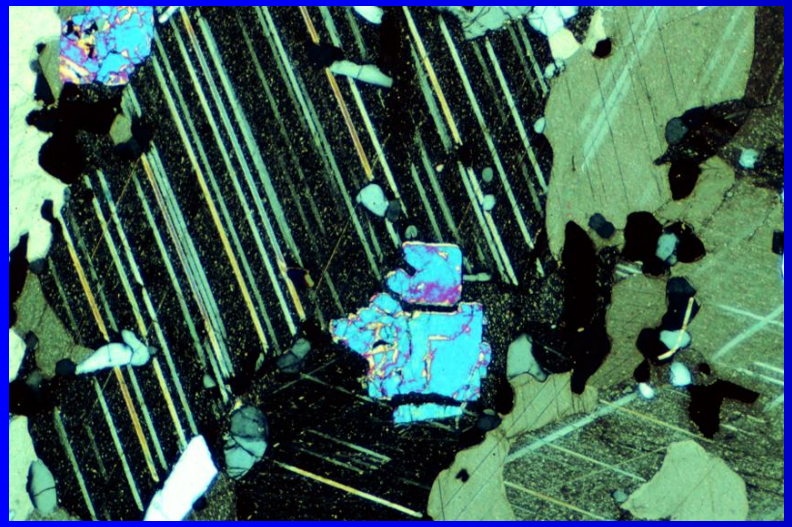
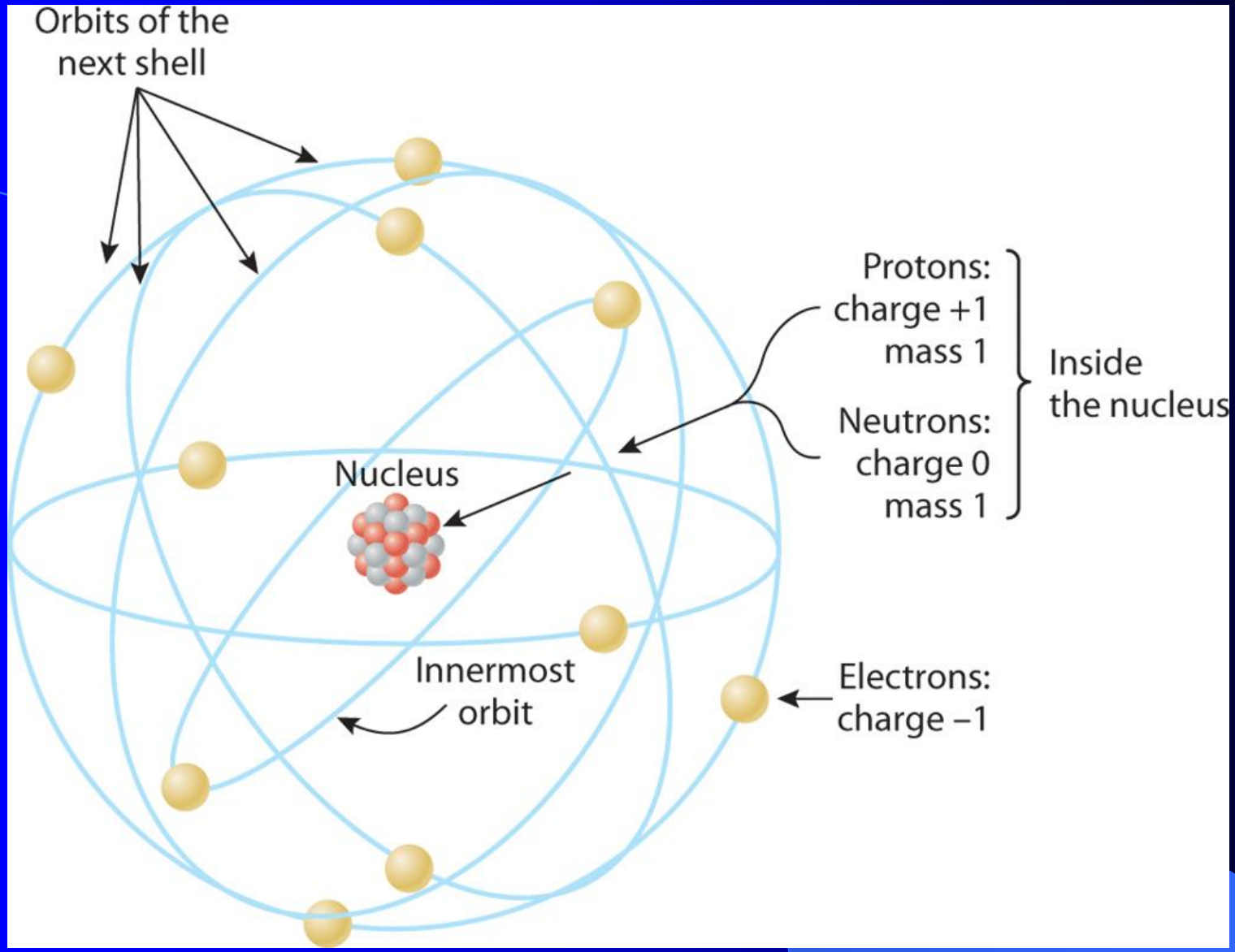
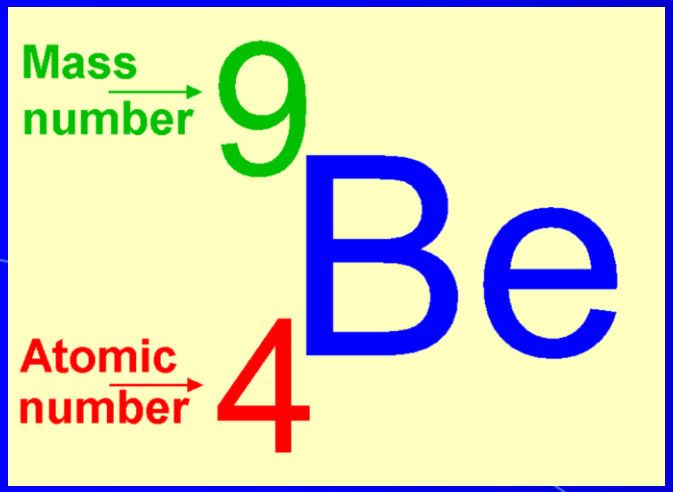
Earth Materials I

Crystal Structures




Orbits of the next shell
Protons: charge +1 mass 1
Neutrons: charge 0 mass 1
Inside the nucleus
Nucleus
Innermost orbit
Electrons: charge –1



Isotopes – same atomic number, different numbers of neutrons, different atomic mass.

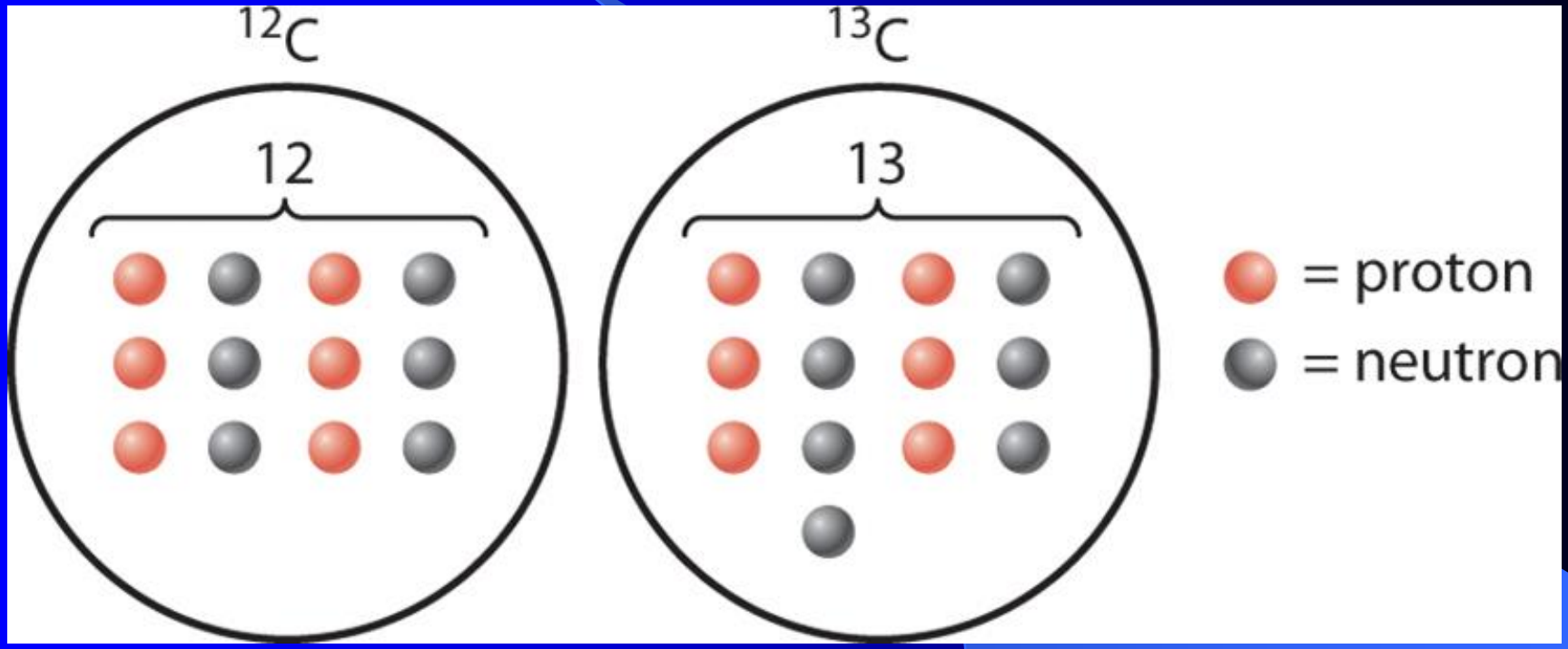
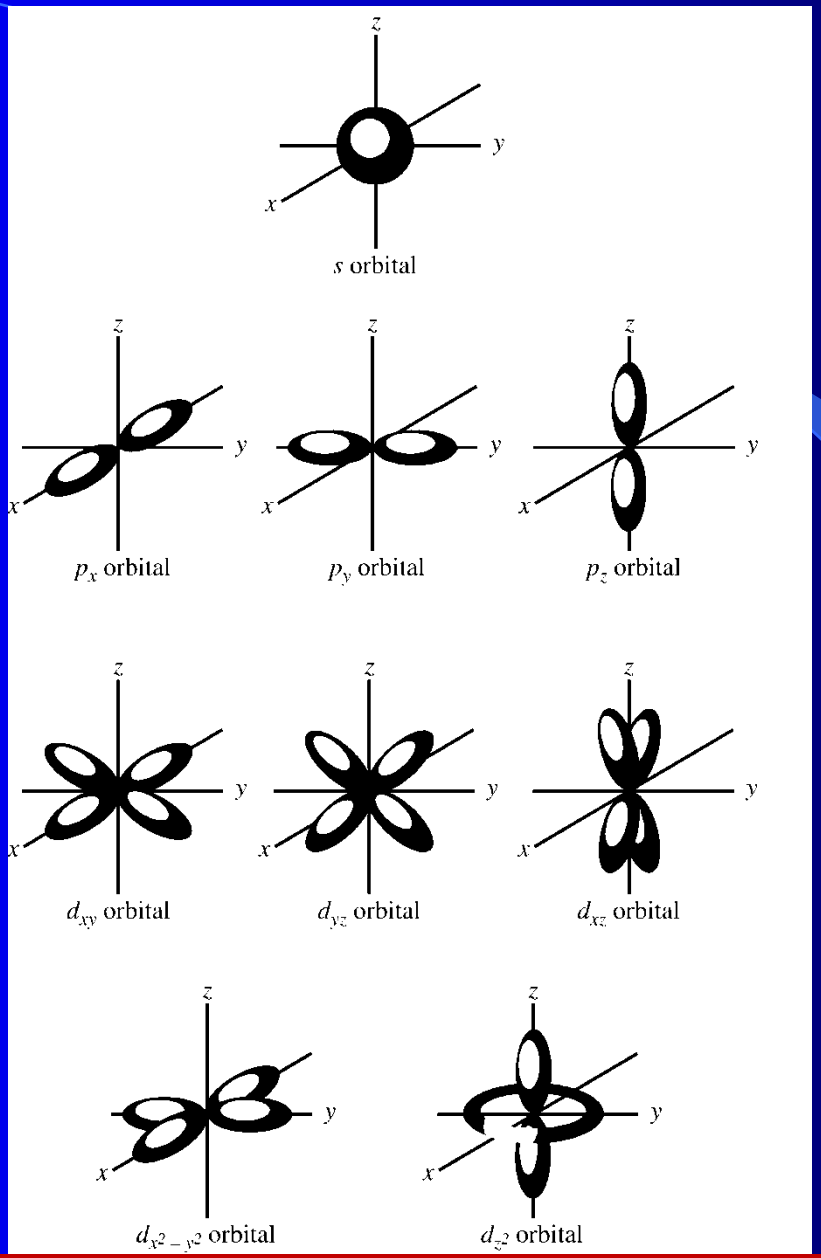


Table 1-1. Summary of quantum numbers

Name	Symbol	Values
Principal	n	1, 2, 3, ... ,
Azimuthal	l	n - 1, n - 2, n - 3, ... ,0
Magnetic	m	0, ±1, ±2, ... , ±(l - 1), ±l
Spin	s	± 1/2



Shape of various electron orbitals. From Brownlow (1996).

