

Pauling's Rules and Silicate Structures

Lecture 4

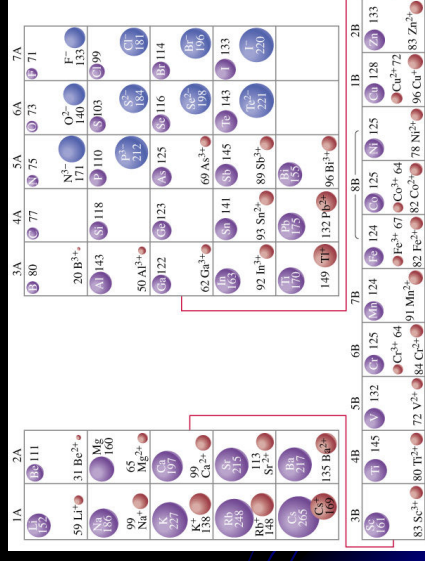
Elemental Abundance in Crust

Element	% by wt	mol wt	% by mol
O	46.6	16.0	62.6
Si	27.7	28.1	21.2
Al	8.1	27.0	6.4
Fe	5.0	55.8	1.9
Ca	3.6	40.1	1.9
Na	2.8	23.0	2.6
K	2.6	39.1	1.4
Mg	2.1	24.3	1.9

Elemental Abundance in Crust

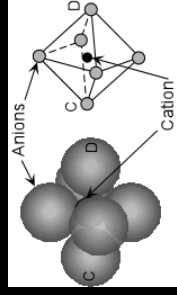
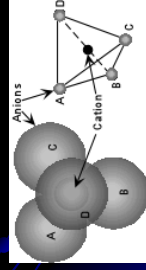
Element	Ionic Radius (R)	R/R _{Oxygen}
O ²⁻	1.32	1.00
Si ⁴⁺	0.30	0.23
Al ³⁺	0.39/0.54	0.30/0.42
Mg ²⁺	0.72	0.55
Fe ²⁺	0.78	0.59
Fe ³⁺	0.65	0.49
Ca ²⁺	1.00/1.12	0.76/0.86
Na ⁺	1.02/1.18	0.78/0.89
K ⁺	1.51/1.64	1.14/1.24
C ⁴⁺	0.08	0.06

Atoms and Ions Have Different Radii

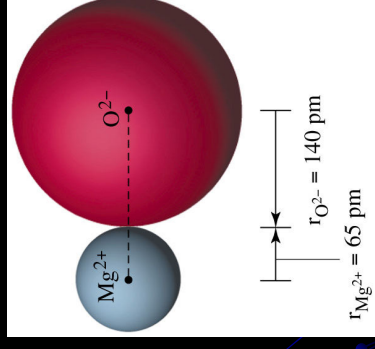


Pauling's Rules

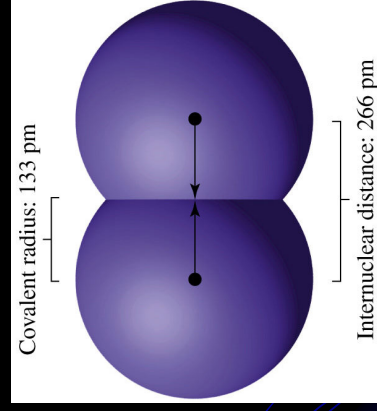
- **RULE 1:** Around every cation, a coordination polyhedron of anions forms, in which the cation-anion distance is determined by the radius sums and the coordination number is determined by the radius ratio.



Cation-Anion Distance (Ionic)



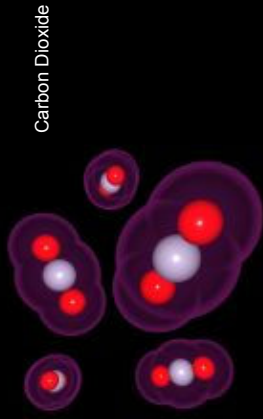
Covalent Radius IS Smaller than Ionic Radius



