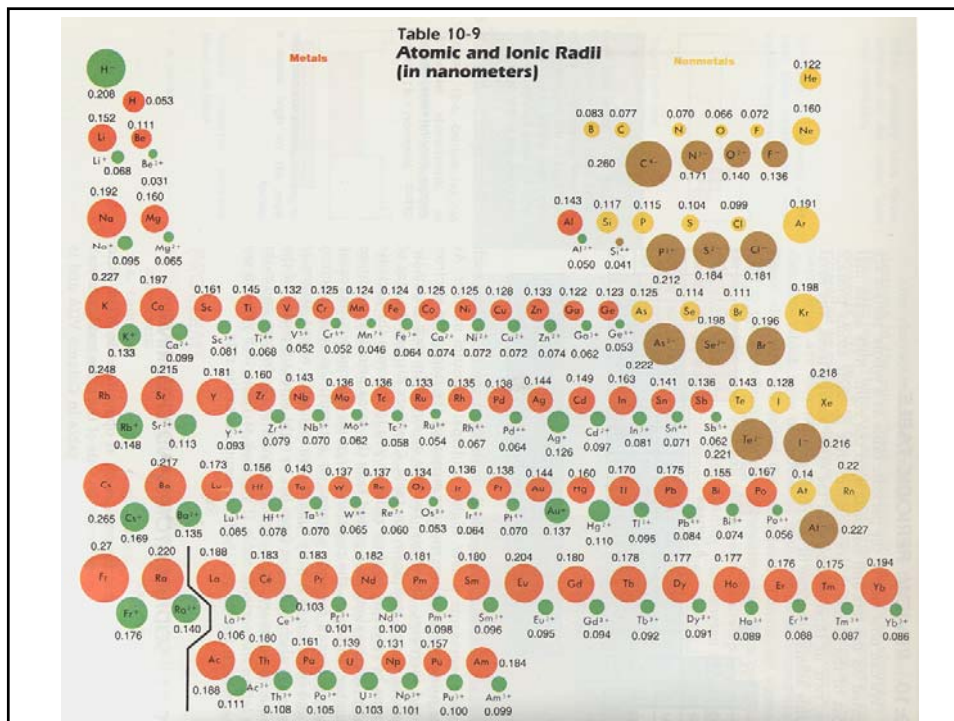# Earth and Planetary Materials

Spring 2013
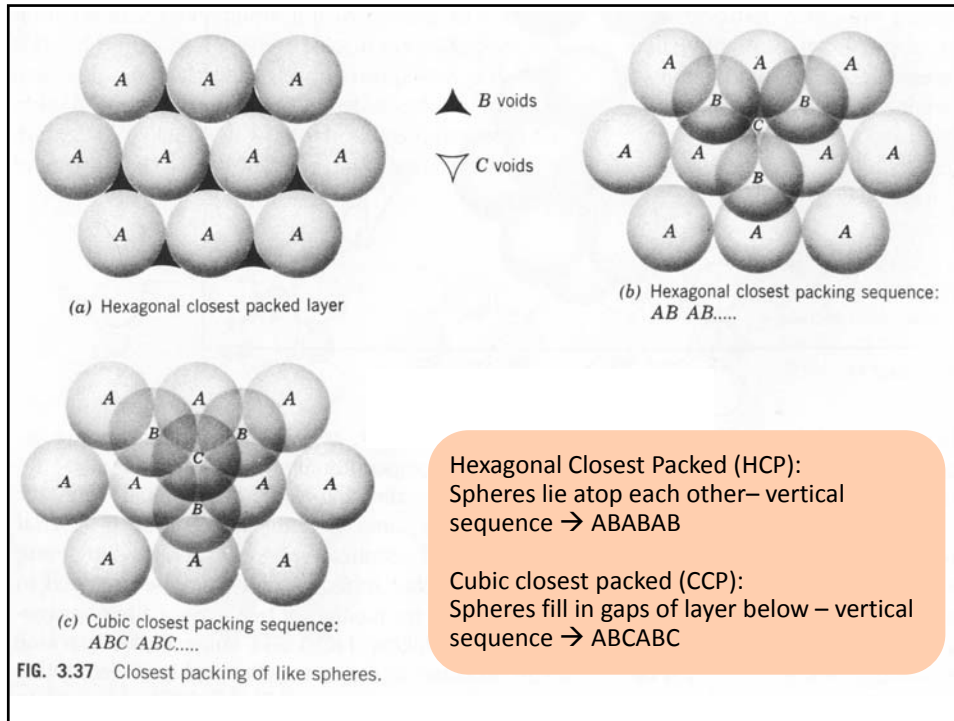
Lecture 3
2013.01.14

Close-Packed Anion Arrays

Closest Packing

- Coordination number (C.N.) : number of anions bonded to a cation → larger cation, higher C.N.
- Anions are much larger than most cations → anion arrangements in 3D = packing

