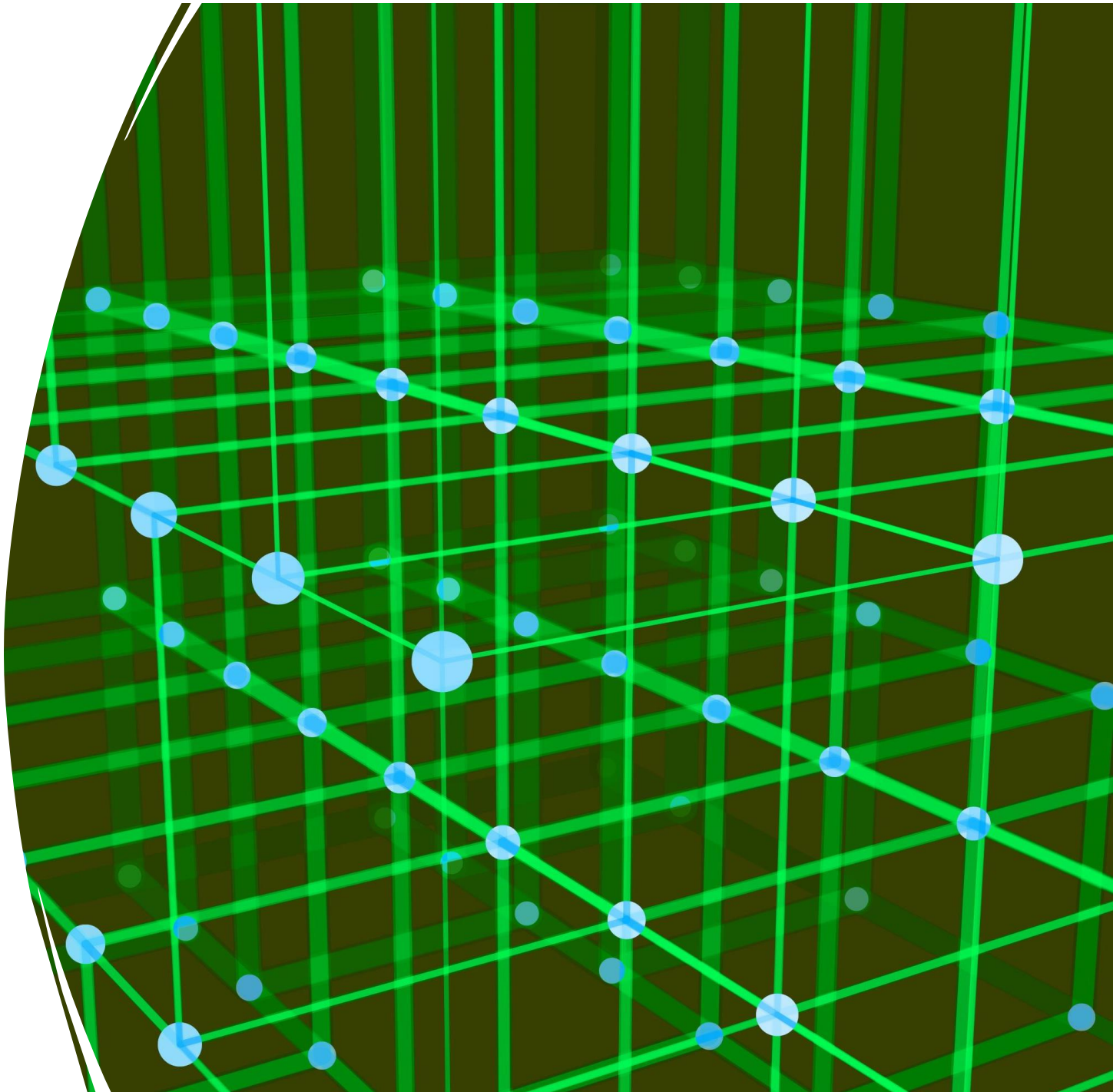
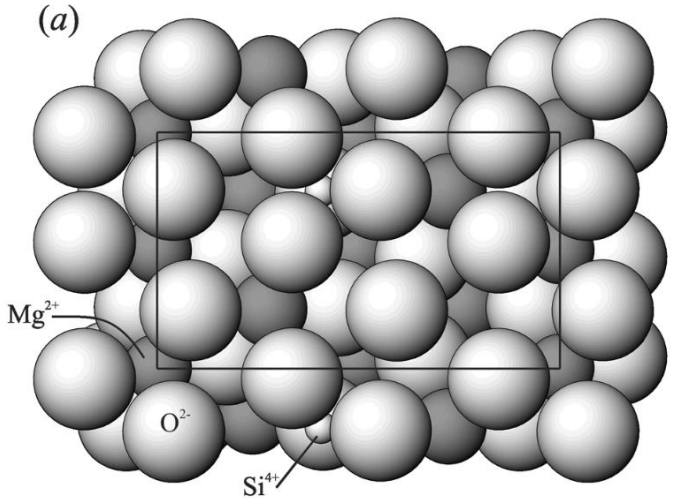
Crystal structure



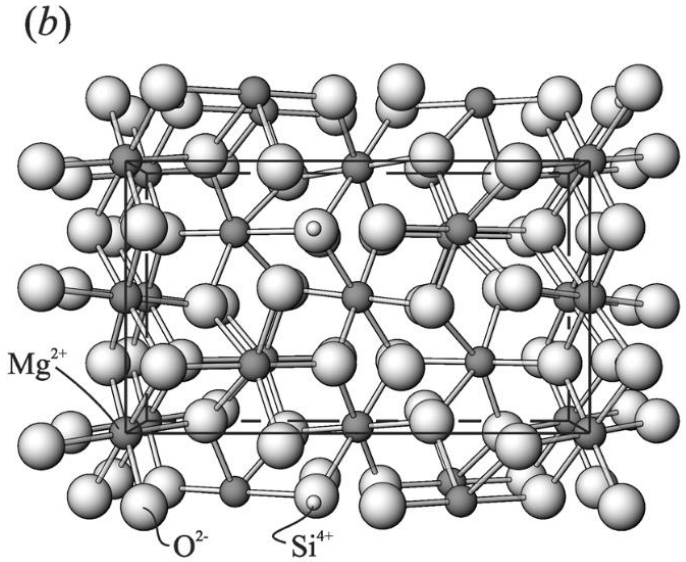
Dr. Tapabrato Sarkar

Mineral structures

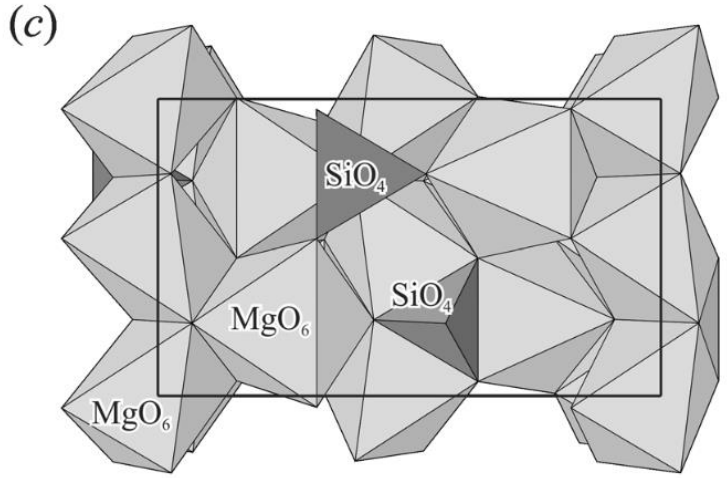
How are mineral structures illustrated?



