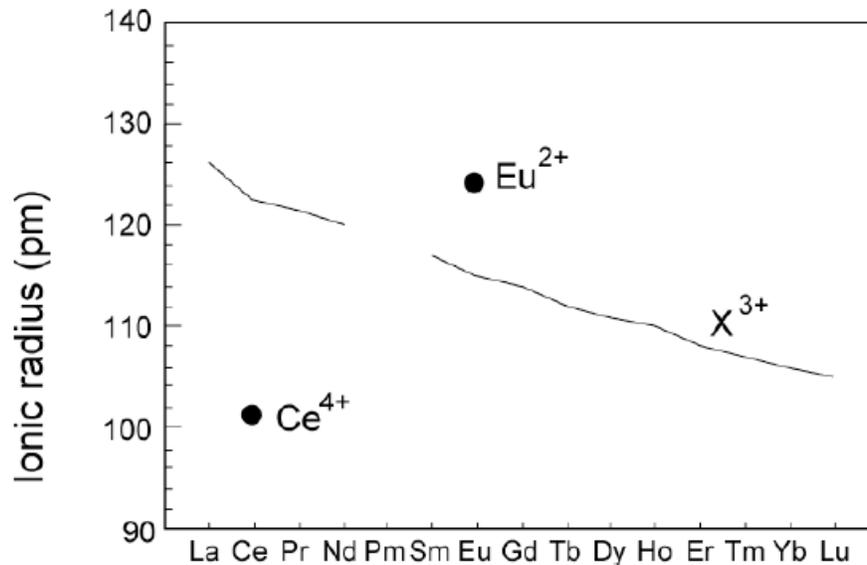


EESC 4701: Igneous and Metamorphic Petrology
THE MANTLE
LAB 5

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*...

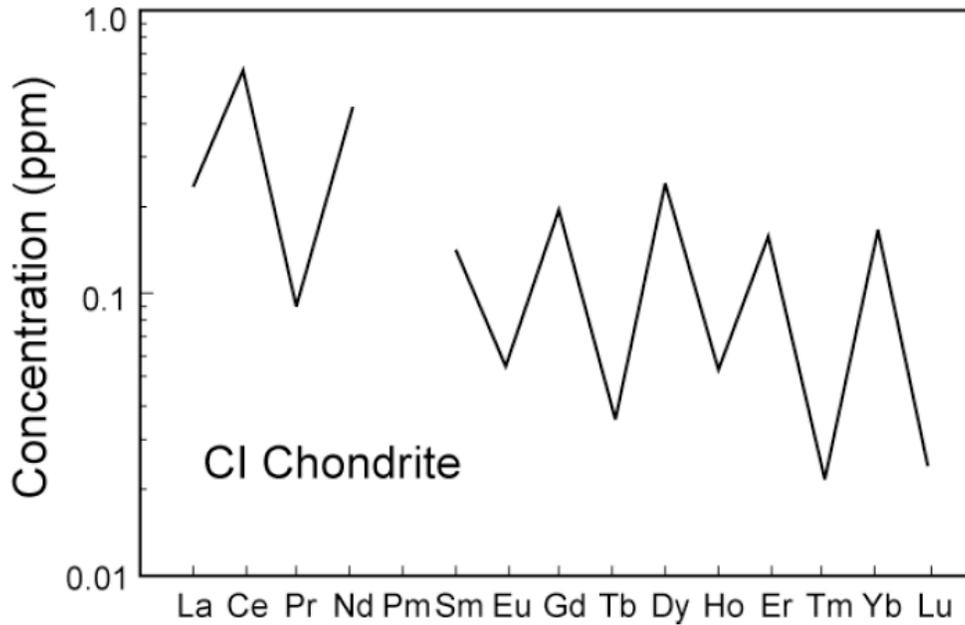


Because of their high charge and large radii, the rare earth elements are usually relatively **incompatible** in silicate minerals. However, due to the lanthanide contraction, the heavier rare earths are smaller and thus can "fit" within some lattice sites (although there must be charge compensation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

