

CHAPTER 4

Crystal Structure

- We can assume minerals to be made of orderly packing of atoms or rather ions or molecules.
- Many mineral properties like symmetry, density etc are dependent on how the atoms or ions are packed
- We can approximate the atoms or ions in a metal to be rigid spherical balls

- Think of a box full of ping pong balls.
- The densest packing is one on which a layer of balls sit on the hollow between the balls in the layer below.
- The two closest packing are:
 - Hexagonal close packing (ABCABC)
 - Cubic close packing (ABAB)

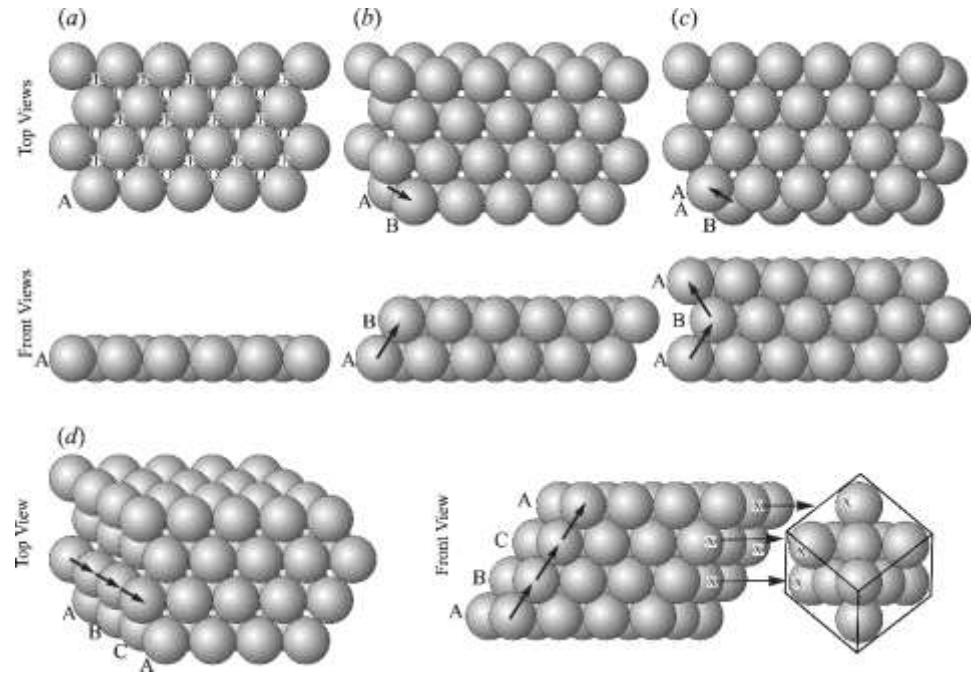


Figure 4.1 Closest packing of spheres.

- Some what less dense packing is body centered cubic packing, seen in Iron.
- Because they can be packed so closely, metals have high density

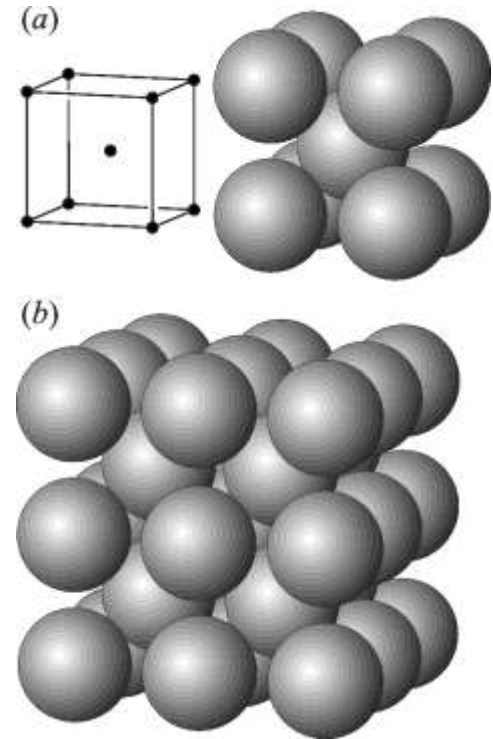


Figure 4.2 Body-centered cubic packing. (a) Bodycentered lattice (left) and with atoms at each lattice node (right). (b) Eight unit cells. Each sphere is in contact with eight neighbors.

Covalent and Molecular Bonds

- Covalent bonds are strong therefore covalent crystals are strong and have high melting point
- Because atoms need to be placed in a specific orientation only, covalent crystals do not show a close packing.
- The bonds in molecular crystals are weak, hence these tend to be soft. The geometry of the structure is determined by the shape and charge distribution in the molecules (e.g., Hydrogen bond in water)

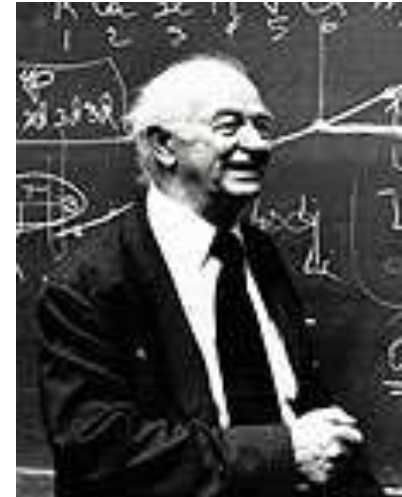
Ionic Bonds

- For minerals formed largely by ionic bonding, the ion geometry can be simply considered to be spherical
- Spherical ions will geometrically pack (*coordinate*) oppositely charged ions around them as tightly as possible while maintaining charge neutrality
- For a particular ion, the surrounding coordination ions define the apices of a polyhedron
- The number of surrounding ions is the *Coordination Number*

Pauling's Rules of Mineral Structure

Rule 1: A coordination polyhedron of anions is formed around each cation, wherein:

- the cation-anion distance is determined by the sum of the ionic radii, and
- the coordination number of the polyhedron is determined by the cation/anion radius ratio ($R_a:R_x$)



Linus Pauling

Radius Ratio of Cation and Anion (R_c/R_a), Coordination number and Coordination polyhedra