(a) Hexagonal closest packed layer

(b) Hexagonal closest packing sequence: AB AB.....

B voids

C voids

(c) Cubic closest packing sequence: ABC ABC.....

FIG. 3.37 Closest packing of like spheres.

Hexagonal Closest Packed (HCP):
Spheres lie atop each other– vertical sequence → ABABAB

Cubic closest packed (CCP):
Spheres fill in gaps of layer below – vertical sequence → ABCABC

Pauling's rules

The Nobel Prize in Chemistry (1954)

"… for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"

Linus Carl Pauling
(1901 – 1994)

California Institute of Technology

Pauling's rules

- Rule 1: The coordination principle
- Rule 2: The electrostatic valency principle
- Rule 3: Sharing of polyhedral elements I
- Rule 4: Sharing of polyhedral elements II
- Rule 5: The principle of parsimony

Rule 1: The coordination Principle

- A coordinated polyhedron of anions is formed about each cation

- The cation – anion distance is determined by the sum of their radii

$$d = R_{anion} + R_{cation}$$

- The cation coordination number (CN) is determined by the radius ratio

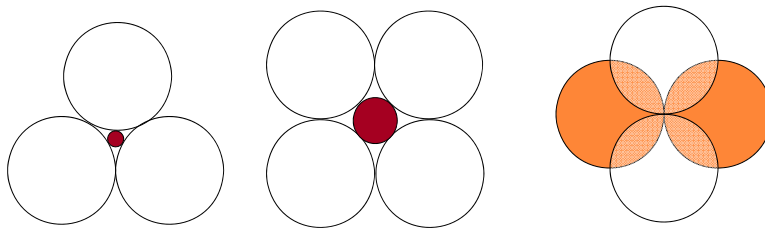$$R_{cation}/R_{anion}$$

5

C.N. calculations

- Application of pythagorean theorem:

  $$c^2 = a^2 + b^2$$

- End up with ranges of R_c/R_a values corresponding to different C.N.

- Calculation (see handout)

R_c/R_a	Expected coordination	C.N.
<0.15	2-fold coordination	2
0.15	Ideal triangular	3
0.15-0.22	Triangular	3
0.22	Ideal tetrahedral	4
0.22-0.41	Tetrahedral	4
0.41	Ideal octahedral	6
0.41-0.73	Octahedral	6
0.73	Ideal cubic	8
0.73-1.0	Cubic	8
1.0	Ideal dodecahedral	12
>1.0	dodecahedral	12

