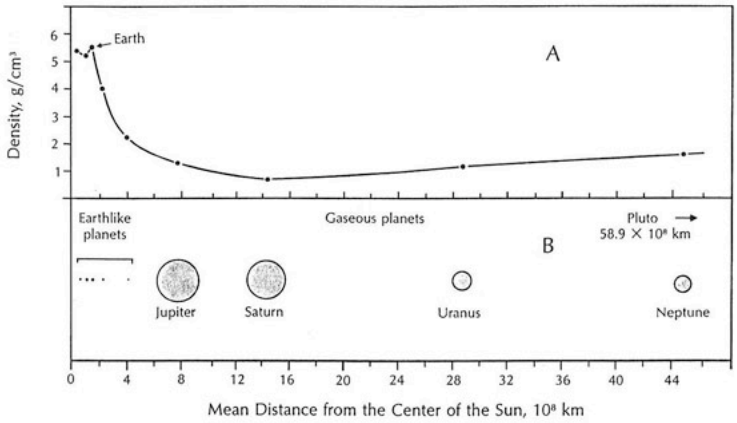


Figure 3.1 **A:** Variation of density of the planets with mean distance from the Sun. Note that the Earth has the highest density among the earthlike planets, which, as a group, are more dense than the outer gaseous planets. **B:** The planets of the solar system magnified 2000 times relative to the 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_2O_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_2O	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).

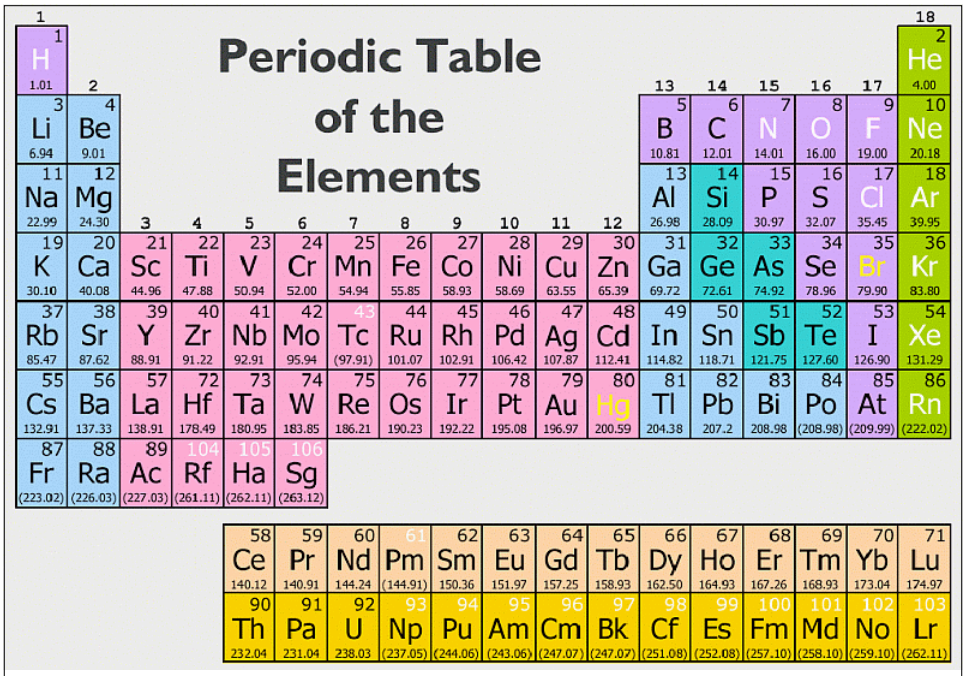
TABLE 21-2
Estimated compositions of the whole Earth, the mantle, and the continental crust, in weight percent

	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_2O_3	3.9	3.4	15.2	17.3
Fe_2O_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_2O	0.25	0.4	3.0	3.2
K_2O	0.02	0.1(?)	2.9	1.5
P_2O_5				0.21
H_2O				1.0

Table 4.8 Chemical Composition of Dry Air

	Concentration by Volume	
Constituent	*%*	*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_2O	—	0.5

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



What controls the periodicity of behavior of the elements?

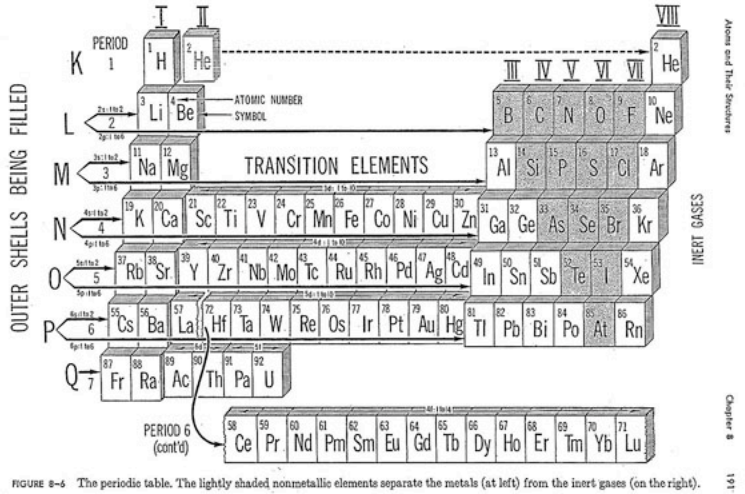


FIGURE 8–6 The periodic table. The lightly shaded nonmetallic elements separate the metals (at left) from the inert gases (on the right).