Minimum Radius Ratio	Coordination number	Packing geometry
~1.0	12	Corners of a cuboctahedron (close packing)
0.732-1	8	Corners of a cube
0.414-0.732	6	Corners of an octahedron
0.225-0.414	4	Corners of a tetrahedron
0.155-0.225	3	Corners of an equilateral triangle
<0.155	2	Linear

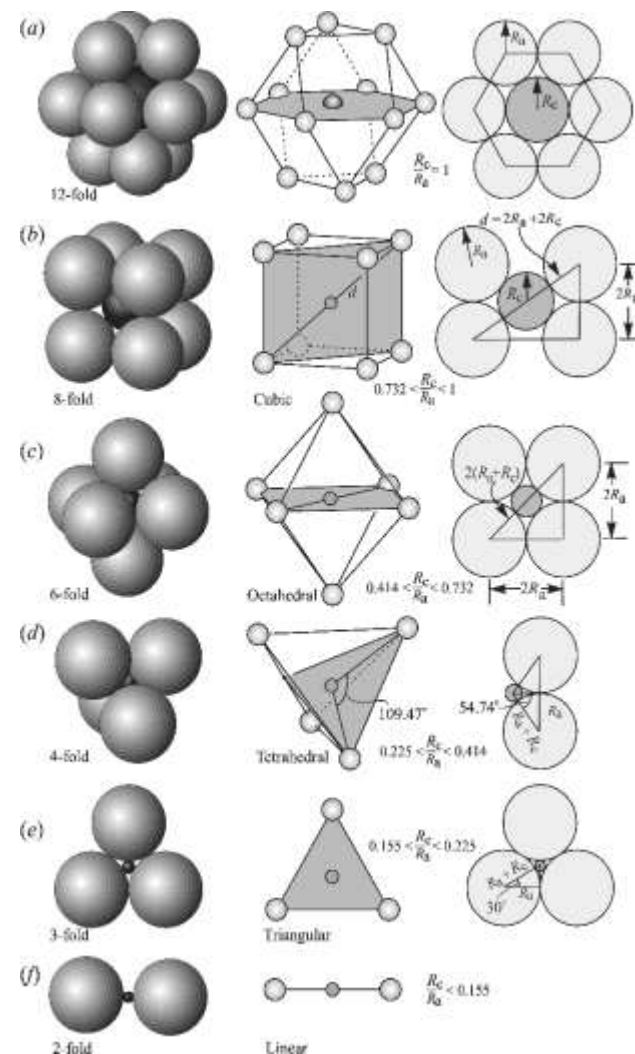


Figure 4.3 Coordination polyhedra. Anions with radius R_a are shown with light shading, cations with radius R_c with dark. Left view shows cation and anions drawn to scale.

Pauling's Rules of Mineral Structure

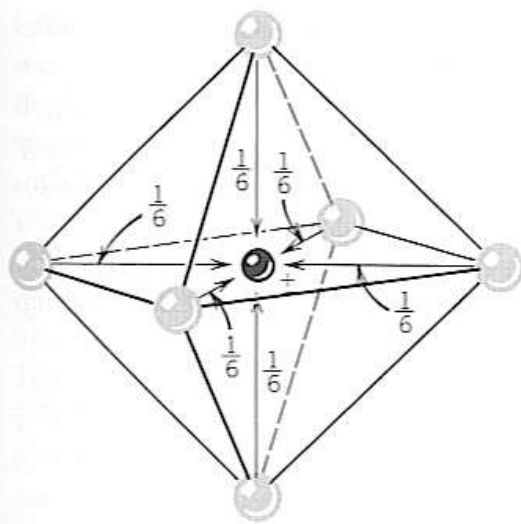
Rule 2: The electrostatic valency principle

The strength of an ionic (electrostatic) bond (e.v.) between a cation and an anion is equal to the charge of the anion (z) divided by its coordination number (n):

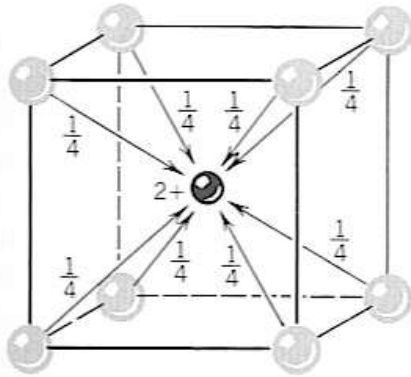
$$\text{e.v.} = z/n$$

In a stable (neutral) structure, a charge balance results between the cation and its polyhedral anions with which it is bonded.

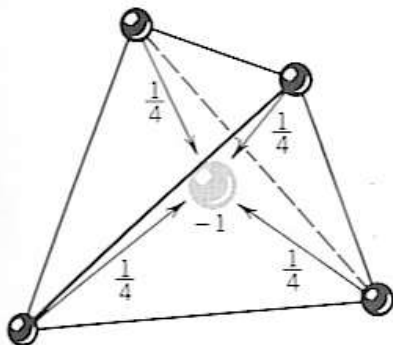
Charge Balance of Ionic Bonds



C. N. = 6; e. v. = $\frac{1}{6}$
 $6 \times (\frac{1}{6}) = 1$



C. N. = 8; e. v. = $\frac{1}{4}$
 $8 \times (\frac{1}{4}) = 2$



C. N. = 4; e. v. = $\frac{1}{4}$
 $4 \times (\frac{1}{4}) = 1$

Uniform Bond Strength

- **Isodesmic:** where all ionic bonds are of equal strength
- Anions tend to pack around the cation in highly symmetric and generally close packing arrangement
- Most of the minerals crystallize in highly symmetric systems like isometric, tetragonal or hexagonal systems
- Oxides, Fluorides, Chlorides are common examples

