SILICATES
• Based on silica tetrahedra
• Tetrahedra are linked
  • to one another by bonds that have a mixed character, and
  • to cations by ionic bonds
• Tetrahedral site may also be occupied by Al$^{3+}$
• Crystal structure determined by ratio of tetrahedral sites to oxygen anions

References
ELEMENTAL ABUNDANCE IN THE EARTH’S CRUST

- Silicates are the major rock-forming minerals present in the Earth’s crust. They consist of the two most abundant elements in the crust, oxygen and silicon, combined with various cations.
- Oxygen is the commonest element in the crust (nearly half by weight and over 90% by volume). Thus, mineral structures are generally determined by the way the oxygen ions are arranged (coordinated) around a central cation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>46.60</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>27.72</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>8.13</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>5.00</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>3.63</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>2.83</td>
</tr>
<tr>
<td>Potassium</td>
<td>K</td>
<td>2.59</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>2.09</td>
</tr>
</tbody>
</table>


Figure 2-14 The silica tetrahedron shown from (a) top and (b) side views. A central silicon ion is surrounded by four oxygen ions. (From S. Judson, M. E. Kauffman, and L. D. Leet, *Physical Geology*, 7th ed., copyright © 1987 by Prentice-Hall, Inc., Englewood Cliffs, N.J.)
SILICATE STRUCTURE

- The **coordination number** is the number of oxygen ions arranged around the central cation. It varies from 2 to 12, depending on the ratio of the radius of the cation to that of the anion.
- The radius ratio of silicon to oxygen (~0.20) results in **tetrahedral coordination** of oxygen anions around a central silicon cation. This silica tetrahedra is the basis of silicate structures.
- Silicate structures are made up of these tetrahedra arranged in various ways, with cations in the spaces. Most cations occur in only one type of coordination in silicate minerals; however, others such as **aluminium** occur in several.
- The Si-O bond in silicate minerals has a dual **ionic-covalent** character. Si shares one of its outer shell electrons with each oxygen ion, i.e., $[\text{Si}^{4+}(\text{O}^{2-})_{4}]^{4-}$. In addition, silica tetrahedra may share electrons (oxygen ions) with other tetrahedra to build a network or isolated tetrahedra may be linked only by ionic bonding to other cations.
- Aluminium may take the place of silicon in the tetrahedra or be **octahedrally coordinated** to adjacent silica tetrahedra by an ionic bond.
- Remember, cations that have a similar ionic radii and charge tend to substitute for each other to form mixed compounds called **solid solutions**, e.g., olivines, $\text{Mg}_2\text{SiO}_4 \leftrightarrow \text{Fe}_2\text{SiO}_4$.

GEOMETRY OF TETRAHEDRA LINKAGES IN SILICATES

- **Island silicates** – independent silica tetrahedra linked by the electrostatic attraction of the intersecting (interstitial) cations, e.g., olivine, where the presence of $[\text{SiO}_4]$ in the mineral formula is indicative of this type of configuration.

- **Cyclosilicates or ring silicates** – adjacent tetrahedra share two oxygen to form a ring, e.g., beryl, $\text{BeAl}_2\text{Si}_6\text{O}_{18}$, and tourmaline, which form **hexagonal** or **trigonal** crystals.

- When tetrahedra are linked to two others to form **chains**, there are two possible configurations. **Single chain silicates** are linked only by cations, e.g., pyroxenes, whereas **double chain silicates** are linked by both cations and shared oxygens, e.g., amphiboles. Major cations in chain silicates are $\text{Mg}^{2+}$, $\text{Fe}^{2+}$, $\text{Ca}^{2+}$ and $\text{Na}^+$.
- Chain silicate minerals always have a prismatic to blocky habit and two cleavage planes meeting at $90^\circ$ (pyroxenes) and $\sim120^\circ$ (amphiboles) that are planes of weakness between the chain units.
**TABLE 3-2**