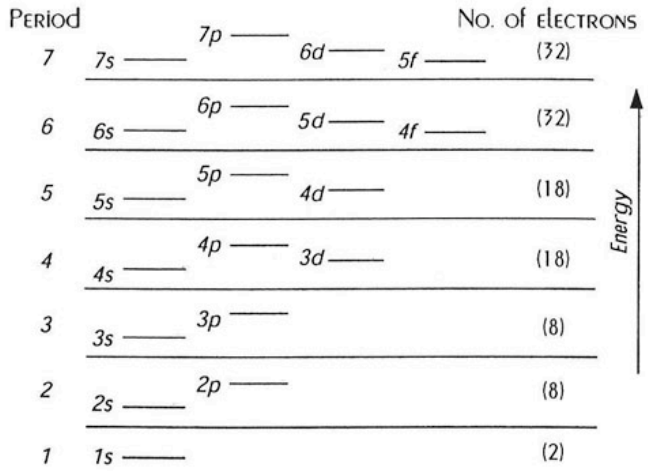
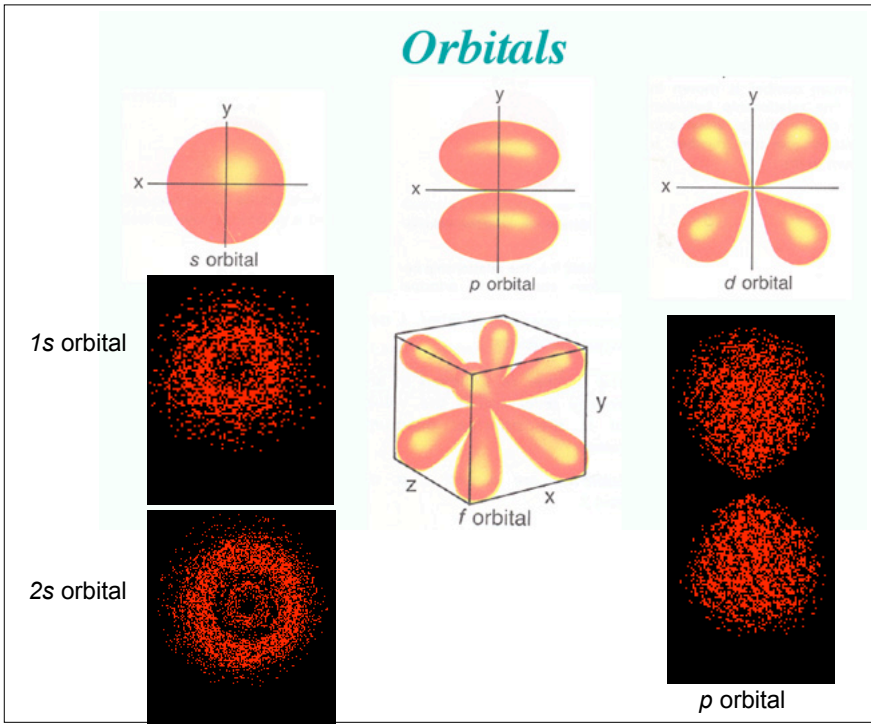
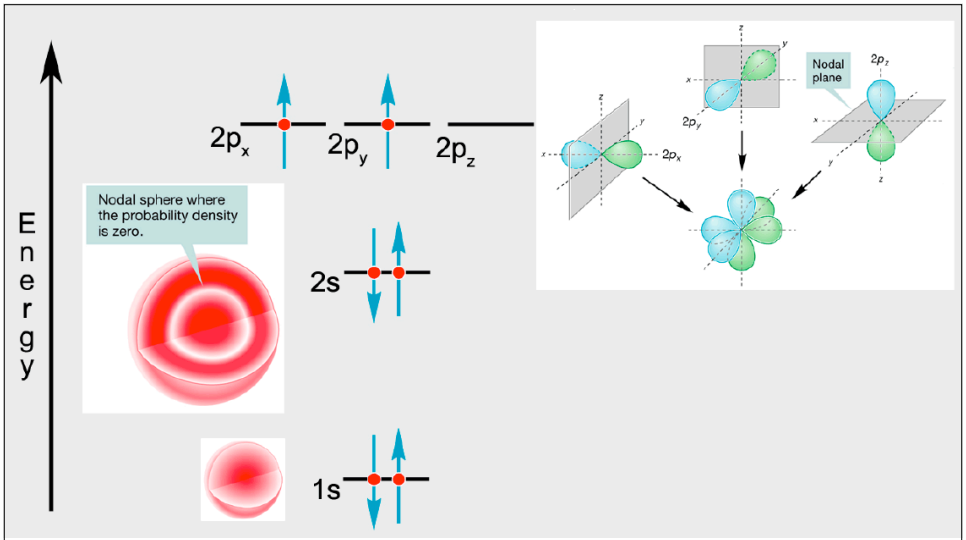