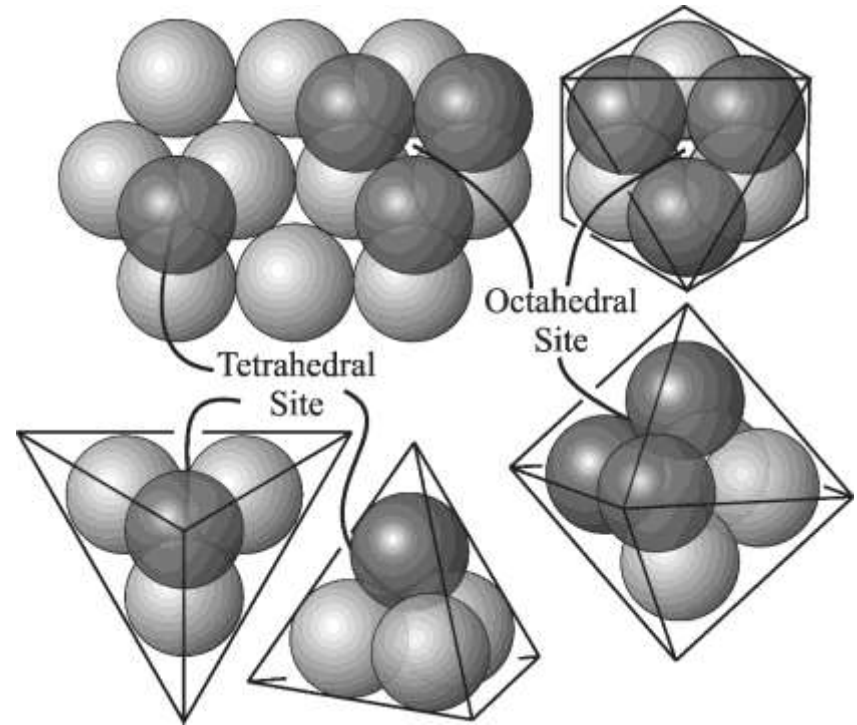


Figure 4.4 Tetrahedral and octahedral sites in close-packed structures. A layer of anions (light) is shown with just four anions from an adjacent layer (dark).

Nonuniform Bond Strength

- Some anion-cation bonds are stronger than others: cations forming stronger bonds are smaller and have a high charge
 - Ex: C^{4+} , S^{6+} , P^{5+} , Si^{4+}
 - These strongly charged cations form CO_3^{2-} , SO_4^{4-} , PO_4^{3-} , SiO_4^{4-} anionic groups
- Have lower symmetry, irregular coordination polyhedra

Formation of Anionic Groups

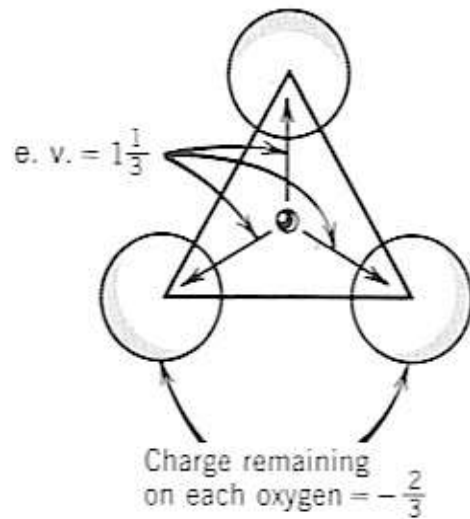
Anisodesmic Bonds results from high valence cations with electrostatic valencies greater than half the valency of the polyhedral anions; other bonds with those anions will be relatively weaker.

Mesodesmic: anion-cation bond takes exactly half othe available anion-cation charge

Triangular (CO_3)²⁻ group

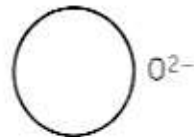
C. N. = 3; e. v. = $\frac{4}{3} = 1\frac{1}{3}$

Carbonate



(a)

