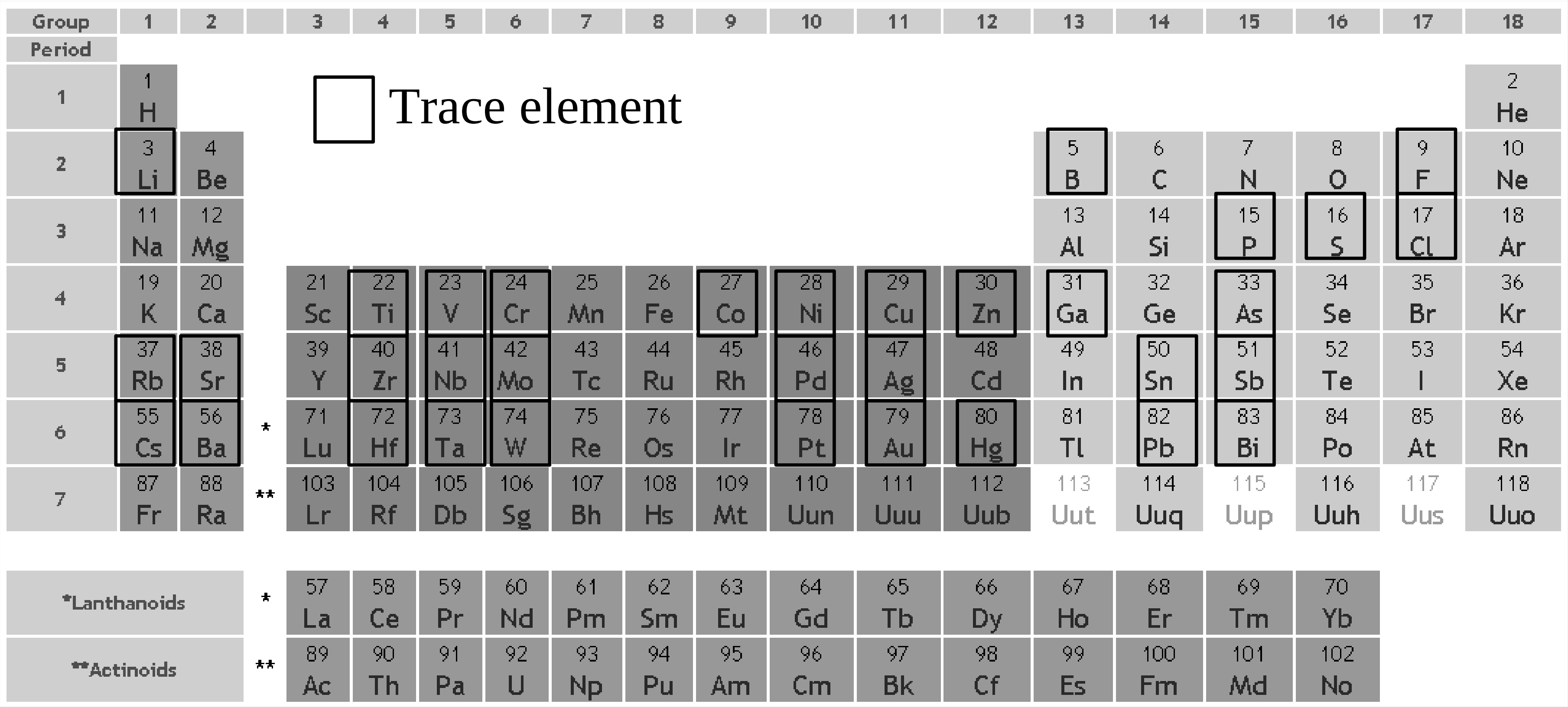
Trace Elements

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



☐ Trace element

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	☐ 3 Li	4 Be												☐ 5 B	6 C	7 N	8 O	☐ 9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	☐ 15 P	☐ 16 S	☐ 17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	☐ 22 Ti	☐ 23 V	☐ 24 Cr	25 Mn	26 Fe	☐ 27 Co	☐ 28 Ni	☐ 29 Cu	☐ 30 Zn	☐ 31 Ga	32 Ge	☐ 33 As	34 Se	35 Br	36 Kr
5	☐ 37 Rb	☐ 38 Sr		39 Y	☐ 40 Zr	☐ 41 Nb	☐ 42 Mo	43 Tc	44 Ru	45 Rh	☐ 46 Pd	☐ 47 Ag	48 Cd	49 In	☐ 50 Sn	☐ 51 Sb	52 Te	53 I	54 Xe
6	☐ 55 Cs	☐ 56 Ba	*	71 Lu	☐ 72 Hf	☐ 73 Ta	☐ 74 W	75 Re	76 Os	77 Ir	☐ 78 Pt	☐ 79 Au	☐ 80 Hg	81 Tl	☐ 82 Pb	☐ 83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

