

Figure 3.1 **A:** Variation of density of the planets with mean distance from the Sun. Note that the Earth has the highest density among the earthlike planets, which, as a group, are more dense than the outer gaseous planets. **B:** The planets of the solar system magnified 2000 times relative to the distance scale. The earthlike planets are very small in relation to the Sun and the gaseous planets of the solar system.

Differentiaton:

Redistribution of mass (elements) and energy by chemical & physical processes.

Goal: Quantitative understanding of those processes.

TABLE 1-9 Chemical Compositions of Mercury, Venus, Earth, and Mars

Mantle and crust (%)	Mercury	Venus	Earth	Mars
SiO ₂	43.6–47.1	40.4–49.8	45	36.8–49.6
TiO ₂	0.33	0.2–0.3	0.15	0.2–0.3
Al ₂ O ₃	4.7–6.4	3.4–4.1	3.3	3.1–6.4
MgO	33.7–54.6	33.3–38.0	40	30
FeO	3.7	5.4–18.7	8.0	15.8–26.8
CaO	1.8–5.2	3.2–3.4	2.65	2.4–5.2
Na ₂ O	0.08	0.1–0.28	0.34	0.1–0.2
Core (%)				
Fe	93.5–94.5	79–89	85.5–86.2	64–88
Ni	5.5	4.8–5.5	4.8–5.5	8.0–8.2
S	0–0.35	1.0–5.1	1.0–9.0	3.5–9.3
O	—	8.0–9.8	0–8.0	0–18.7
Relative masses				
Mantle and crust	32.0–35.2	68.0–76.4	67.6	81–82
Core	64.8–68.0	23.6–32.0	32.4	18–19

Data from Taylor (1982, 385–386 and 403).

TABLE 21-2
Estimated compositions of the whole Earth, the mantle, and the continental crust, in weight percent

	Whole Earth	Mantle	Continental crust	Andesite
SiO ₂	47.9	45.7	60.2	57.6
TiO ₂	0.02	0.09	0.7	0.77
Al ₂ O ₃	3.9	3.4	15.2	17.3
Fe ₂ O ₃			2.5	3.1
FeO	8.9	8.0	3.8	4.3
MnO	0.14	0.14	0.1	0.15
MgO	34.1	38.4	3.1	3.6
CaO	3.2	3.1	5.5	7.2
Na ₂ O	0.25	0.4	3.0	3.2
K ₂ O	0.02	0.1(?)	2.9	1.5
P ₂ O ₅				0.21
H ₂ O				1.0

Table 4.8 Chemical Composition of Dry Air

Constituent	Concentration by Volume	
	%	ppm
N ₂	78.084	—
O ₂	20.946	—
CO ₂	0.033	—
Ar	0.934	—
Ne	—	18.18
He	—	5.24
Kr	—	1.14
Xe	—	0.087
H ₂	—	0.5
CH ₄	—	2
N ₂ O	—	0.5

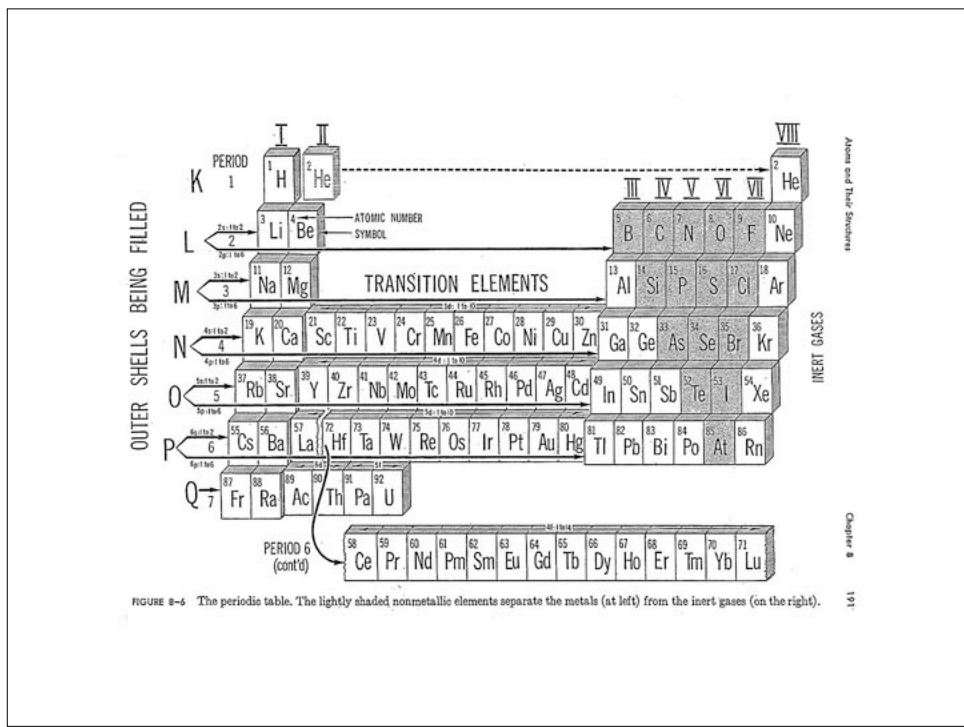
Data from the *CRC Handbook of Chemistry and Physics* (Weast et al., 1986).