Spheres to scale

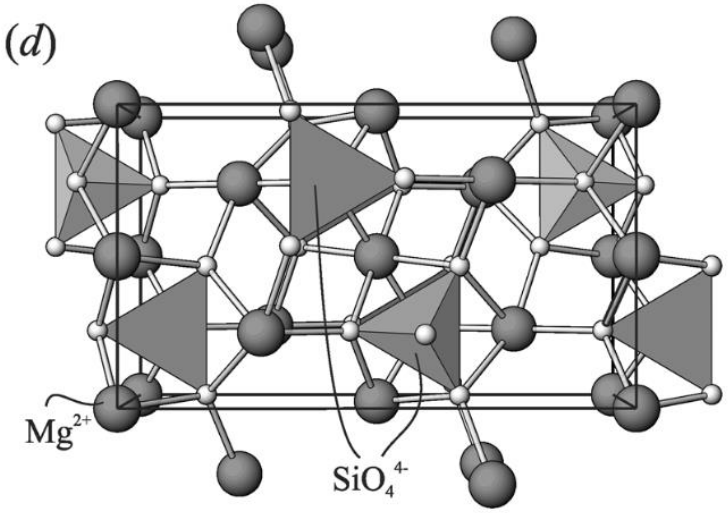


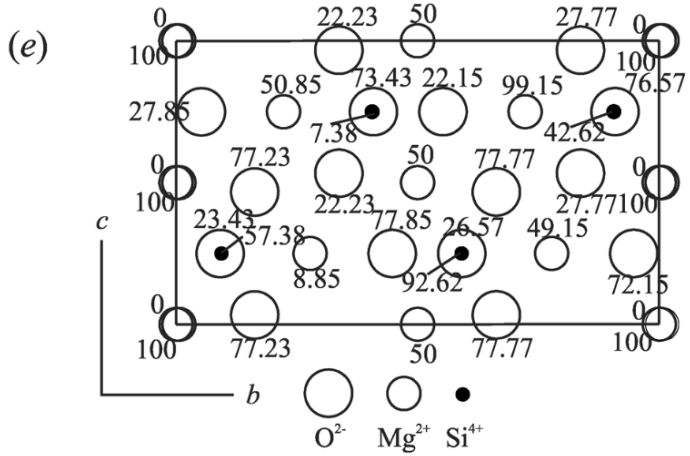
Stick-and-ball: Reduced sphere size



Polyhedral. Only the polyhedral framework is shown

Hybrid polyhedra and stick-and-ball





"Mapped" structure.

Crystal structures

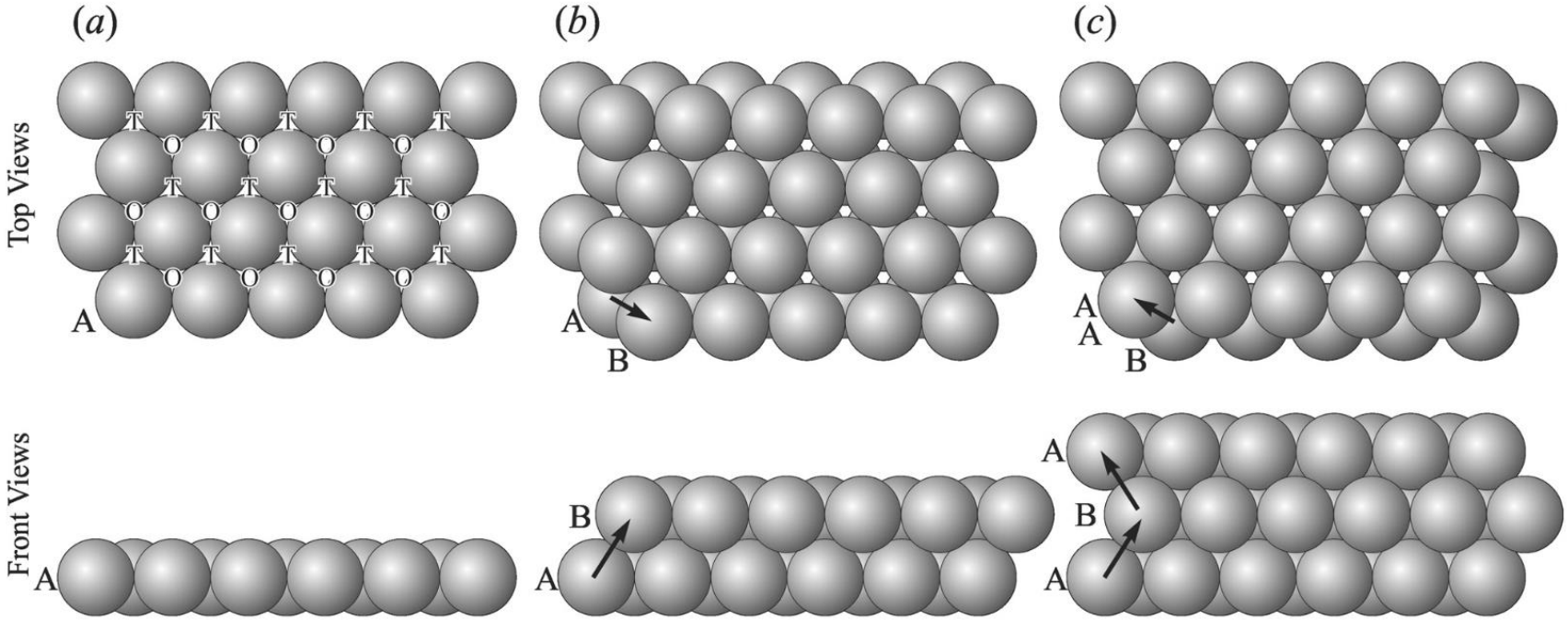
❑ Structure controls with metallic bonding

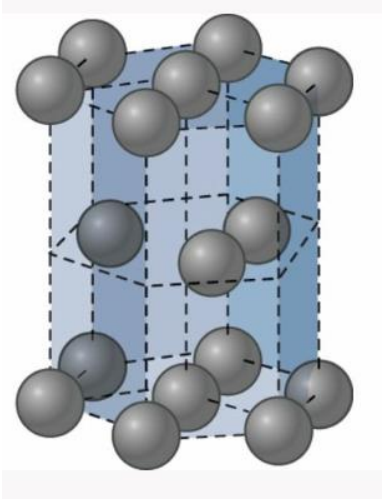
The metal atoms tend to pack together in highly ordered arrangements that minimize void space.

- **Packing of spheres:**

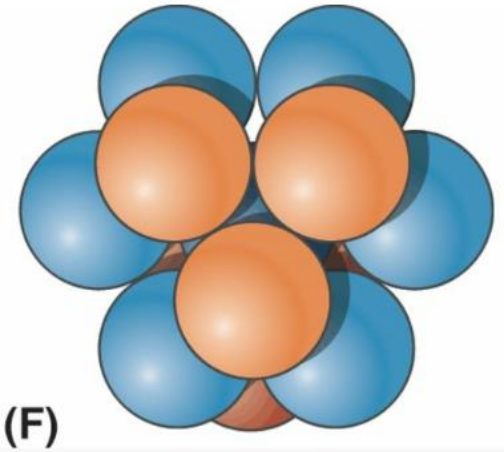
Hexagonal Closest Packing

✓ Close-packed (A) layer of spheres. Each sphere is in contact with six neighbors.
✓ The T site is surrounded by four spheres and the O sites are surrounded by six spheres.
✓ Third layer is stacked directly above the first





