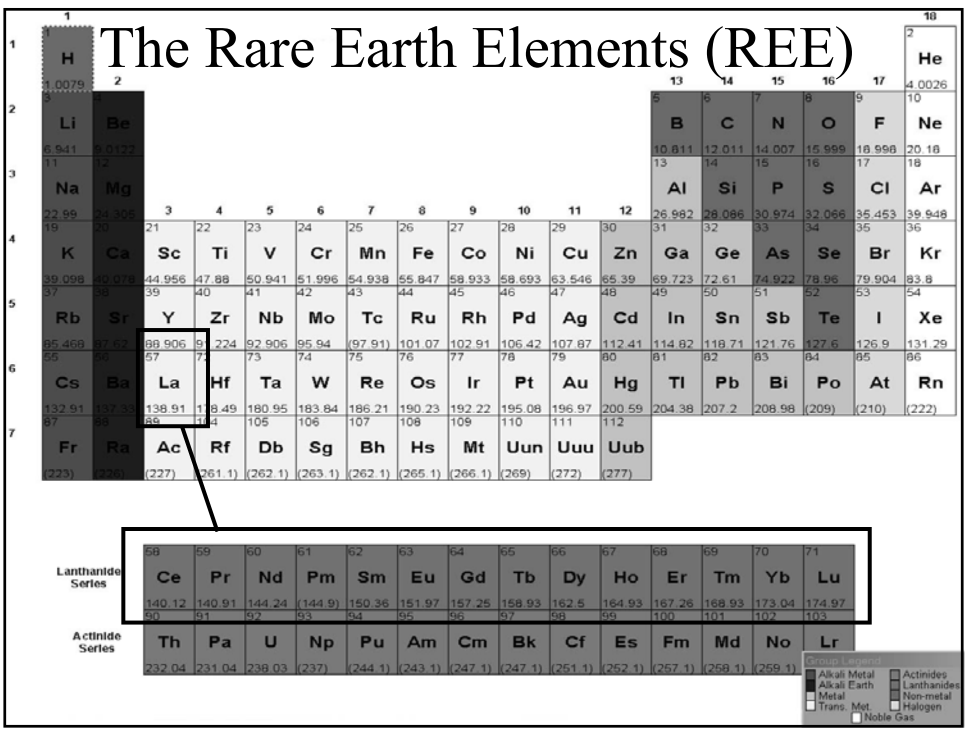
Lecture 16 Rare Earth Elements
and Spider Diagrams

Monday, March 21st, 2005

The Rare Earth Elements (REE)



Contrasts and similarities in the D values:

All are incompatible

Also Note:

HREE are less incompatible

Especially in garnet

Eu can → 2+ which conc. in plagioclase

Table 9-1. Partition Coefficients for some commonly used trace elements in basaltic and andesitic rocks

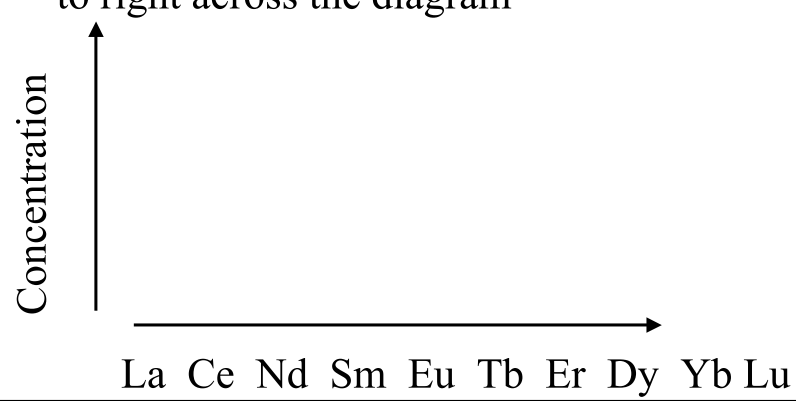
	Olivine	Opx	Cpx	Garnet	Plag	Amph
Rb	0.006	0.02	0.04	0.001	0.1	0.3
Sr	0.01	0.01	0.14	0.001	1.8	0.57
Ba	0.006	0.12	0.07	0.002	0.23	0.31
Ni	14	5	2.6	0.4	0.01	3
Cr	2.1	10	8.4	0.17	10	1.6
La (Rare Earth Elements)	0.007	*0.02*	0.08	0.05	0.14	0.27
Ce	0.009	0.02	0.34	0.05	0.14	0.34
Nd	0.009	0.05	0.6	0.07	0.08	0.19
Sm	0.009	0.05	0.9	0.06	0.08	0.91
Eu	0.008	0.05	0.9	0.9	0.1/1.5*	1.01
Tb	*0.01*	0.05	1	5.6	0.03	1.4
Er	0.013	0.31	1	18	0.08	0.48
Yb	0.014	0.34	0.2	30	0.07	0.97
Lu	0.016	0.11	0.82	35	0.08	0.89