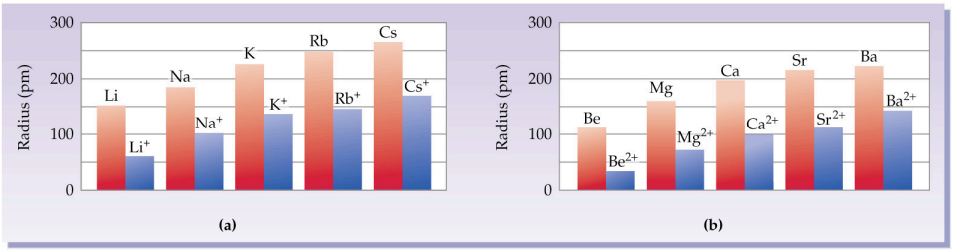
Figure 1.2. The predicted sequence of orbital energies for electrons in atoms. *S* levels can hold 2 electrons, *p*, *d*, and *f* can hold 6, 10, and 14 respectively.

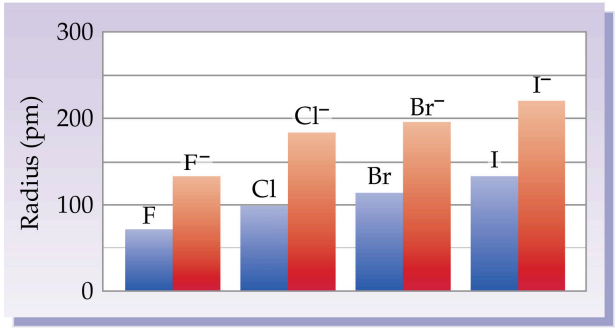


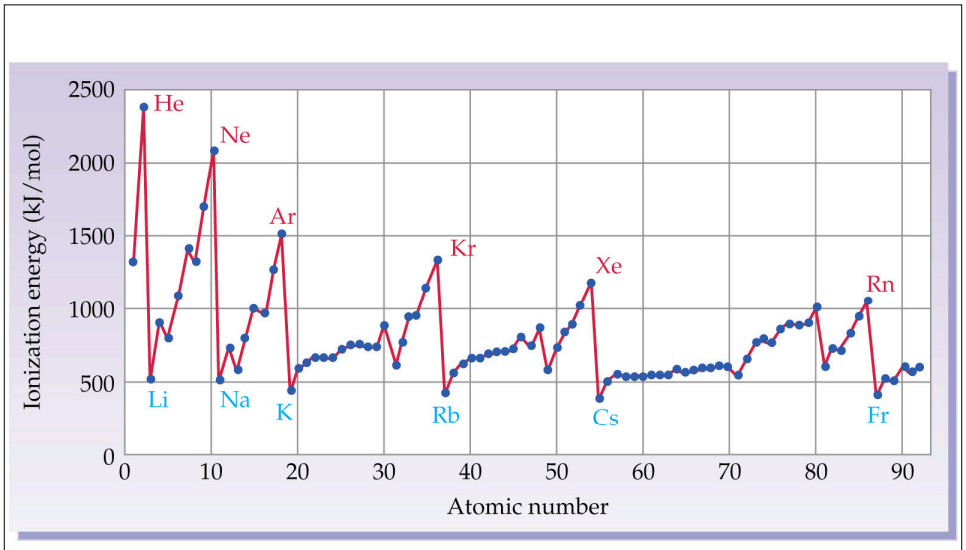


The atomic orbital diagram for the carbon atom (6e + 6p + 6,7, or 8n);
$1s^2\ \ 2s^2\ \ 2p_x^1\ \ 2p_y^1$

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







Ionization energies of the first 92 elements.