FIG. 4.11 Change in coordination from 6 to 8 in alkali chlorides as a function of increasing cation size. (a), (b), (c), and (d) have sodium chloride type structures with 6-fold coordination; (e) and (f) have cesium chloride type structures with 8-fold coordination.
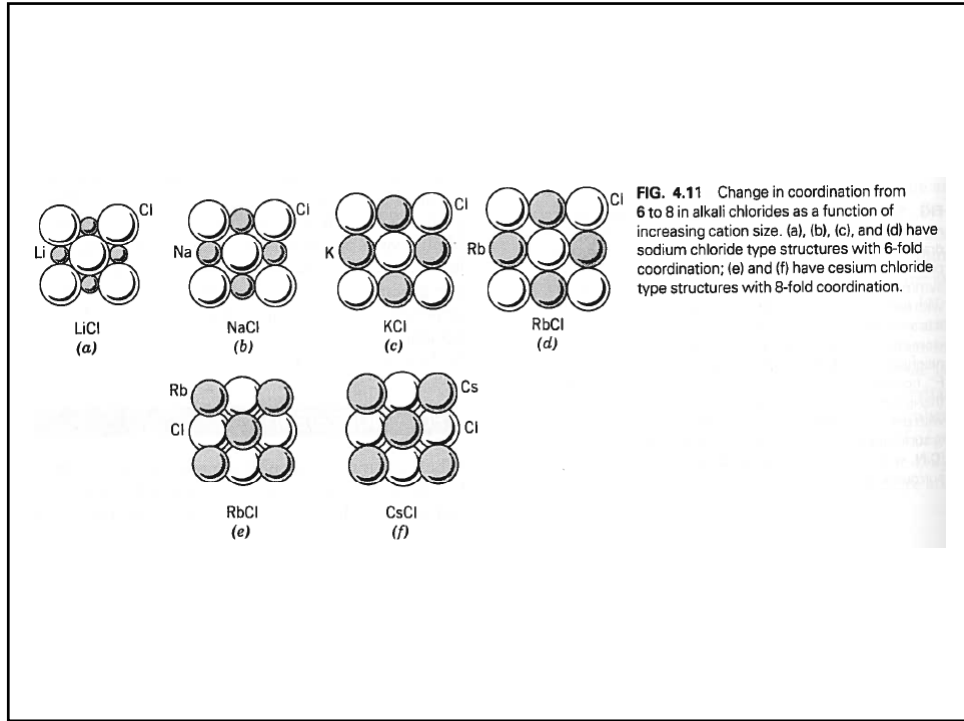
TABLE 3.12 Some Common Ions (Exclusive of Hydrogen) that Occur in Rock-Forming Minerals, Arranged in Decreasing Ionic Size

| Ion	Coordination Number with Oxygen		Ionic Radius Å
O^{2-}			1.36 [3]
K^+	8–12		1.51 [8]–1.64 [12]
Na^+	8–6	cubic to	1.18 [8]–1.02 [6]
Ca^{2+}	8–6	octahedral	1.12 [8]–1.00 [6]
Mn^{2+}	6		0.83 [6]
Fe^{2+}	6		0.78 [6]
Mg^{2+}	6	octahedral	0.72 [6]
Fe^{3+}	6		0.65 [6]
Ti^{4+}	6		0.61 [6]
Al^{3+}	6		0.54 [6]
Al^{3+}	4		0.39 [4]
Si^{4+}	4	tetrahedral	0.26 [4]
P^{5+}	4		0.17 [4]
S^{6+}	4		0.12 [4]
C^{4+}	3	triangular	−0.08 [3]

Rule 2: The electrostatic valency principle

The total strength of the valency bonds that reach an anion from all neighboring cations is equal to the charge of the anion

- Bond strength = cation valence / C.N.

- Sum of bonds to a ion = charge on that ion

- Works both ways: anion → cation; cation → anion

Example – quartz (SiO_2)

Si^{4+} O^{2-}
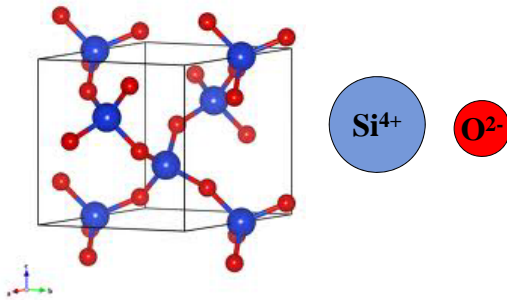
Si^{4+}:   CN = 4; Charges donated to coordinated O = (+4)/4 = +1

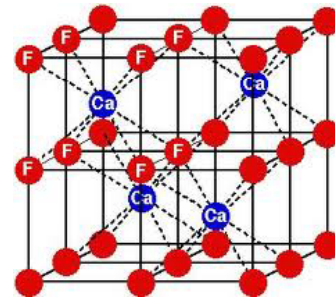O^{2-}:   CN = 2; Total valence reaching O = (+1) × 2 = +2

⇓

Charge on the O = -2
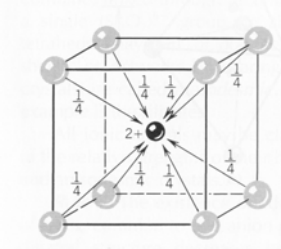
Example – Fluorite (CaF$_2$)

Ca^{2+}

- CN = 8
- Each Ca donates (+2)/8 = +1/4 to the coordinated F

F

- Each F is bonded to 4 Ca^{2+} ions
- Total valence reaching F = (+1/4) × 4 = +1
- Charge on the anion = -1

For minerals containing > 2 different ions

Relative bond strengths can be:

- Isodesmic : All bonds have same relative strength
- Example?