Periodic Table of the Elements

1 H 1.01																	18 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (208.98)	85 At (209.99)	86 Rn (222.02)
87 Fr (223.02)	88 Ra (226.03)	89 Ac (227.03)	104 Rf (261.11)	105 Ha (262.11)	106 Sg (263.12)												

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.91)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237.05)	94 Pu (244.06)	95 Am (243.06)	96 Cm (247.07)	97 Bk (247.07)	98 Cf (251.08)	99 Es (252.08)	100 Fm (257.10)	101 Md (258.10)	102 No (259.10)	103 Lr (262.11)

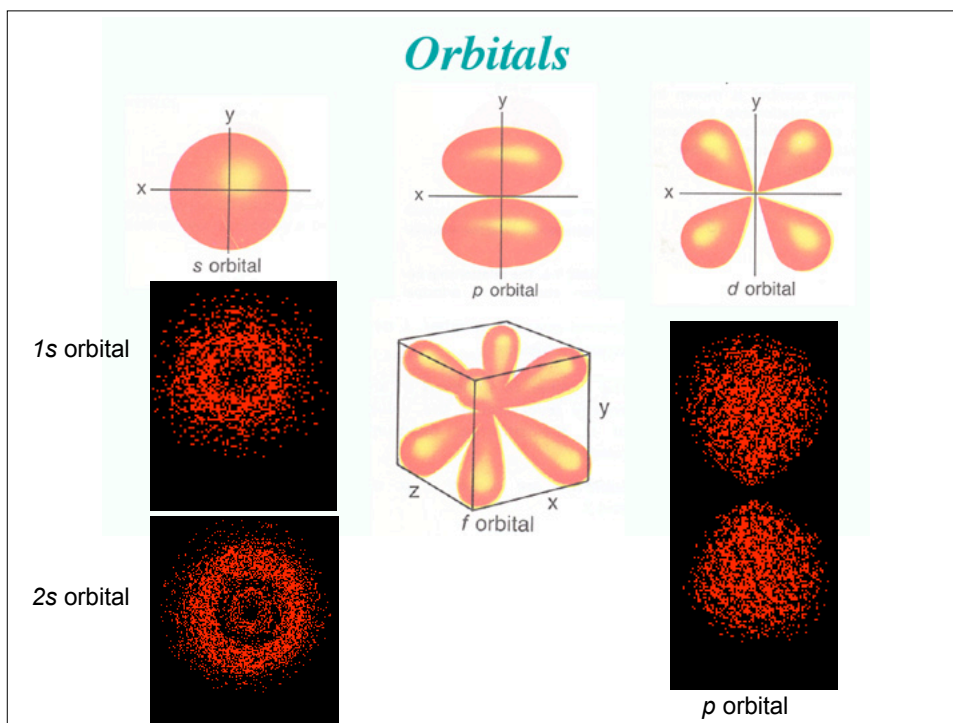
What controls the periodicity of behavior of the elements?

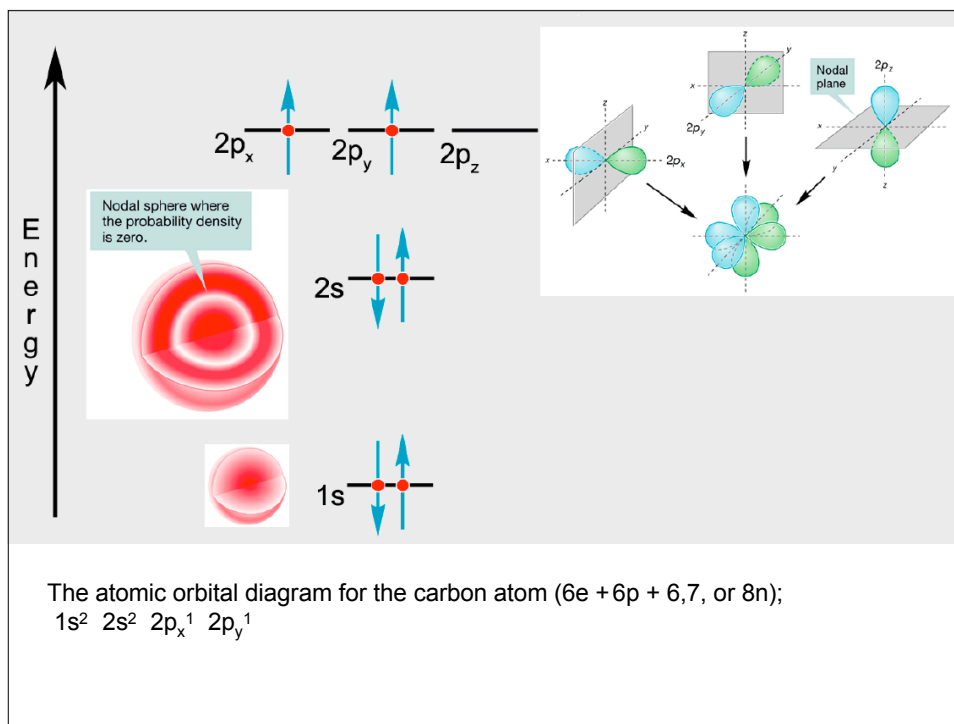


PERIOD					NO. of ELECTRONS
7	7s	7p	6d	5f	(32)
6	6s	6p	5d	4f	(32)
5	5s	5p	4d		(18)
4	4s	4p	3d		(18)
3	3s	3p			(8)
2	2s	2p			(8)
1	1s				(2)

