Lecture 38

Igneous geochemistry

Read White Chapter 7 if you haven't already

Today

1. Magma mixing/AFC
2. Spot light on using the Rare Earth Elements (REE) to constrain mantle sources and conditions of petrogenesis

Modeling Igneous Petrogenesis

However, other concurrent processes can obscure the signatures of melt-crystal equilibrium, such as:

- Contamination (by wall rocks of a magma chamber)
- Mixing of two distinct magmas that came from two different histories (T, P, source composition, % melt,).

Banded pumice from Mount Lassen volcano recording fluid mixing and hybridization of two magmas prior to and during the 1915 eruption.

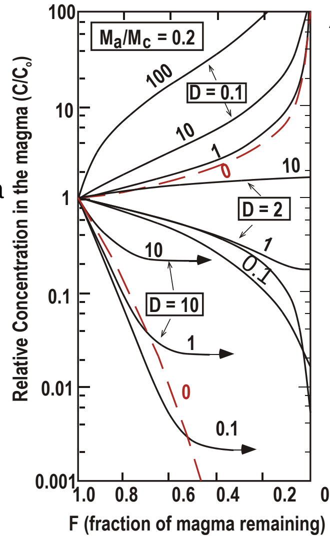
http://mineralsciences.si.edu/

Melt Contamination

when magmas interact with country rock while crystallization is occurring, they can assimilate components of the wall rock.

This process is governed by mineral-melt K_ds.

Here's one model, in which a wall rock melts and mixes with the magma as it crystallizes.



Assimilation-Fractional Crystallization

The change in concentration of an element, C, in a magma undergoing assimilation and fractional crystallization (AFC) is given by:

$$C_m/C_m^o = F^{\pm z} + \left(\frac{R}{R \pm 1}\right)\frac{C_a}{zC_m^o}(1 \pm F^{\pm z})$$

C_m = concentration in the evolving magma
C_m^o = original concentration in the magma
C_a = concentration in the assimilated material
F = mass fraction of original magma remaining
R = the ratio of mass assimilated/crystallized
D = the distribution coefficient
$z = \frac{R + D \pm 1}{R \pm 1}$

Figure 12.23. Variation of concentration during assimilation-fractional crystallization. Short dashed red lines are for simple fractional crystallization. Numbers on the curves refer to values of C_a/C_m^o, the ratio of the concentration in the assimilant to the original concentration in the magma. After DePaolo (1981a).

The special case of the Rare earth Elements (REE)

This unique group of elements numbered 57-71 (La-Lu) is useful for examining the details of igneous petrogenesis because as a group they behave similarly in a range of geochemical situations.

Ionic radii decrease thru the group ("lanthanide contraction")

All the REE have *similar valence* configurations: $6s^2 5d^1 4f^x$ and thus take charges of +3 (losing both 6s and their one 5d electrons).

Eu and Ce are exceptions. Often they are also +3 charged, but they can also form Eu^{+2} and Ce^{+4} at certain magma pE.

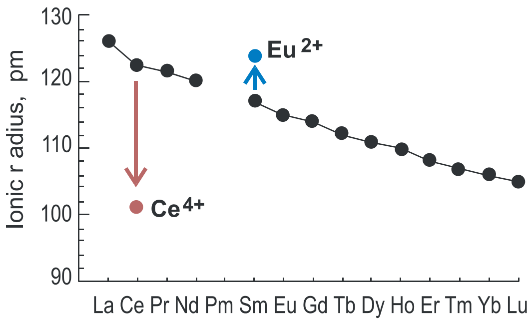


Figure 7.5. Ionic radii of the lanthanide rare earth elements (3+ state except where noted). Promethium (Pm) has no isotope with a half-life longer than 5 years.
modified from White, Geochemistry

REE distribution coefficients

Their similar chemistry, (mostly) same charge, but different radii translate to a smoothly varying range of K_d behaviors that in turn contribute to their usefulness. These attributes account for a range of REE signatures during magmagenesis.