Hexagonal Prism



Crystal structures

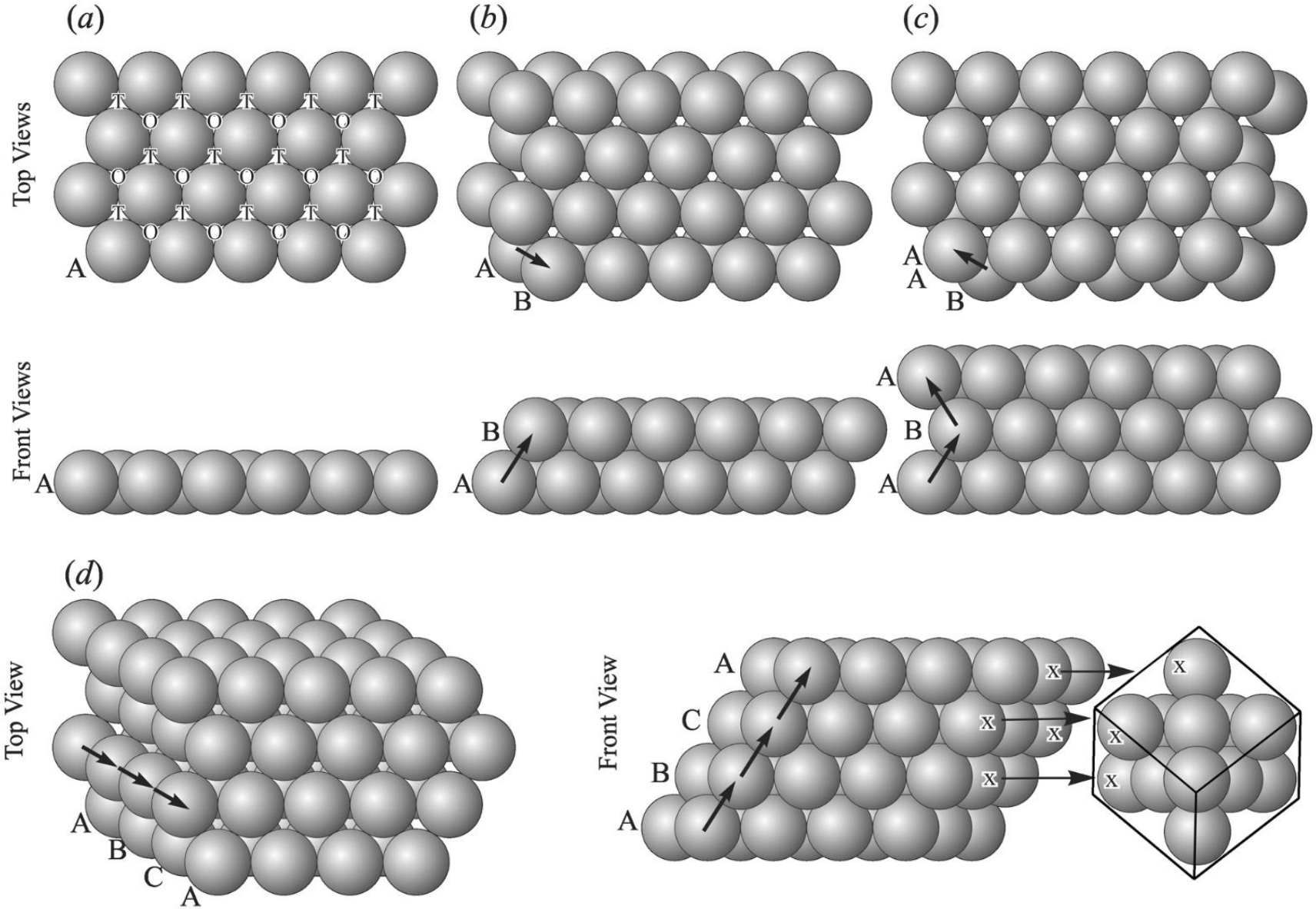
❑ Structure controls with metallic bonding

The metal atoms tend to pack together in highly ordered arrangements that minimize void space.

- **Packing of spheres:**

Cubic Closest Packing

✓ The C layer is shifted in the same direction as B, so the C spheres are directly above the O sites in the A layer



Crystal structures

❑ Structure controls with ionic bonding

(a) 12-fold coordination (based on cubic closest packing). The coordination polyhedron is not a regular shape.

R_c = Radius of cation
R_a = Radius of anion

$R_c/R_a = 1$

(b) 8-fold, or **cubic**, coordination.

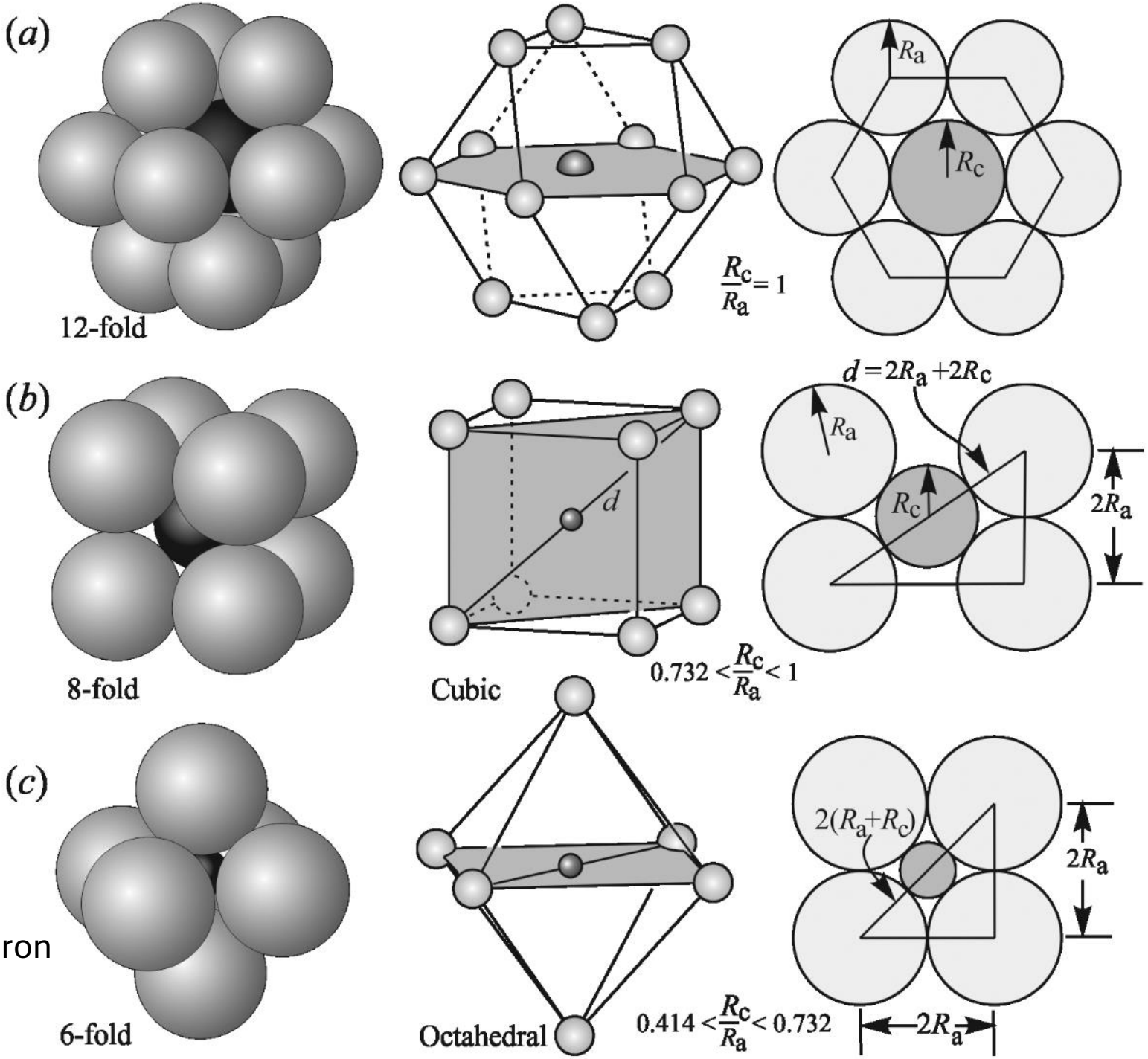
8 anions around a cation, making a cube

$R_c/R_a = 0.732 – 1$

(c) 6-fold, or **octahedral**, coordination.

6 anions around a cation, making an octahedron

$R_c/R_a = 0.414 – 0.732$



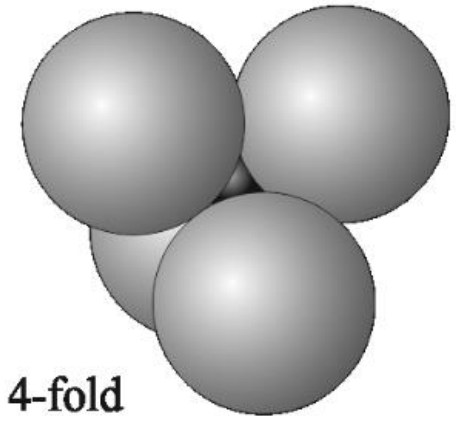
Crystal structures

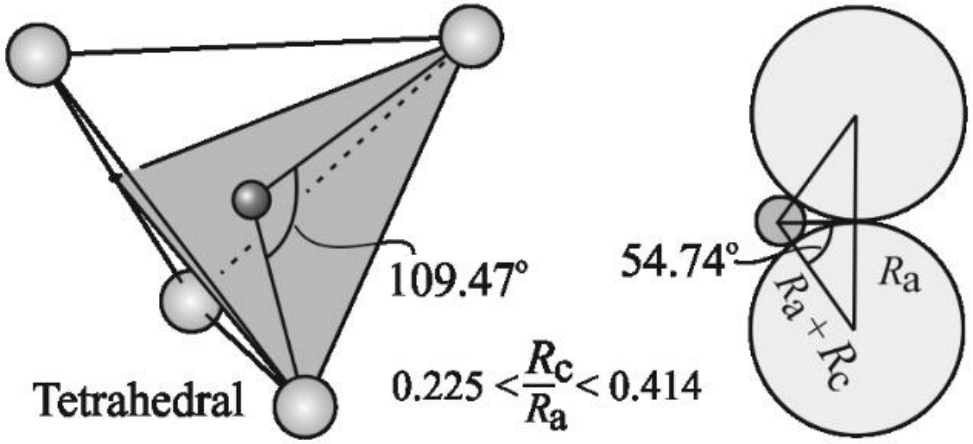
❑ Structure controls with ionic bonding

(d) 4-fold, or **tetrahedral**, coordination.