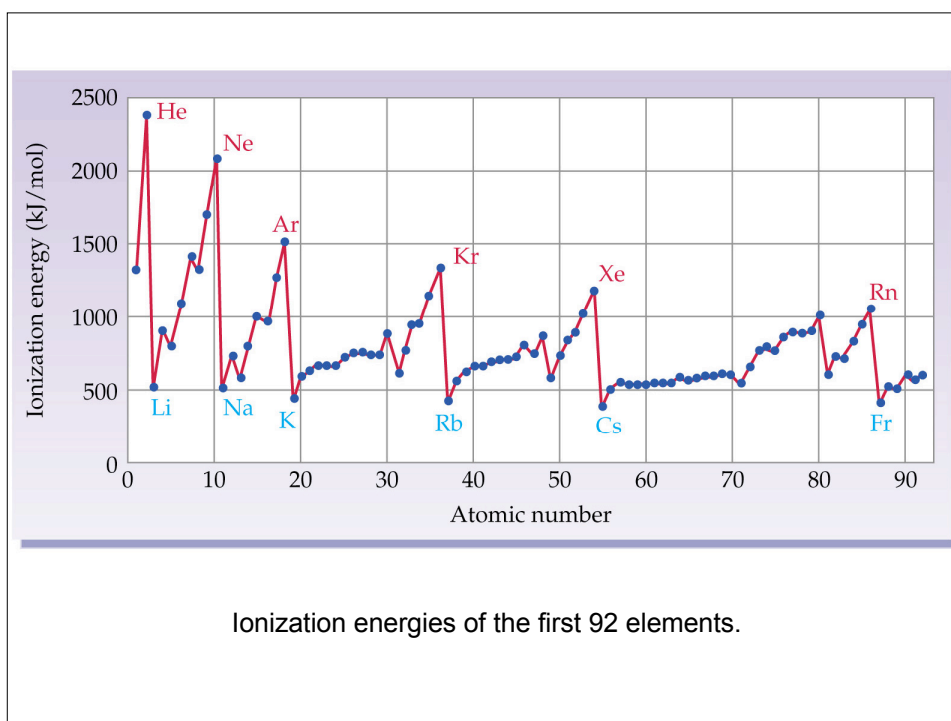
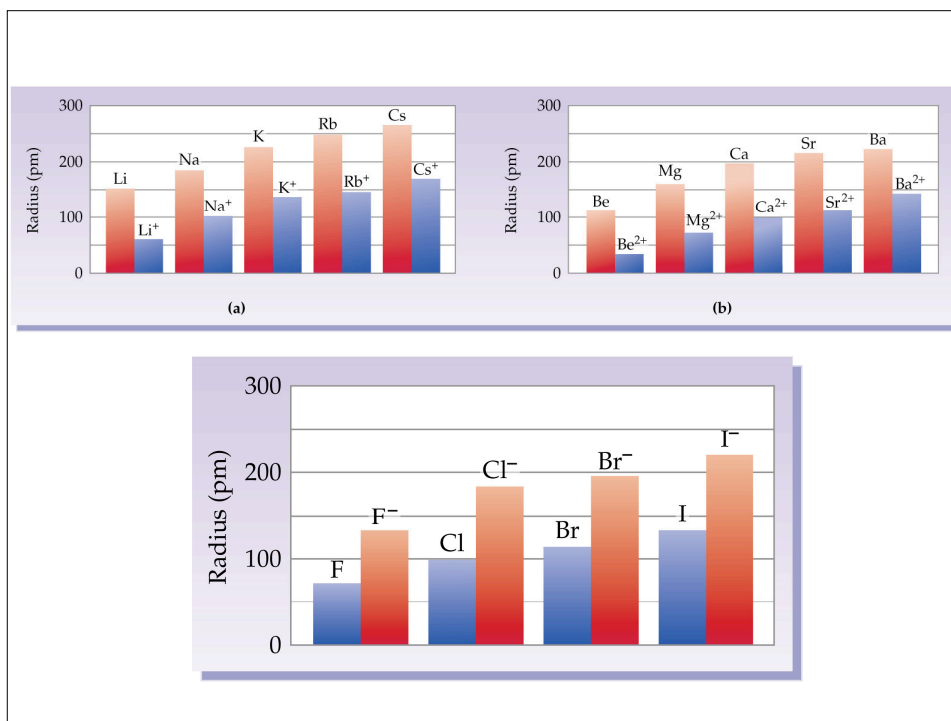
Energy ↑

Figure 1.2. The predicted sequence of orbital energies for electrons in atoms. *s* levels can hold 2 electrons, *p*, *d*, and *f* can hold 6, 10, and 14 respectively.





B: $1s^2 2s^2 2p^1$	or	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow}{\quad}$	$\frac{\quad}{2p}$	$\frac{\quad}{\quad}$
C: $1s^2 2s^2 2p_x^1 2p_y^1$	or	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow}{\quad}$	$\frac{\uparrow}{2p}$	$\frac{\quad}{\quad}$
N: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	or	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow}{\quad}$	$\frac{\uparrow}{2p}$	$\frac{\uparrow}{\quad}$
O: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	or	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow\downarrow}{\quad}$	$\frac{\uparrow}{2p}$	$\frac{\uparrow}{\quad}$
F: $1s^2 2s^2 2p^5$	or	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow\downarrow}{\quad}$	$\frac{\uparrow\downarrow}{2p}$	$\frac{\uparrow}{\quad}$
Ne: $1s^2 2s^2 2p^6$	or	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow\downarrow}{\quad}$	$\frac{\uparrow\downarrow}{2p}$	$\frac{\uparrow\downarrow}{\quad}$



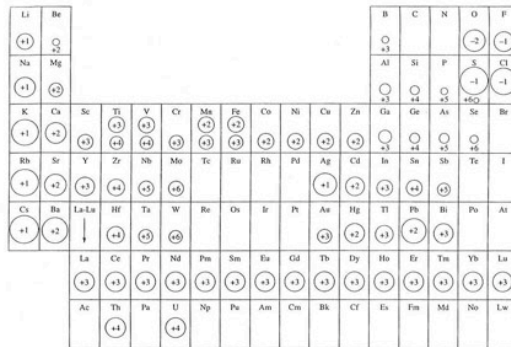
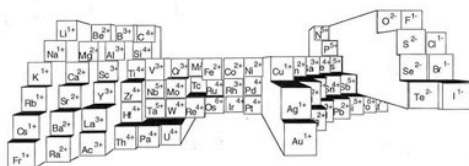
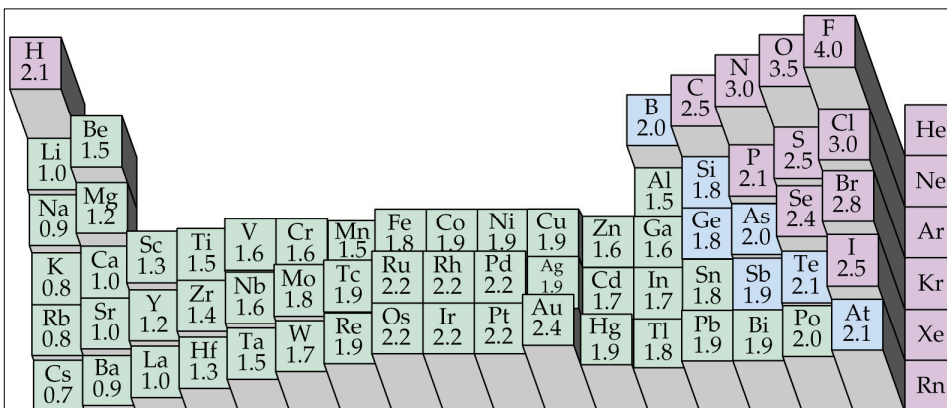