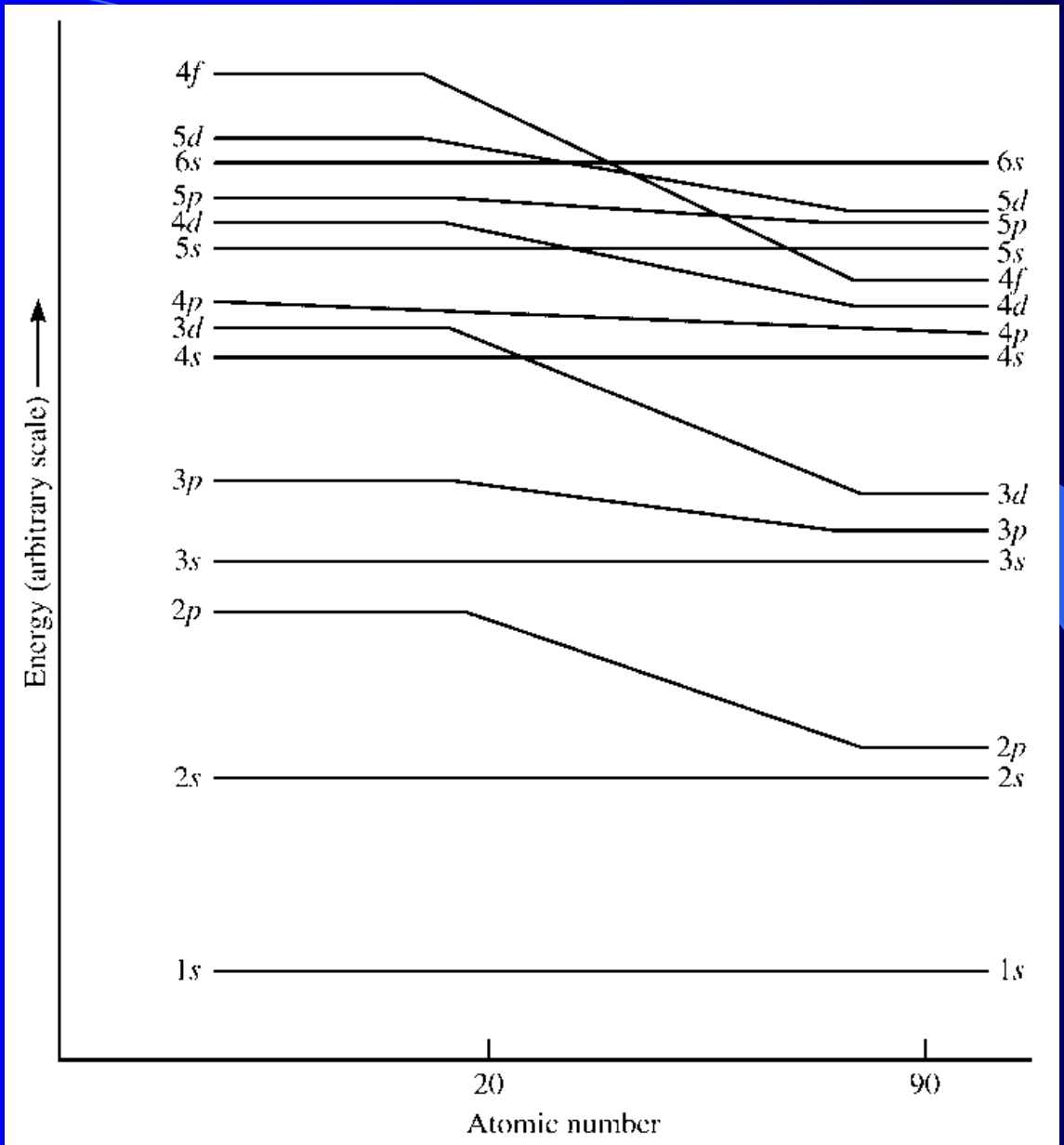
Table 4.6 Summary of the three quantum numbers.

Principal quantum number, n (shell)	Azimuthal quantum number, l (subshell)	Subshell designation	Magnetic quantum number, m	Number of orbitals in subshell	Maximum number of electrons
1 (K)	0	1s	0	1	2
2 (L)	0	2s	0	1	2 } 8
	1	2p	−1, 0, +1	3	6 }
3 (M)	0	3s	0	1	2
	1	3p	−1, 0, +1	3	6 } 18
	2	3d	−2, −1, 0, +1, +2	5	10
4 (N)	0	4s	0	1	2
	1	4p	−1, 0, +1	3	6
	2	4d	−2, −1, 0, +1, +2	5	10 } 32
	3	4f	−3, −2, −1, 0, +1, +2, +3	7	14

Table 4.7 Electron configurations of atoms with atomic number 1–54.

Shell	K	L		M			N				O					P		Q	
Element	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	7*s*
1. H	1																		
2. He	2																		
3. Li	2	1																	
4. Be	2	2																	
5. B	2	2	1																
6. C	2	2	2																
7. N	2	2	3																
8. O	2	2	4																
9. F	2	2	5																
10. Ne	2	2	6																
11. Na	2	2	6	1															
12. Mg	2	2	6	2															
13. Al	2	2	6	2	1														
14. Si	2	2	6	2	2														
15. P	2	2	6	2	3														
16. S	2	2	6	2	4														
17. Cl	2	2	6	2	5														
18. Ar	2	2	6	2	6														
19. K	2	2	6	2	6		1												
20. Ca	2	2	6	2	6		2												
21. Sc	2	2	6	2	6	1	2												
22. Ti	2	2	6	2	6	2	2												
23. V	2	2	6	2	6	3	2												
24. Cr	2	2	6	2	6	5	1												
25. Mn	2	2	6	2	6	5	2												
26. Fe	2	2	6	2	6	6	2												
27. Co	2	2	6	2	6	7	2												
28. Ni	2	2	6	2	6	8	2												
29. Cu	2	2	6	2	6	10	1												
30. Zn	2	2	6	2	6	10	2												
31. Ga	2	2	6	2	6	10	2	1											
32. Ge	2	2	6	2	6	10	2	2											
33. As	2	2	6	2	6	10	2	3											
34. Se	2	2	6	2	6	10	2	4											
35. Br	2	2	6	2	6	10	2	5											
36. Kr	2	2	6	2	6	10	2	6											
37. Rb	2	2	6	2	6	10	2	6			1								
38. Sr	2	2	6	2	6	10	2	6			2								
39. Y	2	2	6	2	6	10	2	6	1		2								
40. Zr	2	2	6	2	6	10	2	6	2		2								
41. Nb	2	2	6	2	6	10	2	6	4		1								
42. Mo	2	2	6	2	6	10	2	6	5		1								
43. Tc	2	2	6	2	6	10	2	6	5		2								
44. Ru	2	2	6	2	6	10	2	6	7		1								
45. Rh	2	2	6	2	6	10	2	6	8		1								
46. Pd	2	2	6	2	6	10	2	6	10										
47. Ag	2	2	6	2	6	10	2	6	10		1								
48. Cd	2	2	6	2	6	10	2	6	10		2								
49. In	2	2	6	2	6	10	2	6	10		2	1							
50. Sn	2	2	6	2	6	10	2	6	10		2	2							
51. Sb	2	2	6	2	6	10	2	6	10		2	3							
52. Te	2	2	6	2	6	10	2	6	10		2	4							
53. I	2	2	6	2	6	10	2	6	10		2	5							
54. Xe	2	2	6	2	6	10	2	6	10		2	6							

Note: This range of atomic numbers is similar to that of Table 4.4.



Variation of energy levels for the various subshells as a function of atomic number. From Brownlow (1996).

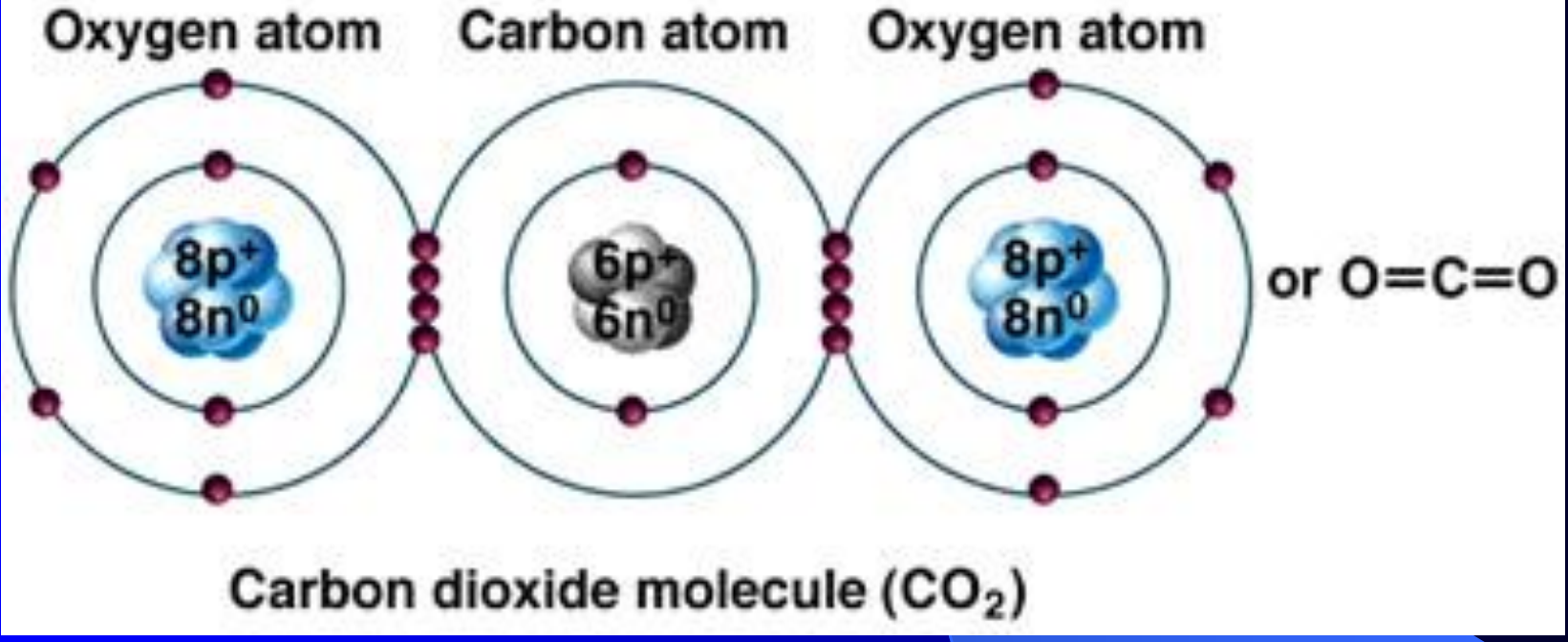
Periodic Table of the Elements

- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- poor metals
- nonmetals
- noble gases
- rare earth metals