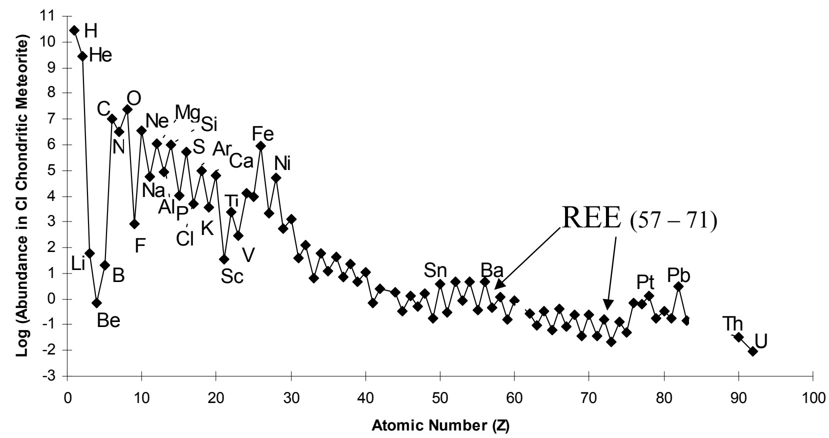
data from Henderson (1982) * Eu^{3+}/Eu^{2+} *Italics* are estimated

REE Diagrams

Plots of concentration as the ordinate (y-axis) against increasing atomic number

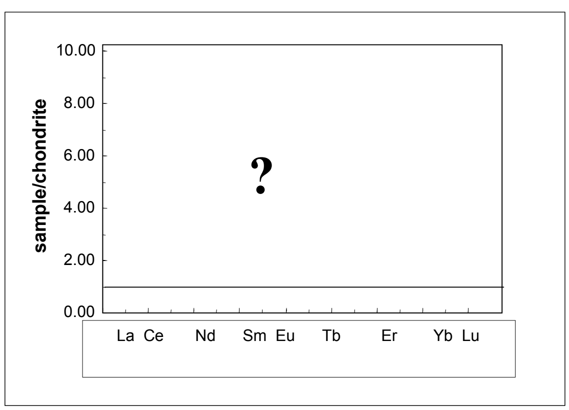
- Degree of compatibility increases from left to right across the diagram





- Eliminate Oddo-Harkins effect and make y-scale more functional by normalizing to a standard
  - estimates of primordial mantle REE
  - chondrite meteorite concentrations

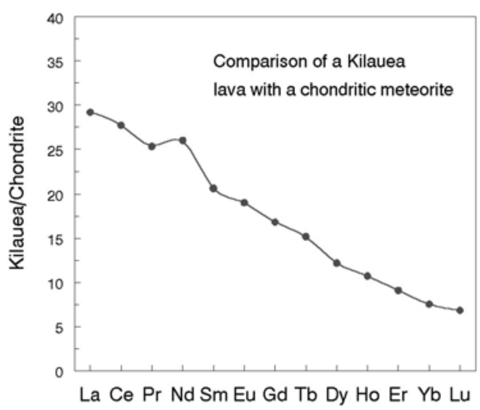
What would an REE diagram look like for an analysis of a chondrite meteorite?



Comparison of REE in a Kilauea lava with Chondrite abundances (data in ppm)

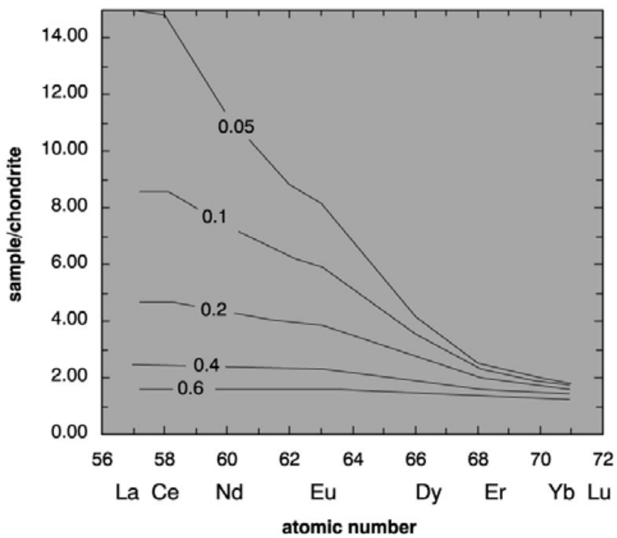
REE	Chondrite	Kilauea	Kilauea/Chondrite
La	0.31	9.05	29.19
Ce	0.808	22.4	27.72
Pr	0.122	3.09	25.33
Nd	0.600	15.6	26.00
Sm	0.195	4.02	20.61
Eu	0.0735	1.40	19.04
Gd	0.259	4.36	16.83
Tb	0.0474	0.72	15.19
Dy	0.322	3.93	12.20
Ho	0.0718	0.77	10.72
Er	0.210	1.91	9.095
Yb	0.209	1.58	7.55
Lu	0.0322	0.22	6.83

