Ionic Coordination and Silicate Structures

Pauling’s Rules

- A coordination polyhedron of anions forms around a cation
- Ionic distance determined by radii
- Coordination number determined by radius ratio.

May result in a complex ion

Atoms and Ions Have Different Radii

Elemental Abundance in Crust

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionic Radius (R)</th>
<th>R/R_{Oxygen}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O^{2-}</td>
<td>1.32</td>
<td>1.00</td>
</tr>
<tr>
<td>Si^{4+}</td>
<td>0.30</td>
<td>0.23</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>0.39/0.54</td>
<td>0.30/0.42</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>0.72</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>0.78</td>
<td>0.59</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>0.65</td>
<td>0.49</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>1.00/1.12</td>
<td>0.76/0.86</td>
</tr>
<tr>
<td>Na^{+}</td>
<td>1.02/1.18</td>
<td>0.78/0.89</td>
</tr>
<tr>
<td>K^{+}</td>
<td>1.51/1.64</td>
<td>1.14/1.24</td>
</tr>
<tr>
<td>C^{4+}</td>
<td>0.08</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Coordination Number

- **Coordination number**: total number of neighbors around a central atom
- Controlled by ratio of ionic radii
- Arranged for closest packing

Styrofoam Ball Investigation of Coordination Number

- Four sizes of styrofoam balls
- Exercise 1: CN of Si and O
  - Largest = O, Smallest = Si
- Exercise 2: CN of Fe and O
  - Largest = O, Medium = Al
- Exercise 3: CN of Ca and O
  - Largest balls = O, Large = Ca

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<tr>
<td>Ca $^{2+}$</td>
<td>1.12</td>
<td>0.85</td>
</tr>
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</table>

CN=4: Tetrahedral

- Top view
- Side view

CN=6: Octahedral

- Diagram of an octahedral coordination structure.
Coordination and Silicate Structures

**CN=8: Cubic**

![Cubic Coordination](image)

**CN=12: Hexagonal or Cubic Close Packed**

![Hexagonal Coordination](image)

**Coordination of Common Crustal Ions**

<table>
<thead>
<tr>
<th>Element</th>
<th>R/R(_{Oxygen})</th>
<th>CN</th>
<th>Coordination with O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(^{4+})</td>
<td>0.23</td>
<td>4</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>0.30/0.42</td>
<td>4/6</td>
<td>Tetrahedral/Octahedral</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.55</td>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>0.59</td>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>0.49</td>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.76/0.86</td>
<td>6/8</td>
<td>Octahedral/Cubic</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.78/0.89</td>
<td>6/8</td>
<td>Octahedral/Cubic</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.14/1.24</td>
<td>8/12</td>
<td>Cubic/Closest</td>
</tr>
</tbody>
</table>

**General Formula for Silicates**

- Ions in silicates... tetrahedral, octahedral, or cubic/closest packed coordination
- General Formula: \(X_m\ Y_n\ (Z_p\ O_q)\ W_r\)
  - \(X\) = Cubic/Closest
  - \(Y\) = Octahedral
  - \(Z\) = Tetrahedral
  - \(O\) = Oxygen
  - \(W\) = OH, F, Cl

<table>
<thead>
<tr>
<th>Site</th>
<th>CN</th>
<th>Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>4</td>
<td>Si(^{4+}), Al(^{3+})</td>
</tr>
<tr>
<td>Y</td>
<td>6</td>
<td>Al(^{3+}), Fe(^{3+}), Fe(^{2+}), Mg(^{2+}), Mn(^{2+}), Ti(^{2+})</td>
</tr>
<tr>
<td>X</td>
<td>8</td>
<td>Na(^+), Ca(^{2+})</td>
</tr>
<tr>
<td></td>
<td>8-12</td>
<td>K(^+), Ba(^{2+}), Rb(^+)</td>
</tr>
</tbody>
</table>
Mineral Formula Examples

- General Formula
  \[ X_m Y_n (Z_p O_q) W_r \]
- Augite
  \((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6\)
- Muscovite
  \(KAl_2(Si_3Al)O_{10}(OH,F)_2\)
- Plagioclase
  \((Na,Ca)(Si,Al)_4O_8\)

Requirements of Pauling’s Rules

- Stable coordination numbers for Si produces complex anion \((SiO_4)^4^-\)
- \((SiO_4)^4^-\) must bond to balance charge
- Insufficient cations
- Tetrahedra commonly bond with other complex anions

Pauling’s Rules

- Shared edges or faces of polyhedra decrease stability.
  - The closer the cations… the greater the repulsion
  - The higher the cation charge… the greater the repulsion

Requirements of Pauling’s Rules

- Si\(^{4+}\) has high charge and low coordination number
  - Silica tetrahedra will not share sides or faces
- Arrangements of silica tetrahedra based on sharing of apices
Isolated Tetrahedra 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
Coordination and Silicate Structures

**Ring Silicates**
- 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

**Chain Silicates: Cleavage**
- Amphibole Cleavage (120 / 60)
- Pyroxene Cleavage (90)
**Chain Silicates: Habit**

- Pyroxene
- Amphibole

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

**Sheet Silicates**

- Biotite (Crystal)
- Biotite (Broken)

**Framework Silicates (Tectosilicates)**
- Tetrahedra share all 4 oxygens to form a 3-D network
- If all tetrahedra cored by silicon then no charge imbalance
  - e.g., quartz (SiO$_2$)
- If some tetrahedra cored by Al, remaining charge balance achieved by bonding with cations
  - e.g., feldspar (NaAlSi$_3$O$_8$)
Feldspar (Orthoclase)  Nepheline

**Framework Silicates**

**Silicon Content of Silicates**

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>EXAMPLE FORMULA</th>
<th>Si:O Ratio</th>
</tr>
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<tbody>
<tr>
<td>Nesosilicates</td>
<td>Mg$_2$SiO$_4$</td>
<td>1:4</td>
</tr>
<tr>
<td>Sorosilicates</td>
<td>Zn$_4$(OH)$_2$Si$_2$O$_7$·H$_2$O</td>
<td>1:3.5</td>
</tr>
<tr>
<td>Cyclosilicates</td>
<td>Al$_2$Be$_3$Si$<em>6$O$</em>{18}$</td>
<td>1:3</td>
</tr>
<tr>
<td>Inosilicates (Single Chain)</td>
<td>CaMgSi$_2$O$_6$</td>
<td>1:3</td>
</tr>
<tr>
<td>Inosilicates (Double Chain)</td>
<td>Ca$_2$Mg$_2$(Si$<em>4$O$</em>{11}$)OH$_2$</td>
<td>1:2.75</td>
</tr>
<tr>
<td>Phyllosilicates</td>
<td>Al$_2$Si$<em>4$O$</em>{10}$·(OH)$_2$</td>
<td>1:2.5</td>
</tr>
<tr>
<td>Tectosilicates</td>
<td>SiO$_2$</td>
<td>1:2</td>
</tr>
</tbody>
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