- all mineral-melt K_d <1 except apatite & HREE ("heavy REE") in garnet.
- the steep pattern (HREE vs LREE = "light REE") for garnet
- the flat HREE and gently sloping LREE pattern for clinopyroxene and hornblend.
- the flat pattern for olivine and plagioclase, with the exception of the positive Eu spike for plagioclase.

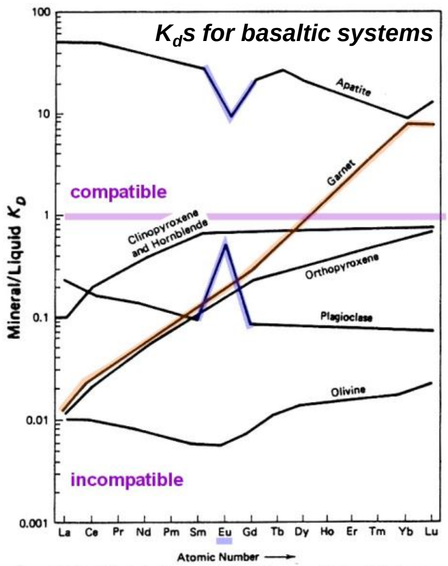


Figure 11.22 Typical distribution coefficients for rare earth elements between various minerals and basaltic melt, after Zielinski (1975). REE concentrations are normalized to values in chondritic meteorites. All of these phases are intolerant of REE (that is, have K_D values less than 1) except apatite (and garnet for the heavy rare earths). The positive Eu anomaly in plagioclase occurs because some of this element is in the divalent state and can substitute for Ca^{2+} ions.

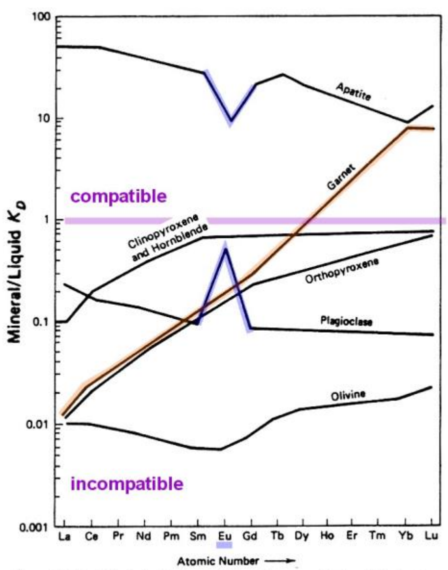
REE distribution coefficients

- REE compatibility?

Notice that *besides apatite*..

None of the phases preferentially retains LREE

HREE are also compatible in garnet



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REE distribution coefficients

- Eu anomalies:

The positive Eu spike for plagioclase results from Eu^{+2} for Ca^{+2} substitution in crystal lattices.

Rocks that have accumulate plagioclase or have had plagioclase removed show *positive* or *negative* Eu anomalies (peaks or troughs in REE patterns), respectively.

Mathematically, the Eu anomaly (Eu*) is:

$$Eu^* = Eu_{meas}/Eu_{expected} = \frac{Eu_{meas}}{(Sm_{meas})^{1/2} \times (Gd_{meas})^{1/2}}$$

Melting Effects

The different REE k_d values in various minerals provide strong bounds on melting processes and conditions.

Using models like those we've been discussing, we can construct predicted REE patterns for a given set of conditions (e.g., the model dynamic melting patterns shown earlier).

Note that the **presence or absence of garnet in a source dramatically changes REE patterns when the source melts**.

Garnet is stable only at depths deeper than 60-100 km in the mantle, so a garnet signature is a strong control on depth of melting.