Coordination Number

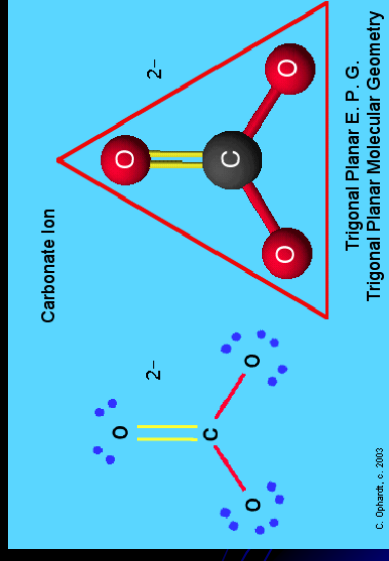
- **Coordination number (c.n.)** is the sum of the total number of neighbors of a central atom in a compound
- Controlled by the ratio of radii of the ions
 - What arrangement of ions of a given size will allow them to be the most closely packed?
- Coordination number affects ionic radii
 - Larger CN results in larger ionic radius

CN=2: Linear



- Not important in minerals

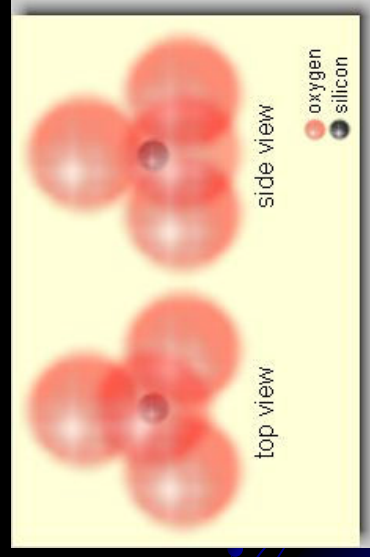
CN=3: Triangular



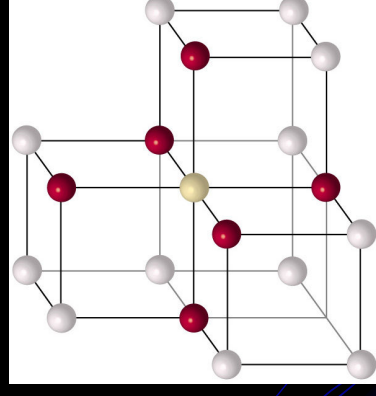
Trigonal Planar E. P. G.
Trigonal Planar Molecular Geometry

C. Ophardt, c. 2009

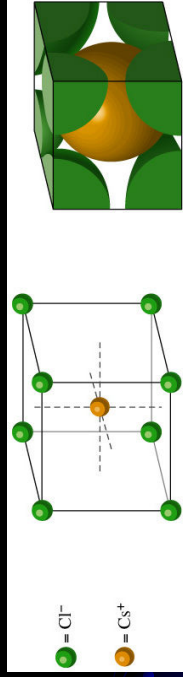
CN=4: Tetrahedral



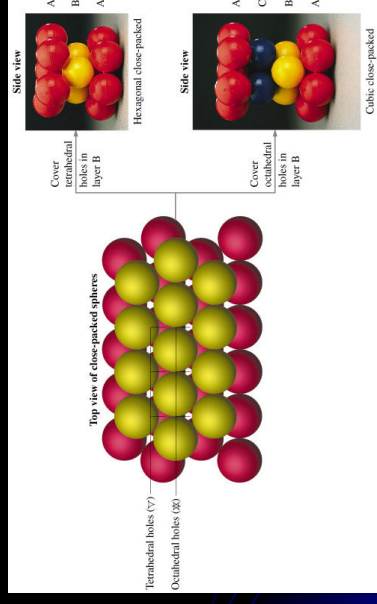
CN=6: Octahedral



CN=8: Cubic



CN=12: Hexagonal or Cubic Close Packed



Coordination of Common Crustal Ions

Element	R/R _{Oxygen}	CN	Coordination with O
Si ⁴⁺	0.23	4	Tetrahedral
Al ³⁺	0.30/0.42	4/6	Tetrahedral/Octahedral
Mg ²⁺	0.55	6	Octahedral
Fe ²⁺	0.59	6	Octahedral
Fe ³⁺	0.49	6	Octahedral
Ca ²⁺	0.76/0.86	6/8	Octahedral/Cubic
Na ⁺	0.78/0.89	6/8	Octahedral/Cubic
K ⁺	1.14/1.24	8/12	Cubic/Closest