For minerals containing > 2 different ions

Relative bond strengths can be:

- Anisodesmic : Strength of one bond is much stronger than the others → Simplify the much stronger part to an anionic entity
- Examples: SO_4^{2-}, NO_3^-, CO_3^{2-}
- Calculations?

For minerals containing > 2 different ions

Relative bond strengths can be:

- Mesodesmic: Cation-anion bond strength = ½ charge, meaning identical bond strength available for further bonding to cation or other anion
- Example?

Mesodesmic subunit – SiO_4^{4-}

- Each Si-O bond has strength of 1

- This is ½ the charge of O^{2-}

- O^{2-} then can make an equivalent bond to cations or to another Si^{4+} (two Si^{4+} then share an O)

- Reason silicate can easily polymerize to form a number of different structural configurations (and why silicates are hard)
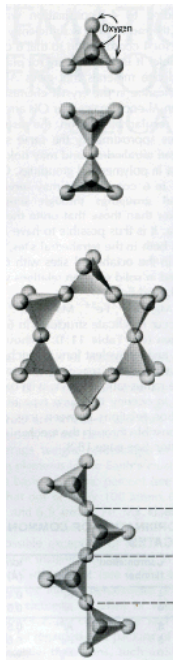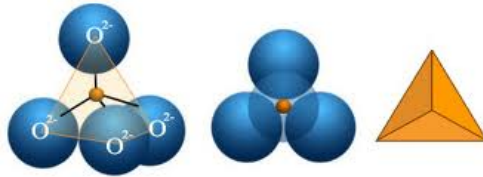
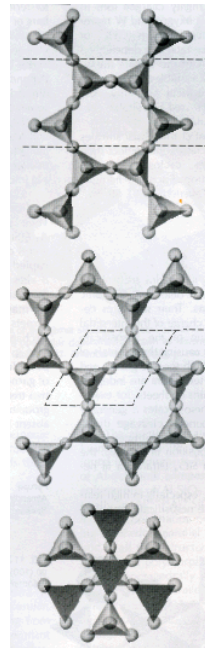

Nesosilicates
– SiO_4^{4-}

Sorosilicates
– $Si_2O_7^{6-}$

Cyclosilicates
– $Si_6O_{18}^{12-}$

Inosilicates (single)
– $Si_2O_6^{4-}$

Inosilicates (double)
– $Si_4O_{11}^{6-}$

Phyllosilicates
– $Si_2O_5^{2-}$

Tectosilicates
– SiO_2^0

Rule 3: Sharing of polyhedral elements I

- Shared edges and especially faces between two anion polyhedra decreases stability
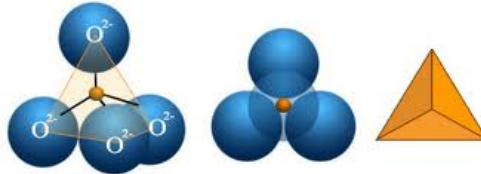
Cations like to be far apart!

- Cation-cation repulsion due to much shorter cation-cation distances with shared edges and faces

- A sample calculation: edge shared tetrahedra (looking down)
- Application?
  - M-M distance as detected experimentally → geometry

