Trace Elements

Fractionation in igneous rocks
Trace element properties

- Present in concentrations < 0.1 weight percent (<1000 ppm)
- Includes elements Rb, Sr, Zr, Ba, Li, Ni, Cu, V, W, Ag, Au, Cr, Co, Sn, etc. (some are economic)
- Many are members of the transition metal portion of the periodic table
- Trace elements have a wide range of valence states and ionic radii
# Periodic Table of Elements: Trace elements

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- **Trace element**

*Lanthanoids*

**Actinoids**
Goldschmidt’s Chemical Environments

• Siderophile elements: elements that prefer the metallic phase (Fe, Co, Ni, Pd, Pt, Au, Sn, W, Cu, Mo, As, Sb)
• Chalcophile elements: elements that prefer the sulfide phase (S, Zn, Hg, Pb, Bi, Cu, Ga, Sn, As, Fe, Mo)
• Lithophile elements: elements that prefer the silicate phase (H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, B, Al, REE, Si, Ti, Hf, Th, P, V, Nb, Ta, O, Cr, U, F, Cl, Mn, Fe)
Substitution parameters

- Ionic radius: must be close in value for substitution ($\text{Mg}^{2+}=0.65; \text{Fe}^{2+}=0.76; \text{K}^+=1.33$)
- Ionic charge: Must be equal
- Other factors being equal, the smaller ion will preferentially substitute in the solid lattice
Common Substitutions

- **K site (12):** Na, Sr, Ba, Rb, Cs, Pb
- **Al site (6):** Ti, Ga
- **Si site (4):** Ge, Al
- **Ca site (6):** Sr, Mn, REE
- **Mg site (6):** Fe, Li, Mn
- **Fe2+ site (6):** Mg, Ni, Co, Sc, Mn
- **Fe3+ site (6):** Cr, V
- **Ti site (6):** Hf, REE
Distribution Coefficients

- $a = (\gamma)c$ (chemical activity = activity coefficient times concentration)
- Henry’s Law: as concentrations are lowered $\gamma$ becomes $= 1.0$, and $a = c$
- $K_D = C_S / C_L$ (distribution coefficient = $K_D$)
- $D = K_{D1}P_1 + K_{D2}P_2 + K_{D3}P_3 + \ldots$ (D = bulk distribution coefficient; P = proportion of mineral)
- $D > 1.0$: trace element is compatible
- $D < 1.0$: trace element is incompatible
Fractionation Equation

- $C_L/C_O = F^{(D-1)}$
- $F =$ proportion of melt in a melt+solid system
- $D =$ bulk distribution coefficient for trace element of interest
- $C_L =$ concentration of trace element in liquid (melt)
- $C_O =$ original concentration of trace element
Example Problem (part A)

• Given a mantle peridotite containing 5 ppm Rb find Rb concentration in a 7% partial melt. Peridotite is 45% Olivine + 55% Orthopyroxene. $K_{D(\text{oliv})} = 0.006$ and $K_{D(\text{opx})} = 0.02$.

• $D = 0.45(0.006) + 0.55(0.02) = 0.0137$

• $C_{L} = (0.07)^{(0.0137-1)} \times (5 \text{ ppm}) = 69 \text{ ppm}$
Example problem (part B)

- \( C_L = 69 \text{ ppm} \) (from previous step)
- Concentration in solid \( (C_S) \):
  - Original conc. = \( (C_L)(0.07) + (C_S)(0.93) \)
  - 5 ppm = \( (69 \text{ ppm})(0.07) + (C_S)(0.93) \)
  - \( C_S = [5 \text{ ppm} - (69 \text{ ppm})(0.07)] / 0.93 \)
  - \( C_S = 0.2 \text{ ppm} \)
Rare Earth Elements

- Elements La to Lu having oxidation state of +3
- Large ionic radius in range 1.14 to 0.85 angstroms
- Show little substitution for major elements in silicates
- Relatively impervious to alteration, metamorphosis, and/or weathering
## Periodic Table: REE

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### Lanthanoids
- La
- Ce
- Pr
- Nd
- Pm
- Sm
- Eu
- Gd
- Tb
- Dy
- Ho
- Er
- Tm
- Yb

### Actinoids
- Ac
- Th
- Pa
- U
- Np
- Pu
- Am
- Cm
- Bk
- Cf
- Es
- Fm
- Md
- No
REE Variation Diagrams

- Normalized to chondritic meteorite abundance (La=0.33ppm, Ce=0.88, Pr=0.112, Nd=0.60, Sm=0.181, Eu=0.069, Gd=0.249, Tb=0.047, Ho=0.070, Er=0.2, Tm=0.03, Yb=0.2, Lu=0.034)
- Plotted as a histogram of element versus the log of normalized abundance (Rock/Chondrite)
Chondritic REE Abundances
Chondrite REE Trends

• Chondrite values are assumed to represent original solar system (primordial) abundances
• Note that the even atomic number REE are more abundant than the following odd atomic number REE
• Light REE occur at higher absolute abundance
REE Trends in Rocks

REE FRACTIONATION PATTERNS

Log (Rock/Chondrite) vs REE

MORB
Arc Tholeiite
Peridotite
Alkali basalt
REE Fractionation Trends

- Fractional crystallization tends to enrich melt in light REE, depletes heavy REE
- Eu will display a negative anomaly if plagioclase is involved in fractional crystallization
- Restite will display a corresponding enrichment of heavy REE
- Primitive magma will display a “flat” trend
Quantitative REE Calculations

- Fractionation should obey mass balance rules
- Source ppm = (melt ppm)(x) + (restite ppm)(1-x)
- Assume that MORB basalt is source rock, peridotite is restite, and alkali basalt is suspected melt.
- 3.2=(5.02)(x)+(0.76)(1-x) therefore x=0.573
- If the solution for x (melt fraction) is consistent for all REE then the alkali basalt could have been the melt in equilibrium with peridotite restite