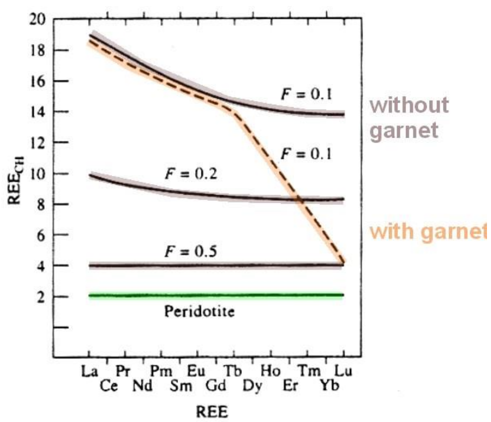

Figure 8-8 Chondrite-normalized REE contents of melts produced by equilibrium melting of peridotite and garnet peridotite. REE_{CH} is obtained by dividing sample concentration by chondrite value for a given element. The original REE content of peridotite is assumed to be a flat pattern at 2× chondrite abundances. The mineral assemblage in peridotite is 55 percent olivine, 25 percent orthopyroxene, and 20 percent calcic clinopyroxene. The mineral assemblage in garnet peridotite is 55 percent olivine, 20 percent orthopyroxene, 20 percent calcic clinopyroxene, and 5 percent garnet. *F* is the fraction of melt in the rock. Compare the strongly fractionated $(HREE)_{CH}$ pattern produced by melting garnet peridotite (dashed line) with the relatively unfractionated pattern in the melts derived from peridotite (solid lines denoted with *F*). (Reprinted by permission of the publishers from ORIGINS OF IGNEOUS ROCKS by Paul C. Hess, Cambridge, Mass: Harvard University Press, Copyright © 1989 by the President and Fellows of Harvard College.)

REE patterns and magmagenesis

Commonly, REE concentrations are **normalized to chondritic** or primitive mantle:

a. To "smooth-out" the odd-even atomic abundance differences between elements (which makes a “saw tooth” pattern in un-normalized abundances

b. To provide a genetic link back to the primordial mantle.

Note, since REE are

(1) all refractory elements during condensation and

(2) are not siderophiles, and

(3) because the core is about a third of the mass of the Earth,

estimated primitive-mantle REE concentrations are all about three times the C1 chondritic average values.

Crystallization Effects

In the lunar crust, there’s a general mirror-image similarity of REE patterns for the lunar mare basalts and the lunar anorthosites; coupled with opposing Eu anomalies, these imply that the two types of rocks share a genetic relationship.

Fractional crystallization modeling demonstrates that plagioclase loss and accumulation, respectively, can produce this signature. The lunar anorthosites appear to be plagioclase-rich cumulates whereas the mare magmas lost a large amount of plagioclase before eruption of the basalts.

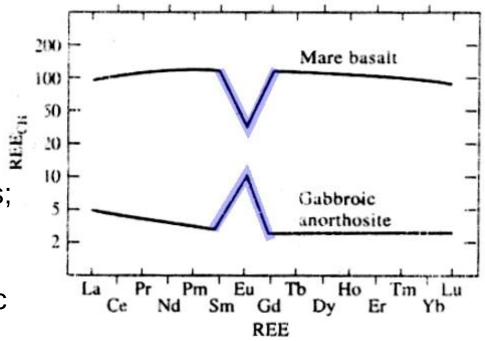

Figure 8-10 Chondrite-normalized REE patterns for basalt with a negative europium anomaly and a gabbroic anorthosite with a positive europium anomaly. Both samples are lunar igneous rocks characterized by very high Eu^{2+}/Eu^{3+} ratios (representative of formation under reducing conditions). The basalt is from the mare regions, and the gabbroic anorthosite is from the lunar highlands of the Moon. The mare basalt is relatively depleted in Eu as a result of the fractional crystallization of plagioclase, whereas the anorthosite has accumulated plagioclase. After Hess (1989).

Crystallization Effects

- The effect of plagioclase fractional crystallization is to increase overall REE abundance while developing a negative Eu anomaly after 40% of the rock's plagioclase was removed is demonstrated below.

Otherwise, patterns have almost the same overall *shape*, as expected from the plagioclase K_d pattern.

Note, "BCR-1" is a commonly analyzed basalt standard (from the Columbia River Flood basalt province).