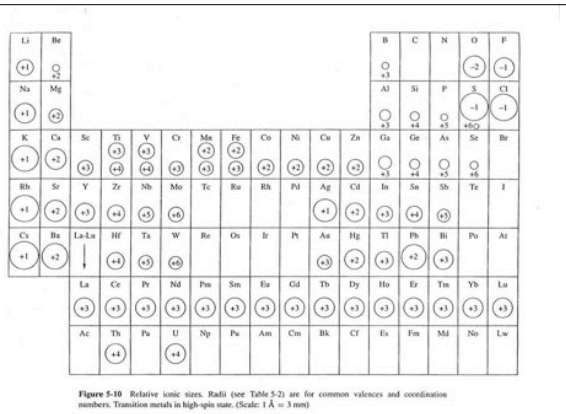


Figure 5-10 Relative ionic sizes. Radii (see Table 5-2) are for common valences and coordination numbers. Transition metals in high-spin state. (Scale: 1 Å = 3 mm)

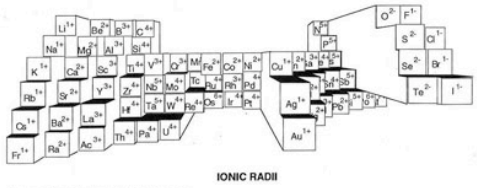
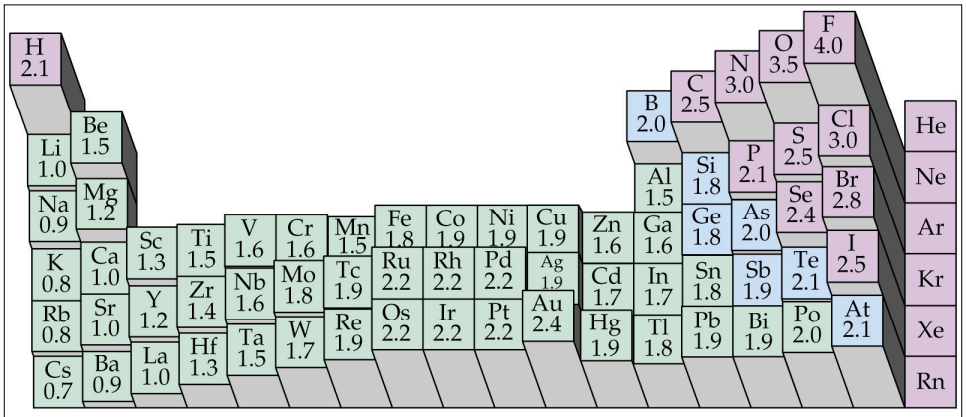
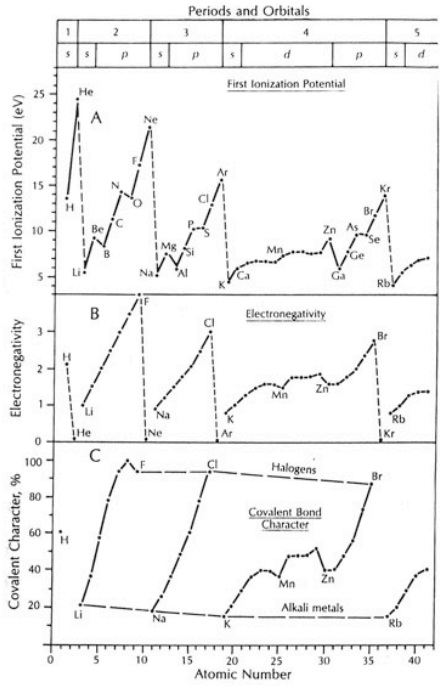


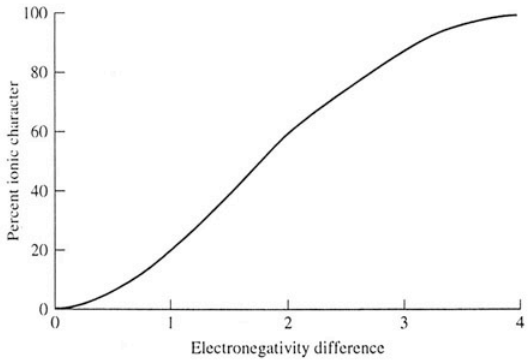
Figure 1.8. Ionic radii of the elements.



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





"As the electronegativity difference between two atoms increases the bonding electrons are increasingly drawn toward the more electronegative atom.
When the electronegativity difference becomes extreme the electrons are really no longer shared but can be thought of being transferred from the cation to the anion (ionic bonding)."