COORDINATION POLYHEDRA

Trigonal

Tetrahedral

Sharing corners

Sharing corners

Sharing edges

Octahedral

Sharing corners

Sharing edges

Cubic

Sharing corners

Sharing edges

Sharing faces
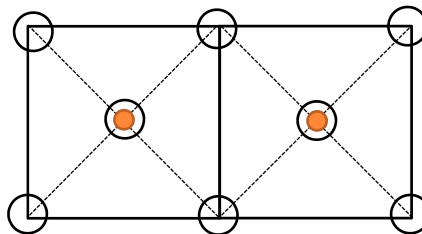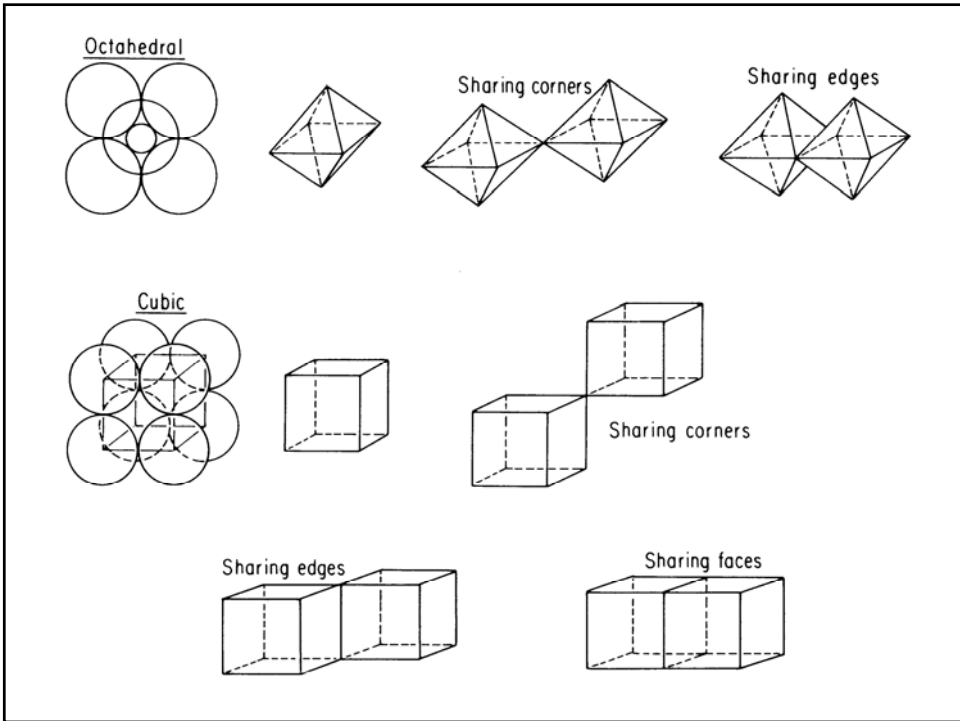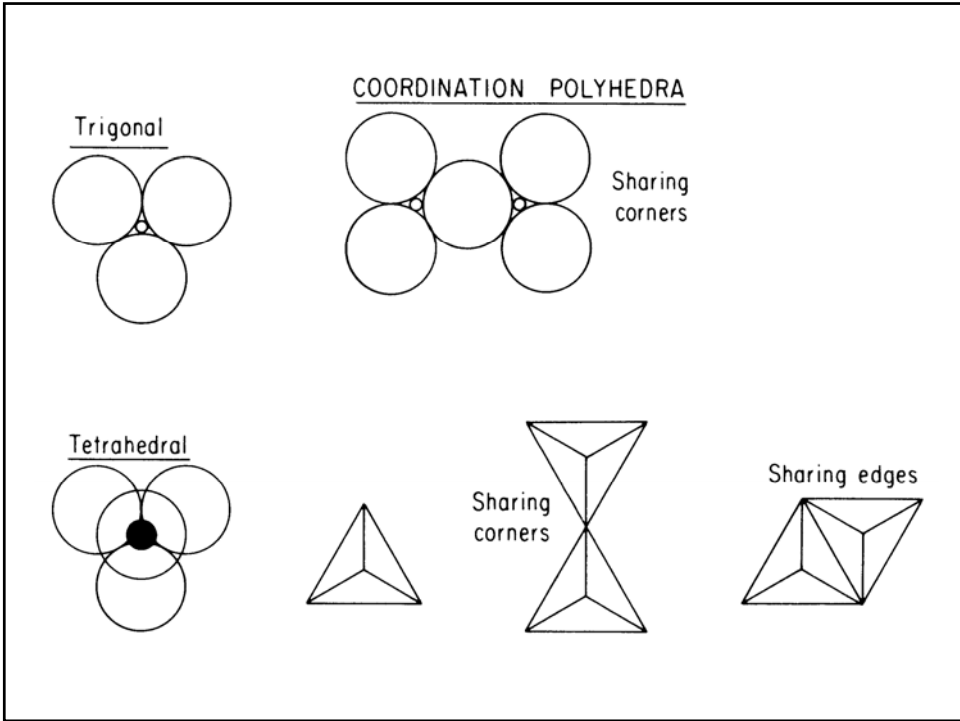
Rule 4: Sharing of polyhedral elements II