4 anions around a cation, making a tetrahedron

$R_c/R_a = 0.225 - 0.214$

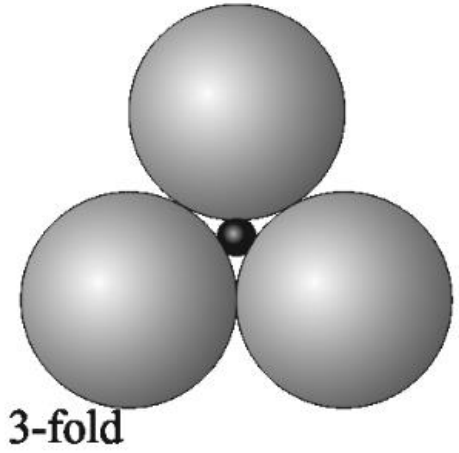


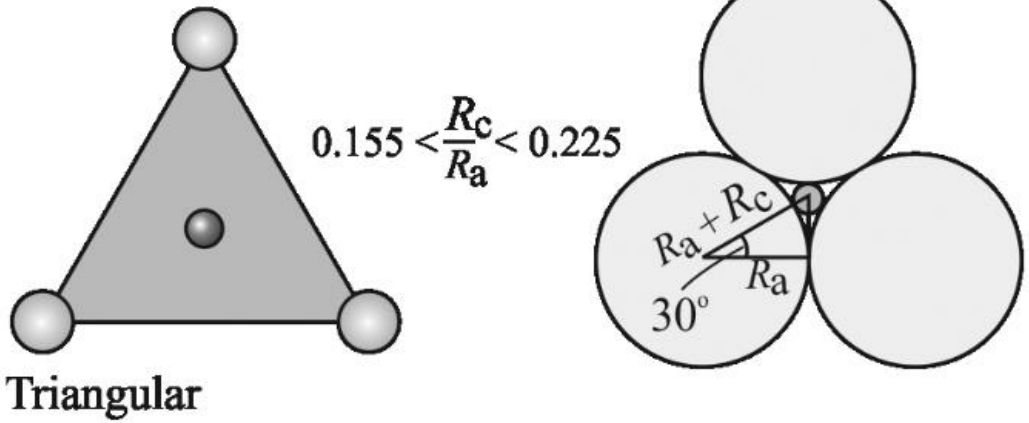


(e) 3-fold, or **triangular**, coordination.

3 anions around a cation, making a triangle

$R_c/R_a = 0.155 - 0.225$

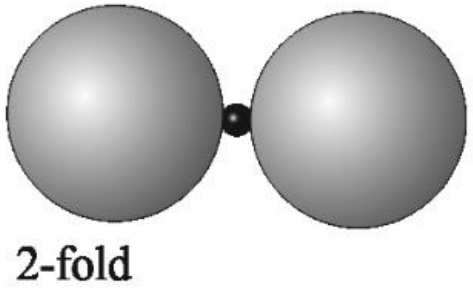


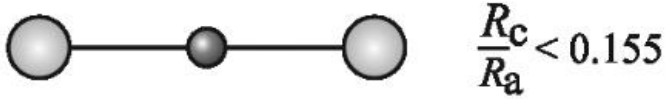


(f) 2-fold, or **linear**, coordination.

2 anions around a cation, making a line

$R_c/R_a < 0.155$



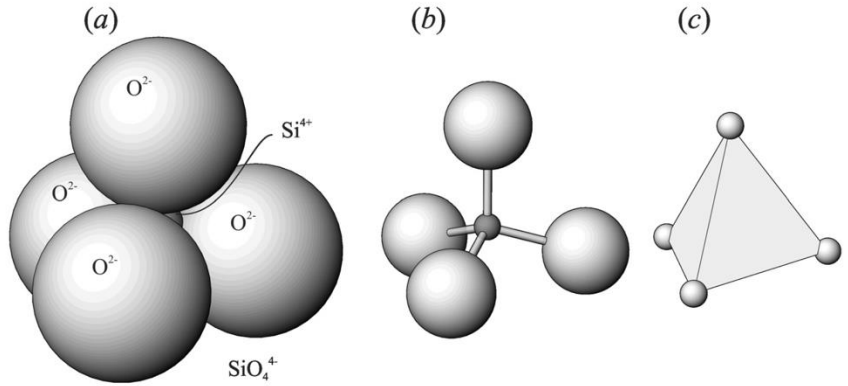


Crystal structures

- Structure controls with ionic bonding

Table 4.2 Cation Sizes Appropriate for Regular Coordination Polyhedra When Coordinating with O^{2-} (~1.26 Å)

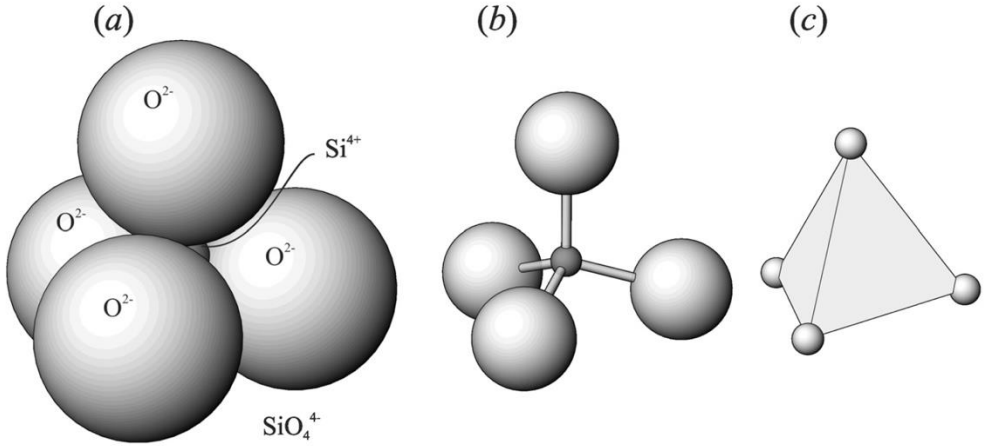
Coordination	Radius Ratio	Minimum Radius (Å)	~Maximum Radius (Å)	Common Cations
12	~1.00	1.26	N/A	K^+, Ca^{2+}, Na^+
8	0.732–1.00	0.92	1.26	Fe^{2+}, Ca^{2+}, Na^+, Mg^{2+}
6	0.414–0.732	0.52	0.92	Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}
4	0.225–0.414	0.28	0.52	Si^{4+}, Al^{3+}, S^{6+}, P^{5+}
3	0.155–0.225	0.20	0.28	C^{4+} [a]
2	<0.155	N/A	0.20	None