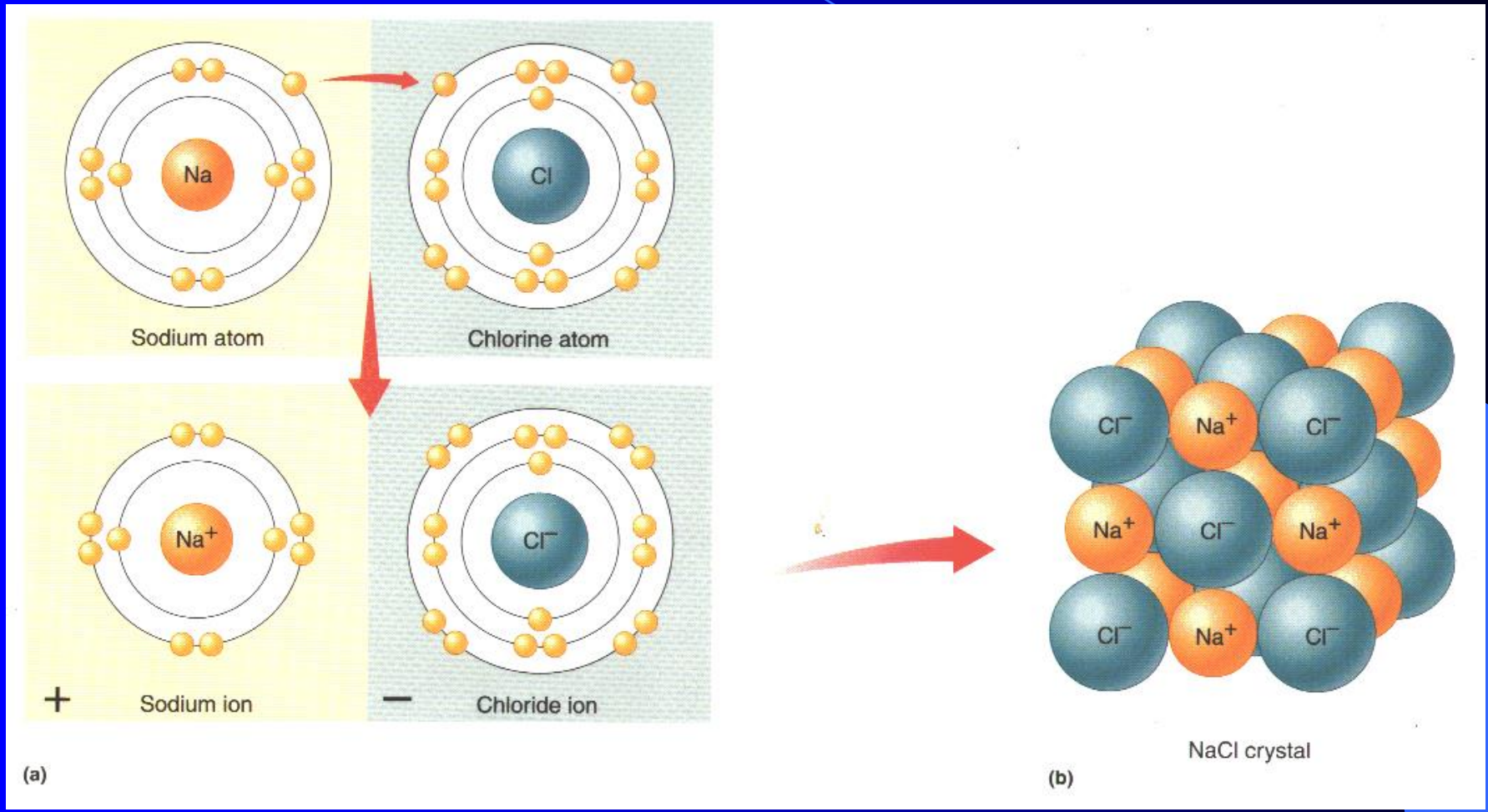
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	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
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

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	71 Lu
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	103 Lr