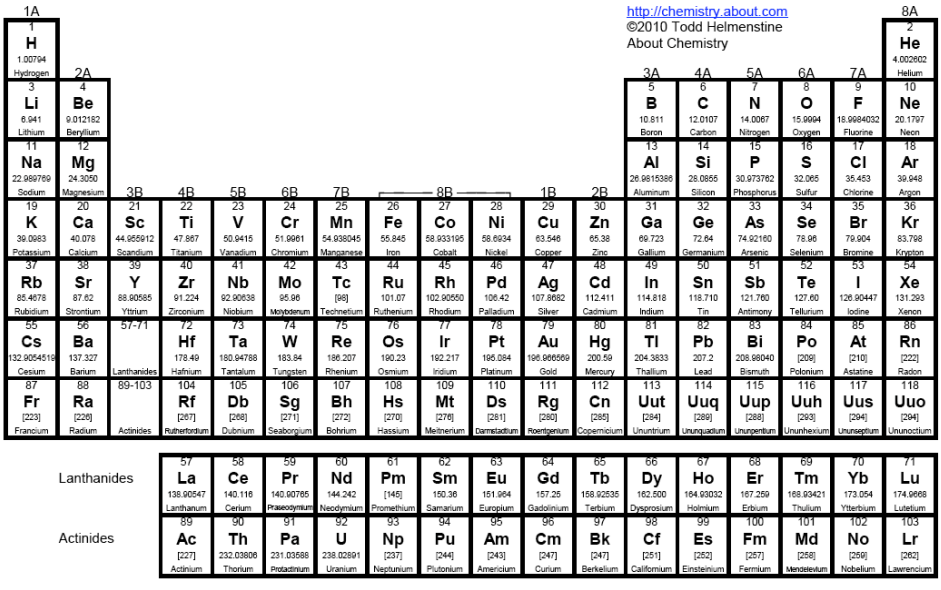
Figure 5-2 Relation between electronegativity difference and percent ionic character. The largest difference there can be in a bond is 3.3, which is the difference between the most electronegative element F (4.0), and the least electronegative element Cs (0.7). (After R. Chang, *General*

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.

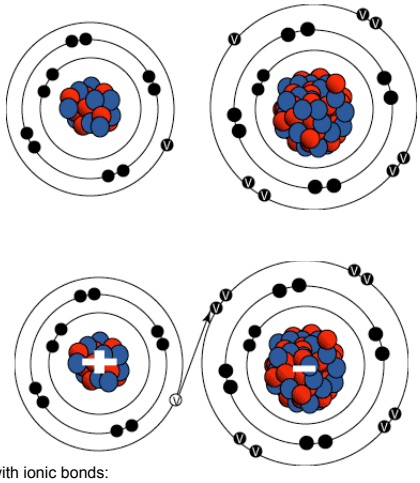
Periodic Table of the Elements



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 Walls** - very weak bond caused by attraction of dipole molecules, or emf of one molecule induces polarity of e^- orbits in another and resulting attraction

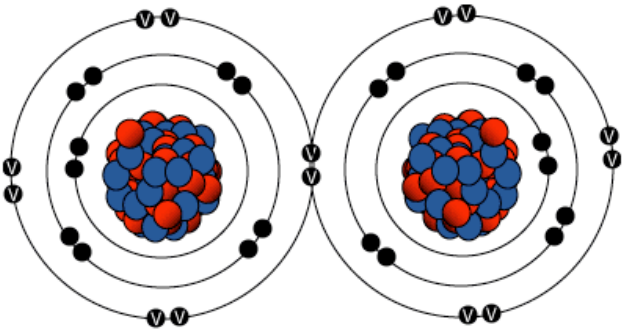
Ionic Bonding



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.

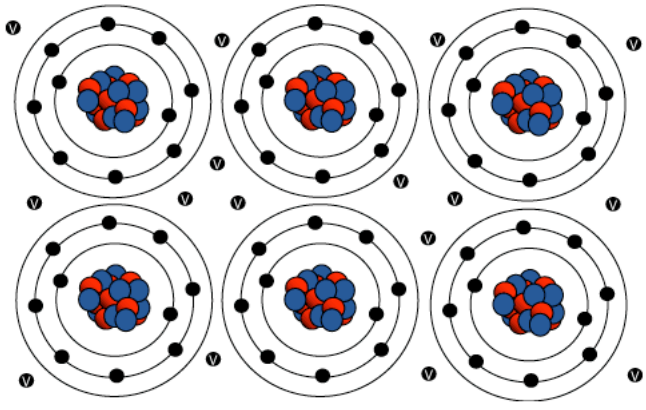
Covalent Bonding



Some Common Features of Materials with Covalent Bonds:

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

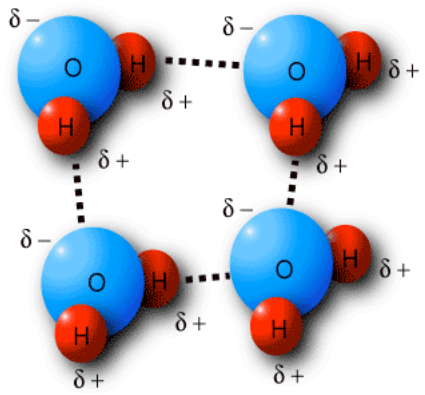
Metallic Bonding



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

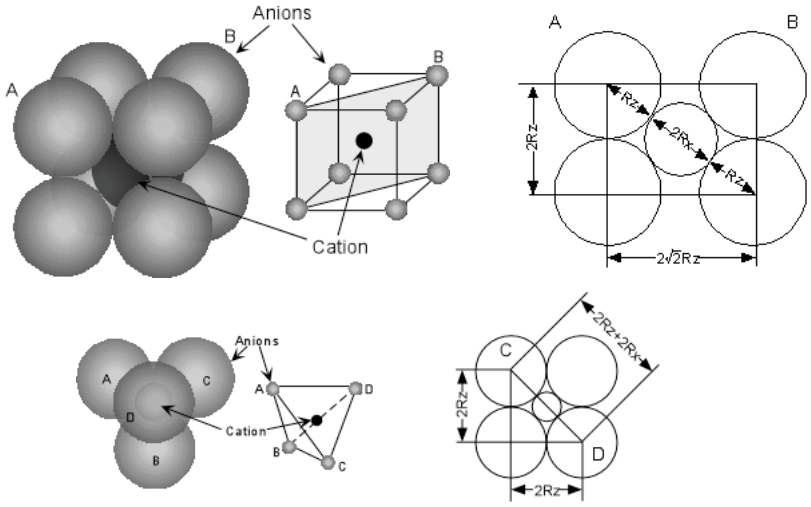
- **Pauling's Rules!**
  - Rule #1: Coordination Principle and Radius Ratios
    - Each cation is surrounded by a ***coordination polyhedron (CP)***. The form of the CP is defined by the cation and anion radii and the number of anions in the CP is fixed by the relative size of the cation and anion
    - 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

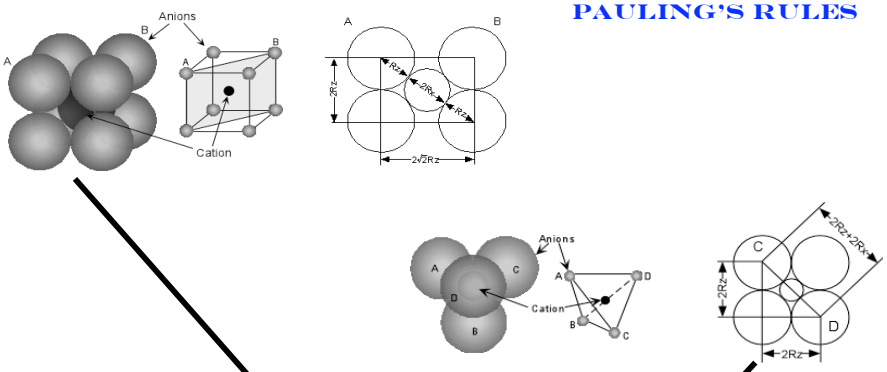
Rule #1: Coordination Principle and Radius Ratios

a. coordination polyhedra

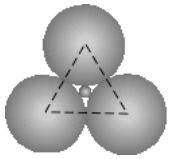
b. coordination number



PAULING'S RULES



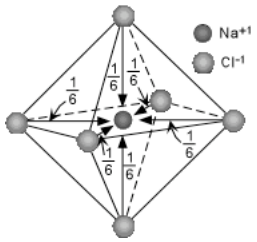
Rx/Rz	C.N.	Type
1.0	12	Hexagonal or Cubic Closest Packing
1.0 - 0.732	8	Cubic
0.732 - 0.414	6	Octahedral
0.414 - 0.225	4	Tetrahedral
0.225 - 0.155	3	Triangular
<0.155	2	Linear



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.

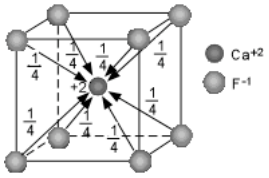


In NaCl each Na+ is surrounded by 6 Cl- ions. The Na is thus in 6 fold coordination and C.N. = 6.

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*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*1/4 or 2. So, again the charge is balanced.



PAULING'S RULES

Rule #2: Electrostatic Valency Principle

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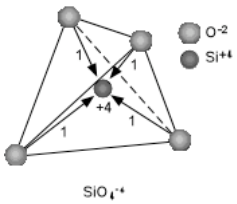
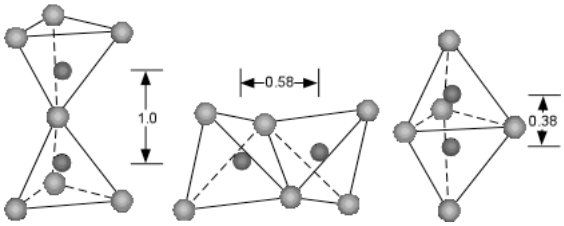


A third case arises when the charge reaching the cation is exactly 1/2 the charge on the anion. This is the case for Si+4 in tetrahedral coordination with O^{-2}. Here, the charge. reaching the Si is 4/4 =1.