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 (Mg^{2+}=0.65; Fe^{2+}=0.76; 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
- 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

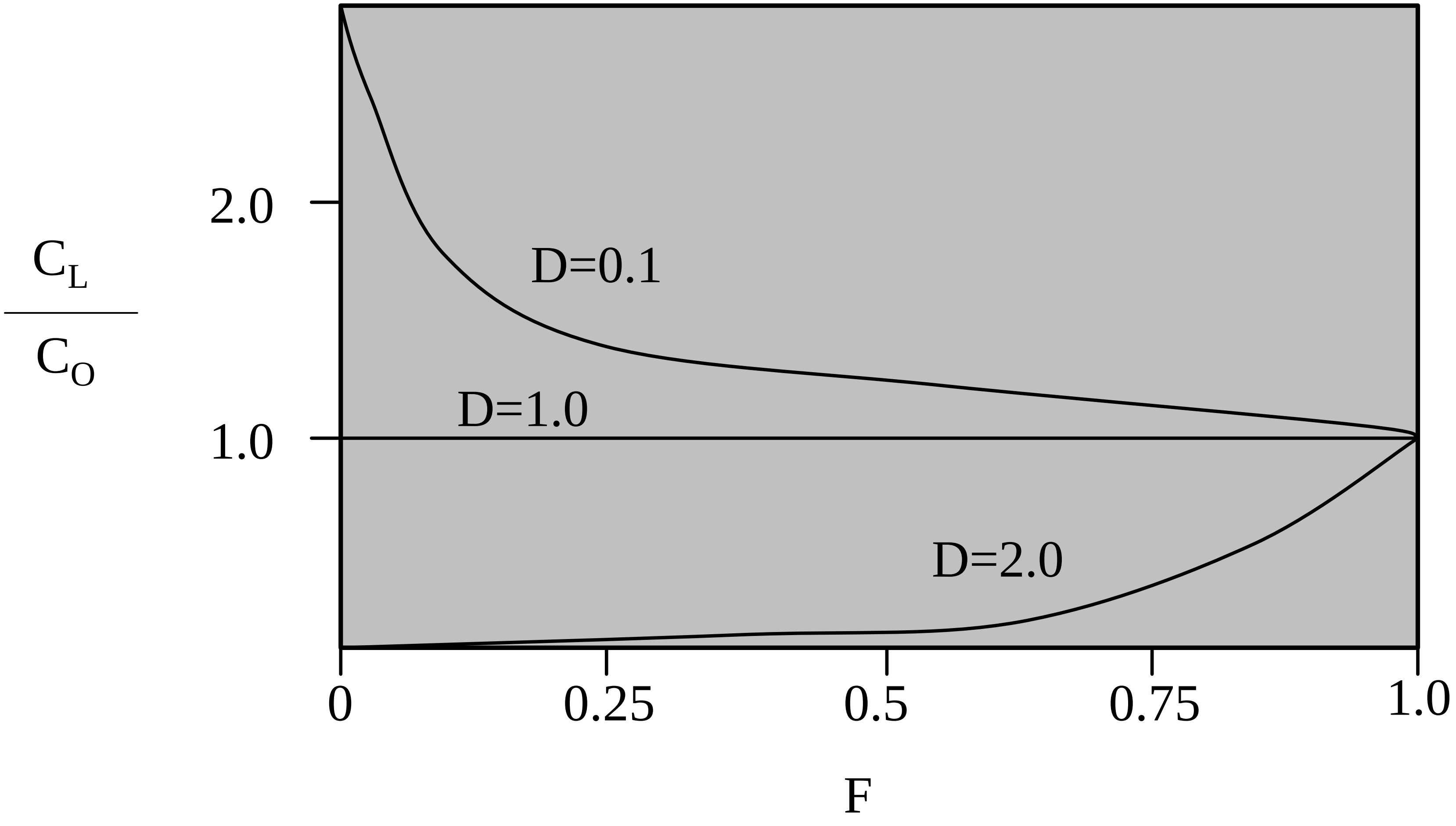
Distribution Coefficients

- a = (γ)c (chemical activity = activity coefficient times concentration)
- Henry's Law: as concentrations are lowered γ 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