Divide sample by chondritic abundance



Plot of preceding Kilauea data.

REE diagrams using batch melting model of a garnet lherzolite for various values of F:

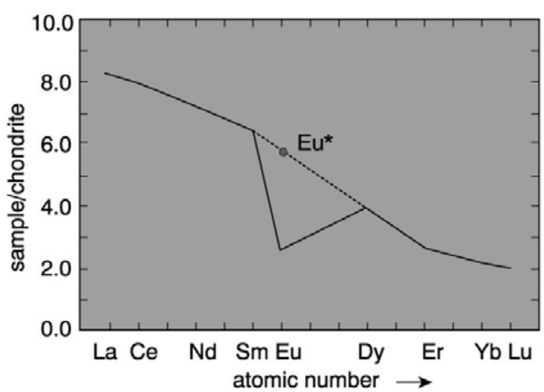


See Ch. 9 p. 62 for worked example

Figure 9-4. Rare Earth concentrations (normalized to chondrite) for melts produced at various values of F via melting of a hypothetical garnet lherzolite using the batch melting model (equation 9-5). From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

- Europium anomaly when plagioclase is
  - a fractionating phenocryst

    or
  - a residual solid in source



Eu is divalent in contrast with other REE's which are trivalent. Consequently it behaves like Sr

Figure 9-5. REE diagram for 10% batch melting of a hypothetical lherzolite with 20% plagioclase, resulting in a pronounced negative Europium anomaly. From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

Spider Diagrams

An extension of the normalized REE technique to a broader spectrum of elements

Chondrite-normalized spider diagrams are commonly organized by (the author's estimate) of increasing incompatibility L ← R

Different estimates → different ordering (poor standardization)

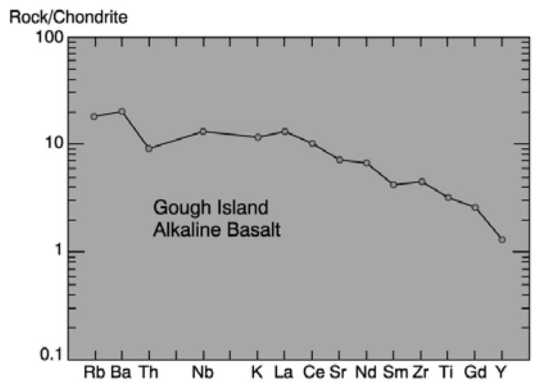


Fig. 9-6. Spider diagram for an alkaline basalt from Gough Island, southern Atlantic. After Sun and MacDonough (1989). In A. D. Saunders and M. J. Norry (eds.), Magmatism in the Ocean Basins. Geol. Soc. London Spec. Publ., **42**. pp. 313-345.

MORB-normalized Spider

Separates LIL and HFS

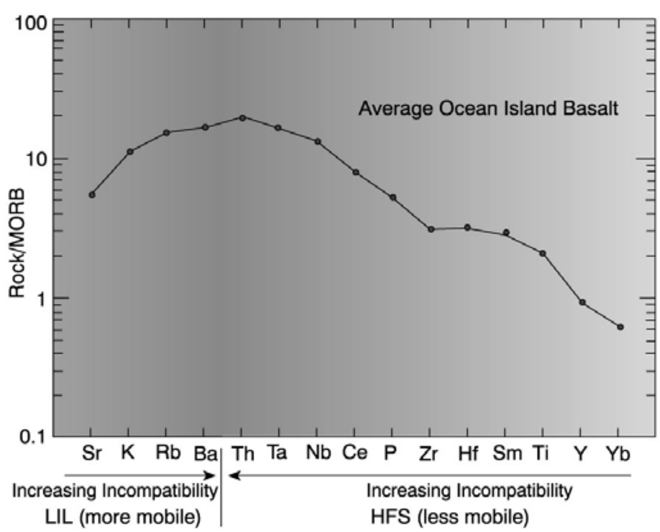


Figure 9-7. Ocean island basalt plotted on a mid-ocean ridge basalt (MORB) normalized spider diagram of the type used by Pearce (1983). Data from Sun and McDonough (1989). From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