Figure 5-10 Relative ionic sizes. Radii (see Table 5-2) are for common valences and coordination numbers. Transition metals in high-spin state. (Scale: 1 Å = 3 mm)



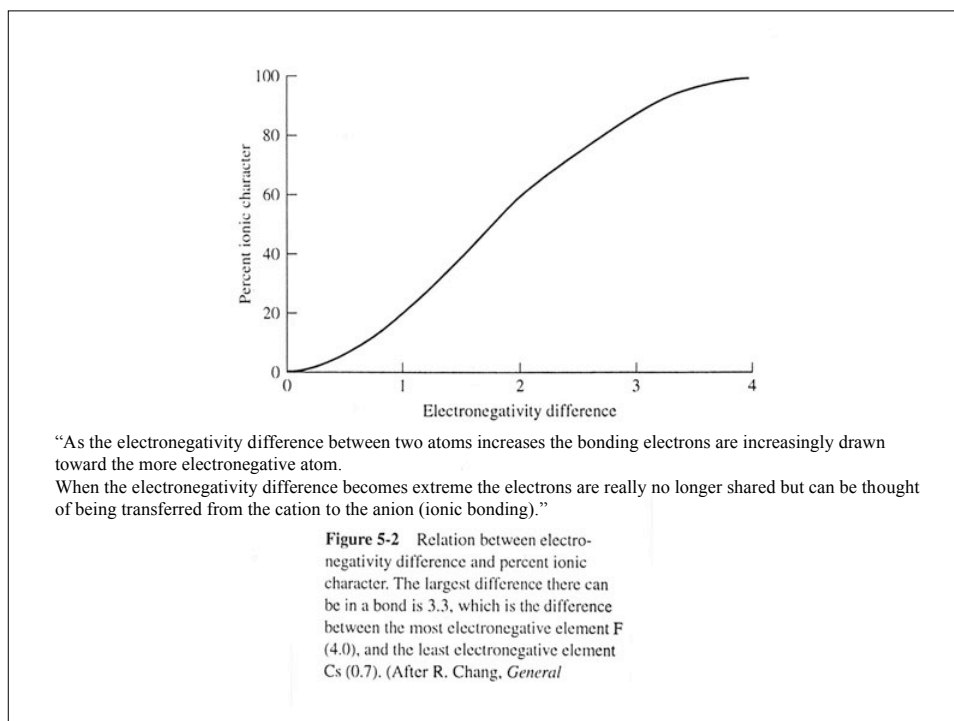
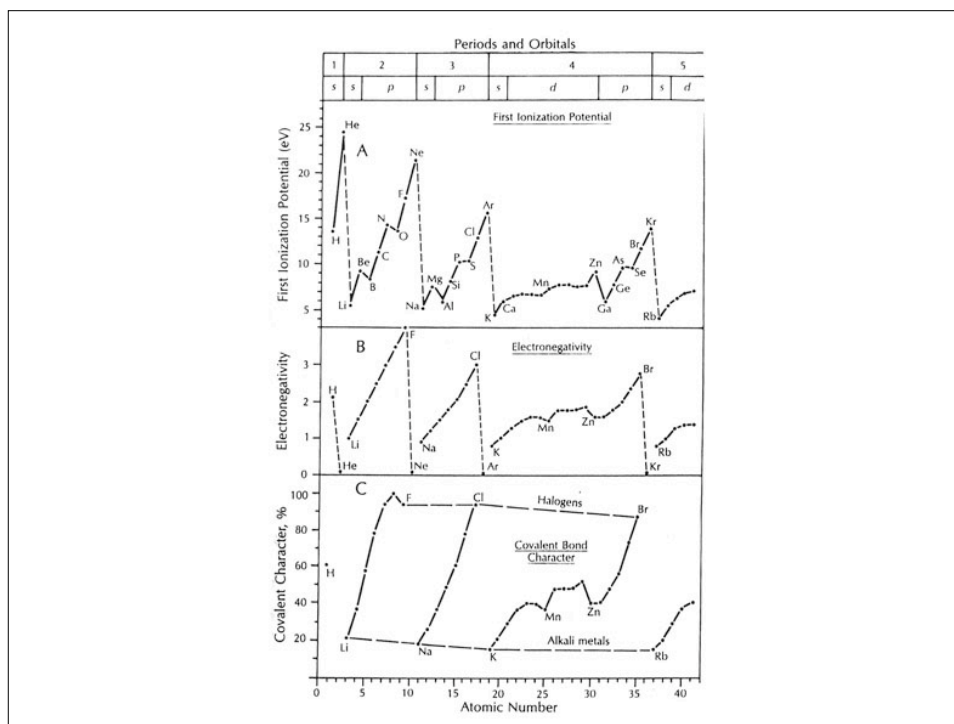
IONIC RADII

Figure 1.8. Ionic radii of the elements.



Electronegativity trends in the periodic table. Electronegativity increases from left to right and generally decreases from top to bottom.

Low electronegativity = electron donors
High electronegativity = electron acceptors



Outline (on the periodic table) of the primary element groups:

- rare earth elements, actinides, special cases to return to later.
- noble gases (unreactive, filled electron shells)
- alkali metals (reactive, singly charged, large radii)
- alkaline earths (reactive, doubly charged, smaller radii)
- halogens (very reactive, negative charge)
- PGE's (cogners of Fe, Ni, Co; rare elements; small radii, can occur in native state)
- HFSE (high charge to small radius ratio) Ti-V to Hf-Ta; will see importance of ratio
- Finally note the LILE's

Conclude – now have some general intuition of what elements will behave similarly, and therefore during differentiation which elements will group together.