General Formula for Silicates

- Ions in silicates will be in tetrahedral, octahedral, or cubic/closest packed coordination

General Formula:

- $X_m Y_n (Z_p O_q) W_r$
 - X = 8-12 CN
 - Y = 6 CN
 - Z = 4 CN
 - O = Oxygen
 - W = OH, F, Cl

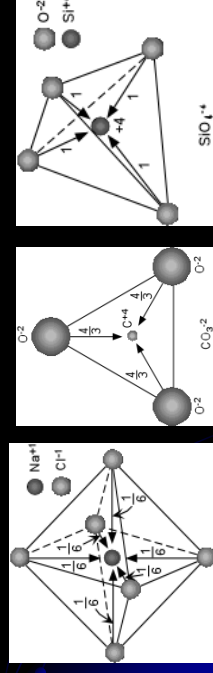
Site	CN	Ions
Z	4	Si ⁴⁺ , Al ³⁺
Y	6	Al ³⁺ , Fe ³⁺ , Fe ²⁺ , Mg ²⁺ , Mn ²⁺ , Ti ²⁺
X	8	Na ⁺ , Ca ²⁺
	8-12	K ⁺ , Ba ²⁺ , Rb ⁺

Mineral Formula Examples

- General Formula
 $X_m Y_n (Z_p O_q) W_r$
- Augite
 $(Ca, Na)(Mg, Fe, Al, Ti)(Si, Al)_2 O_6$
- Muscovite
 $KAl_2(Si_3Al)O_{10}(OH, F)_2$
- Plagioclase
 $(Na, Ca)(Si, Al)_4 O_8$

Pauling's Rules

- **RULE 2: Ionic Bond Strength**
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.
- Electrostatic Valency = Cation Charge/CN
- Measure of bond strength

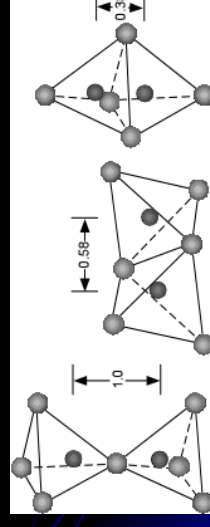


Requirements of Rules 1 and 2

- Stable coordination numbers for Si and Al result in complex ions
- Si tetrahedra and Al octahedra must bond with other ions to balance negative charge
- Insufficient cations to balance negative charge
- Tetrahedra and octahedra must commonly share oxygens with other complex ions

Pauling's Rules

- **RULE 3:**
Shared edges, and particularly faces of two anion polyhedra in a crystal structure decreases its stability.
- Maximizes distance between cations, and therefore minimizes repulsion



Requirements of Rule 3

- In silicates the tetrahedra will share oxygens with neighboring tetrahedra, as well as with neighboring octahedra

Pauling's Rules

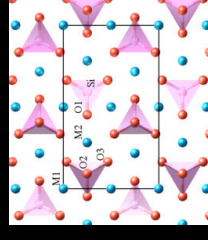
- **RULE 4:**
In a crystal structure containing several cations, those of high valency and small coordination number tend not to share polyhedral elements.
 - A follow-up to Rule 3

Requirements of Rules 3 and 4

- Si^{4+} has a high valency and low coordination number (4 with oxygen), so silica tetrahedra will not share sides or faces
- Arrangements of silica tetrahedra must be based on the sharing of apices

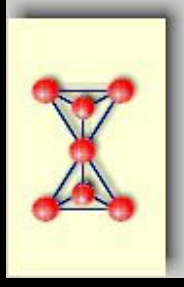
Isolated Tetraheda Silicates (Nesosilicates)

- Tetrahedra do not share any oxygens with neighboring silicon ions
- Charge balance achieved by bonding with cations
- e.g., Olivine, Garnet, Kyanite