○ Really a specialization of Rule 3

○ Cations of high valence and small CN do not share anions easily with other cations due to high degree of repulsion
   • e.g. $[SiO_4]$ tetrahedra

Rule 5: The principle of Parcimony

Relatively few types of cation and anion sites

⇩

The number of essentially different kinds of constituents in a crystal tends to be small

⇩

In structures with complex chemical compositions, a number of different ions can occupy the same structural position (site)

⇩

Solid Solution

Example – Amphibole

Table 24. Amphibole analyses

	1	2	3	4	5
SiO_2	55.00	40.75	55.57	49.01	58.54
TiO_2	0.35	0.25	0.18	0.05	—
Al_2O_3	2.11	19.81	0.89	0.00	0.79
Fe_2O_3	1.59	1.22	0.06	0.00	0.22
FeO	13.45	19.29	17.48	44.99	0.37
MnO	0.25	0.25	0.45	0.37	tr.
MgO	23.97	13.81	21.85	3.17	24.45
CaO	0.97	0.27	1.29	0.31	13.59
Na_2O	0.33	1.92	0.13	0.04	0.27
K_2O	0.05	0.04	0.01	0.00	0.12
H_2O^+	1.51	2.68	2.01	1.28	2.12
H_2O^-	0.04	—	0.06	0.31	0.00
F	—	0.01	—	1.00	—
	99.62	100.38	99.98	100.63	100.47
$-O \equiv F,Cl$	—	0.00	—	0.42	—
Total	99.62	100.38	99.98	100.21	100.47

Deer, Howie and Zussman (1992) An Introduction to the Rock Forming Minerals. 2nd Edition, Prentice Hall
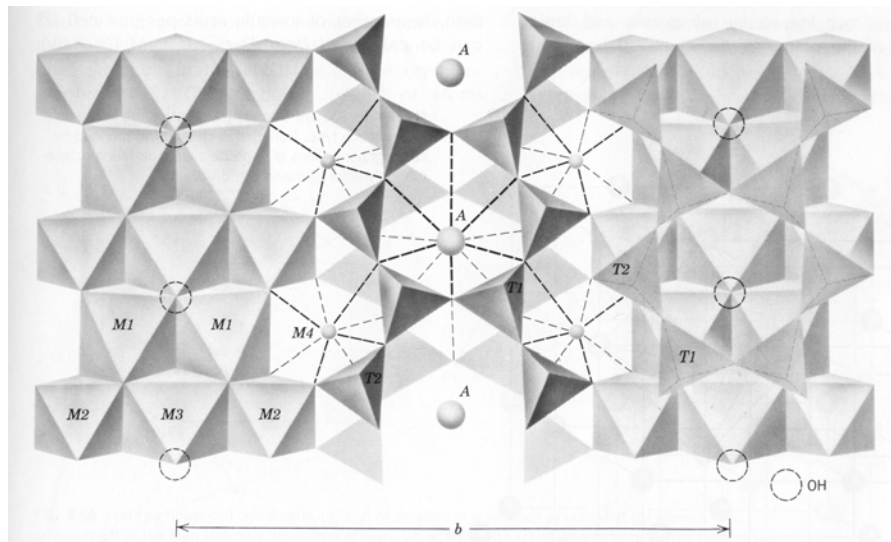
Example – Amphibole structure

Table 1-8

COMMON IONIC SUBSTITUTION PAIRS

Ion	CN	Radius (Å)	Ion	CN	Radius (Å)
Mg	VI	0.80	Fe^{2+}	VI	0.86
Al	IV	0.47	(OH⁻)	IV	0.34
F	VI	1.25	O	VI	1.32
Ba	IX	1.55	K	IX	1.63
Ge	IV	0.48	Si	IV	0.34
Ga	VI	0.70	Al	VI	0.61
Hf	VIII	0.91	Zr	VIII	0.92
Mn^{4+}	VI	0.62	Fe^{3+}	VI	0.73
Mn^{2+}	VI	0.91	Fe^{2+}	VI	0.86
La–Lu	VIII	1.26–1.05	Ca	VIII	1.20
Na	VIII	1.24	Ca	VIII	1.20

Review for Pauling's Rules

- Coordination polyhedron of anions surrounding the cation
- Local charge balance
- Shared polyhedral elements
- Dispersion of high-valence cations
- Rule of parsimony

Review for Pauling's Rules

Using "Pauling's rules" to discuss crystal structure means:

- Focusing on the cation-centered polyhedra and the shared polyhedral elements
- For a fixed anion size (e.g., oxides) the coordination number (CN) depends on the size of the cation:

  small cation → small coordination number (e.g. Si)

  large cation → large coordination number (e.g. K)
- The arrangement of cations and anions satisfies local electrostatic charge balance

Unit cell

The building block

Elements and Minerals

►FIGURE 1.3
This diagram shows the relationships between atoms; molecules, which are compounds of several atoms; unit cells made up of several molecules; a collection of unit cells, and mineral crystals.