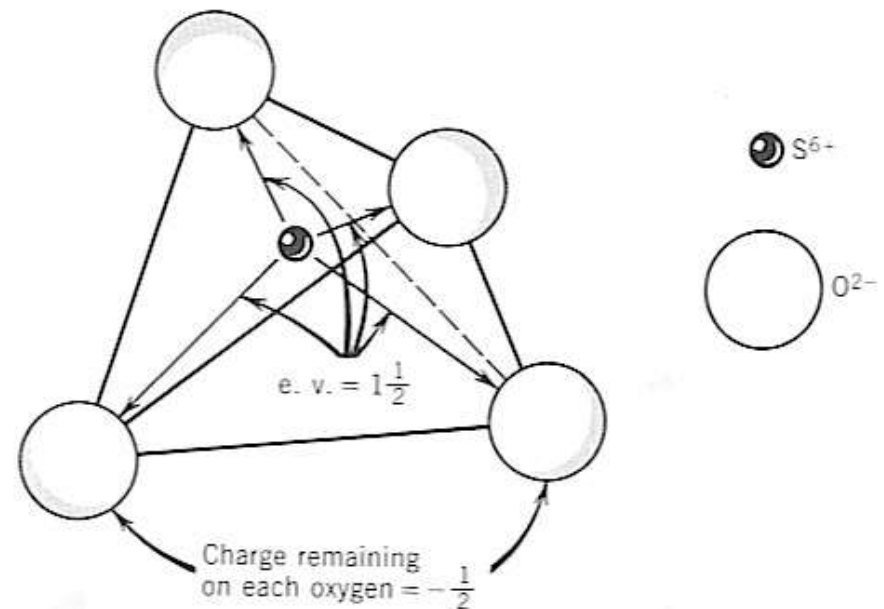
C^{4+}



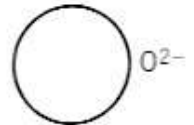
Tetrahedral (SO_4)²⁻ group

C. N. = 4; e. v. = $\frac{6}{4} = 1\frac{1}{2}$

Sulfate



S^{6+}



Anisodesmic

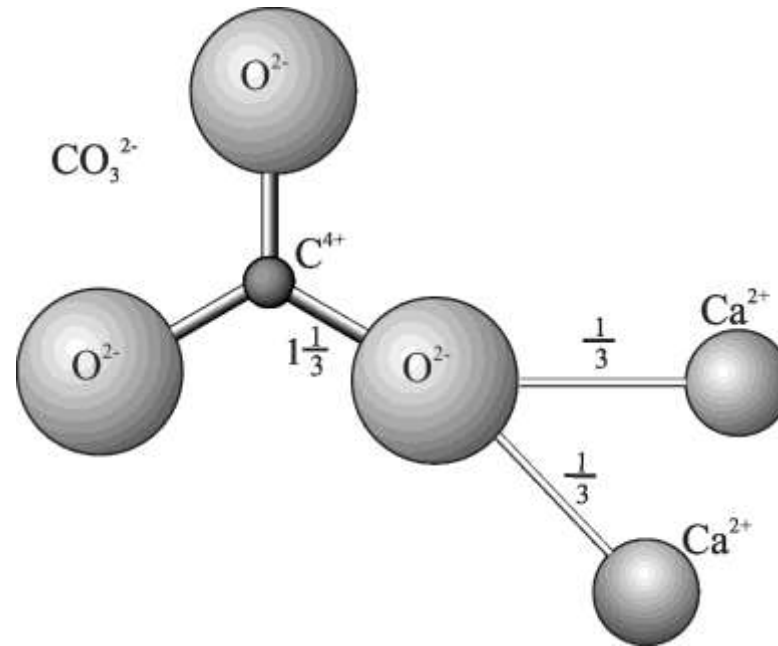


Figure 4.5 Anisodesmic carbonate (CO_3^{2-}) group. Each O–C bond occupies 1.33 of the available -2 charge on oxygen; only two-thirds of a charge on the oxygen is available to bond with other cations such as Ca^{2+} .

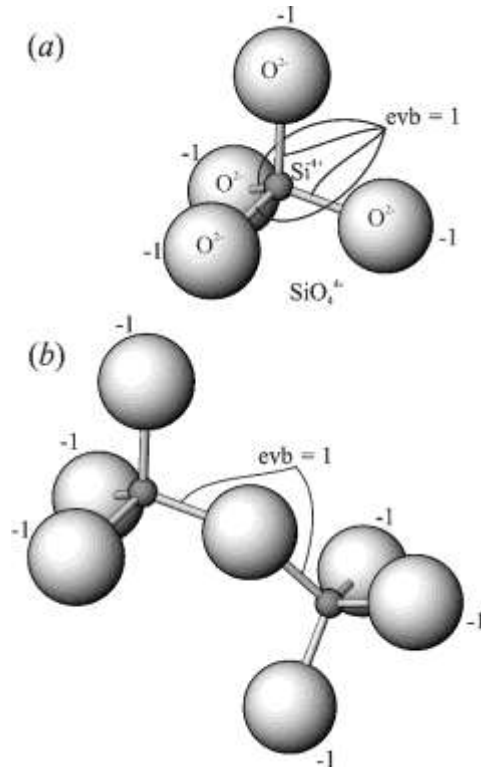


Figure 4.6 Mesodesmic silicon tetrahedra.

Pauling's Rules of Mineral Structure

- **Rule 3:** Anion polyhedra that share edges or faces decrease their stability due to bringing cations closer together; especially significant for high valency cations
- **Rule 4:** In structures with different types of cations, those cations with high valency and small CN tend not to share polyhedra with each other; when they do, polyhedra are deformed to accommodate cation repulsion

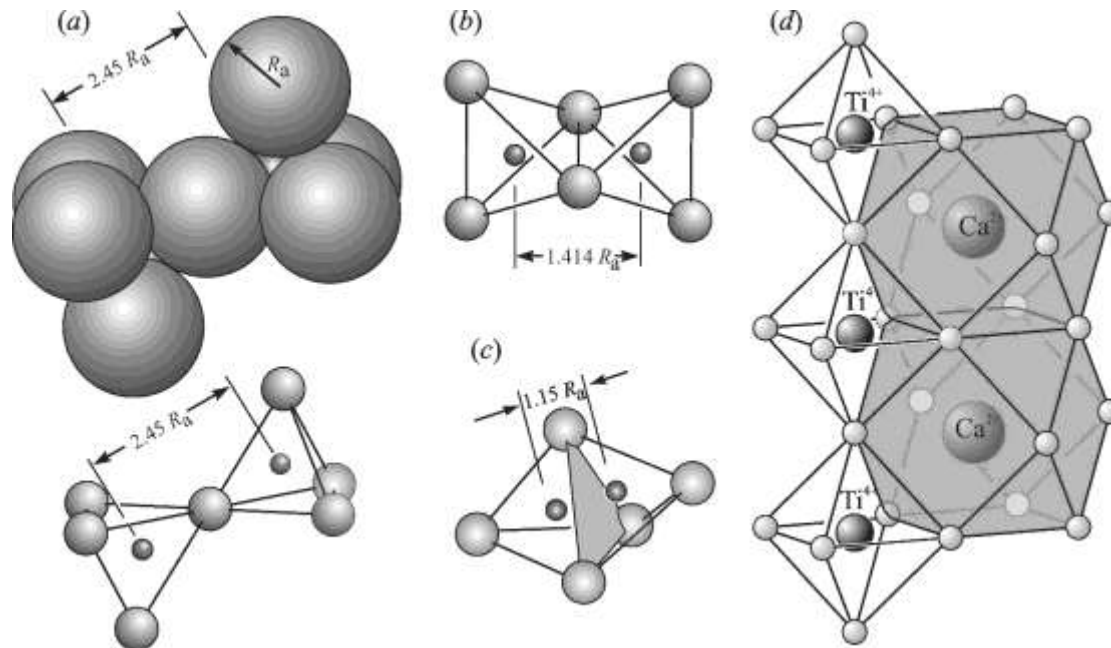


Figure 4.7 Sharing anions between polyhedra.

Pauling's Rules of Mineral Structure

- **Rule 5:** The principle of parsimony : nature tends towards simplicity

Because the number and types of different structural sites tends to be limited, even in complex minerals, different ionic elements are forced to occupy the same structural positions – leads to solid solution.