Periodic Table of the Elements

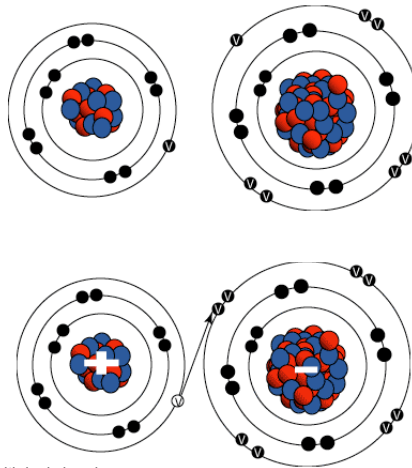
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About Chemistry

1A 1 H 1.00794 Hydrogen																	2 He 4.002602 Helium
3 Li 6.941 Lithium	4 Be 9.012182 Beryllium											5 B 10.811 Boron	6 C 12.0107 Carbon	7 N 14.0067 Nitrogen	8 O 15.9994 Oxygen	9 F 18.9984032 Fluorine	10 Ne 20.1797 Neon
11 Na 22.989769 Sodium	12 Mg 24.3050 Magnesium											13 Al 26.9815386 Aluminum	14 Si 28.0855 Silicon	15 P 30.973762 Phosphorus	16 S 32.065 Sulfur	17 Cl 35.453 Chlorine	18 Ar 39.948 Argon
19 K 39.0983 Potassium	20 Ca 40.078 Calcium	21 Sc 44.955912 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938045 Manganese	26 Fe 55.845 Iron	27 Co 58.933195 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.64 Germanium	33 As 74.92160 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.798 Krypton
37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.90585 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90638 Niobium	42 Mo 95.96 Molybdenum	43 Tc 101.07 [98] Technetium	44 Ru 101.07 [98] Ruthenium	45 Rh 102.90550 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.90447 Iodine	54 Xe 131.293 Xenon
55 Cs 132.9054519 Cesium	56 Ba 137.327 Barium	57-71 Lanthanides	72 Hf 178.49 Hafnium	73 Ta 180.94788 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.966569 Gold	80 Hg 200.59 Mercury	81 Tl 204.3833 Thallium	82 Pb 207.2 Lead	83 Bi 208.98040 Bismuth	84 Po [209] Polonium	85 At [210] Astatine	86 Rn [222] Radon
87 Fr [223] Francium	88 Ra [226] Radium	89-103 Actinides	104 Rf [261] Rutherfordium	105 Db [268] Dubnium	106 Sg [271] Seaborgium	107 Bh [272] Bohrium	108 Hs [270] Hassium	109 Mt [276] Meitnerium	110 Ds [281] Darmstadtium	111 Rg [280] Roentgenium	112 Cn [285] Copernicium	113 Uut [284] Ununtrium	114 Uuq [289] Ununquadium	115 Uup [288] Ununpentium	116 Uuh [289] Ununhexium	117 Uus [294] Ununseptium	118 Uuo [294] Ununoctium
Lanthanides			57 La 138.90547 Lanthanum	58 Ce 140.118 Cerium	59 Pr 140.90765 Praseodymium	60 Nd 144.242 Neodymium	61 Pm [145] Promethium	62 Sm 150.36 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.92535 Terbium	66 Dy 162.500 Dysprosium	67 Ho 164.93032 Holmium	68 Er 167.259 Erbium	69 Tm 168.93421 Thulium	70 Yb 173.054 Ytterbium	71 Lu 174.9668 Lutetium
Actinides			89 Ac [227] Actinium	90 Th 232.03806 Thorium	91 Pa 231.03688 Protactinium	92 U 238.02891 Uranium	93 Np [237] Neptunium	94 Pu [244] Plutonium	95 Am [243] Americium	96 Cm [247] Curium	97 Bk [247] Berkelium	98 Cf [251] Californium	99 Es [252] Einsteinium	100 Fm [257] Fermium	101 Md [258] Mendelevium	102 No [259] Nobelium	103 Lr [262] Lawrencium

Bond Types

- **Ionic** - electron transferred from one atom to another
- **Covalent** - electron shared between atoms
- **Metallic** - electron location not constrained; “sea of electrons”
- **van der Waals** - very weak bond caused by attraction of dipole molecules, or emf of one molecule induces polarity of e^- orbits in another and resulting attraction

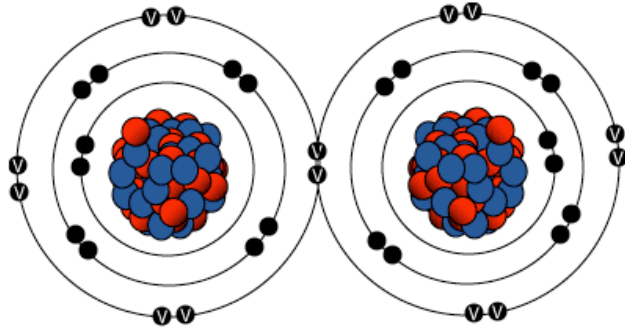
Ionic Bonding



Generally, solid materials with ionic bonds:

- * are hard because particles cannot easily slide past one another.
- * are good insulators because there are no free electrons or ions (unless dissolved or melted).
- * are transparent because their electrons are not moving from atom to atom and less likely to interact with light photons.
- * are brittle and tend to cleave rather than deform because bonds are strong.
- * have high melting point because ionic bonds are relatively strong.