Fractionation (graphical)



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. $K_{D(oliv)}=0.006$ and $K_{D(opx)}=0.02$.
- $D=0.45(0.006)+0.55(0.02)=0.0137$
- $C_L=(0.07)^{(0.0137-1)}$ x(5ppm) = 69ppm

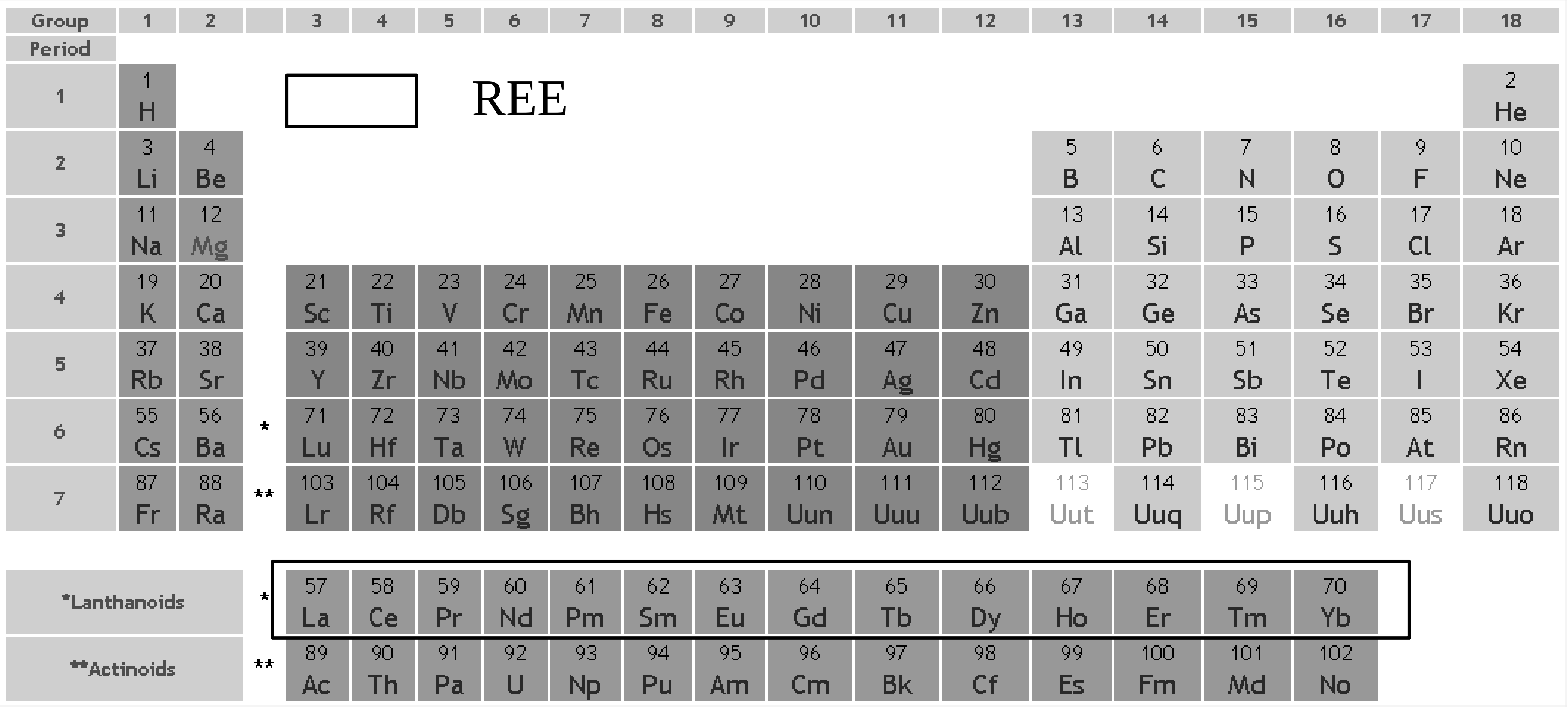
Example problem (part B)