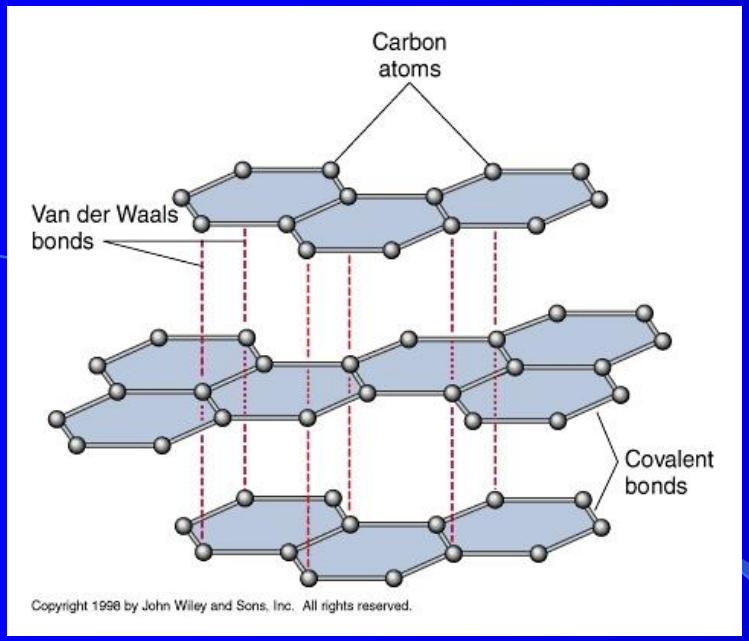
Formation of Covalent Bonds

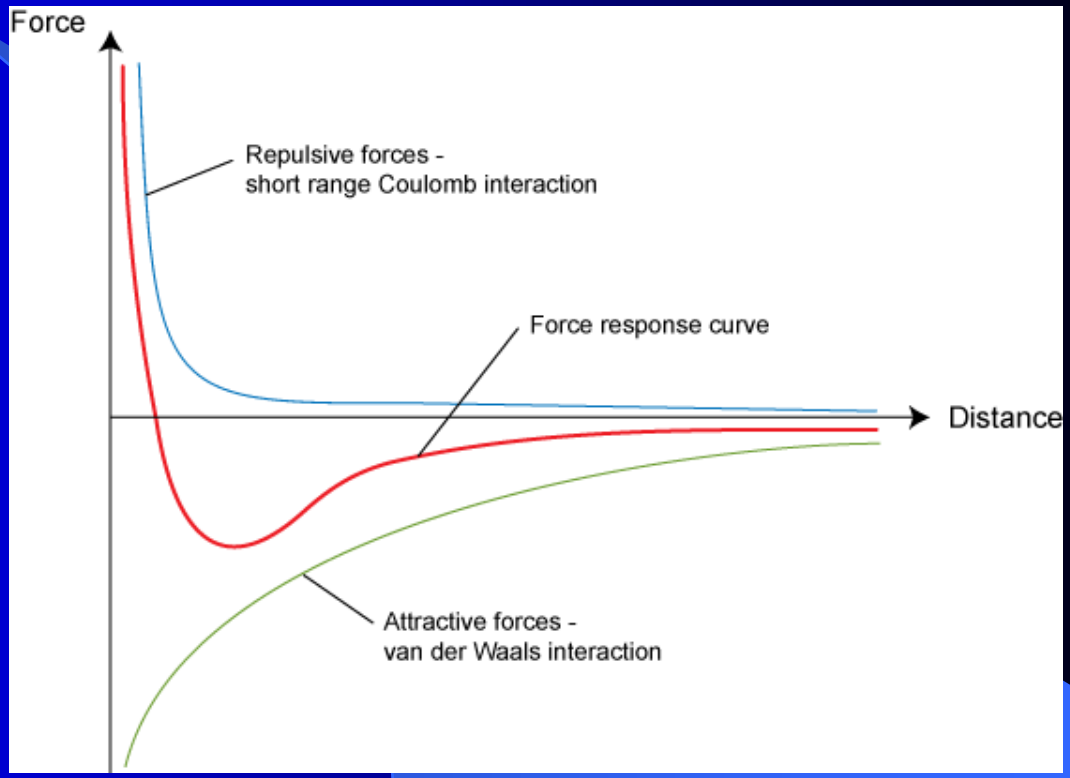


Ionic Bonding

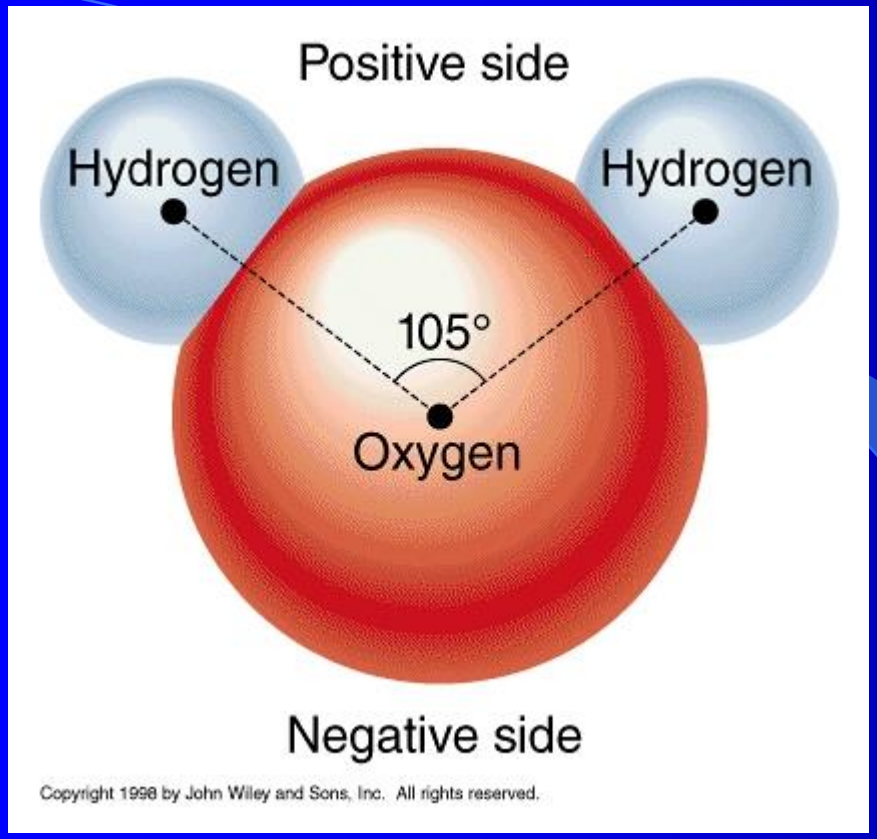


van der Waals Bonding





Hydrogen Bonding



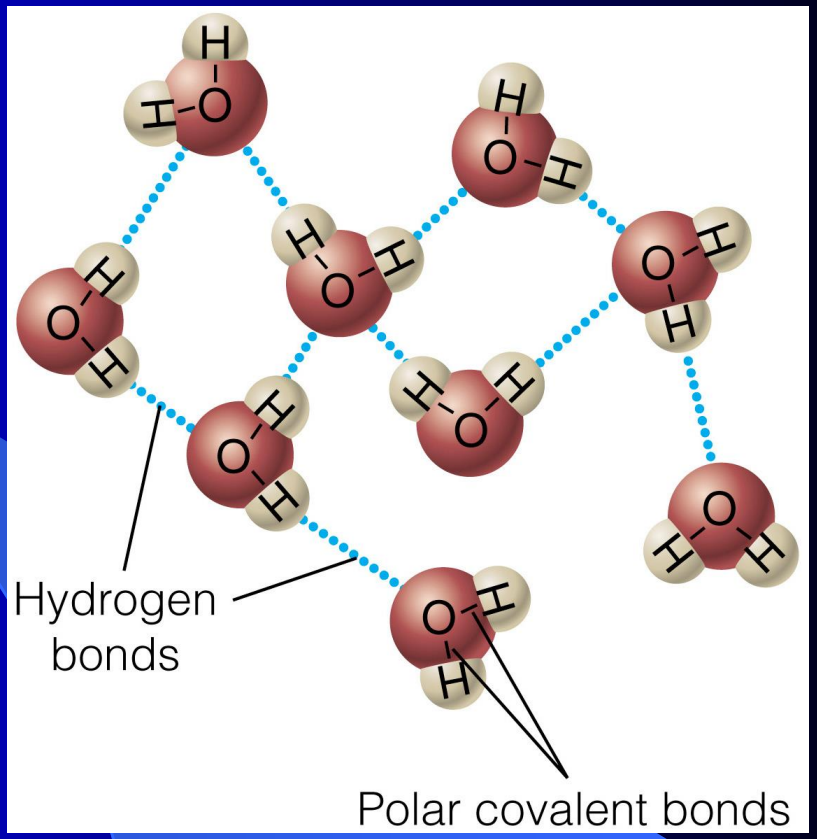


Table 7-2. Electronegativities

Z	Ion	Electro-negativity	Z	Ion	Electro-negativity	Z	Ion	Electro-negativity
1	H^{+}	2.20	33	As^{5+}	2.18	65	Dy^{3+}	1.22
3	Li^{+}	0.98	34	Se^{2-}	2.55	67	Ho^{3+}	1.23
4	Be^{2+}	1.57	35	Br^{-}	2.96	68	Er^{3+}	1.24
5	B^{3+}	2.04	37	Rb^{+}	0.82	69	Tm^{3+}	1.25
6	C^{4+}	2.55	38	Sr^{2+}	0.95	70	Yb^{3+}	---
7	N^{5+}	3.04	39	Y^{3+}	1.22	71	Lu^{3+}	1.0
8	O^{2-}	3.44	40	Zr^{4+}	1.33	72	Hf^{4+}	1.3
9	F^{-}	3.98	41	Nb^{5+}	1.6	73	Ta^{5+}	1.5
11	Na^{+}	0.93	42	Mo^{6+}	2.16	74	W^{6+}	1.7
12	Mg^{2+}	1.31	43	Tc^{2+}	2.10	75	Re^{7+}	1.9
13	Al^{3+}	1.61	44	Ru^{2+}	2.2	76	Os^{6+}	2.2
14	Si^{4+}	1.90	45	Rh^{2+}	2.28	77	Ir^{6+}	2.2
15	P^{5+}	2.19	46	Pd^{2+}	2.20	78	Pt^{4+}	2.2
16	S^{2-}	2.58	47	Ag^{+}	1.93	79	Au^{+}	2.4
17	Cl^{-}	3.16	48	Cd^{2+}	1.69	80	Hg^{2+}	1.9
19	K^{+}	0.82	49	In^{3+}	1.78	81	Tl^{3+}	1.8
20	Ca^{2+}	1.00	50	Sn^{2+}	1.96	82	Pb^{2+}	1.8
21	Sc^{3+}	1.36	51	Sb^{5+}	2.05	83	Bi^{3+}	1.9
22	Ti^{4+}	1.54	52	Te^{2-}	2.1	84	Po^{4+}	2.0
23	V^{3+}	1.63	53	I^{-}	2.66	85	At^{5+}	2.2
24	Cr^{3+}	1.66	55	Cs^{+}	0.79	87	Fr^{+}	0.7
25	Mn^{2+}	1.55	56	Ba^{2+}	0.89	88	Ra^{2+}	0.9
26	Fe^{2+}	1.83	57	La^{3+}	1.10	89	Ac^{3+}	1.1
27	Co^{2+}	1.88	58	Ce^{3+}	1.12	90	Th^{4+}	1.3
28	Ni^{2+}	1.91	59	Pr^{3+}	1.13	91	Pa^{4+}	1.5
29	Cu^{+}	1.90	60	Nd^{3+}	1.14	92	U^{6+}	1.7
30	Zn^{2+}	1.65	62	Sm^{3+}	1.17	93	Np^{3+}	1.3
31	Ga^{3+}	1.81	64	Gd^{3+}	1.20	94	Pu^{4+}	1.3
32	Ge^{4+}	2.01						

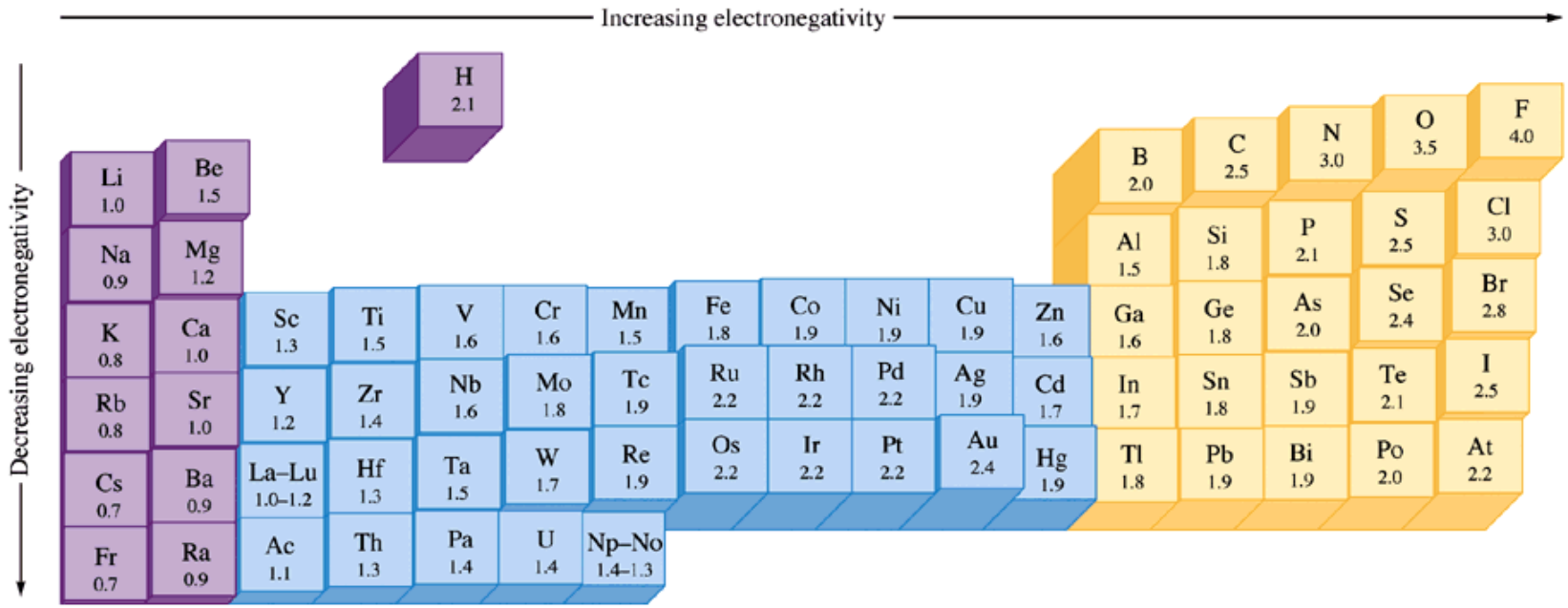

Increasing electronegativity
Decreasing electronegativity
H 2.1
Li 1.0
Be 1.5
Na 0.9
Mg 1.2
K 0.8
Ca 1.0
Rb 0.8
Sr 1.0
Cs 0.7
Ba 0.9
Fr 0.7
Ra 0.9
Sc 1.3
Ti 1.5
V 1.6
Cr 1.6
Mn 1.5
Fe 1.8
Co 1.9
Ni 1.9
Cu 1.9
Zn 1.6
Y 1.2
Zr 1.4
Nb 1.6
Mo 1.8
Tc 1.9
Ru 2.2
Rh 2.2
Pd 2.2
Ag 1.9
Cd 1.7
La–Lu 1.0–1.2
Hf 1.3
Ta 1.5
W 1.7
Re 1.9
Os 2.2
Ir 2.2
Pt 2.2
Au 2.4
Hg 1.9
Ac 1.1
Th 1.3
Pa 1.4
U 1.4
Np–No 1.4–1.3
B 2.0
C 2.5
N 3.0
O 3.5
F 4.0
Al 1.5
Si 1.8
P 2.1
S 2.5
Cl 3.0
Ga 1.6
Ge 1.8
As 2.0
Se 2.4
Br 2.8
In 1.7
Sn 1.8
Sb 1.9
Te 2.1
I 2.5
Tl 1.8
Pb 1.9
Bi 1.9
Po 2.0
At 2.2

Table 7-3. Percent ionic character of a single chemical bond

Difference in electronegativity	Ionic character, %	Difference in electronegativity	Ionic character, %
0.1	0.5	1.7	51
0.2	1	1.8	55
0.3	2	1.9	59
0.4	4	2.0	63
0.5	6	2.1	67
0.6	9	2.2	70
0.7	12	2.3	74
0.8	15	2.4	76
0.9	19	2.5	79
1.0	22	2.6	82
1.1	26	2.7	84
1.2	30	2.8	86
1.3	34	2.9	88
1.4	39	3.0	89
1.5	43	3.1	91
1.6	47	3.2	92

Table 4.1 The 29 most common, naturally occurring elements and their common ionic states.

Atomic number	Element	Ion	Atomic number	Element	Ion
3	Lithium	Li^{+}	24	Chromium	Cr^{3+}
4	Beryllium	Be^{2+}	25	Manganese	Mn^{2+}
5	Boron	B^{3+}			Mn^{4+}
6	Carbon	C^{4+}	26	Iron	Fe^{2+}
8	Oxygen	O^{2-}			Fe^{3+}
9	Fluorine	F^{-}	27	Cobalt	Co^{2+}
11	Sodium	Na^{+}	28	Nickel	Ni^{2+}
12	Magnesium	Mg^{2+}	29	Copper	Cu^{+}
13	Aluminum	Al^{3+}			Cu^{2+}
14	Silicon	Si^{4+}	30	Zinc	Zn^{2+}
15	Phosphorus	P^{5+}	38	Strontium	Sr^{2+}
16	Sulfur	S^{2-}	40	Zirconium	Zr^{4+}
		S^{6+}	47	Silver	Ag^{+}
17	Chlorine	Cl^{-}	56	Barium	Ba^{2+}
19	Potassium	K^{+}	82	Lead	Pb^{2+}
20	Calcium	Ca^{2+}	92	Uranium	U^{4+}
22	Titanium	Ti^{4+}			

Table 4.2 Thirteen of the most common elements (exclusive of hydrogen) that make up 99% of the Earth's crust.

O	Ti
K	Al
Na	Si
Ca	P
Mn	S
Fe	C
Mg	

Note: Elements are listed in order of decreasing size of their most common ionic state. Ionic radii are given in Table 4.4.