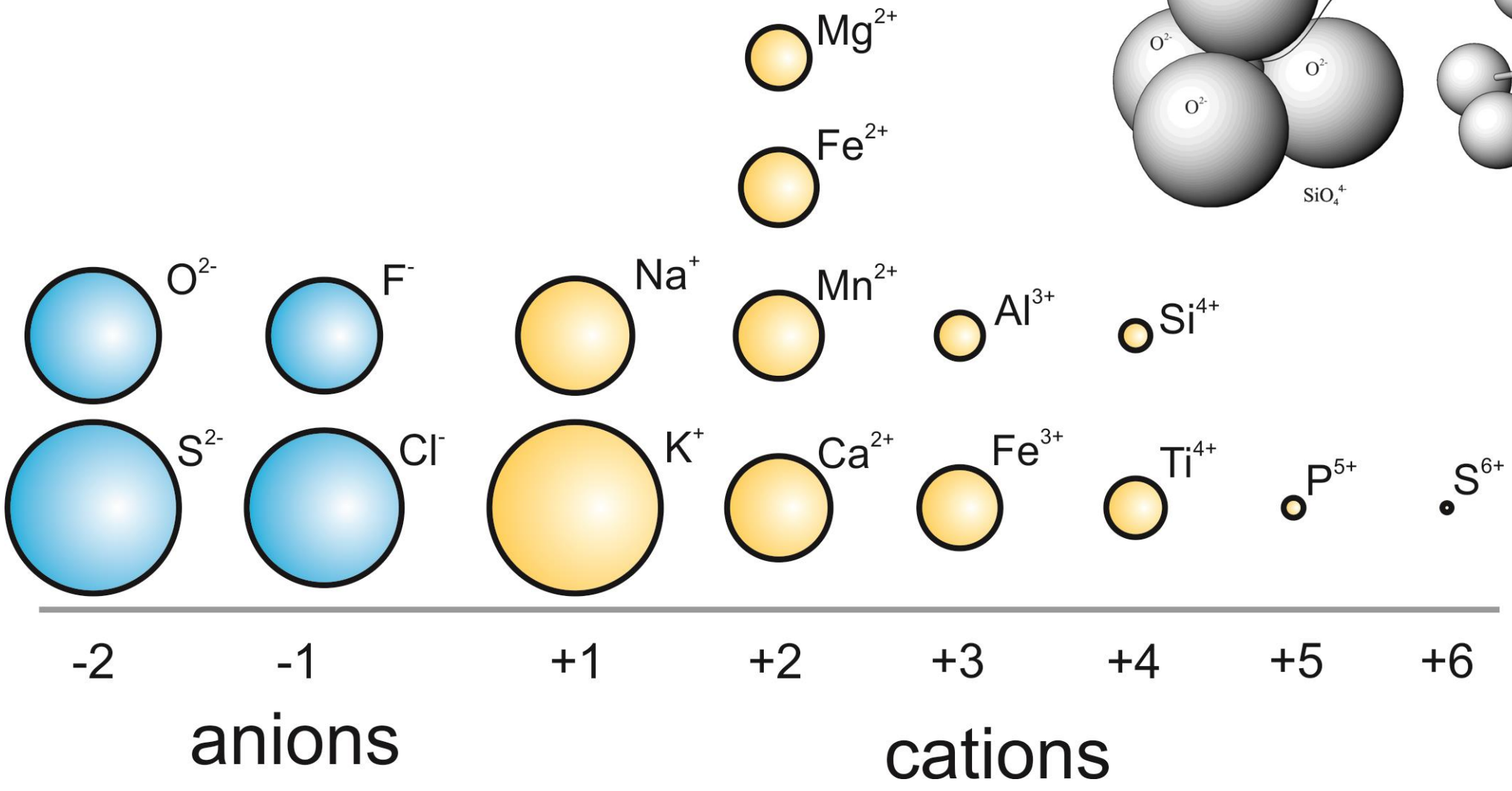


Check for effective ionic radii of elements in Appendix A (Nesse)

Crystal structures

- **Structure controls with ionic bonding**



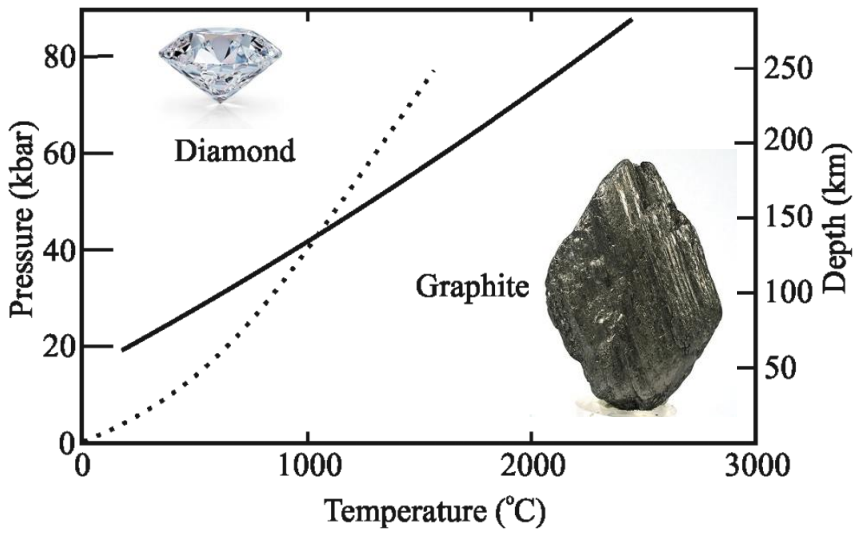


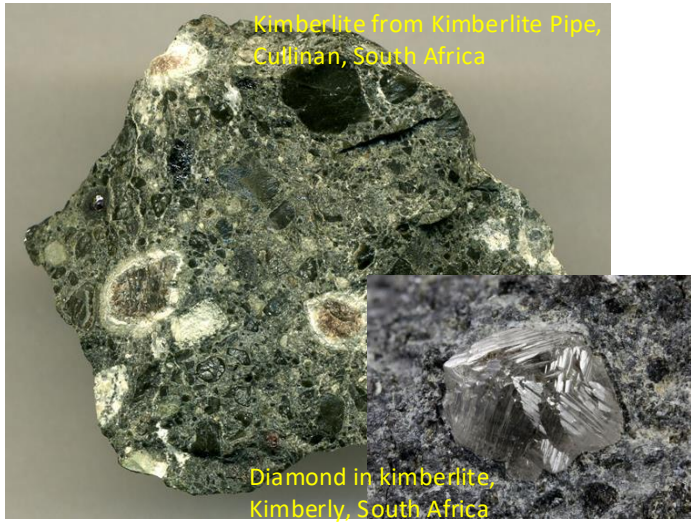
Check for effective ionic radii of elements in Appendix A (Nesse)

Structural variation in minerals

Polymorphism: The ability of a chemical compound to crystallize with more than one structure

- ✓ At a given T and P, one structure may represent the lowest energy configuration, therefore stable
- ✓ At other T and P, a different structure may be more stable.
- ✓ In general, ***high pressures*** favor tightly packed structures, reflected in higher mineral density.





- ✓ ***High temperature*** tends to favor somewhat more open, lower density structures and structures that allow greater diversity in the occupancy of specific structural sites.
- ✓ Different polymorphs of the same substance are stable under different sets of conditions
- ✓ The presence of a given polymorph in a rock may indicate the conditions under which the rock was formed or to which it has been subjected.