Application of Trace Elements to Igneous Systems

1. Use like major elements on variation diagrams to document FX, assimilation, etc. in a suite of rocks
   - More sensitive → larger variations as process continues

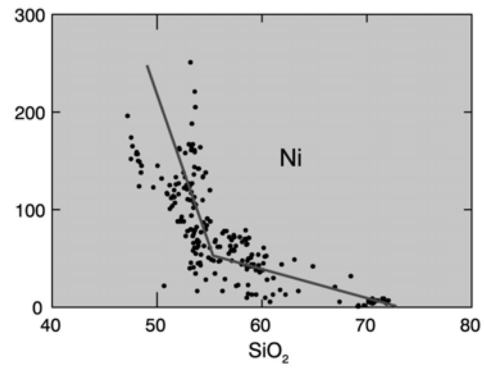


Figure 9-1a. Ni Harker Diagram for Crater Lake. From data compiled by Rick Conrey. From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

2. Identification of the source rock or a particular mineral involved in either partial melting or fractional crystallization processes

Garnet concentrates the HREE and fractionates among them

Thus if garnet is in equilibrium with the partial melt (a residual phase in the source left behind) expect a steep (-) slope in REE and HREE

Shallow (< 40 km) partial melting of the mantle will have plagioclase in the resuduum and a Eu anomaly will result

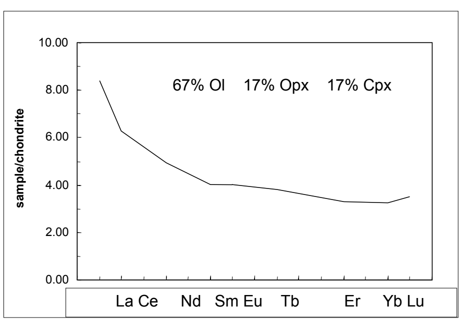
Table 9-1. Partition Coefficients for some commonly used trace elements in basaltic and andesitic rocks

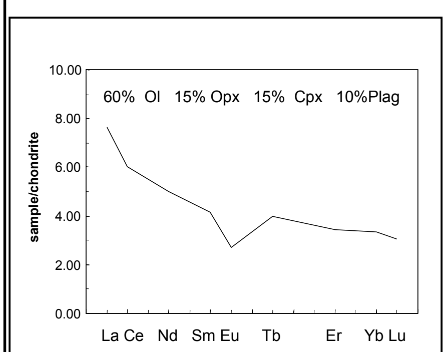
	Olivine	Opx	Cpx	Garnet	Plag	Amph
Rb	0.006	0.02	0.04	0.001	0.1	0.3
Sr	0.01	0.01	0.14	0.001	1.8	0.57
Ba	0.006	0.12	0.07	0.002	0.23	0.31
Ni	14	5	2.6	0.4	0.01	3
Cr	2.1	10	8.4	0.17	10	1.6
Rare Earth Elements: La	0.007	*0.02*	0.08	0.05	0.14	0.27
Ce	0.009	0.02	0.34	0.05	0.14	0.34
Nd	0.009	0.05	0.6	0.07	0.08	0.19
Sm	0.009	0.05	0.9	0.06	0.08	0.91
Eu	0.008	0.05	0.9	0.9	0.1/1.5*	1.01
Tb	*0.01*	0.05	1	5.6	0.03	1.4
Er	0.013	0.31	1	18	0.08	0.48
Yb	0.014	0.34	0.2	30	0.07	0.97
Lu	0.016	0.11	0.82	35	0.08	0.89

data from Henderson (1982) * Eu^{3+}/Eu^{2+} *Italics* are estimated

Garnet and Plagioclase effect on HREE

Same REE conc and extent of melting. All that changes is the mantle source mineralogy which is pressure (depth) related.