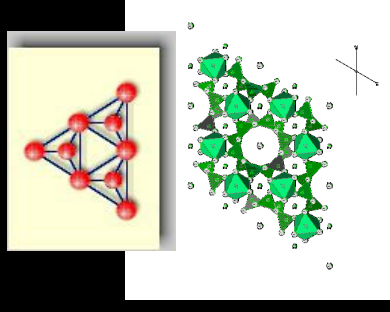
Paired Silicates (Sorosilicates)

- Pairs of tetrahedra share one oxygen
- Remaining charge balance achieved by bonding with cations
- e.g., Epidote



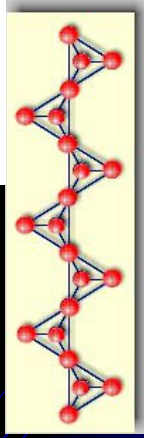
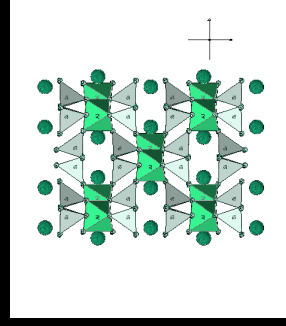
Ring Silicates (Cyclosilicates)

- Sets of tetrahedra share two oxygens to form a ring
- Remaining charge balance achieved by bonding with cations
- e.g., tourmaline, beryl



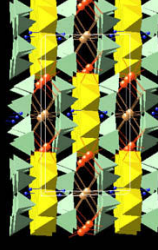
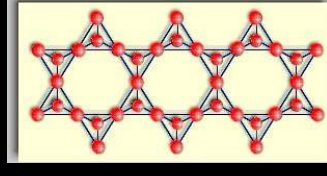
Single-Chain Silicates (Inosilicates)

- Sets of tetrahedra share two oxygens to form a chain
- Remaining charge balance achieved by bonding with cations
- e.g., pyroxenes



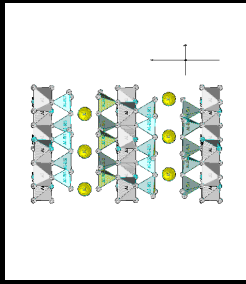
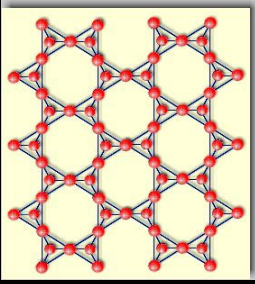
Double-Chain Silicates (Inosilicates)

- Sets of tetrahedra share oxygens (2 and 3 alternation) to form a chain
- Remaining charge balance achieved by bonding with cations
- e.g., amphiboles



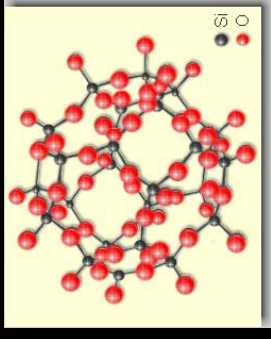
Sheet Silicates (Phyllosilicates)

- Sets of tetrahedra share three oxygens to form a sheet
- Remaining charge balance achieved by bonding with cations
- e.g., micas



Framework Silicates (Tectosilicates)

- Sets of tetrahedra share all 4 oxygens in 3 dimensions to form a 3-D network
- If all tetrahedra are cored by silicon then there is no charge imbalance
 - e.g., quartz
- If some tetrahedra are cored by Al, then the remaining charge balance achieved by bonding with cations
 - e.g., feldspars



Silicon Content of Silicates

STRUCTURE	EXAMPLE FORMULA	Si:O Ratio
Nesosilicates	Mg_2SiO_4	1:4
Sorosilicates	$Zn_x(OH)_2Si_2O_7 \cdot H_2O$	1:3.5
Cyclosilicates	$Al_2Be_3Si_6O_{18}$	1:3
Inosilicates (Single Chain)	$CaMgSi_2O_6$	1:3
Inosilicates (Double Chain)	$Ca_2Mg_2(Si_4O_{11})OH_2$	1:2.75
Phyllosilicates	$Al_2Si_4O_{10}(OH)_2$	1:2.5
Tectosilicates	SiO_2	1:2