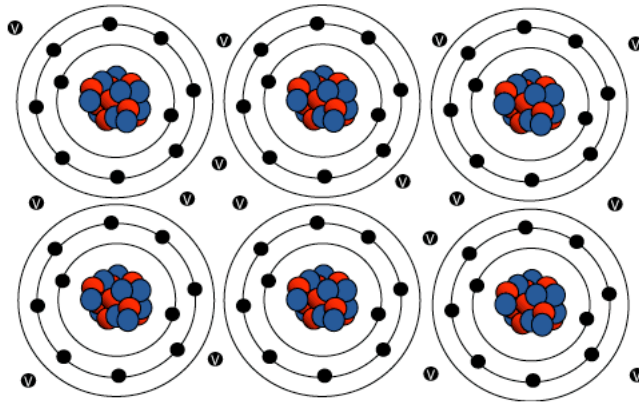
Covalent Bonding



Some Common Features of Materials with Covalent Bonds:

- * Hard
- * Good insulators
- * Transparent
- * Brittle or cleave rather than deform

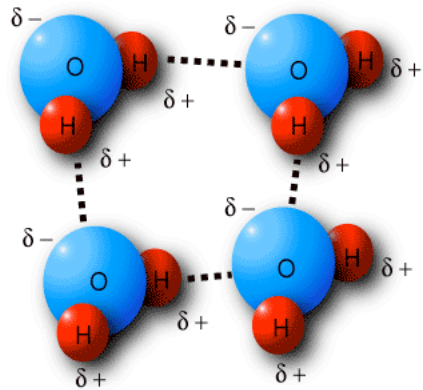
Metallic Bonding



Some Common Features of Materials with Metallic Bonds:

- * Good electrical and thermal conductors due to their free valence electrons
- * Opaque
- * Relatively ductile

van der Waals Bonding



Polar water molecules
H–O–H bond angle = 104.5°

Structural Controls on Ionic Bonding

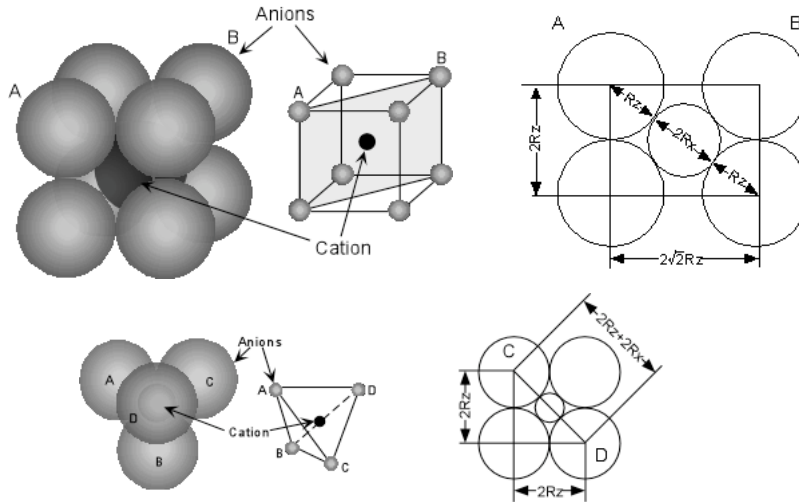
- **Pauling's Rules!**

- Rule #1: Coordination Principle and Radius Ratios
 - Each cation is surrounded by a *coordination polyhedron (CP)*. The form of the CP is defined by the cation and anion radii and the number of anions in the CP is fixed by the relative size of the cation and anion
 - The CP and the coordination number (CN) are related and yield well-defined geometric relationships
- Rule# 2: Electrostatic Valency Principle
 - The total strength of the valence bonds that reach an anion from all nearest neighbor cations is equal to the charge of the anion
- Rule#3: Sharing of Polyhedral Elements I
 - Face and edge sharing of individual CP within a crystal structure tends to *decrease* its overall stability
- Rule#4: Sharing of Polyhedral Elements II
 - In a crystal with different cations, those with large valence (high positive charge) and small coordination number *tend to not share CP elements* (edges and faces)
- Rule#5: Principle of Parsimony
 - The number of different constituents in a crystal structure tends to be small

PAULING'S RULES

Rule #1: Coordination Principle and Radius Ratios

- a. coordination polyhedra
- b. coordination number



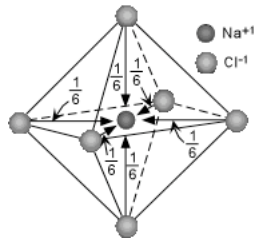
PAULING'S RULES

R_x/R_z	C.N.	Type
1.0	12	Hexagonal or Cubic Closest Packing
1.0 - 0.732	8	Cubic
0.732 - 0.414	6	Octahedral
0.414 - 0.225	4	Tetrahedral
0.225 - 0.155	3	Triangular
<0.155	2	Linear

PAULING'S RULES

Rule #2: Electrostatic Valency Principle

An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an ion equal the charge on that ion.

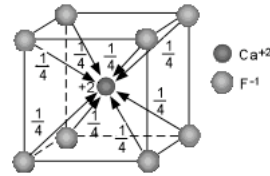


In NaCl each Na⁺ is surrounded by 6 Cl⁻ ions. The Na is thus in 6 fold coordination and C.N. = 6.

So 1/6 of a negative charge reaches the Na ion from each Cl. The +1 charge on the Na ion is balanced by $6 \times 1/6 = 1$ negative charge from the 6 Cl ions.

Similarly, in the CaF₂ structure, each Ca⁺² ion is surrounded by 8 F⁻ ions in cubic or 8-fold coordination. The charge reaching the Ca ion from each of the F ions is thus 1/4.

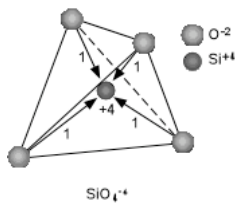
Since there are 8 F ions, the total charge reaching the Ca ion is $8 \times 1/4$ or 2. So, again the charge is balanced.



PAULING'S RULES

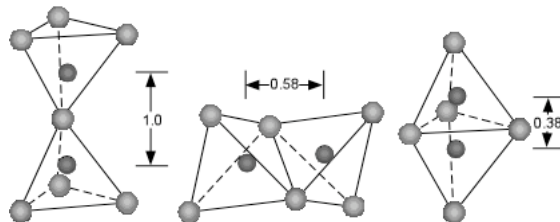
Rule #2: Electrostatic Valency Principle

An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an ion equal the charge on that ion.