TABLE 8-7 Rare-Earth Element Data

Z	REE	r	BCR-1	C_M	BCR-1/C_M (chondrite normalized)	K_D	40 PL (40% plag removal)
57	La	1.26	24.2	0.367	65.9	0.14	102.0
58	Ce	1.22	53.7	0.957	56.1	0.14	87.0
59	Pr	1.22	6.5	0.137	47.4	—	—
60	Nd	1.20	28.5	0.711	40.1	0.08	64.1
61	Pm	—	—	—	—	—	—
62	Sm	1.17	6.70	0.231	29.0	0.08	46.4
63	Eu	1.15	1.95	0.087	22.4	0.32	31.7
64	Gd	1.14	6.55	0.306	21.4	0.10	33.9
65	Tb	1.12	1.08	0.058	18.6	—	—
66	Dy	1.11	6.39	0.381	16.8	0.09	26.7
67	Ho	1.10	1.33	0.0851	15.6	—	—
68	Er	1.08	3.70	0.249	14.9	0.08	23.8
69	Tm	1.07	0.51	0.0356	14.3	--	—
70	Yb	1.06	3.48	0.248	14.0	0.07	22.5
71	Lu	1.05	0.55	0.0381	14.4	0.08	23.0

r = ionic radius in angstroms for cubic coordinated, trivalent REE (Whittaker and Muntus 1970)
BCR-1 = REE concentration in ppm in USGS basaltic rock standard (Taylor and McLennan 1985)
C_M = average REE concentration in ppm in Type 1 carbonaceous chondrites (Evensen et al. 1978); 1.5× original data **Chon ~ PM / 3 for REE**
K_D = average distribution coefficient for plagioclase in mafic rocks (Henderson 1982)
40 PL = C/C_M in residual melt after 40 percent extraction of plagioclase from original melt composition taken as BCR-1 (40 percent fractionation of plagioclase)
Source: From *Basic Analytical Petrology*, by Paul C. Ragland. Copyright © 1989 by Oxford University Press, Inc. Reprinted by permission.

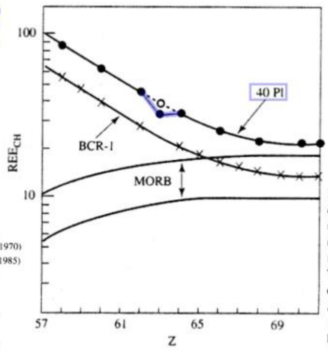

Figure 8-9 Chondrite-normalized REE concentrations for MORB basalts, basalt rock standard BCR-1, and daughter rock (40 Pl) calculated for plagioclase extraction from melt with the composition of BCR-1. The daughter rock has a small negative europium anomaly. (From *Basic Analytical Petrology*, by Paul C. Ragland. Copyright © 1989 by Oxford University Press, Inc. Reprinted by permission.)

Mantle Source Effects

Fig. 8-9 (repeated below) shows another important feature of the REE:

- The difference in shape between the BCR curve ("LREE" enriched) and MORB ("LREE Depleted").

➢ There is no common mantle mineral that preferentially retains the light REE, so this is good evidence that the ocean-ridge source mantle was ***previously depleted*** in the more incompatible elements (light REE relative to the heavy REE).

➢ The relative light REE enrichment in BCR-1 may reflect differences in petrogenesis or source composition relative to the ocean ridges, as we discuss next.

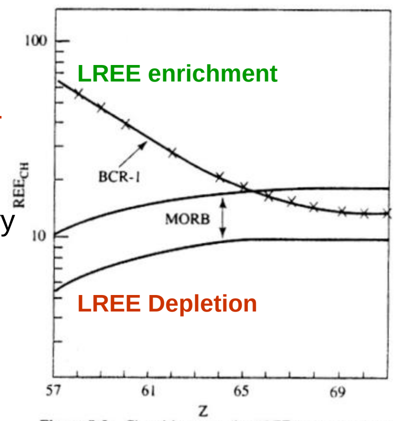

Figure 8-9 Chondrite-normalized REE concentrations for MORB basalts, basalt rock standard BCR-1 ...