- C_L = 69 ppm (from pervious step)
- Concentration in solid (C_S):
  - ✓Original conc. = $(C_L)(0.07)+(C_S)(0.93)$
  - ✓ 5ppm = $(69\text{ppm})(0.07)+(C_S)(0.93)$
  - ✓C_S = 5 ppm – [(69 ppm)(0.07)/(0.93)]
  - ✓C_S = 0.2 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, metamorphism, and/or weathering

Periodic Table: REE



☐ REE

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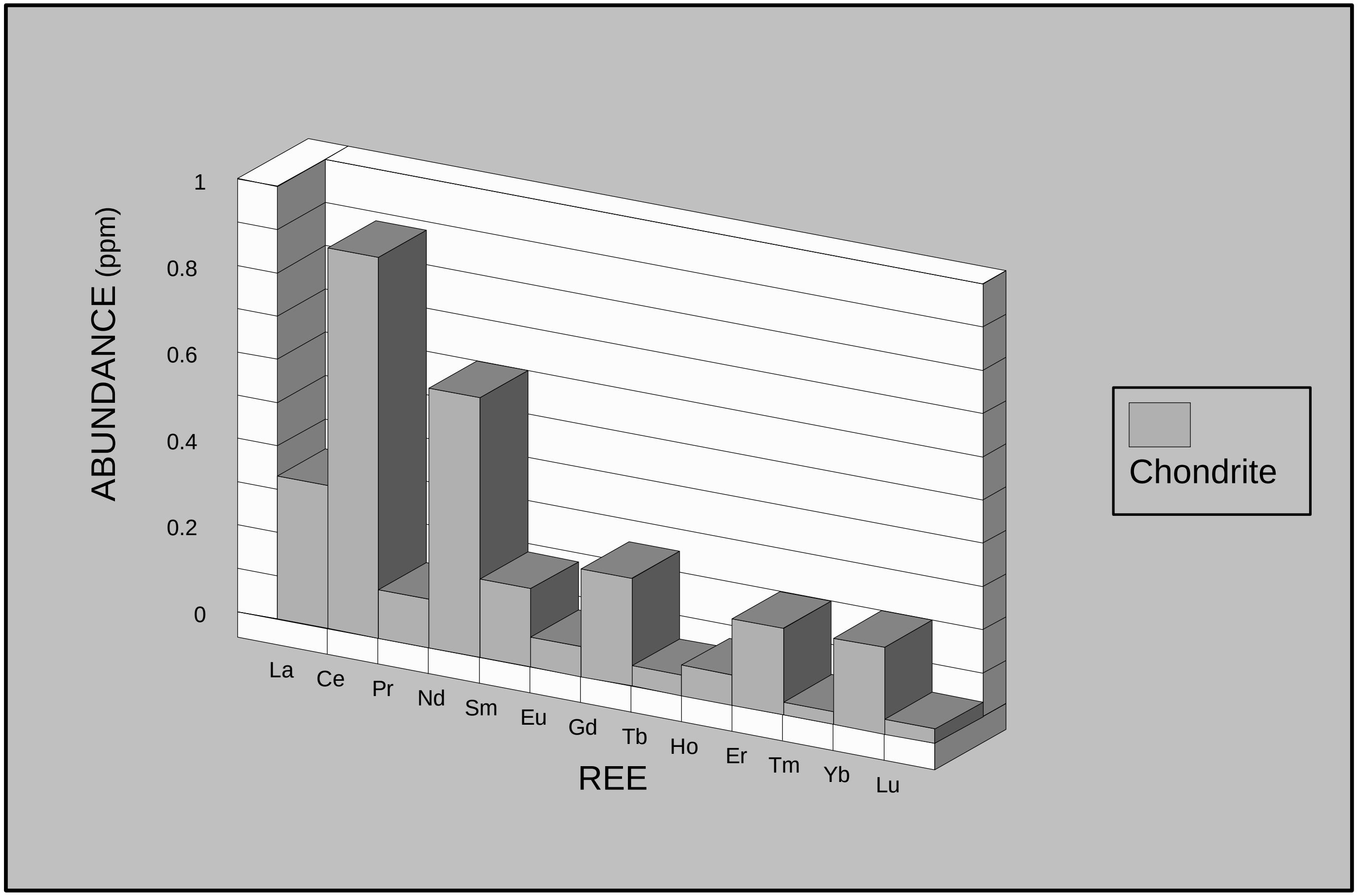
REE Variation Diagrams