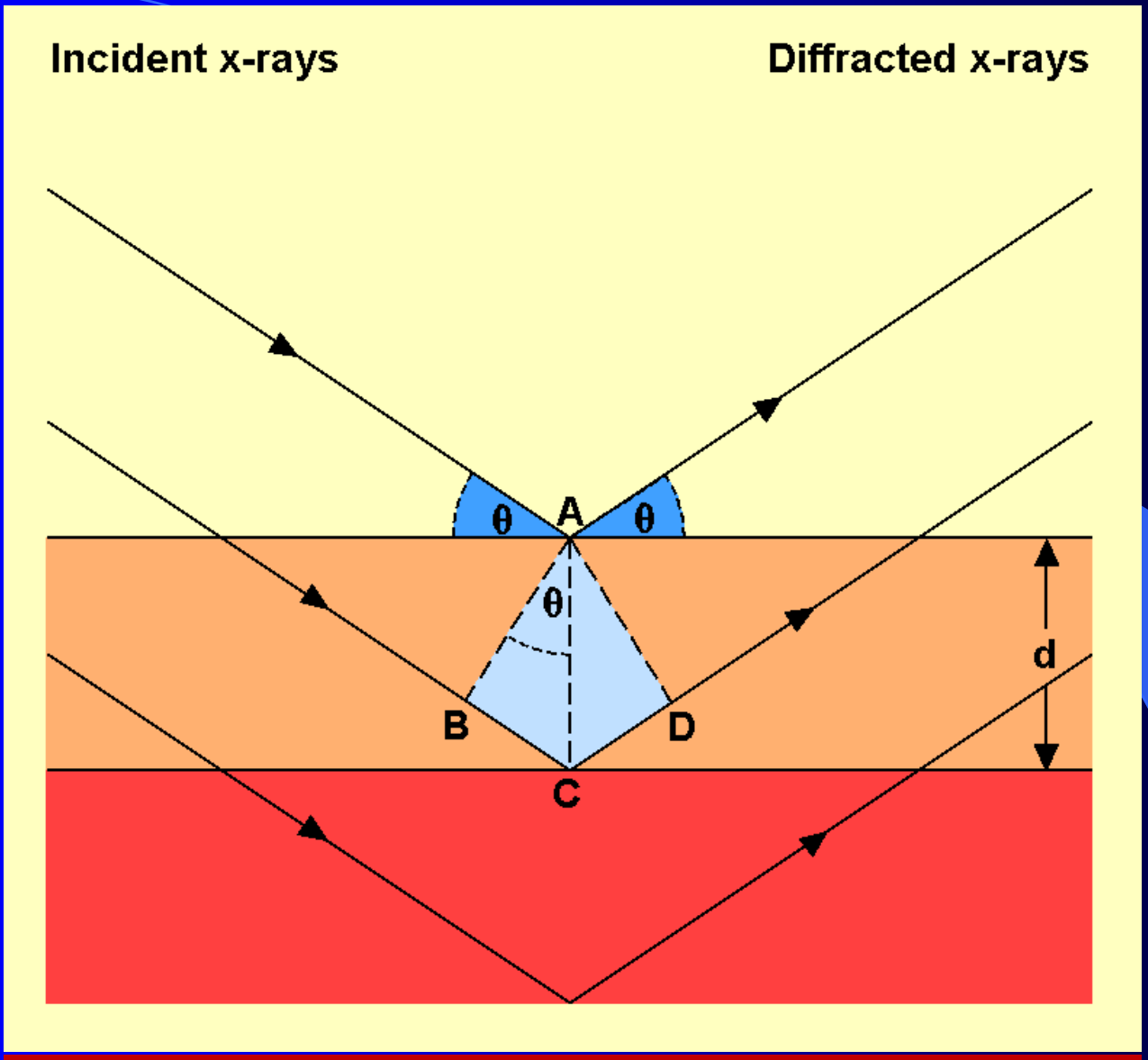
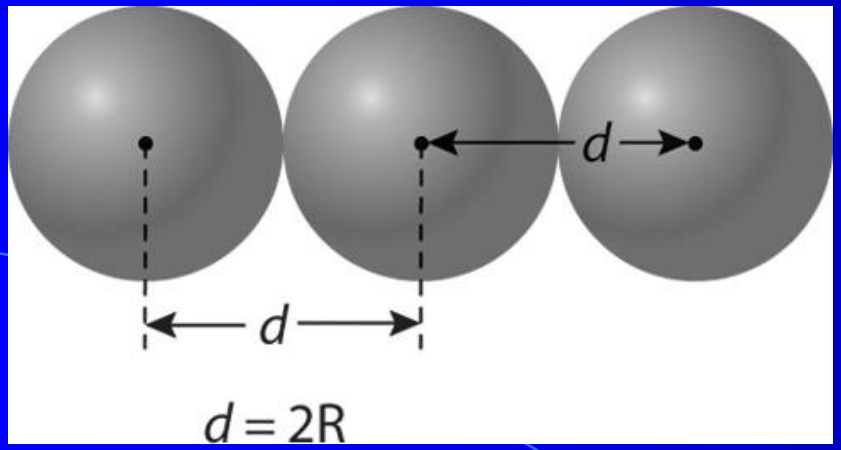


Diagram illustrating Bragg's law. θ = angle of incidence and diffraction when Bragg's law conditions are met. d = interplanar spacing.



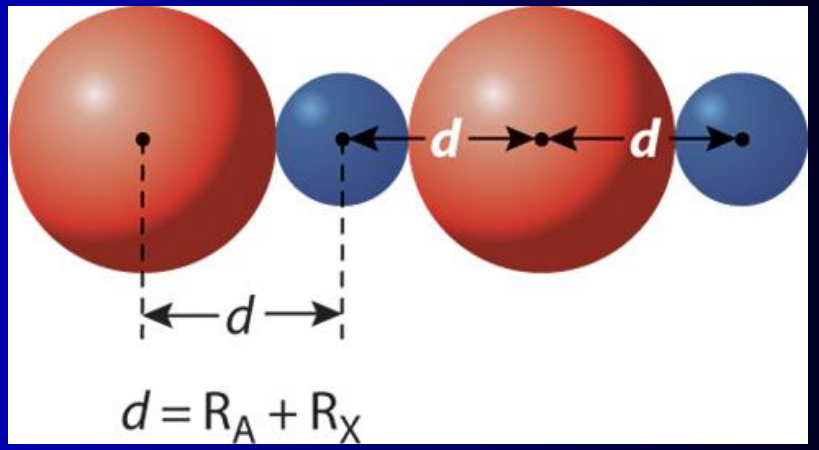


Table 4.3 Atomic radii in Ångstroms for 12-fold coordination.

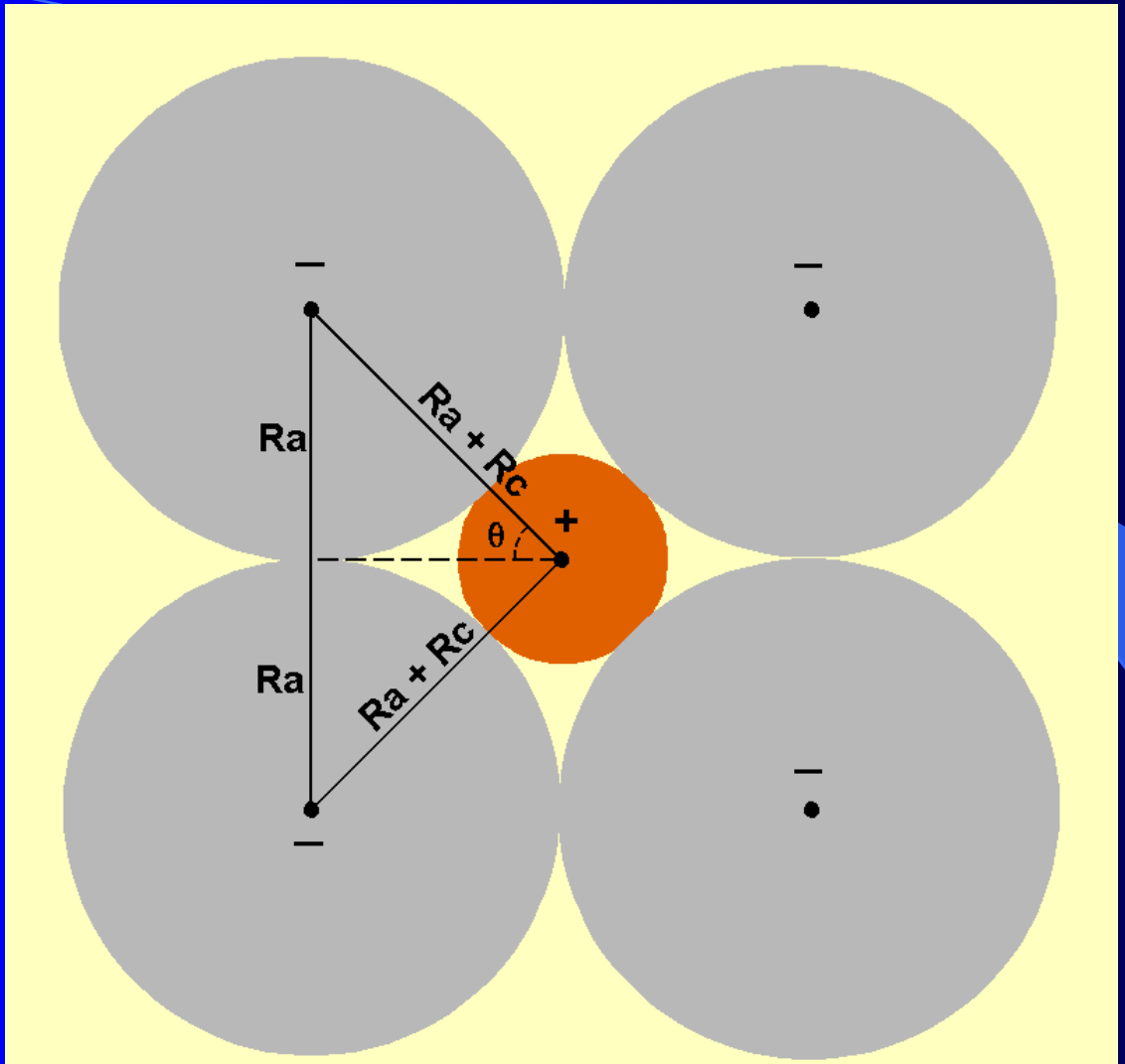
Atom	Radius	Atom	Radius
Li	1.57	Cr	1.29
Be	1.12	Mn	1.37
Na	1.91	Fe	1.26
Mg	1.60	Cu	1.28
Al	1.43	Ag	1.44
K	2.35	Sn	1.58
Ca	1.97	Pt	1.39
Ti	1.47	Au	1.44

Source: Wells (1991)

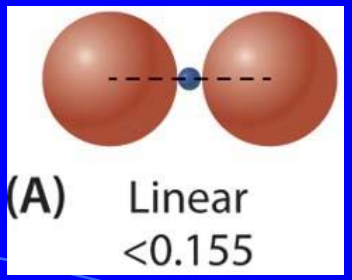
Pauling's Rules – 1. Coordination Principle

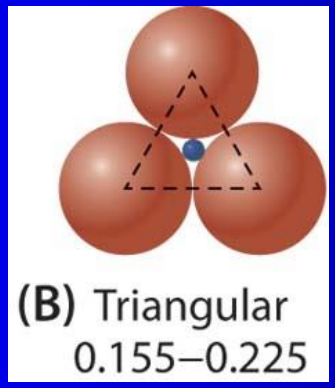
Radius Ratio = Radius cation/Radius Anion

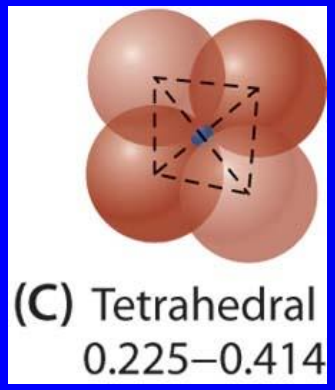
This ratio determines how many anions can be packed around a cation.

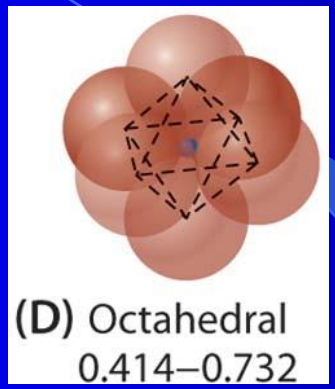


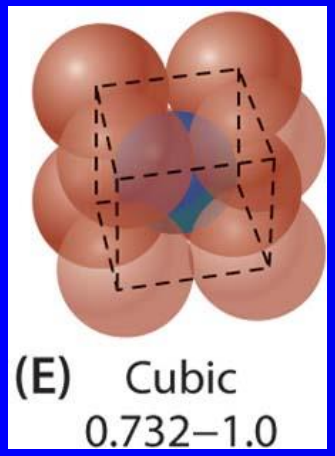
Packing of anions around a cation for a coordination number of 4. The minimum radius ratio can be calculated from the geometry of the packing. R_a and R_c are the radii of the anion and cation, respectively. In this case, $\theta = 45^o$.

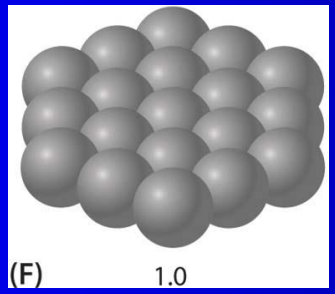












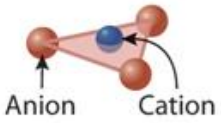
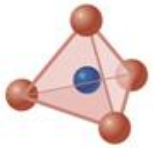
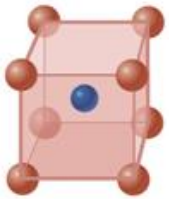
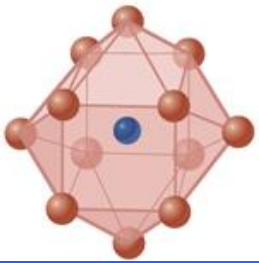
Radius ratio R_A/R_X limits	C.N.	Geometric shape	
0.155 to 0.225	III		Corners of an equilateral triangle (triangular coordination)
0.225 to 0.414	IV		Corners of a tetrahedron (tetrahedral coordination)
0.414 to 0.732	VI		Corners of an octahedron (octahedral coordination)
0.732 to 1.0	VIII		Corners of a cube (cubic coordination)
1.0	XII		Corners of a cuboctahedron (close packing)

Table 4.4 Radii of common ions (in Ångstroms) as a function of coordination number.