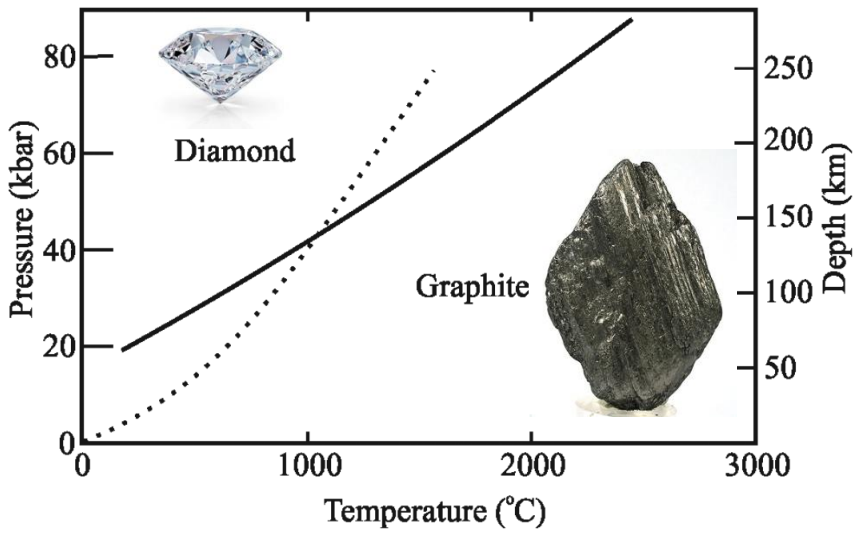
Structural variation in minerals

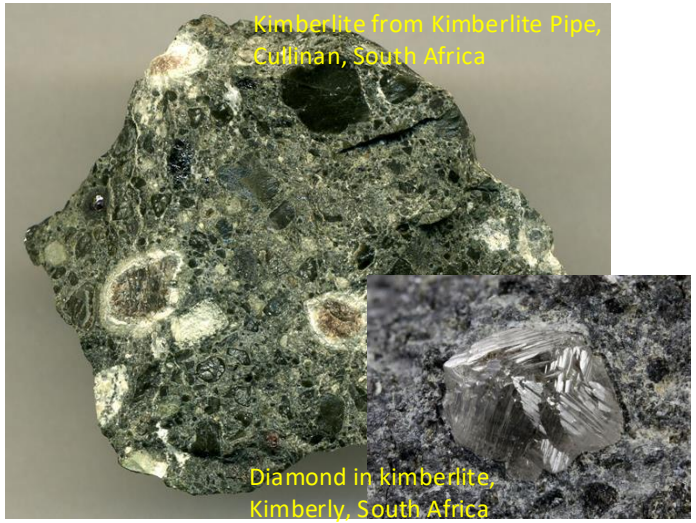
- **Reconstructive polymorphism:**

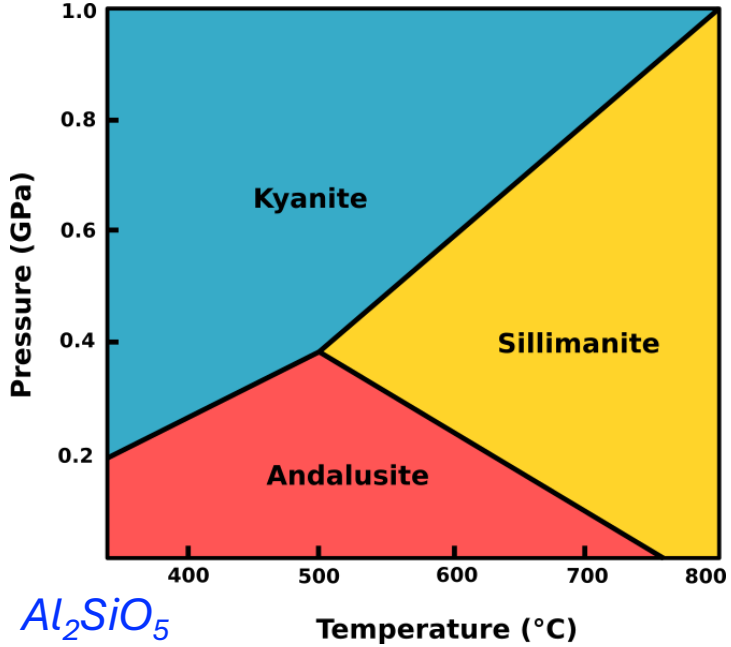
✓ Conversion from one polymorph to another involves a major reorganization of the crystal structure.

✓ The chemical bonds that hold one structure together must be ***broken*** so that the atoms/ions can be ***rearranged*** and bonded into the new structure.

✓ Usually involves a ***large change in energy*** of the structure which must occur at the transformation temperature and/or pressure.







Al_2SiO_5

Kyanite

Sillimanite

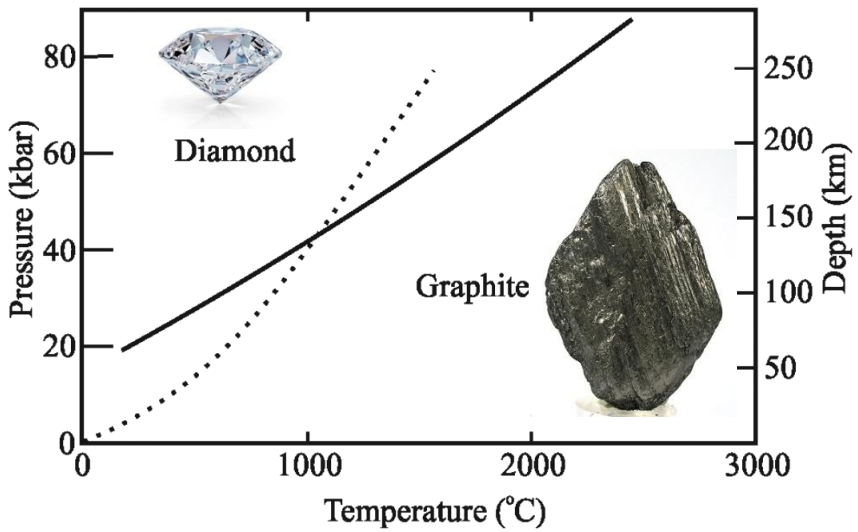
Andalusite

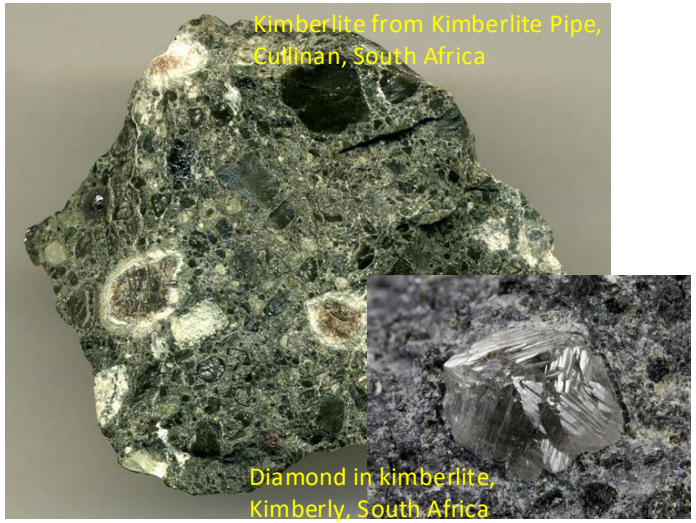
Structural variation in minerals

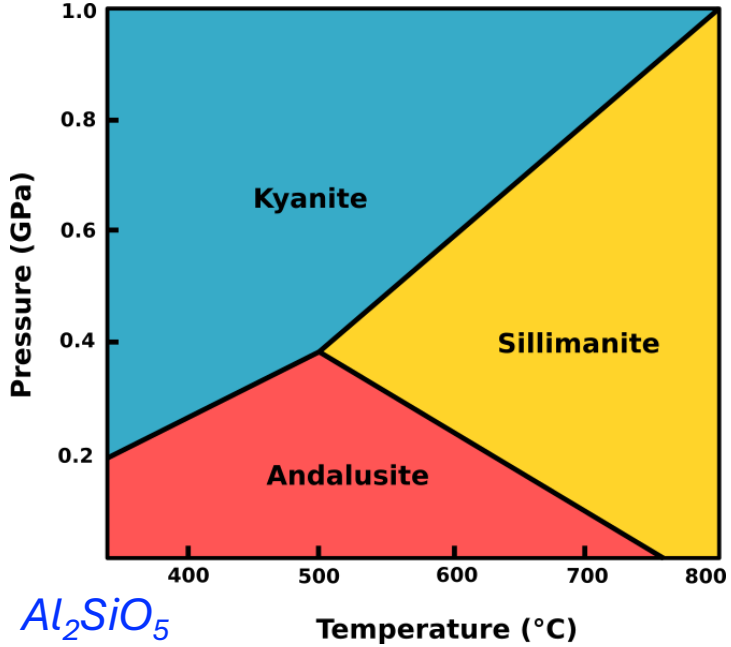
- **Reconstructive polymorphism:**

✓ Because of the extensive rearrangement involved, the rate at which this type of ***transformation*** occurs may be ***very slow***.

✓ If the rate of the transformation is very slow, ***unstable polymorphs*** (metastable) may exist for long periods of time.