Tectonic Setting and REE

This diagram generalizes the REE patterns for the three main tectonic settings where volcanism occurs on earth: spreading centers, convergent margins, and intra-plate (both oceanic and continental).

The *difference* between REE patterns in BCR-1 and MORB *is common* in many igneous rocks from around the globe.

- These two forms of intraplate rocks, continental flood basalts ("CFB") and oceanic hotspots, are depicted using BCR and Hawaii as examples). *Note: a* more general term for oceanic hotspot lavas is "OIB" = oceanic island basalt.

a ***light-REE-enriched pattern*** like that of BCR-1 is ***typical*** of most ***continental basalts and ocean island basalts***.

- Notice also that plate margins (MORB and Island Arc tholeiites = IAB) commonly have flatter REE profiles.

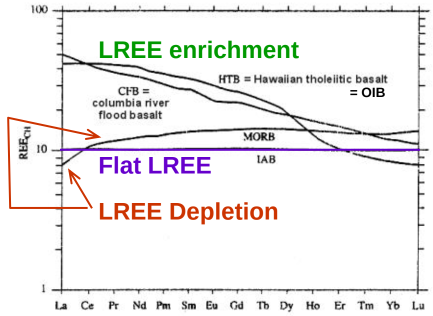

Figure 8-17 Chondrite-normalized plot of rare-earth abundances in typical island arc basalts (IAB), tholeiitic continental flood basalts (CFB), mid-ocean ridge basalts (MORB), and Hawaiian tholeiite basalts (HTB). (After Philpotts, A. R., *Principles of Igneous and Metamorphic Petrology*. Copyright © 1990. Adapted by permission of Prentice Hall, Inc., Upper Saddle River, NJ.)

Tectonic Setting and REE

This basic difference between light-REE-depleted MORB and light-REE-enriched OIB is a worldwide phenomenon.

It cannot be caused by differences in melting conditions or source composition (± garnet), or crystallization of the same homogeneous source.

Instead, it tells us that OIB have a dominant source composition that is not depleted mantle (DM).

Notice that the negative Eu anomalies only occur in some MORB and are largely absent from the OIB. This difference reflects the relative importance of plagioclase crystallization in their respective conditions of petrogenesis.

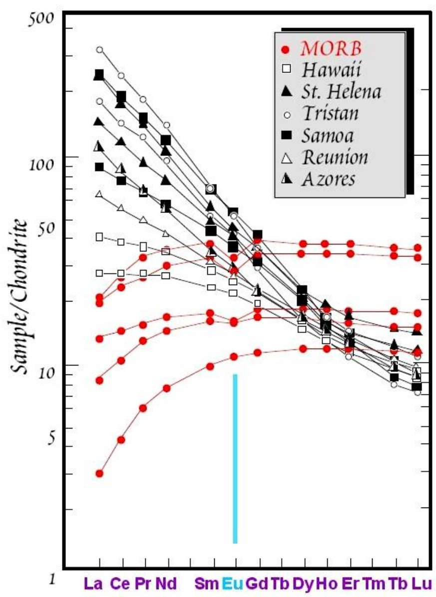

Figure 11.17. Rare earth patterns of mid-ocean ridge basalts and oceanic island basalts.
modified from White, Geochemistry

Tectonic Setting and REE

REE variations in Island Arc Basalts (IAB) display significant variations, from flat to LREE enriched patterns and with variable Eu anomalies.

In general, *IAB are more variable* both within and between volcanoes and volcanoes groups because *petrogenetic conditions are more variable* and *subducted crust* becomes an additional source component that can be added to the mantle melts.