Rock

crystal

collection of unit cells

atoms

molecule
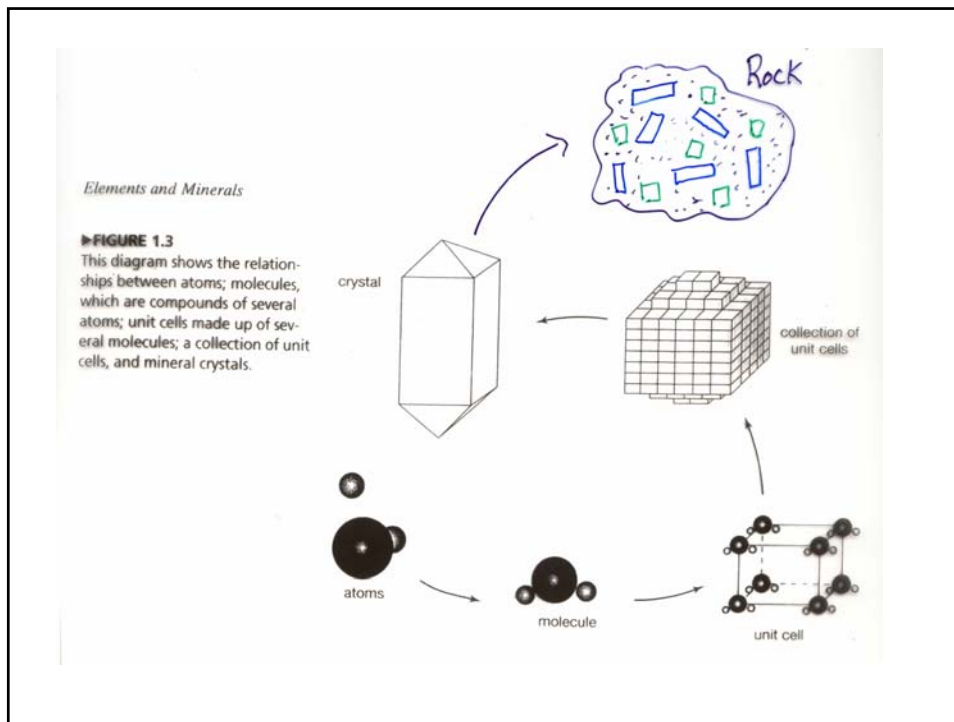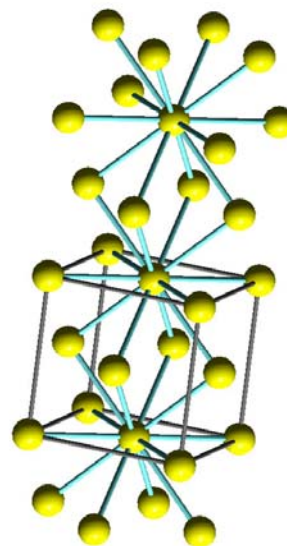
unit cell

Unit cell

- Simplifies the description of atomic arrangements in crystals

- In order to describe the atomic structure, you only need to
  1) describe the arrangement with in the unit cell
  2) state the size and shape of the unit cell

Unit cell

Definition:

Small (often, smallest) parallelopiped within the structure that...