REE Diagrams

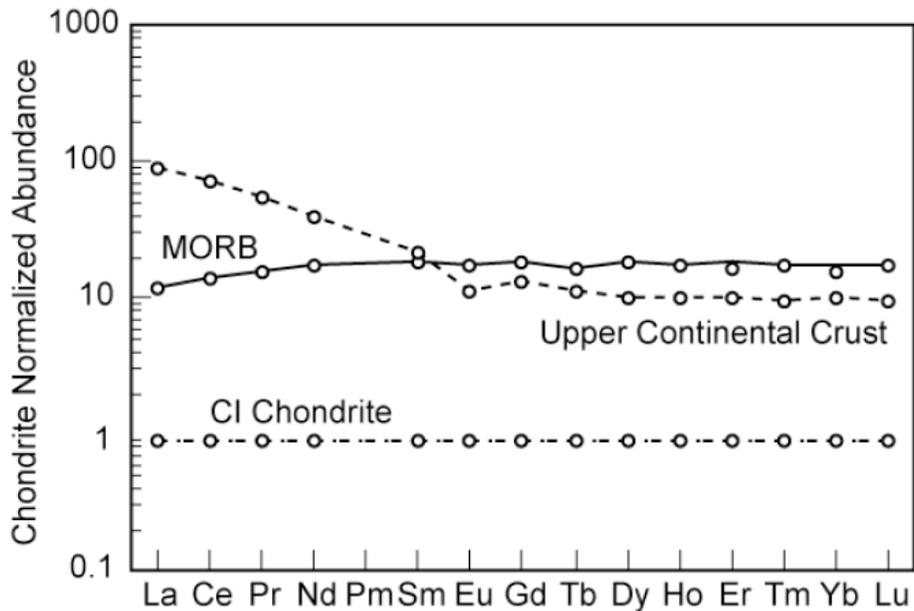
If we plot the concentrations of the rare earth elements as a group on a diagram of abundance versus atomic number, we observe two cosmochemical phenomena:

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



Because these cosmochemical effects are common to all terrestrial rocks, we would rather ignore them in order to accentuate subtler 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.

Distribution (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),

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

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...

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

Also...

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

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:

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

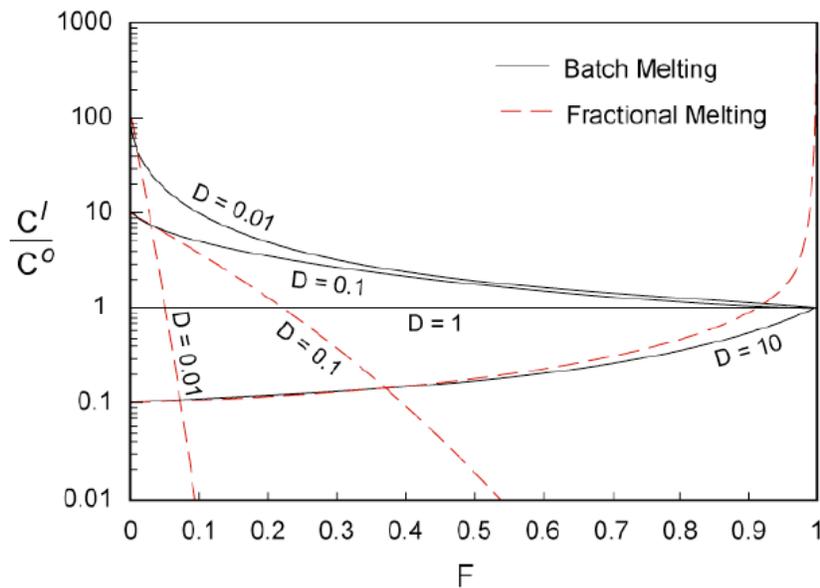
Instantaneous melt composition

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

Aggregated melt composition

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

Instantaneous residue composition



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 $F = 1-X$):

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

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

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

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

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

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

Aggregate (average) crystal composition

