} = D(1 - X)^{(D-1)}$$

Instantaneous crystal composition

$$\frac{\overline{C_i^s}}{C_i^o} = \frac{X^D}{X}$$

Aggregate (average) crystal composition

Class Discussion #7: How do concentrations in the solid and liquid vary depending in equilibrium versus fractional crystallization?



Exercises:

1. I measured the following rare earth element concentrations in a suite of Proterozoic basaltic dikes in northern Minnesota during my undergraduate senior thesis. Plot these 6 samples on a single chondrite-normalized rare earth element diagram (semi-log plot of normalized concentration versus atomic number), using the composition of CI chondrites (see text) for your normalizing values.

Element	KK-35	BE-91-667	AM-91-19	KK-9c	ST-3-708	AM-91-17	AM-91-13
La	2.63	3.79	5.55	7.25	17.59	9.85	37.10
Ce	7.81	9.80	14.7	20.00	35.70	25.20	80.50
Nd	5.53	8.20	11.00	12.00	14.00	17.00	47.00
Sm	1.99	2.75	3.78	4.70	4.99	5.97	11.10
Eu	0.68	1.08	1.31	1.59	1.66	1.91	3.22
Gd	2.74	3.42	4.57	5.47	5.50	7.32	11.83
Tb	0.525	0.62	0.82	0.96	0.94	1.32	1.99
Yb	2.00	2.31	3.2	3.43	3.23	5.14	7.04

2. a) To explore the variation in trace elements in magmas undergoing *fractional crystallization*, develop a numerical model which utilizes the equations for fractional crystallization. An example spreadsheet image is appended to guide you in setting up an efficient model. With your model, calculate the enrichment in the rare earth elements La and Sm, and the ratio La/Sm, in a parental basaltic melt fractionating a crystal assemblage with relative proportions of 40% cpx, 30% plagioclase, and 30% olivine (estimated from phenocryst proportions in the basalts), for X from 0 to 100% in increments of 10%. Use the trace element concentrations of sample KK-35 as the parental composition, C_i^0 , and a set of mineral-melt partition coefficients from your text.
b) Graph the results on a plot of Sm (x-axis) versus La/Sm (y-axis); also graph the compositions of the basaltic dikes from Exercise 1 on the same plot. Based on this diagram, answer the following questions.
 - a. Which of these samples could be related to the parental composition through the calculated fractional crystallization model?
 - b. For those samples that could be “cogenetic” (derived from a common parent magma) through your fractionation model, how much crystallization would need to occur to achieve the entire spectrum of composition?
 - c. How might you explain the compositions of the samples that don’t lie on the fractionation trend?

3. a) To explore the extraction of trace elements from the mantle during partial melting, create a numerical model (for example a spreadsheet) that utilizes the equations for modal equilibrium melting. With your model, calculate the enrichment in the rare earth elements in an equilibrium (batch) modal partial melt of a mantle consisting of 10% cpx, 5% spinel, 25% opx, and 60% olivine, assuming modal melting for $F = 0.01, 0.05, 0.10$ and 0.20 . Assume the concentrations in the mantle are chondritic (same as your REE normalization), and use a set of partition coefficients from your text. Use only the following rare earths: La, Ce, Nd, Sm, Eu, Gd, Dy, Yb. Plot the results on a semi-log plot of chondrite-normalized abundance versus atomic number (i.e. a typical REE plot). Interpolate a curve through all of the REEs (*Hint: If you work only with chondrite-normalized abundances, rather than absolute concentrations, the C_i^0 values will all be 1*).
- b) Examining your model REE patterns, answer the following questions:
- Describe how the enrichment and slope of the REE pattern of the resulting batch melts are related to the degree of melting.
 - Sketch in the REE pattern for the complementary depleted solid residue from equilibrium melting at $F=0.02$.
 - Compare your model REE patterns with that of the basalt with the least enriched composition from Exercise 1. What parameters of the melting model could you vary to produce the basalt with the least enriched composition? What is the effect of changing the aluminous mantle phase (garnet versus spinel)? What about changing the starting mantle composition? What can these models tell us about the mantle source of these basalts?

Extra credit:

Because of the different melting points of various minerals, modal melting is unlikely to be an accurate portrayal of the extraction of basalt from the mantle. Your text derives the equations for non-modal melting, where each mineral has both a modal proportion (in the rock), and a melting proportion (going into the melt). Create a numerical model for non-modal melting, and explore how the resulting melts of a given F vary between modal versus non-modal melting.