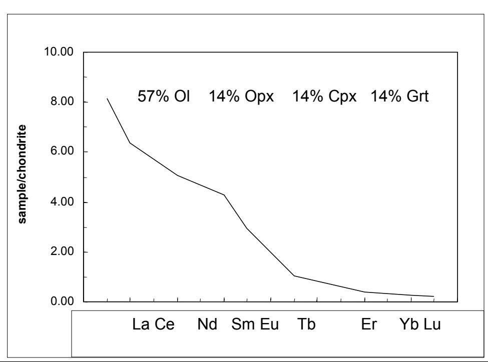


Table 9-6 A brief summary of some particularly useful trace elements in igneous petrology

Element	Use as a petrogenetic indicator
Ni, Co, Cr	Highly compatible elements. Ni (and Co) are concentrated in olivine, and Cr in spinel and clinopyroxene. High concentrations indicate a mantle source.
V, Ti	Both show strong fractionation into Fe-Ti oxides (ilmenite or titanomagnetite). If they behave differently, Ti probably fractionates into an accessory phase, such as sphene or rutile.
Zr, Hf	Very incompatible elements that do not substitute into major silicate phases (although they may replace Ti in sphene or rutile).
Ba, Rb	Incompatible element that substitutes for K in K-feldspar, micas, or hornblende. Rb substitutes less readily in hornblende than K-spar and micas, such that the K/Ba ratio may distinguish these phases.
Sr	Substitutes for Ca in plagioclase (but not in pyroxene), and, to a lesser extent, for K in K-feldspar. Behaves as a compatible element at low pressure where plagioclase forms early, but as an incompatible at higher pressure where plagioclase is no longer stable.
REE	Garnet accommodates the HREE more than the LREE, and orthopyroxene and hornblende do so to a lesser degree. Sphene and plagioclase accommodates more LREE. Eu^{2+} is strongly partitioned into plagioclase.
Y	Commonly incompatible (like HREE). Strongly partitioned into garnet and amphibole. Sphene and apatite also concentrate Y, so the presence of these as accessories could have a significant effect.

Table 9-6. After Green (1980). Tectonophys., **63**, 367-385. From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

Trace elements as a tool to determine paleotectonic environment

- Useful for rocks in mobile belts that are no longer recognizably in their original setting
- Can trace elements be discriminators of igneous environment?
- Approach is empirical on modern occurrences
- Concentrate on elements that are immobile during low/medium grade metamorphism

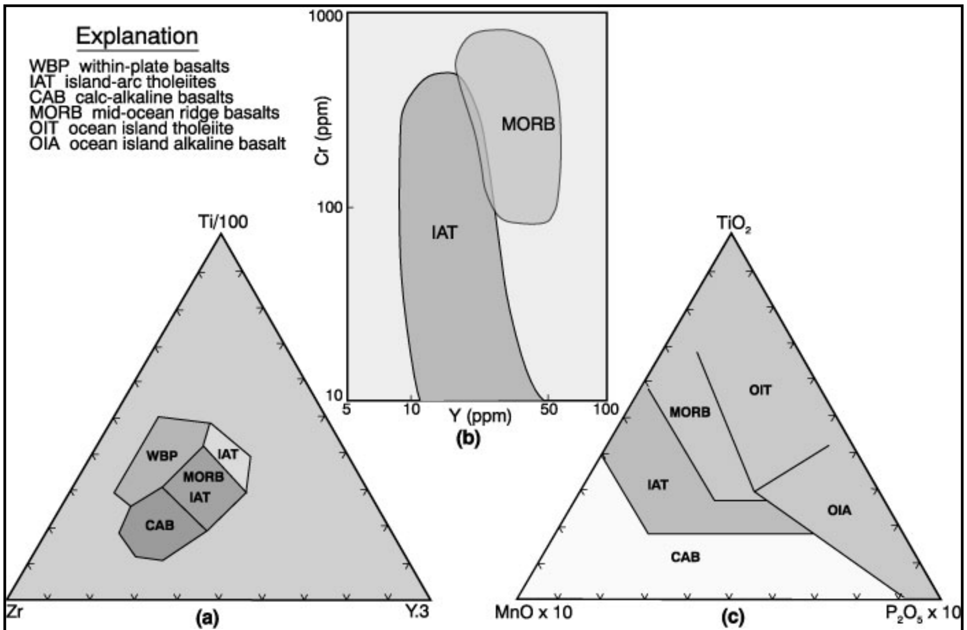


Figure 9-8. (a) after Pearce and Cann (1973), Earth Planet, Sci. Lett., **19**, 290-300. (b) after Pearce (1982) in Thorpe (ed.), Andesites: Orogenic andesites and related rocks. Wiley. Chichester. pp. 525-548, Coish et al. (1986), Amer. J. Sci., **286**, 1-28. (c) after Mullen (1983), Earth Planet. Sci. Lett., **62**, 53-62.