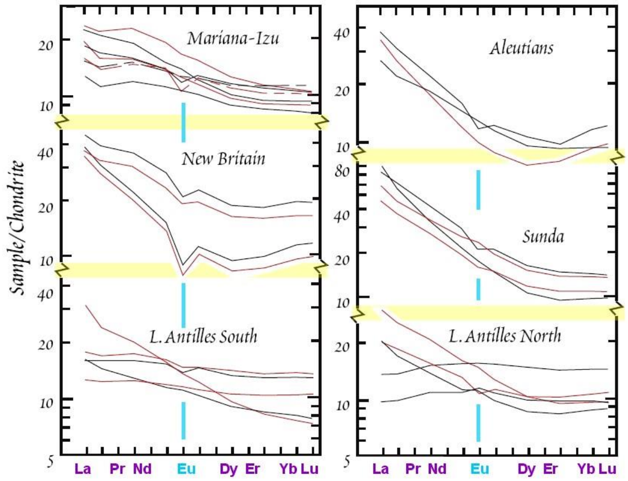

Figure 12.9. Rare earth patterns of some typical island arc volcanics. From White and Patchett (1984). *modified from White, Geochemistry*

Tectonic Setting and extended REE diagrams

Other chondrite-normalized elements can be considered along with the REE concentrations to distinguish IAB from MORB. A type of OIB with alkalic major element composition (and may have DM melts mixed in) is also shown below.

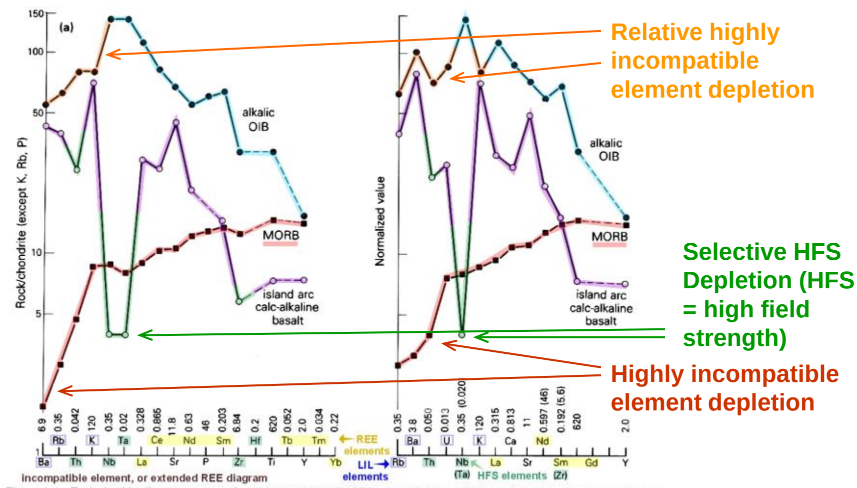

Figure 2.4 Typical ~~spiderdiagram~~ patterns for mid-ocean ridge (MORB), oceanic-island (OIB) and island-arc, basalts normalized according to (a) Thompson *et al.* (1984) and (b) Sun (1980). Values of the normalization constants used are given at the foot of each diagram. *Modified from Wilson, Igneous Petrogenesis*

Tectonic Setting and extended REE diagrams

The additional elements broaden the range of conditions one can examine with the trace element patterns.

Incompatible elements mostly come in two flavors:

- LIL (Large Ion Lithophiles) = BIG ions
- HFS (High Field Strength) = Highly Charged ions

Both types are generally incompatible during MORB and OIB/CFB Petrogenesis, so we usually *relate differences to the mantle sources*.

This can the take the form of

- varying lithological composition
- metasomatism
- melt-rock interaction during melt percolation.

Tectonic Setting and extended REE diagrams

Island Arc Basalt (IAB) results from mantle melts in the presence of subducted hydrated MORB and sediments.

The slab and sediments dehydrate and the water (and fluid-mobile elements, like K, Rb, Sr, U, etc.) infiltrates the otherwise MORB-source-type mantle above the slab, producing characteristic ratios relative to no soluble fluid-mobile elements such as Th.

e.g., Th/U in arcs < Th/U OIB

Ba/Th in arcs > Ba/Th in OIB

Remember, prior depletion makes Th/U and Ba/Th in MORB < OIB

The added water increases the pE (more oxidizing), which makes the HFS (e.g., Nb, Ta) behave compatibly.

In this case, *the difference between LIL and HFS* tells us about the *conditions of petrogenesis*, as well as source differences.