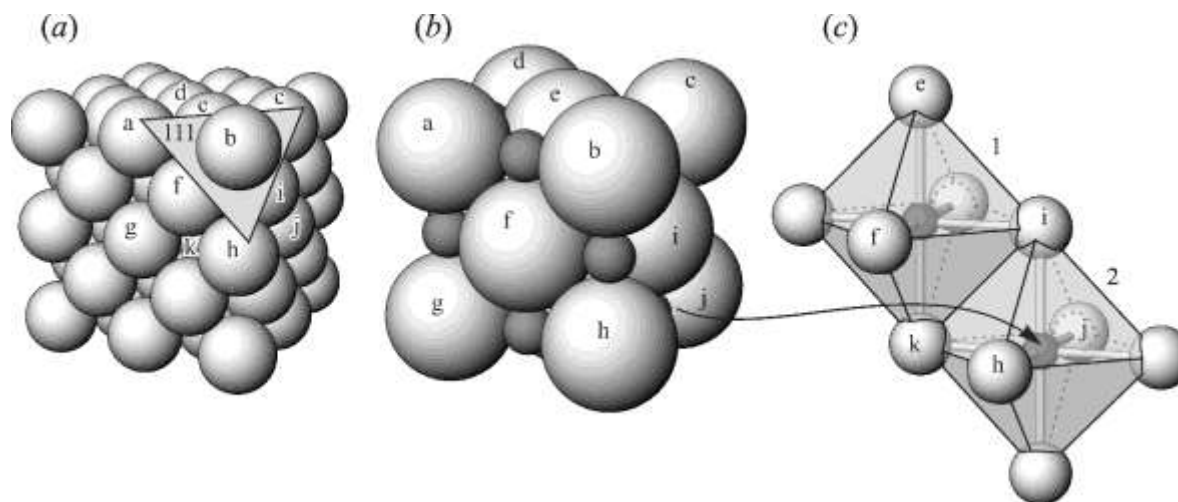


Figure 4.8 NaCl structure.

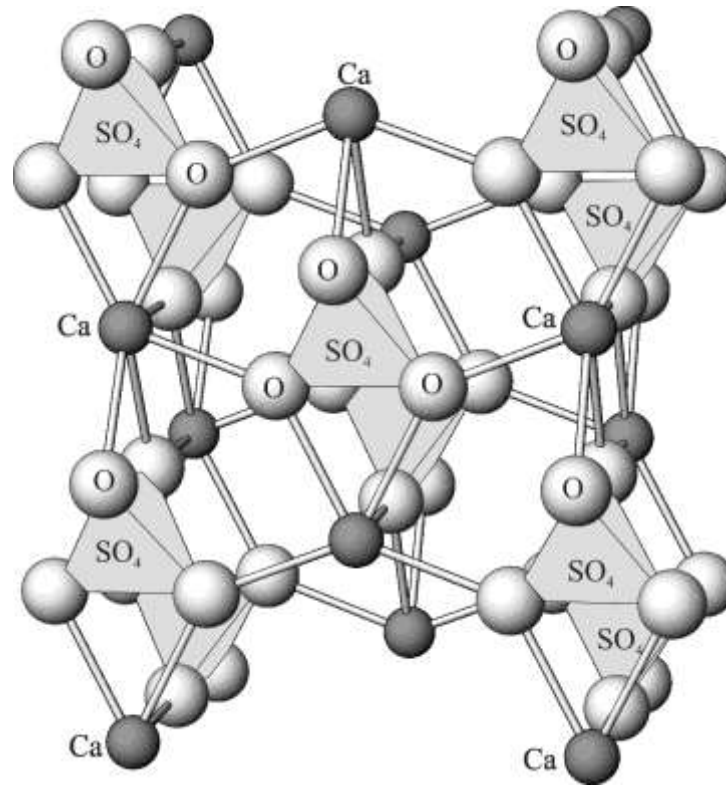
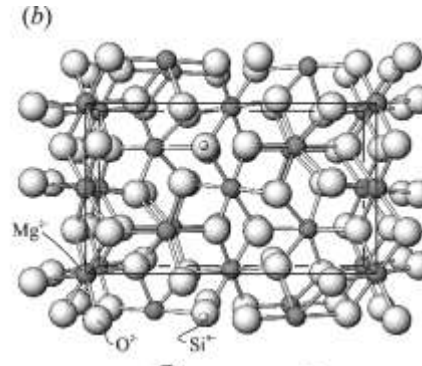
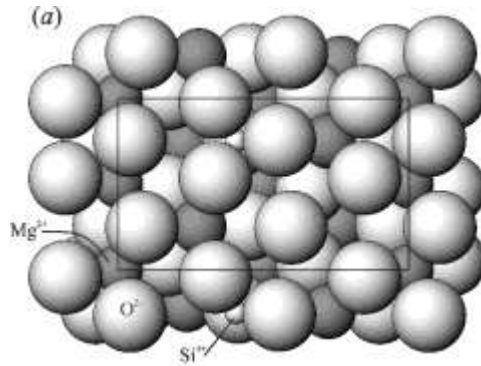


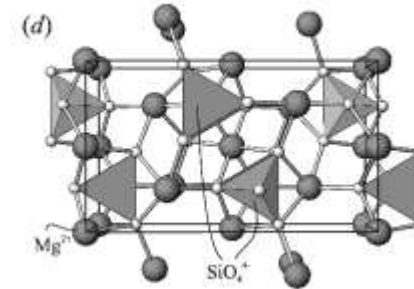
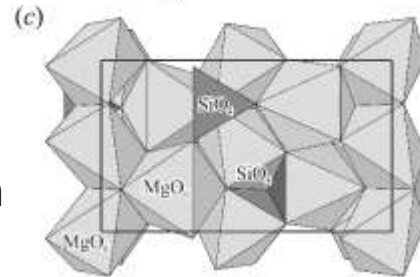
Figure 4.9 Anhydrite structure. Isolated SO_4^{2-} groups are bonded laterally through Ca^{2+} (dark spheres).