- 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)

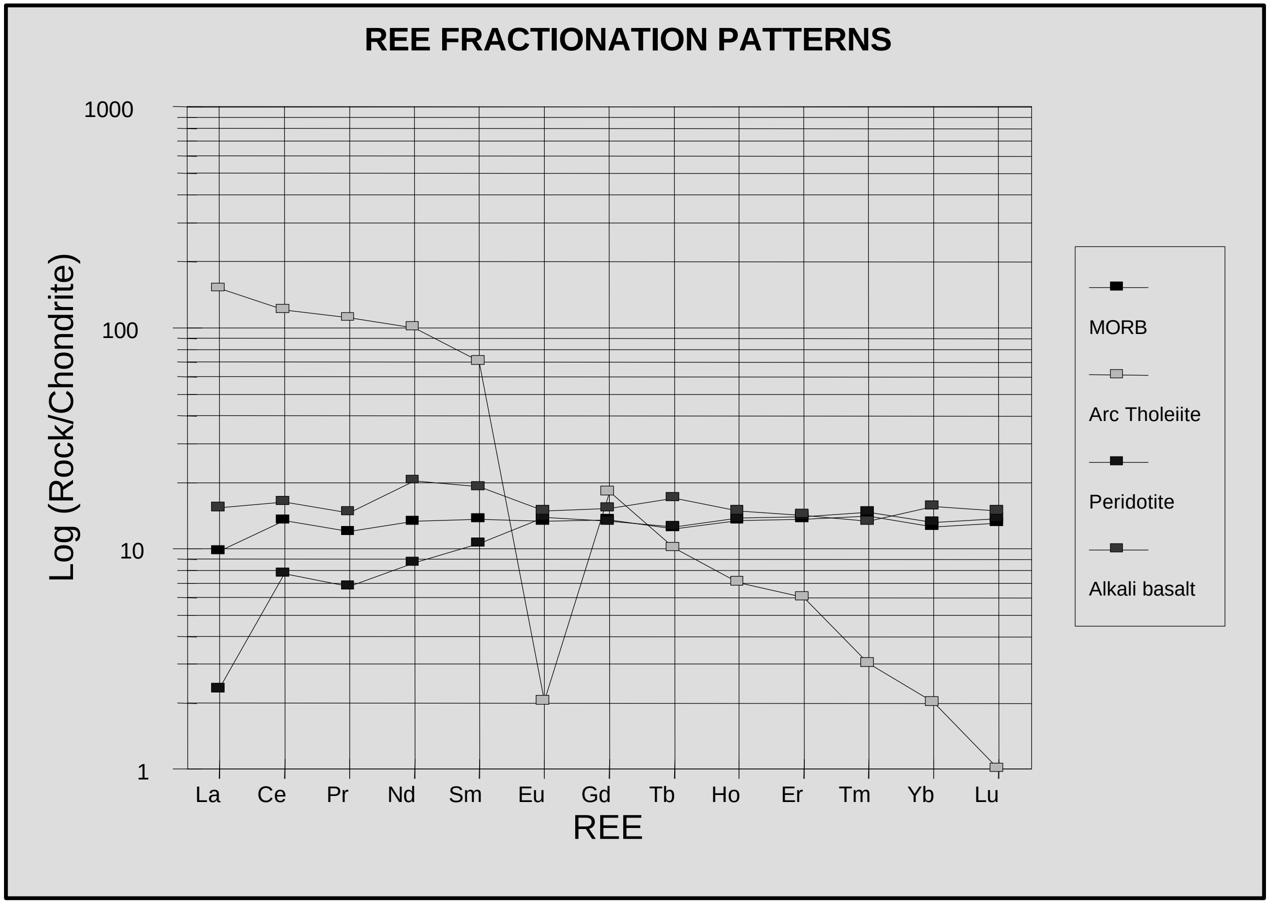
Chondritic REE Abundances



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 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