A third case arises when the charge reaching the cation is exactly 1/2 the charge on the anion. This is the case for Si⁺⁴ in tetrahedral coordination with O⁻². Here, the charge reaching the Si is $4/4 = 1$.

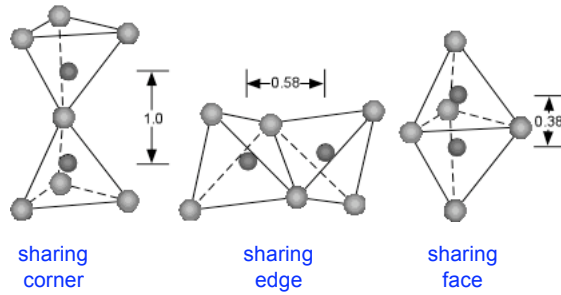
This leaves each Oxygen with a -1 charge that it has not shared. Since this -1 is exactly 1/2 the original charge on O⁻², the Oxygens in the SiO₄⁻⁴ group can be just as tightly bound to ions *outside* the group as to the centrally coordinated Si.



PAULING'S RULES

Rule #3: Sharing of Polyhedral Elements/Components

Shared edges, and particularly faces of two anion polyhedra in a crystal structure decreases its stability. Distance between cations is maximized.



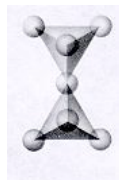
Sharing of only corners of polyhedra places the positively charged cations at the greatest distance from each other.

In the example shown here, for tetrahedral coordination, if the distance between the cations in the polyhedra that share corners is taken as 1, then sharing edges reduces the distance to 0.58, and sharing of faces reduces the distance to 0.38.

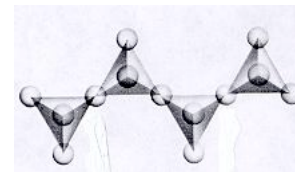
PAULING'S RULES

Rule #3: Sharing of Polyhedral Elements/Components

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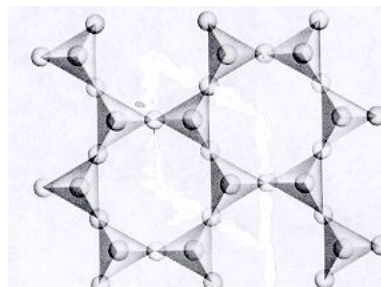
sorosilicate
(e.g., epidote)



Inosilicate
(e.g., pyroxene)



Cyclosilicate
(e.g., tourmaline)



sheet silicate
(e.g., micas)

**Substituting elements into crystals:
Goldschmidt's rules**

- a) Ions of one element can extensively replace those of another if they have the same charge and their radii differ by less than about 15%
- b) Ions whose charges differ by one unit substitute readily for one another provided electrical neutrality of the crystal is maintained (requiring coupled substitution). For more than one unit charge difference, substitution is quite limited.
- c) When two different ions can occupy a position in a crystal lattice, the ion with the higher ionic potential forms a stronger bond with surrounding anions (ionic potential = charge/radius). Therefore, these elements are concentrated in early formed minerals
- d) Even if size and charge are same, substitution may be limited if two ions have different electronegativities, and thus form bonds of different ionic character

















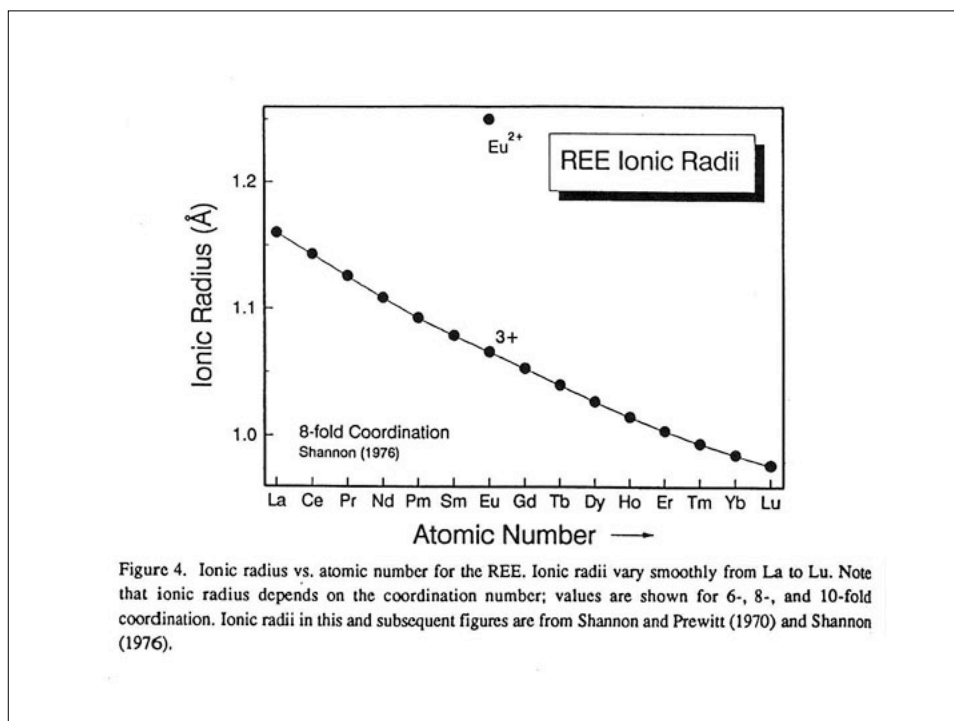
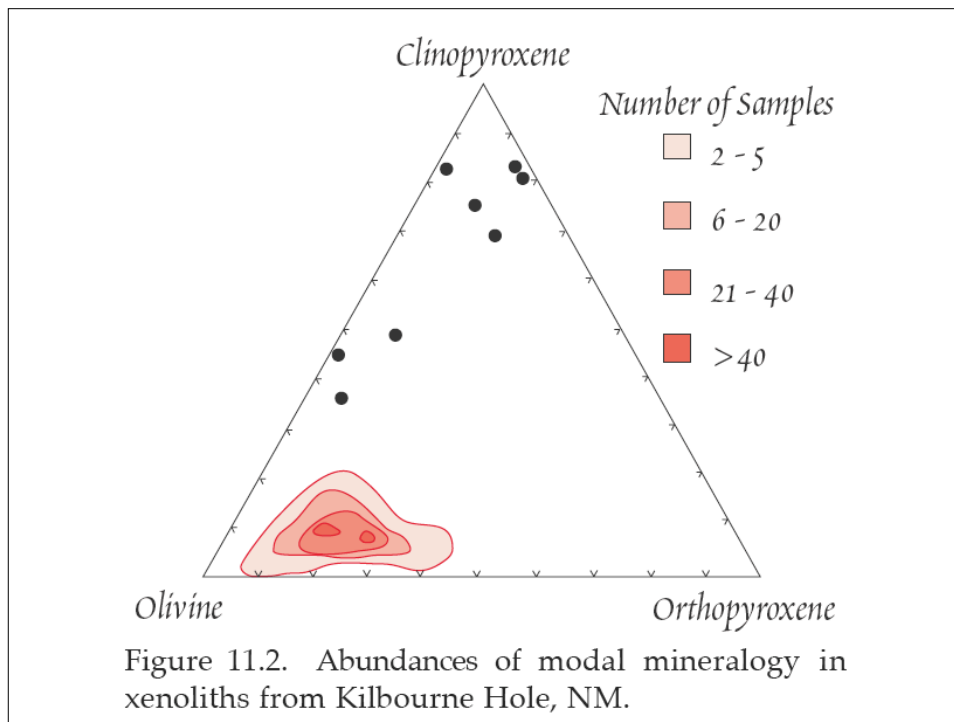
Cations	Radii		Coordination with O^{2-}	Anions
K^+	1.38 Å		8, 12	
Na^+	1.02 Å		6, 8	
Ca^{2+}	1.00 Å		6, 8	
Mn^{2+}	0.83 Å		6	
Fe^{2+}	0.78 Å		6	
Mg^{2+}	0.72 Å		6	
Fe^{3+}	0.64 Å		6	
Ti^{4+}	0.61 Å		6	
Al^{3+}	0.535 Å		4, 6	
Si^{4+}	0.26 Å		4	
C^{4+}	0.15 Å		3	