**Major Silicate Structures**

<table>
<thead>
<tr>
<th>Geometry of linkage of SiO₄ tetrahedra</th>
<th>Si/O ratio</th>
<th>Example mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Isolated tetrahedra</em>: linked by bonds sharing oxygens only through cation</td>
<td>1:4</td>
<td>Olivine</td>
<td>(Mg,Fe)₂SiO₄</td>
</tr>
<tr>
<td><em>Rings of tetrahedra</em>: joined by shared oxygens in three-, four- or six-membered rings</td>
<td>1:3</td>
<td>Beryl</td>
<td>BeAl₂(Si₄O₁₂)</td>
</tr>
<tr>
<td><em>Single chains</em>: reach tetrahedron linked to two others by shared oxygens. Chains bonded by cations</td>
<td>1:3</td>
<td>Pyroxene</td>
<td>(Mg,Fe)SiO₃</td>
</tr>
<tr>
<td><em>Double chains</em>: two chains joined by shared oxygens as well as cations</td>
<td>4:11</td>
<td>Amphibole</td>
<td>(Ca₃Mg₆)Si₄O₁₂(OH)₂</td>
</tr>
<tr>
<td><em>Sheets</em>: each tetrahedron linked to three others by shared oxygens. Sheets bonded by cations or alumina sheets</td>
<td>2:5</td>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
</tr>
<tr>
<td><em>Frameworks</em>: each tetrahedron shares all its oxygens with other SiO₄ tetrahedra (in quartz) or AlO₄ tetrahedra</td>
<td>3:8</td>
<td>Feldspar (albite)</td>
<td>NaAlSi₃O₈</td>
</tr>
</tbody>
</table>

**SHEET SILICATES**

- **Two layer structure (e.g., kaolinite)**
  # silicon-oxygen layer
  # aluminium-hydroxyl layer

- **Three layer structure (e.g., montmorillonite)**
  # silicon-oxygen layer
  # aluminium-iron-magnesium-hydroxyl layer
  # silicon-oxygen layer

- **Four layer structure (e.g., chlorite)**
  # aluminium-iron-magnesium-hydroxyl layer
  # silicon-oxygen layer
  # aluminium-iron-magnesium-hydroxyl layer
  # silicon-oxygen layer
Figure 2-18 The sheet silicates are composed of two types of sheets: (a) A tetrahedral sheet of linked silica tetrahedra (single tetrahedron shown at left) and (b) an octahedral sheet (single octahedron shown at left) in which cations are surrounded by oxygens in octahedral coordination. (From R. E. Grim, Clay Mineralogy, 2d ed., copyright © 1968 by McGraw-Hill, Inc., New York.)
CATION EXCHANGE CAPACITY IN CLAYS

- **Phyllosilicates or sheet silicates** – have a stacked (or multilayered) structure with either a two, three, or four layer structure. A sheet of cations and \((\text{OH})^-\) ions is stacked onto a silicate sheet or between two silicate sheets.
  - **Two layer structure** – clay mineral kaolinite
  - **Three layer structure** – clay mineral montmorillonite (smectite group) and the micas (muscovite and biotite)
  - **Four layer structure** – chlorite
- The layers are linked by weakly bonded interlayer cations (Ca\(^{2+}\), Na\(^+\) and K\(^+\)) in the two and three layer sheet silicates (van der Waals bonds), which is why these minerals have **perfect basal cleavage**. These cations balance the often net negative charge of the silica tetrahedra layers due to substitutions of magnesium and iron for aluminium, and aluminium for silicon.
- Three layer clays have **base exchange properties**, i.e., montmorillonite clays may be more or less ‘sticky’ depending upon the amount of Na and Ca in the interlayer sites. Some multilayer clay minerals (smectite or montmorillonite group) have a tendency to absorb water (situated in between layers) and swell (expand). This is a common cause of structural failure in buildings. Soils containing Na- montmorillonite are more expansive than those containing Ca- montmorillonite.

![Figure 10-28](image)

FRAMEWORK SILICATES – FELDSPARS AND SILICA

- Framework silicates have a three dimensional linkage of silica tetrahedra forming relatively strong bonds in all directions, e.g., feldspar and quartz.