Atomic number	Element	Ion	Radius as a function of coordination number				
			III	IV	VI	VIII	XII
3	Lithium	Li^{+}		0.73	0.90	1.06	
4	Beryllium	Be^{2+}	0.30	0.41	0.59		
5	Boron	B^{3+}	0.15	0.25	0.41		
6	Carbon	C^{4+}	0.06	0.29	0.30		
8	Oxygen	O^{2-}	1.22	1.24	1.26	1.28	
9	Fluorine	F^{-}	1.16	1.17	1.19		
11	Sodium	Na^{+}		1.13	1.16	1.32	1.53
12	Magnesium	Mg^{2+}		0.71	0.86	1.03	
13	Aluminum	Al^{3+}		0.53	0.68		
14	Silicon	Si^{4+}		0.40	0.54		
15	Phosphorus	P^{3+}			0.58		
		P^{5+}		0.31	0.52		
16	Sulfur	S^{2-}			1.70		
		S^{4+}			0.51		
		S^{6+}		0.26	0.43		
17	Chlorine	Cl^{-}			1.67		
19	Potassium	K^{+}		1.51	1.52	1.65	1.78
20	Calcium	Ca^{2+}			1.14	1.26	1.48
22	Titanium	Ti^{4+}		0.56	0.65	0.88	
24	Chromium	Cr^{3+}			0.76		
25	Manganese	Mn^{2+}		0.80	0.97	1.10	
		Mn^{4+}		0.53	0.67		
26	Iron	Fe^{2+}		0.77	0.92	1.06	
		Fe^{3+}		0.63	0.78	0.92	
27	Cobalt	Co^{2+}		0.72	0.88	1.04	
28	Nickel	Ni^{2+}		0.69	0.83		
29	Copper	Cu^{+}		0.74	0.91		
		Cu^{2+}		0.71	0.87		
30	Zinc	Zn^{2+}		0.74	0.88	1.04	
38	Strontium	Sr^{2+}			1.32	1.40	1.58
40	Zirconium	Zr^{4+}		0.73	0.86	0.98	
47	Silver	Ag^{+}		1.14	1.29	1.42	
56	Barium	Ba^{2+}			1.49	1.56	1.75
82	Lead	Pb^{2+}			1.33	1.43	1.63
92	Uranium	U^{3+}			1.17		
		U^{4+}			1.03	1.14	1.31
		U^{6+}		0.66	0.87	1.00	

Note: These data represent the crystal radii reported by Shannon (1976). In textbooks such as Klein and Dutrow (2008) and Dyar et al. (2008), the traditional radii (based on the radius of oxygen = 1.40 Å) are reported. The difference between crystal radii and traditional radii is a constant factor of 0.14 Å.

Table 4.5 Common ions in rock-forming minerals (exclusive of hydrogen) and their **C.N.** as a function of decreasing ionic size.

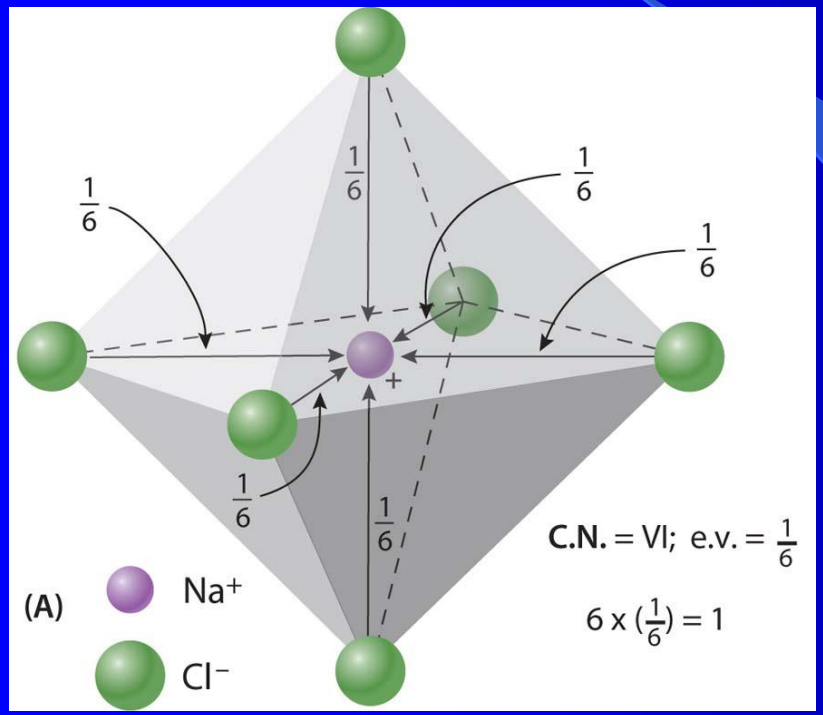
Ion	C.N. with oxygen		Ionic radius in Å
O^{2-}			1.26[IV]
K^{+}	VIII – XII		1.65 [VIII] – 1.78[XII]
Na^{+}	VI – VIII	octahedral to cubic	1.16[VI] – 1.32[VIII]
Ca^{2+}	VI – VIII	octahedral to cubic	1.14[VI] – 1.26[VIII]
Mn^{2+}	VI	octahedral	0.97
Fe^{2+}	VI	octahedral	0.92
Mg^{2+}	VI	octahedral	0.86
Fe^{3+}	VI	octahedral	0.78
Ti^{4+}	VI	octahedral	0.65
Al^{3+}	VI	octahedral	0.68
Al^{3+}	IV	tetrahedral	0.53
Si^{4+}	IV	tetrahedral	0.40
P^{5+}	IV	tetrahedral	0.31
S^{6+}	IV	tetrahedral	0.26
C^{4+}	III triangular		0.06

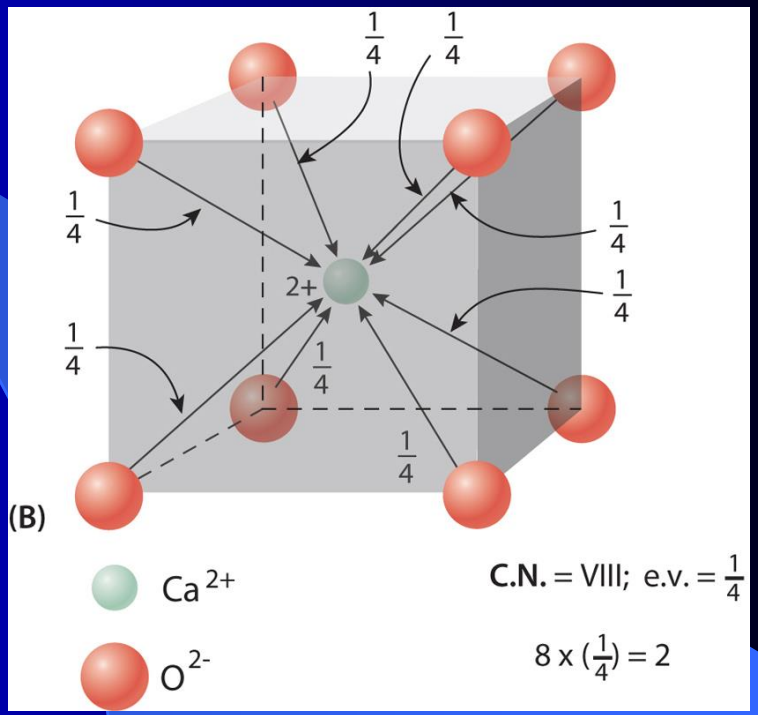
Note: Ionic radii taken from Table 4.4.

Pauling's Rules – 2. Electostatic valency principle

Bond strength (e.v.) = Z/C.N.

Z = charge on ion
C.N. = coordination number





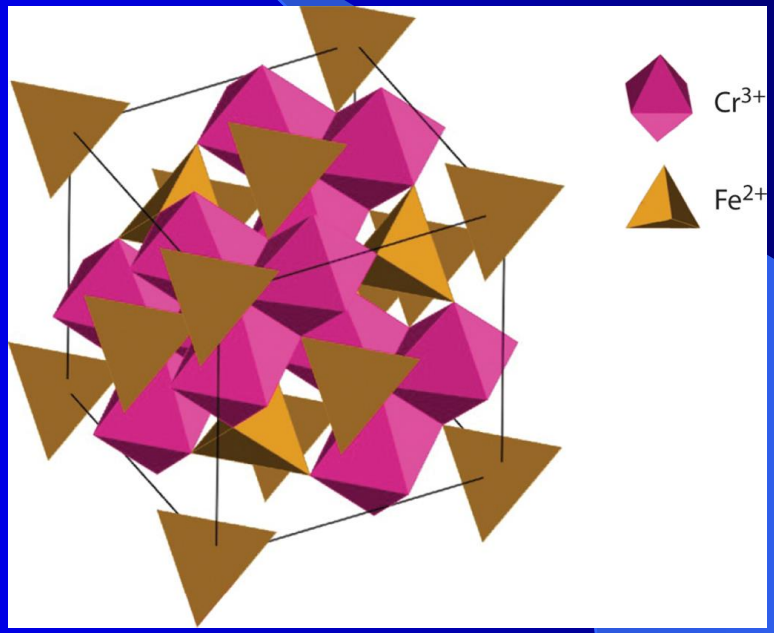
Types of bond strengths

Isodesmic – bonds are of the same strength throughout the structure

Chromite – $FeCr_2O_4$

C.N. – Fe^{IV}, Cr^{VI}

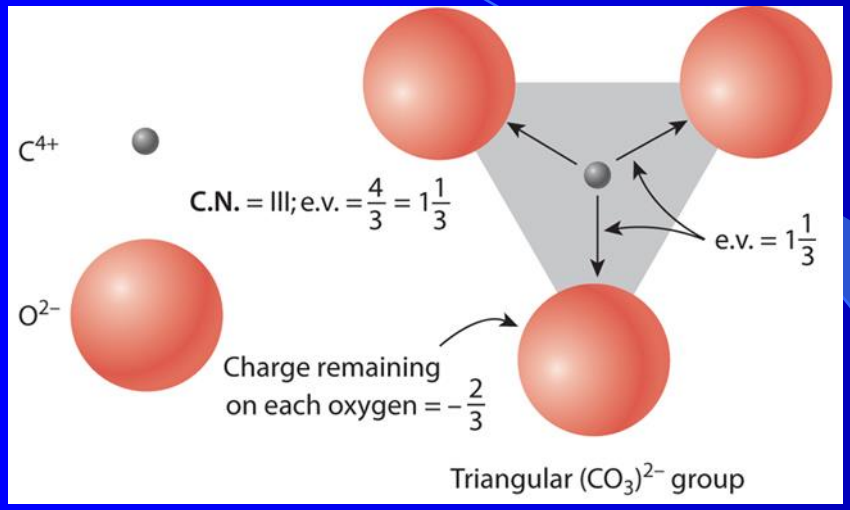
Calculate bond strengths

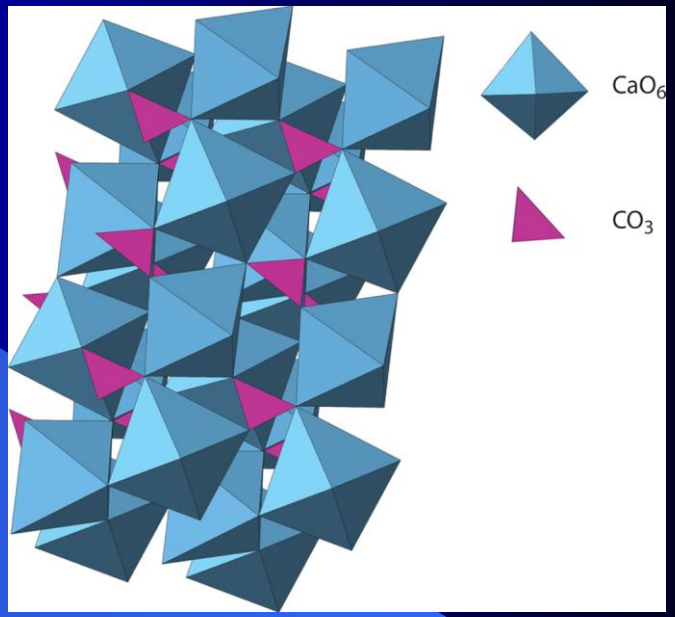


Anisodesmic – bond strengths inside of one type of polyhedra in a structure are different from that of other bonds in the structure