Sphere to scale:
First layer
obscures whatever
is behind



Stick and ball

Polyhedra: only
coordinate
polyhedral are shown



Hybrid: polyhedral
and stick and ball:
anions are omitted

Mapped: Position of each atom
is projected from a axis to the
back wall of the unit cell.
Numbers denote % distance
away from the back wall of the
unit cell.

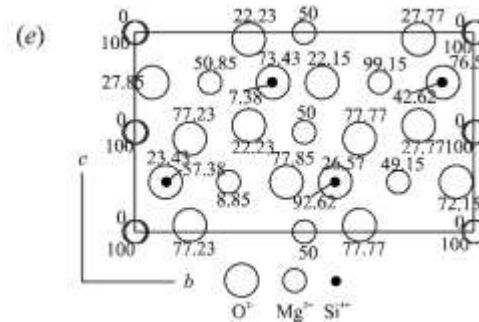


Figure 4.10 Illustration of olivine (Mg_2SiO_4) crystal structure viewed down the a axis. Each unit cell (outlined) contains four formula units.

Isostructural Minerals, Polymorphism

- Two minerals showing same type of crystal structure are called **isostructural**: e.g., carbonate group: calcite, magnesite, siderite etc or halite (NaCl) and galena (PbS)
- Same chemical compound with different crystalline structure or different minerals with the same chemical formula are called **polymorphs**. The phenomenon is Polymorphism and the collection of minerals of the same formula is called a polymorphic group.
e.g., (diamond and graphite), (Kyanite, Andalusite, Sillimanite) (see Table 4.4)
- One of the polymorphs is stable under a particular P,T condition, Generally higher P favors denser, more close packing
- Four types of Polymorphism:
 - Reconstructive,
 - Displacive
 - Order-disorder
 - Polytypism

Reconstructive

Polymorphism: Old bond is broken and new ions are reassembled in new bonds

Example: Diamond and Graphite

Polymorphs do not convert from one to the other form

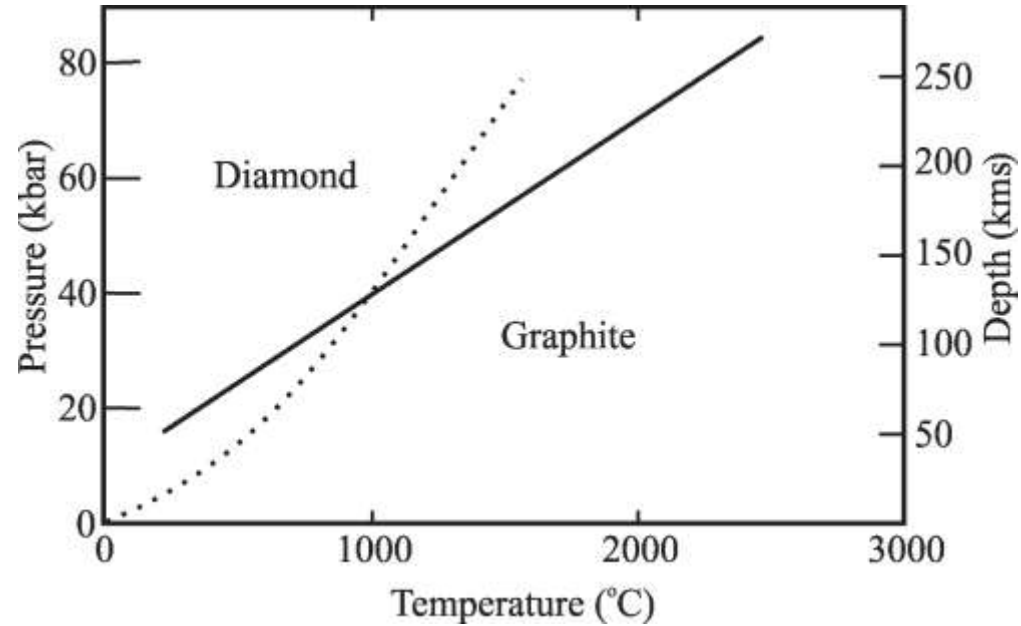


Figure 4.11 Diamond and graphite stability fields.

Displacive Polymorphism: No breaking of structure – involves only bending or distortion of crystal structure

Example: α - quartz and β -quartz (high quartz) : automatic unquenchable conversion takes place at 573 C

- High T forms have higher symmetry
- Crystal form of High T form is retained on conversion but low T forms show signs of internal strain

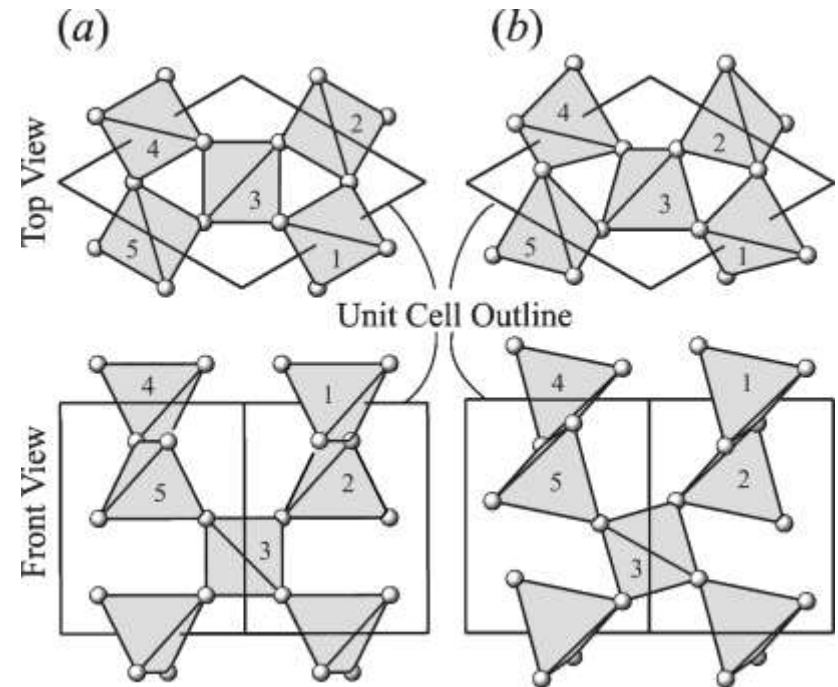


Figure 4.12 Structures of α -quartz and β -quartz. The top view looks down the c axis, the bottom view is from the side. The unit cell is outlined.