**Feldspar minerals**
- Substitution of Al for Si in feldspar requires addition of Na, K, or Ca ions to maintain charge balance.
- Feldspar minerals are initially divided into two compositional groupings.
- **Plagioclase feldspar** – a number of minerals in a solid solution series between a Na-rich (albite) and Ca-rich (anorthite) end-member.
- **Alkali feldspar** – limited solution between a K and a Na end-member (except at high temperatures).
- Striations (parallel lines) on cleavage planes in plagioclase feldspars are due to **twinning**, a crystal defect due to a change in the orientation of the growth direction
- Plagioclase feldspars can show numerous parallel striations (multiple twin planes - **multiple twinning**), whereas alkali feldspars often show a single striation (single twin plane - **simple twinning**)
- In **simple twin** crystals, one part is in the reverse position to the other part, or expressed another way, the second half of the twin may be conceived or conceptualised as being produced by the rotation, about some line, of one half of the crystal through an angle of 180°.
- The extent of solid solution between possible compositional end members in the feldspar group depends on temperature. Feldspars formed at higher temperatures can have a wider range of compositions than those formed at low temperature (perthites)
- **Perthite** is an intergrowth (**exsolution**) of Na feldspar within K feldspar due to physical segregation (separation) during fractional crystallisation, as earlier formed higher temperature feldspars start to become unstable as the magma continues to cool

**Silica types**
- Composed entirely or overwhelmingly of silica tetrahedra in a 3D network
- No cleavage, irregular fracture as there are no planes of weakness along which the mineral will preferential fracture
- Varying colours (in both crystalline and cryptocrystalline silica) reflect minute amounts of elemental impurities within the structure
- Crystalline silica occurs as **quartz** (hexagonal-trigonal), tridymite or cristobalite (polymorphs). **Tridymite** forms at 870°C to 1470°C at atmospheric pressures and is orthorhombic. It inverts to an hexagonal polymorph, quartz, at lower temperatures. **Cristobalite** is a cubic, high-temperature (>1470°C) polymorph.
- **Chalcedony** is a cryptocrystalline silica variety, whereas opal is an amorphous, hydrated silica) variety that may show numerous internal reflections.
Silicates

The feldspars are a group of the most important of the rock-forming minerals and consist of partly discontinuous solid solutions between the end members orthoclase (KAlSi₃O₈), albite (NaAlSi₃O₈), and anorthite (CaAl₂Si₂O₈). Figure 7.9 shows the relations between the feldspars:

\[
\begin{align*}
\text{Orthoclase (Microcline)} & \quad \text{Sandine} \\
\text{Anorthite} & \quad \text{Feldspars series} \\
\text{Albite} & \quad \text{Anorthite} (CaAl₂Si₂O₈)
\end{align*}
\]

Feldspars stable at high temperatures only □ □ Feldspars stable at low temperatures only

7.9 Compositions of the feldspars in terms of the three end-members albite, anorthite, and orthoclase.

Twin crystals
When two closely adjacent crystals have grown together with a crystallographic plane or direction common to both, but one reversed relative to the other, a twin crystal results. In many instances the twin crystal appears as if a single crystal had been divided on a plane, and one half of the crystal rotated relative to the other half on this plane. If the rotation is 180°, points at opposite ends of a crystal are thus brought to the same end as a result of the twinning and re-entrant angles between crystal faces are then frequently produced; they are characteristic of many twins. Examples are shown in Fig. 4.8:

Fig. 4.8. Twin crystals: (a) Augite, showing re-entrant angle R, twin plane parallel to front pinacoid. (b) Arrow head twin of Gypsum. (c) Carlsbad twin of Orthoclase. (d) Multiple twin of Plagioclase (Albite twinning).

7.11 Calcic plagioclase (labradorite) showing characteristic broad lamellae of albite twins. × 30. Crossed nicols.

Albite twinning in plagioclase is often visible with the hand lens and is the best criterion for the distinction of plagioclase from orthoclase in hand-specimens.