Examples are carbonates (CO_3^{2-}), sulfates (SO_4^{2-}), and phosphates (PO_4^{3-})

Calcite ($CaCO_3$) – $Ca^{2+(VI)}$, CO_3^{2-} (e.v. = 4/3)

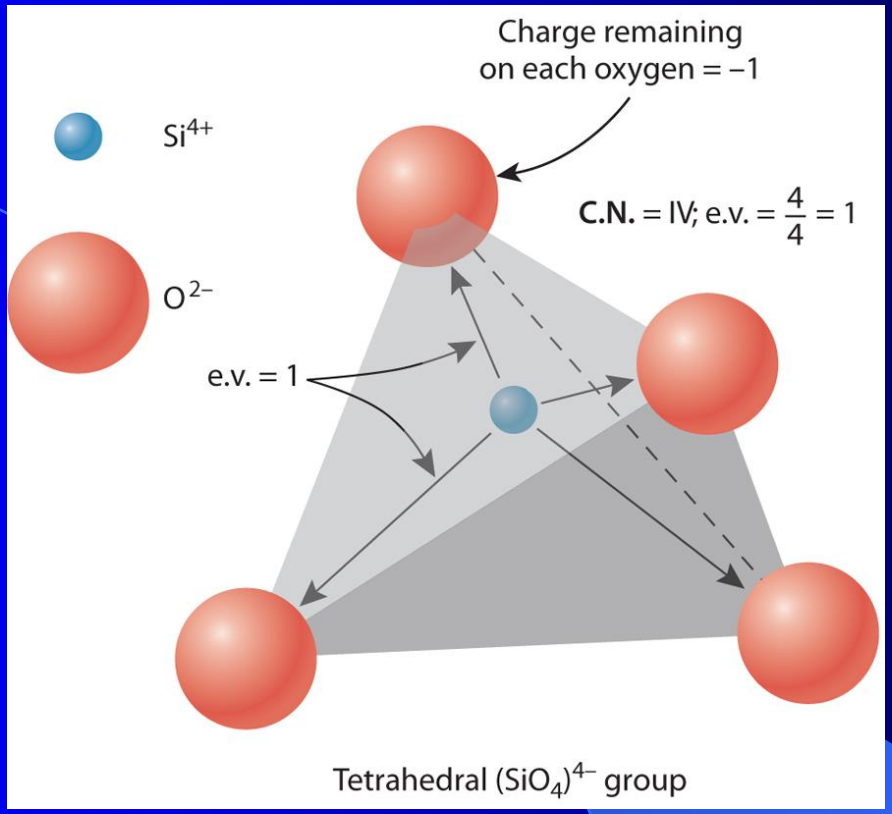




Sulfate - $S^{6+ (IV)}$, e.v. = 3/2

Phosphate – $P^{5+ (IV)}$, e.v. = 5/4

Mesodesmic - e.v. number is equal to1/2 the valence number of the anion



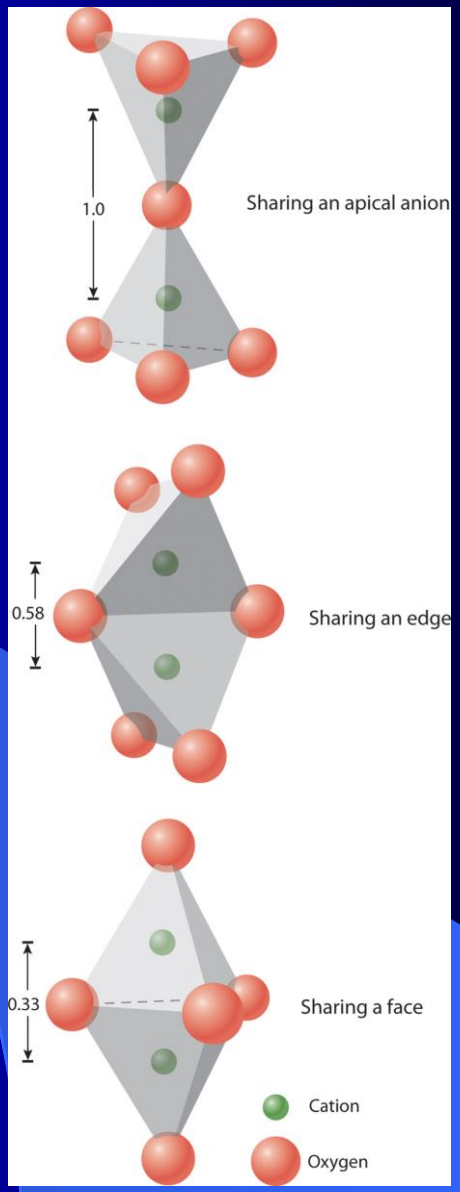
The silica tetrahedron is the basic building block of the silicate minerals

Pauling's Rules – 3. Sharing of polyhedral elements I

Crystal structures become less stable when the polyhedra share edges and even more unstable when the polyhedra share faces.

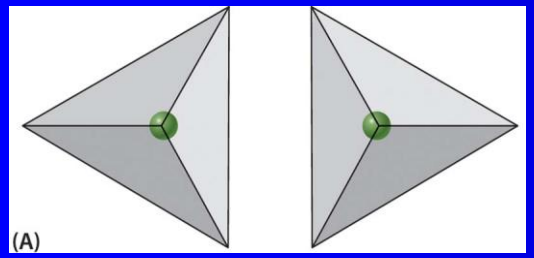
This is because the cations are closer together and like charges repel.

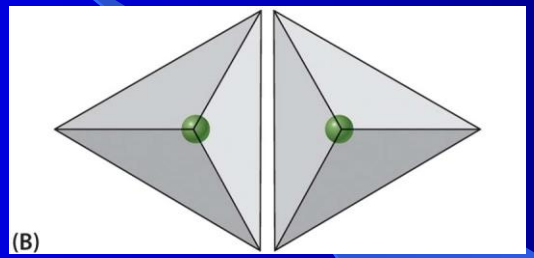
Silica tetrahedra are linked through the oxygens at their apices. These are called bridging oxygens.

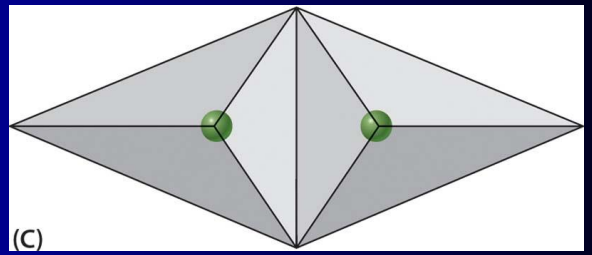


Pauling's Rules – 4. Sharing of polyhedral elements II

In structures containing various cations, those of high charge and small C.N. tend not to share polyhedral elements. If they do, the shared edge contacts and the centers of the cations are displaced away from the shared edge.



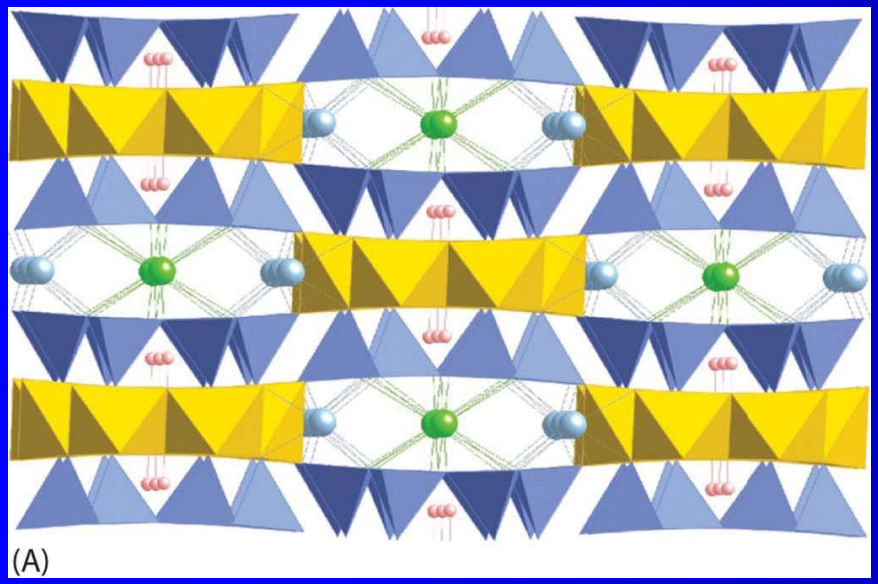




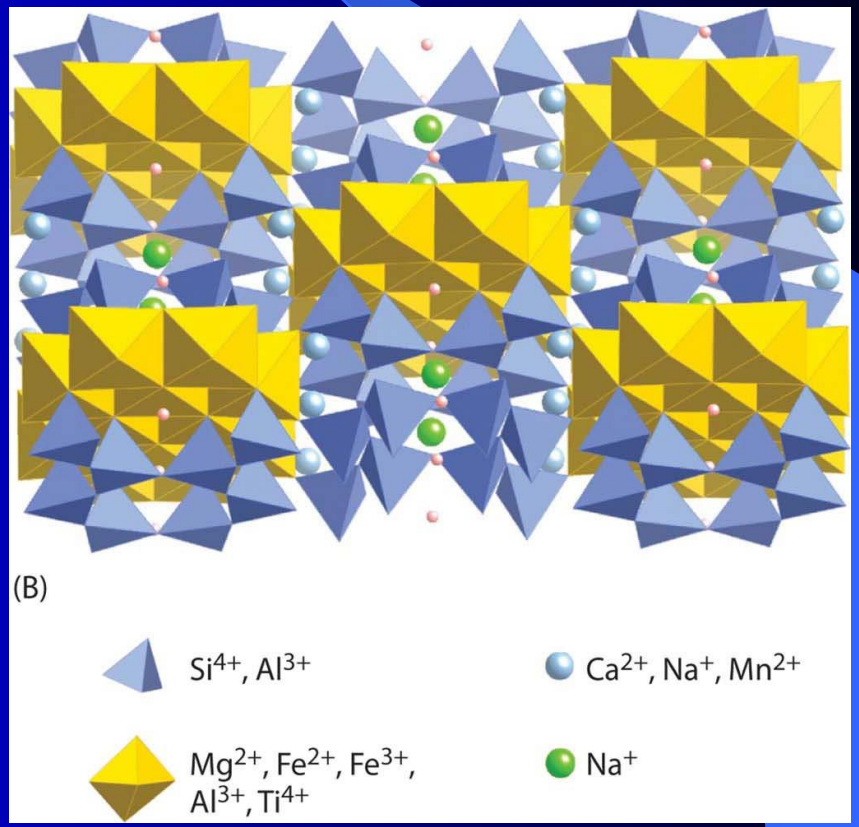
Tetrahedron approach and are distorted because of repulsion of cations.