Al_2SiO_5

Kyanite

Sillimanite

Andalusite

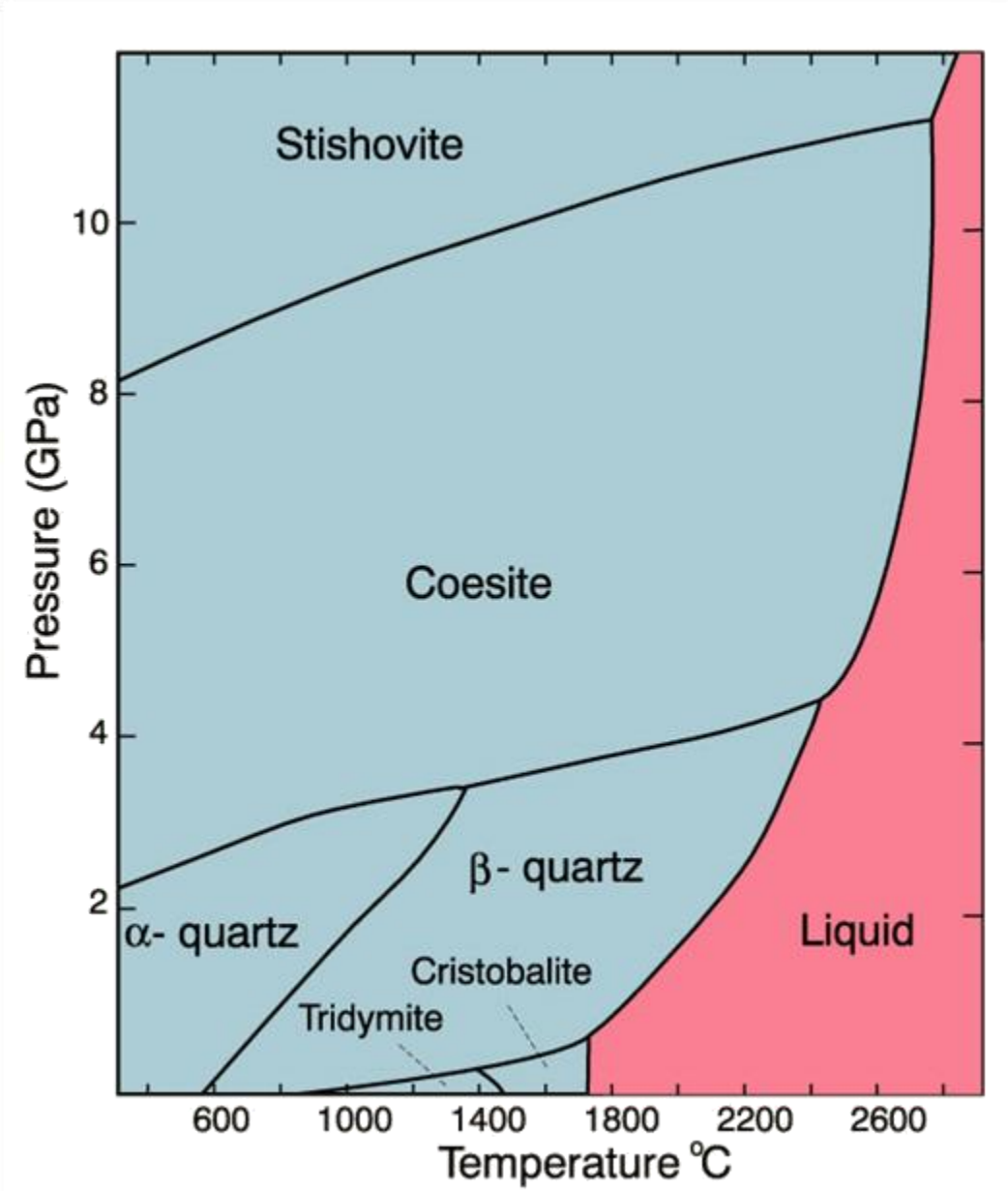
Structural variation in minerals

- **Displacive polymorphism**

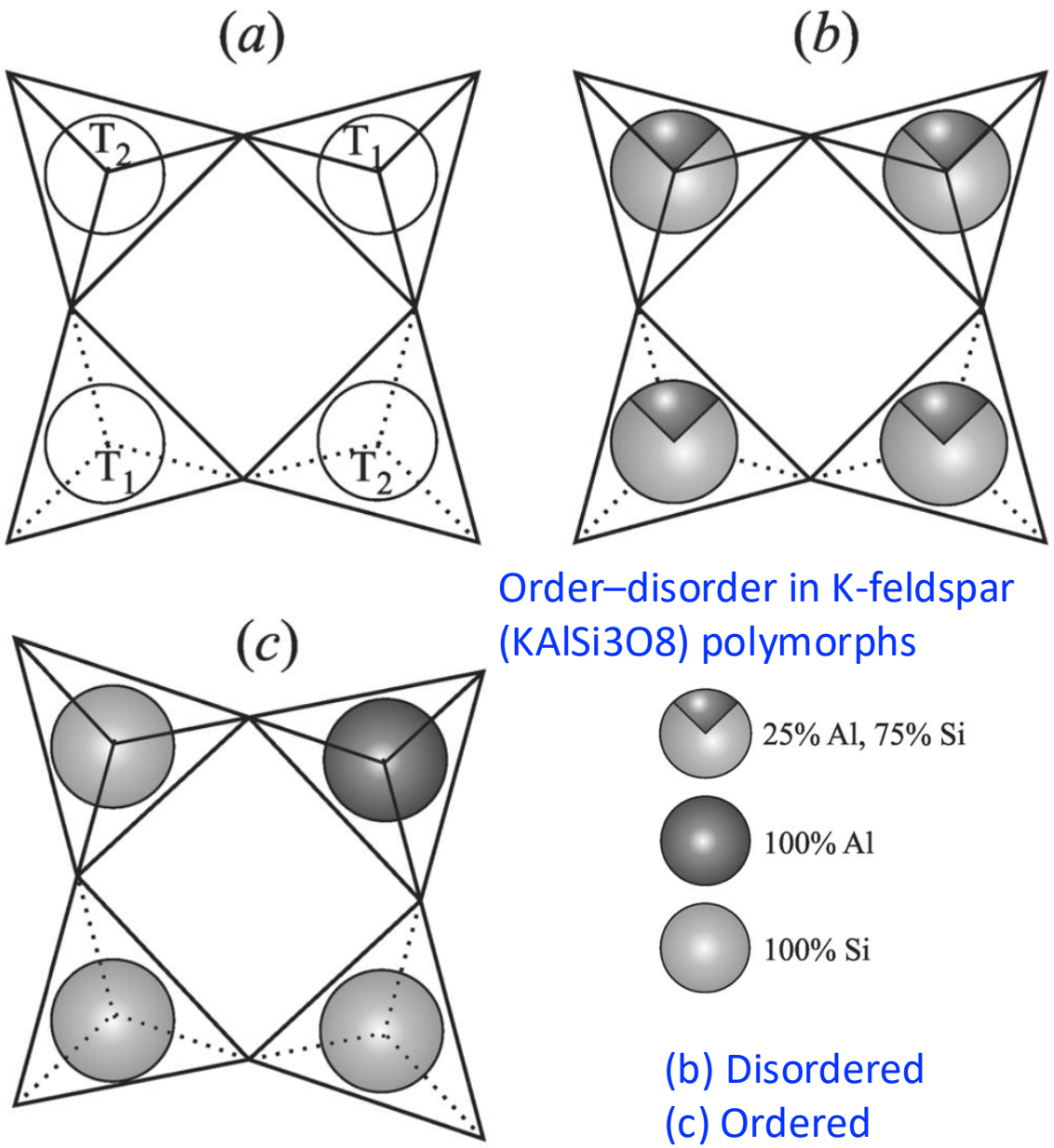
✓ Polymorphic inversions ***do not involve breaking chemical bonds***; the difference between polymorphs is simply a distortion or bending of the crystal structure.

✓ High-temperature forms typically have higher symmetry than low-temperature polymorphs.

✓ The crystal shape of the high-temperature polymorph will be retained on inversion to the low-temperature polymorph, though internal strains in the crystal lattice may lead to the formation of transformation twins



Structural variation in minerals



Order–disorder in K-feldspar ($KAlSi_3O_8$) polymorphs

(b) Disordered
(c) Ordered

- **Order–disorder polymorphism**

✓ The mineral structure remains more or less the same.

✓ Changes in the cation distribution within structural sites.

✓ If two cations X and Y can occupy two equivalent structural sites T1 and T2, the structure is considered ***disordered*** if there is an ***equal probability*** of finding X in either T1 or T2.

✓ If all X (e.g. Al) cations are located in one site T1 and all Y (e.g. Si) cations are in other T1 and T2 sites, the structure is considered fully ***ordered***.