Order-disorder Polymorphism: mineral structure and composition remains the same – only the cation distribution within structural sites change.

Ex; K-Feldspars (KAlSi_3O_8): Contains 1 Al for every 3 Si ions.

- In a disordered state, Al can be found in any one of the four tetrahedral sites (High-Sanidine),
- In a maximum ordered state (low or maximum microcline), Al is found only in one of the Tetrahedral sites, the other three always occupied by Si
- High T favors more disordered state
- Rapid cooling prevents ordering hence Sanidine is found only in volcanic rocks

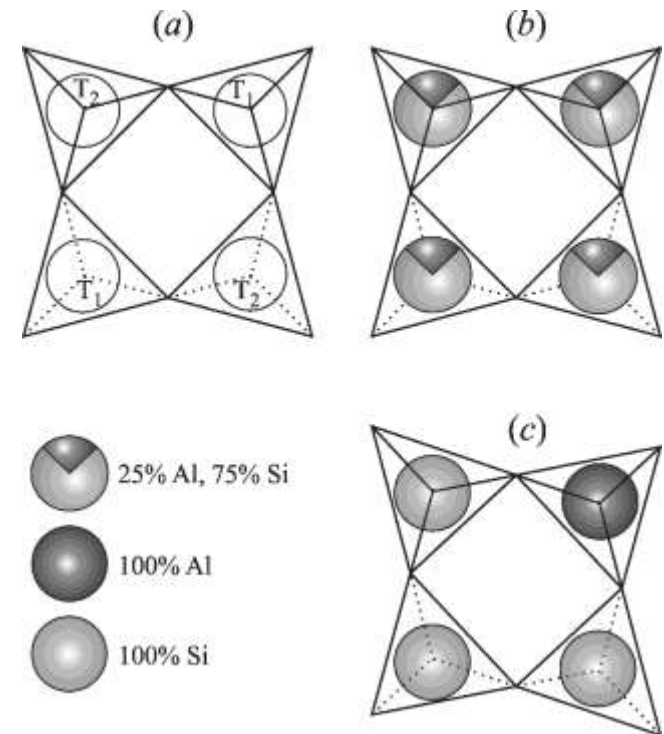


Figure 4.13 Order–disorder in K-feldspar (KAlSi_3O_8) polymorphs.

Polytypism: polymorphs differ only in stacking order. Typically seen in sheet silicates like micas or clay minerals. Also in hexagonal vs Cubic Close Packing as discussed earlier.

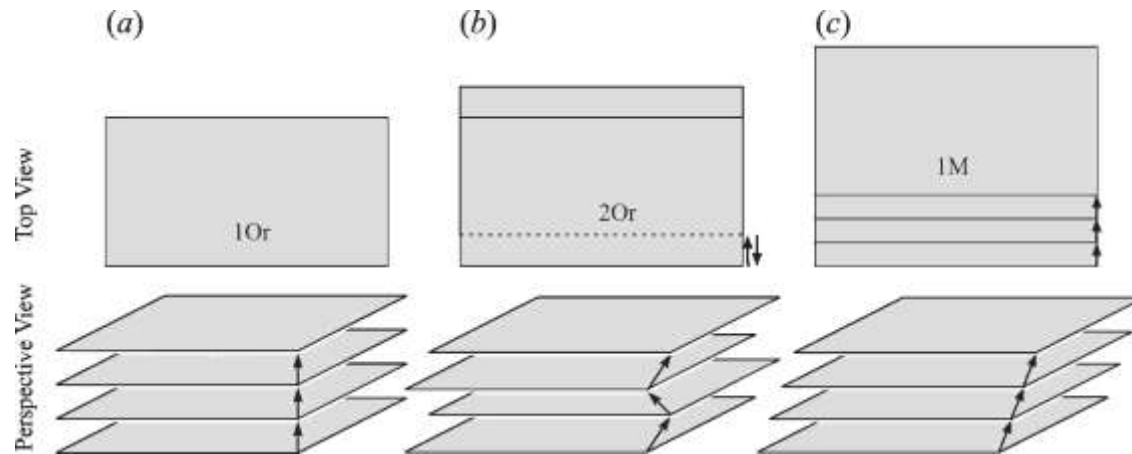


Figure 4.14 Polytypism involves different patterns of stacking identical sheets. The symbols used here are adapted from those used in the sheet silicates.

In a **Solid Solution**, one ion can substitute for the other in the same mineral structure. For example Fe and replace Mg in Olivine ($(\text{Fe},\text{Mg})_2\text{SiO}_4$) (**Simple Substitution**)

- The extreme compositions (e.g., Fe_2SiO_4 and Mg_2SiO_4) are known as **end members**.
- The range of compositions produced by solid solution is called **Solid solution or Substitution Series**.
- A series can be **complete or continuous series** where all intermediate range between the end members is possible.
- Or, **incomplete series** where only a restricted range of composition is found.
- Three types: **Substitution Solid Solution, Omission Solid Solution and Interstitial Solid Solution**
- Substitution: Ions of similar charge and size can substitute each other – usually size differing by less than 15% can substitute extensively. Elements are **Diadochic** if they can occupy the same structural site
- At higher temp more solid solution but at lower temp solid solution can unmix or exsolve.
- In a **Coupled Substitution** a double substitution takes place – one substitution increases charge so to maintain charge neutrality another substitution takes place which decreases charge. Ex: Plagioclase series – $\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$
- Ca^{2+} replaces Na^+ (similar size but different charge) – and charge balance is maintained by one Al^{3+} replacing one Si^{4+}