Pauling's Rules – 5. The principle of parsimony

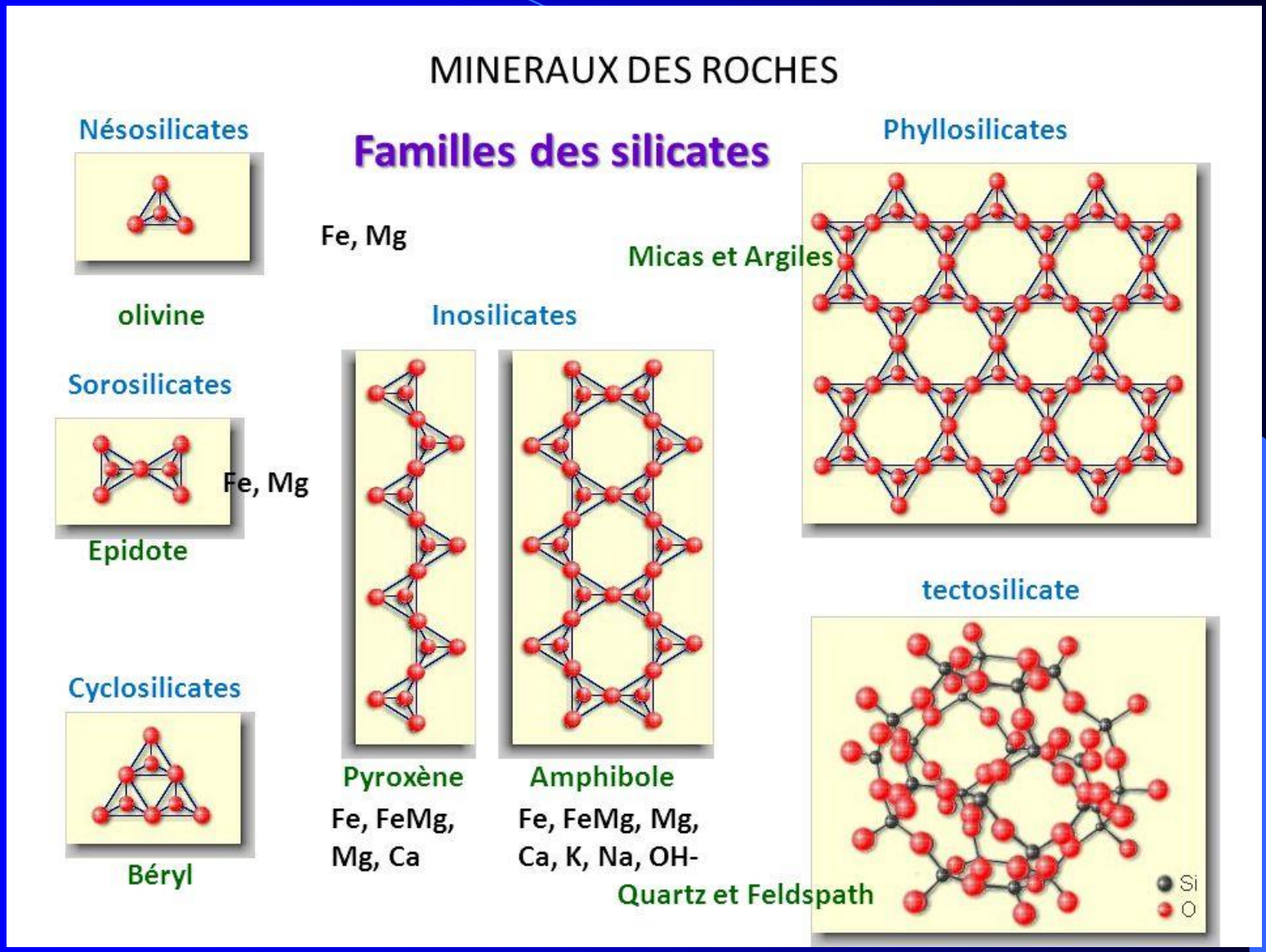
Crystal structures tend to have a limited set of distinctly different cation and anion sites. This leads to extensive replacement in the atomic sites (substitution or solid solution).



Crystal structure of amphibole



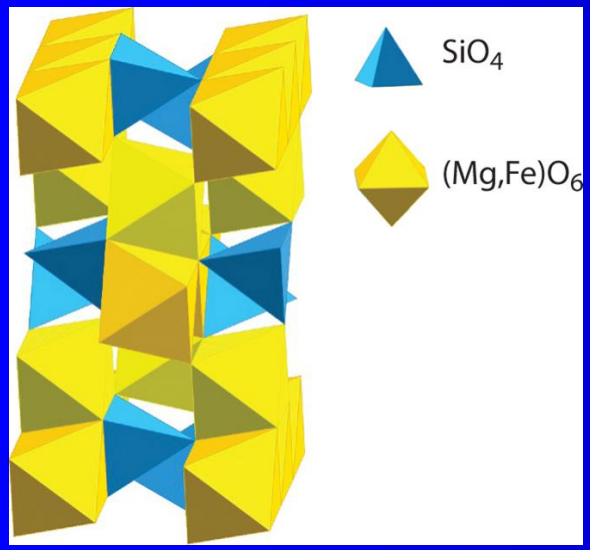
Building blocks for the basic silicate structures. Combine silica tetrahedron in different configurations.

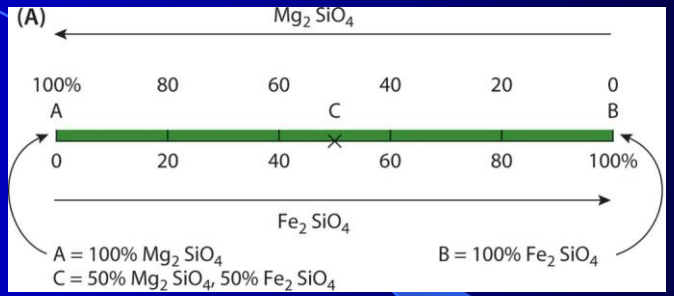


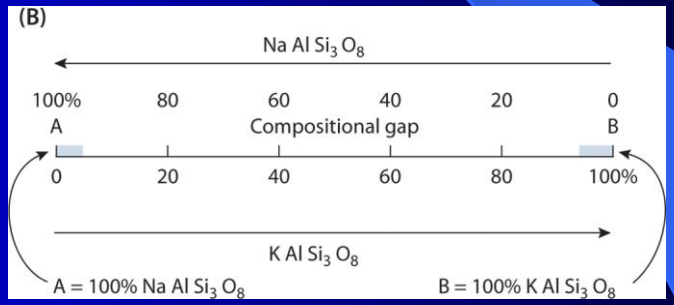
Ionic (book calls it Atomic) Substitution

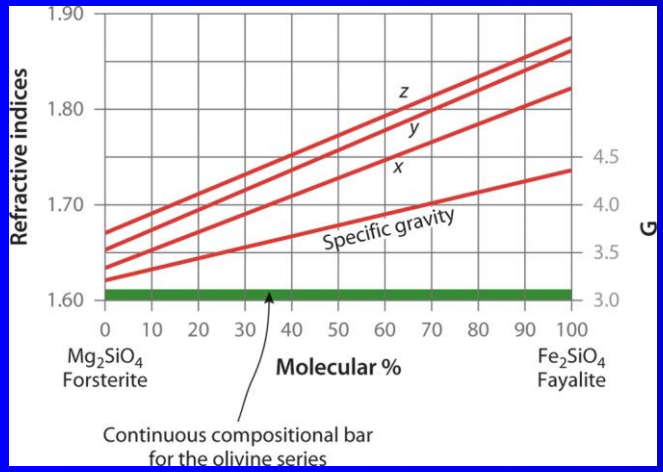
- Ions of one element can substitute for those of another in a crystal structure if their radii differ by less than about 15%
- Ions that differ by one charge unit substitute readily for each other as long as charge neutrality is maintained. Note that this requires a coupled substitution, such as occurs in the plagioclase solid solution series.
- When two ions can occupy the same site in a crystal structure, the ion with the higher ionic potential preferentially enters the site.
- Even if the size and charge of the minor and major ion are similar, substitution may be limited for the minor ion if it has a very different electronegativity and forms a bond of very different character from that of the major ion.

Solid solution series – olivine and feldspar

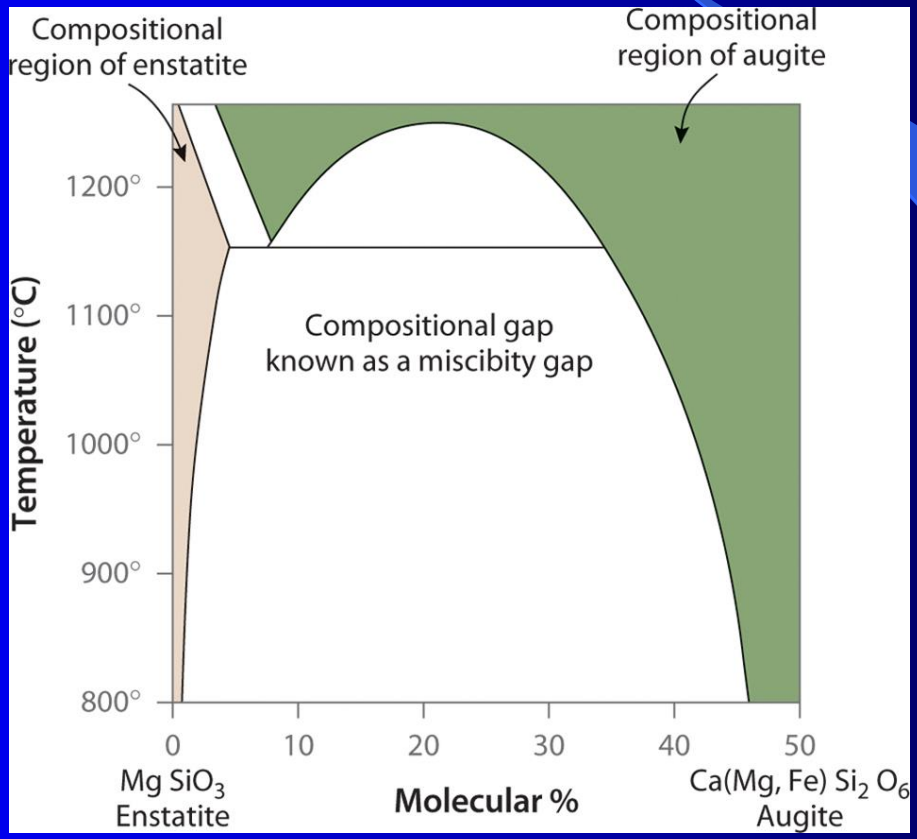








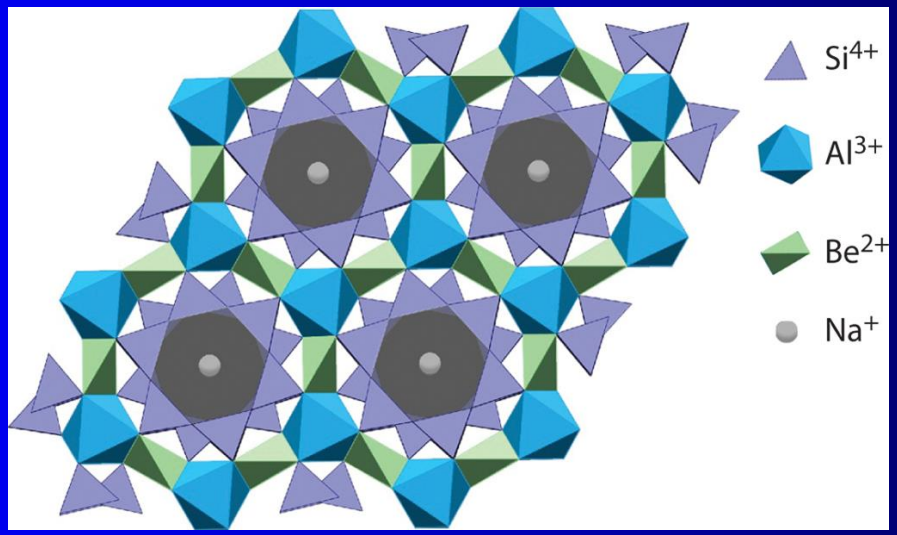
Complete solid solution series and miscibility gap - role of temperature



Types of solid solution

- Substitutional – simple and complex cation and anion substitutions. Ions of similar size and charge.

- Interstitial – ions, ionic groups, or molecules occupy a specific atomic site that is normally empty. Example – ions occupying normally empty channels in the beryl structure.



- Omission – unfilled sites in crystal structure. Example pyrrhotite, $Fe_{1-x}S$. Some of the Fe sites are empty. In order to maintain charge balance, some of the Fe must be oxidized to Fe^{3+}.