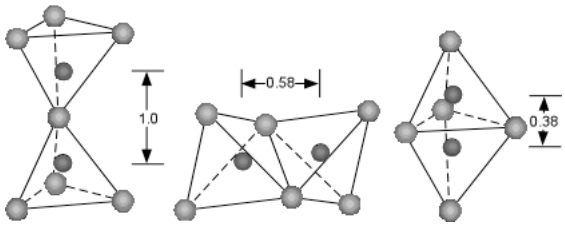
This leaves each Oxygen with a -1 charge that it has not shared. Since this -1 is exactly 1/2 the original charge on O^{-2}, the Oxygens in the SiO_4^{-4} group can be just as tightly bound to ions *outside* the group as to the centrally coordinated Si.



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 corner | sharing edge | sharing face

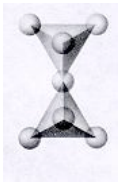
Sharing of only corners of polyhedra places the positively charged cations at the greatest distance from each other.

In the example shown here, for tetrahedral coordination, if the distance between the cations in the polyhedrons 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

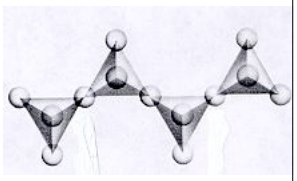
Rule #3: Sharing of Polyhedral Elements/Components

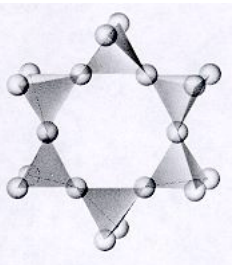
Shared edges, and particularly faces of two anion polyhedra in a crystal structure decreases its stability. Distance between cations is maximized.



sorosilcate
(e.g., epidote)

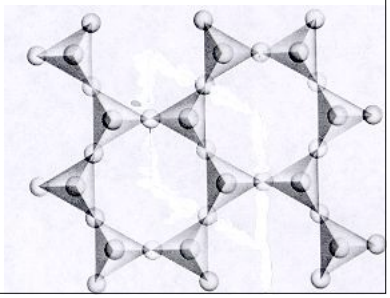
Inosilicate
(e.g., pyroxene)





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

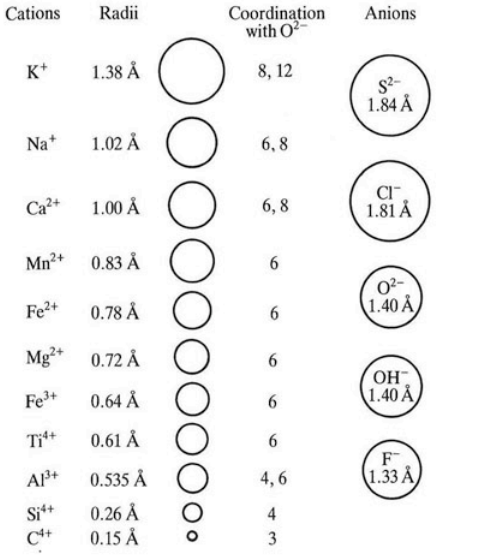


FIGURE 5-3
Radii of common ions in rock-forming minerals. (*Source*: Appendix VI

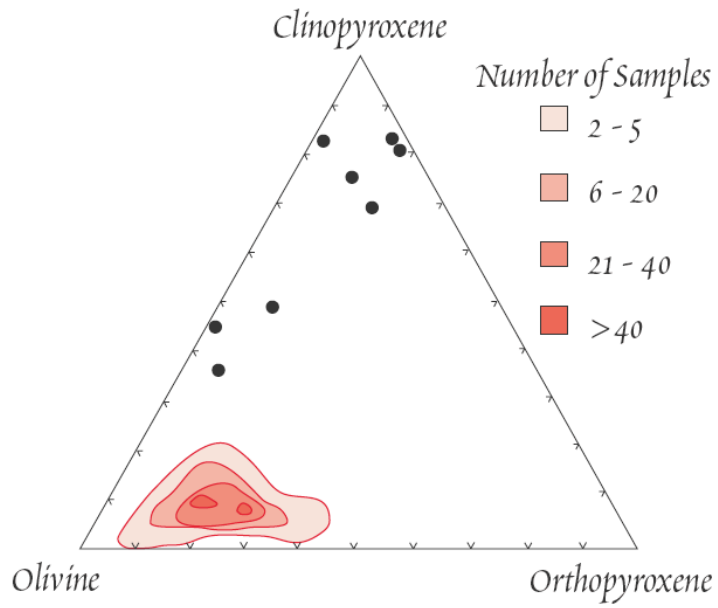


Figure 11.2. Abundances of modal mineralogy in xenoliths from Kilbourne Hole, NM.