- Contains all the types of atoms in the crystal and all the geometrical relationships among them

- Can be used to generate the entire crystal by translation of the unit cell
  a) parallel to its edges
  b) in units of one edge length

- Contains an integral number of formula units, which we will call

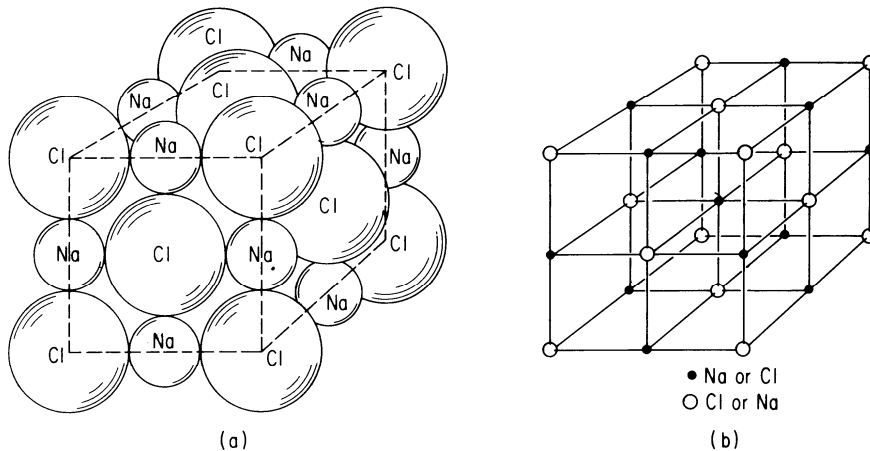$$Z = \text{the cell contents}$$

Figure 2-2 Halite structure. (a) Scale drawing of unit cell with relative sizes of ions shown. (b) Outline of unit cell showing the positions of all contained ions. Both drawings are to the same scale for the unit cell. The unit cell of halite may be shown with either the Na^+ or the Cl^- ions in the FCC positions. All ions are in octahedral coordination.

Size of the unit cell

○ Note that atoms along the outside of the unit cell are shared with adjacent cells

○ How to count the contents of the unit cell - rules are:
  - interior atoms count as 1 each
  - atoms on corners count as 1/8 (each corner shared among eight cells)
  - atoms on edges count as 1/4 (shared among four cells)
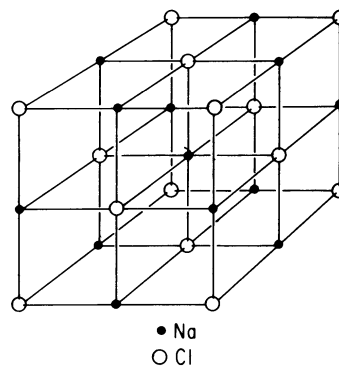 - atoms on faces count as 1/2 (shared between two cells)

Example – NaCl

count Na (filled symbols):

1 interior (in center)

12 edges * 1/4 = 3

Total = 1+ 3 = 4 Na

● Na
○ Cl

Example – NaCl

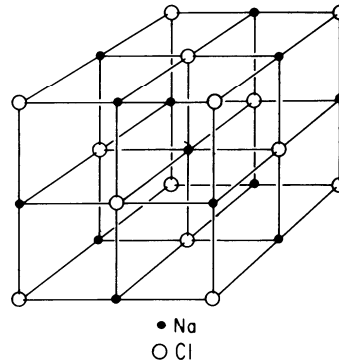count Cl (open symbols):

1 Cl on each corner
8 corners $\times$ 1/8 = 1

one Cl on each face
6 faces $\times$ 1/2 = 3

Total Cl = 1 + 3 = 4 Cl

• Na
○ Cl

So, the total cell contents corresponds to 4*(NaCl)
the cell content Z = 4; note that the cell contains an integral formula unit

---

Basic types of unit cells

○ Simple cubic
  • Atom at each corner of a cube; cell contents: Z = 1

○ Body-centered cubic (BCC)
  • additional atom at the center of the cube (Z = 2)

○ Face-centered cubic (FCC)
  • the atom that occurs at the corners also occurs at the center of each face (e.g., NaCl, Z = 4)

Figure 1-14 Primitive (PC) and body-centered cubic (BCC) structures. (a) The voids in a PC structure have a coordination number of 8. (b) The voids in a BCC structure have a coordination number of 6, but not all at equal distance.

Figure 2-1 Diamond structure. This structure is based on FCC with four additional ions in the interior of the unit cell. The numbered ions are a closest-packed layer. If the interior ions (I) were replaced by Zn^{2+} and the FCC ions by S^{2-}, this structure would be that of sphalerite (Fig. 2-4a). Dashed lines indicate unit-cell outline and solid lines indicate bond directions. Each C ion is bonded to four others.