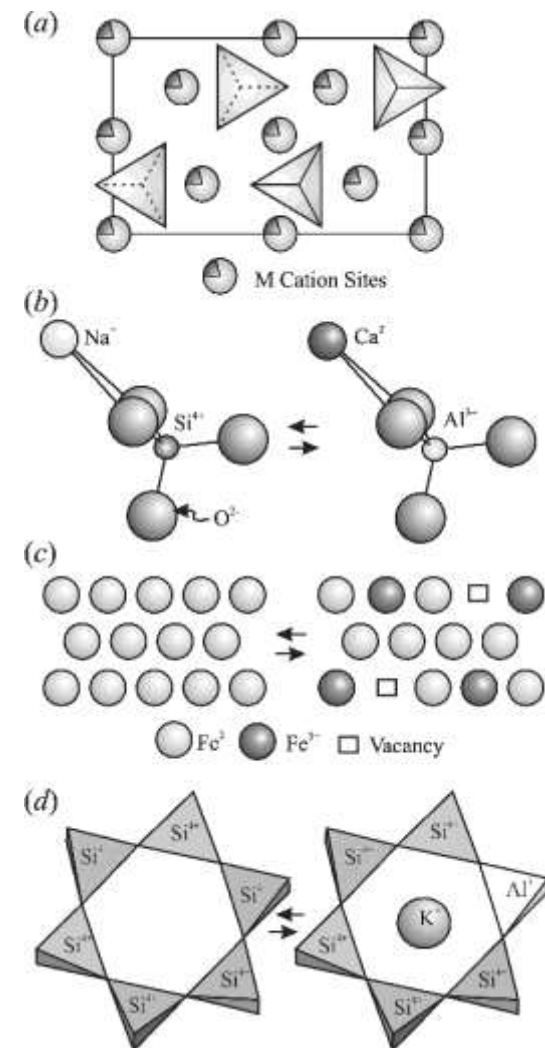


Figure 4.15 Solid solution.

- In **Omission Substitution**, charge balance is maintained by leaving some cation sites vacant.
- In Pyrrhotite (FeS) Fe^{3+} substitutes for Fe^{2+} . To maintain charge balance 3 Fe^{2+} is replaced by 2 Fe^{3+} , leaving one site vacant
- **Interstitial Substitution** is opposite of Omission substitution – extra ions are placed in normally vacant sites.
- Beryl ($\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$) is a ring silicate where ions like K^+ , Rb^+ , Cs^+ etc are placed in the central hollow and is balanced by replacing one Al^{3+} by Si^{4+}

Mineral Formula

- Cations are written first followed by anions or anionic groups
- Charges must balance
- Cations in the same structural sites are grouped together
- Cations in different structural sites are listed in the order of decreasing coordination number



Recalculation of Mineral Analyses

- Chemical analyses are usually reported in weight percent of elements or elemental oxides
- To calculate mineral formula requires transforming weight percent into atomic percent or molecular percent
- It is also useful to calculate (and plot) the proportions of end-member components of minerals with solid solution
- Spreadsheets are useful ways to calculate mineral formulas and end-member components

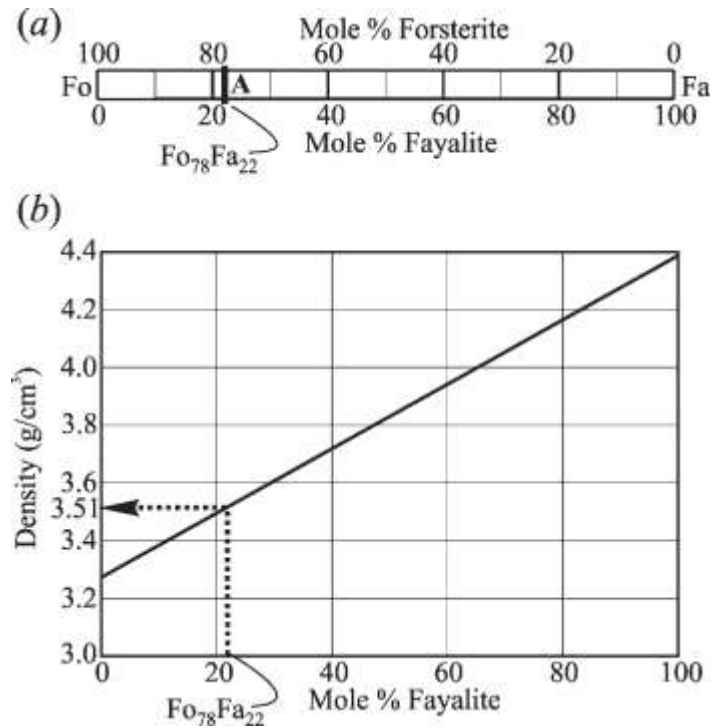


Figure 4.16 Binary diagram of olivine.

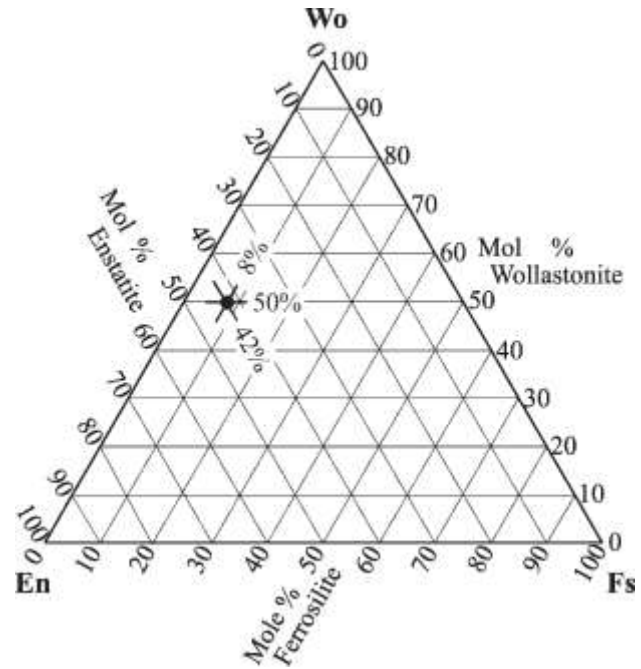


Figure 4.17 Ternary diagram of pyroxene.