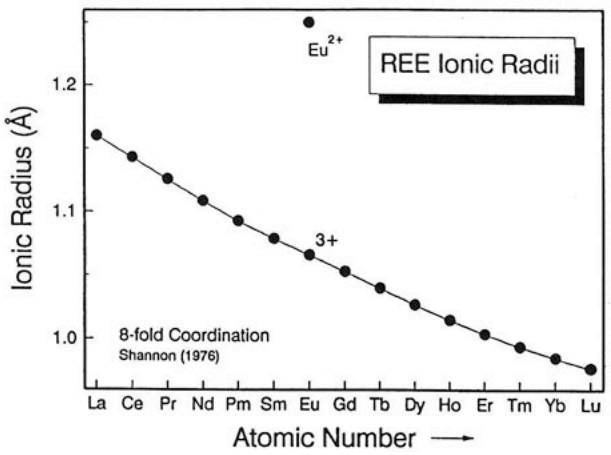


Figure 4. Ionic radius vs. atomic number for the REE. Ionic radii vary smoothly from La to Lu. Note that ionic radius depends on the coordination number; values are shown for 6-, 8-, and 10-fold coordination. Ionic radii in this and subsequent figures are from Shannon and Prewitt (1970) and Shannon (1976).

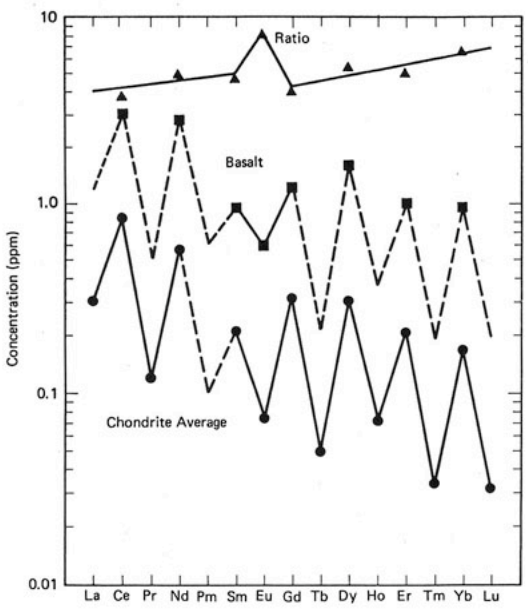
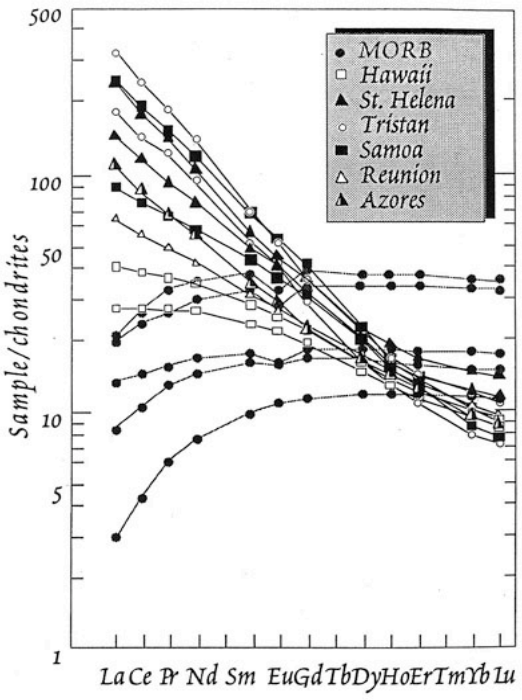
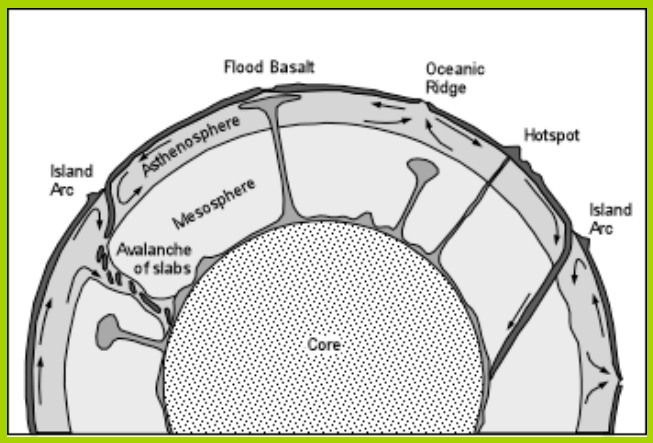


Figure 13.5 Measured abundances of rare earth elements in a basalt and in chondrites. Normalization of the basalt data to chondrites removes the zigzag pattern of odd-even abundances, revealing the pattern imposed during the igneous history of this rock.





Planetary differentiation produced by mantle convection and plate tectonics