FIGURE 5-3
Radii of common ions in rock-forming minerals. (Source: Appendix VI)



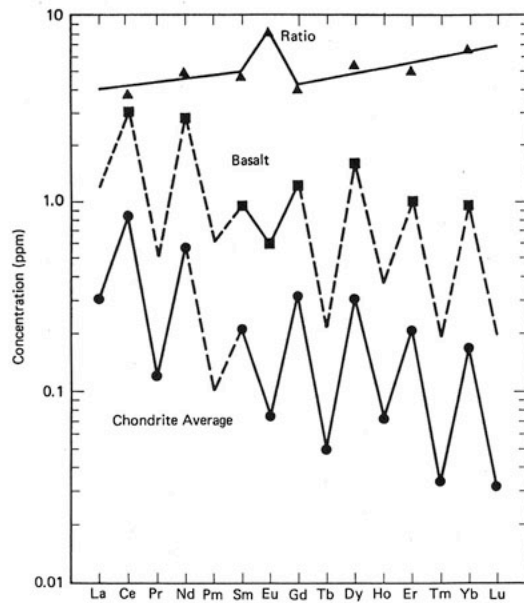
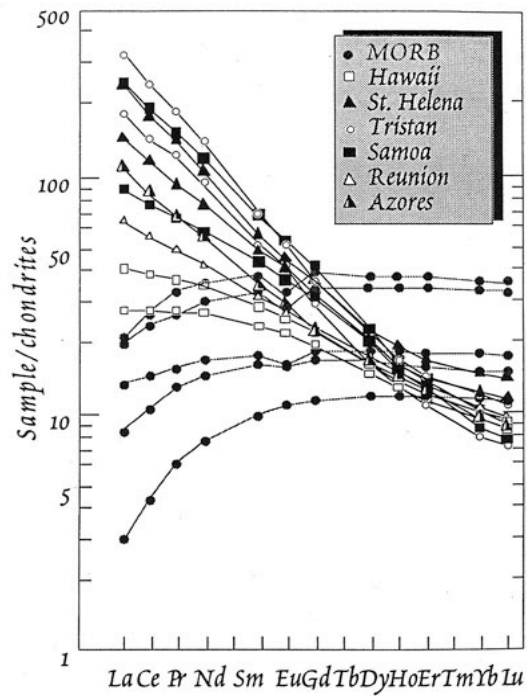
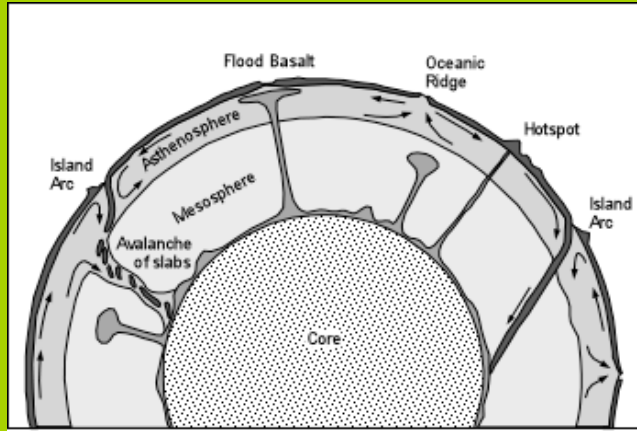


Figure 13.5 Measured abundances of rare earth elements in a basalt and in chondrites. Normalization of the basalt data to chondrites removes the zigzag pattern of odd-even abundances, revealing the pattern imposed during the igneous history of this rock.





Planetary differentiation produced by mantle convection and plate tectonics