Mineral classification

Minerals other than the native elements are conventionally classified based on the identity of the major ***anion*** or ***anionic group***. (First degree of classification)

Differences between '-ides' and '-ates'

Only Anion: '-ides'

Anionic group: '-ates'

Table 4.5 Chemical Classification of Minerals

Mineral Group	Anion or Anionic Group	Mineral Group	Anion or Anionic Group
Native elements	N/A	Carbonates	CO_3
Oxides	O	Nitrates	NO_3
Hydroxides	OH	Borates	BO_3, BO_4
Halides	Cl, Br, F	Chromates	CrO_4
Sulfides	S	Tungstates	WoO_4
Arsenides	As	Molybdates	MoO_4
Antimonides	Sb	Phosphates	PO_4
Selenides	Se	Arsenates	AsO_4
Tellurides	Te	Vanadates	VO_4
Sulfates	SO_4	Silicates	SiO_4

Compositional variation in minerals

- Minerals have a ***definite*** but ***not fixed*** chemical composition (as minerals are crystalline solids).
- Variation in composition takes place keeping the crystal structure constant.

❑ Solid solution

✓ Compositional variation is not a matter of mixing various solutes into a solid solvent.

✓ Compositional variation is a consequence of the ability of different elements, mostly cations, to substitute for each other within the crystal structure.

✓ Compositional variation is possible because different cations can interchangeably occupy the various sites among the anions.

Compositional variation in minerals

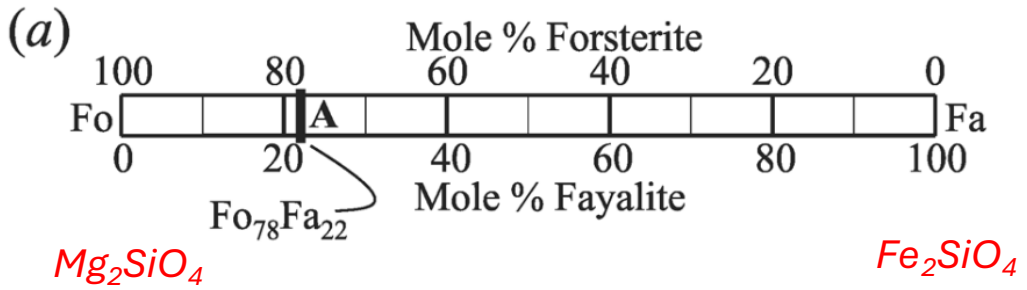
- Minerals have a ***definite*** but ***not fixed*** chemical composition (as minerals are crystalline solids).
- Variation in composition takes place keeping the crystal structure constant.

❖ ***Some important terminologies related to compositional variation***

✓ ***Solid solution series:*** The range of compositions produced by solid solution in a given mineral

✓ ***End members:*** The compositional extremes of a substitution series

✓ A continuous or ***complete substitution*** series is one in which all intermediate compositions are possible.



✓ An incomplete or ***discontinuous substitution*** series is one in which only a restricted range of compositions between the end members is found.

Compositional variation in minerals

❑ Substitution solid solution

Substitution involves interchanging one cation for another in a structural site. ***Two*** requirements control whether substitution can occur.

- **Size**

✓ Ion sizes must be similar.

✓ If the difference in ion size is <15%, extensive substitution is usually possible; if the difference in ion size is >15%, substitution becomes limited.

✓ For example, Si^{4+} and Al^{3+} may substitute in tetrahedral sites; Mg^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+} may substitute in octahedral sites; and Na^{+} and Ca^{2+} may substitute in 12-fold sites.

✓ Temperature has a substantial influence on the degree of substitution

- **Charge**

✓ Charge neutrality must be maintained.

✓ The ions that substitute for each other in a crystal structure may have the same or different charges.

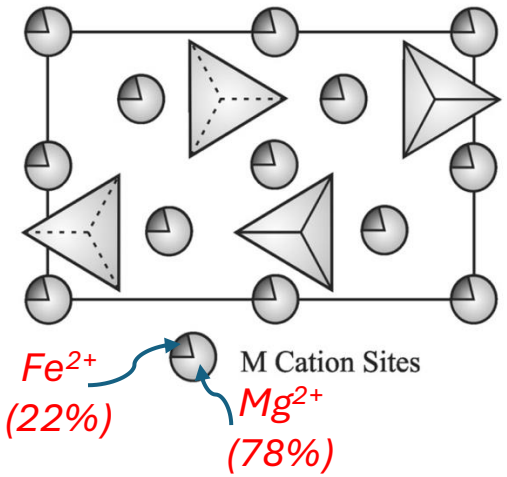
✓ Based on charge difference between the substituting ions, four different substitutions can take place

✓ ***Simple substitution*** is possible if the cations have the same charge.

✓ ***Coupled, omission, or interstitial substitution*** is invoked if cation charges are different.

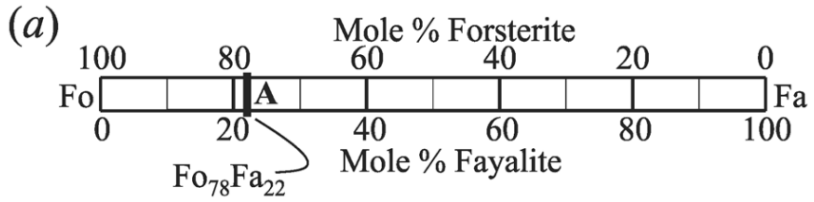
Compositional variation in minerals

- ***Simple substitution***



$Fe^{2+} \leftrightarrow Mg^{2+}$

- ✓ *Radii of Fe^{2+} and Mg^{2+} in octahedral coordination with O^{2-} are 0.75 and 0.86 Å, respectively.*
- ✓ *Same charge*
- ✓ *Readily substituted.*



Mg_2SiO_4 Fe_2SiO_4

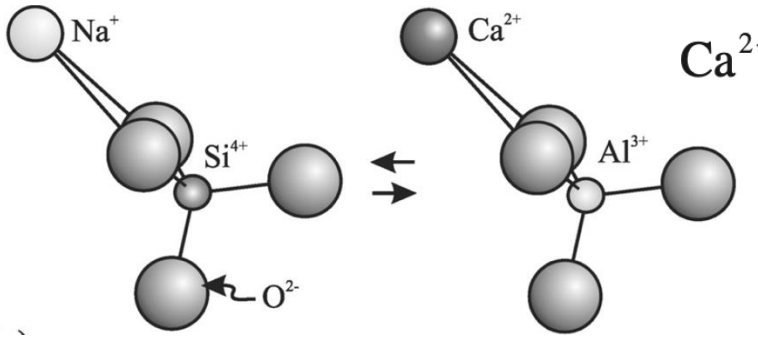
Forsterite Mg_2SiO_4

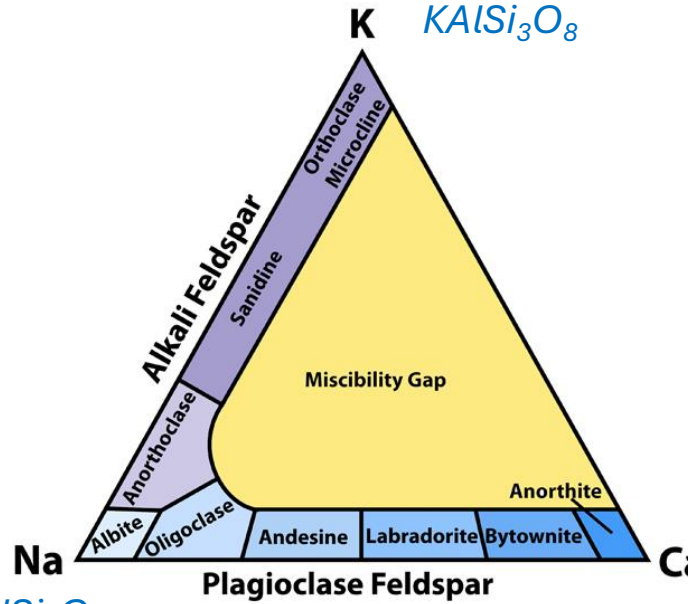
Fayalite Fe_2SiO_4

- ***Coupled substitution***

$CaAl_2Si_2O_8 \leftrightarrow NaAlSi_3O_8$

$Ca^{2+} + Al^{3+} \Leftrightarrow Na^{+} + Si^{4+}$





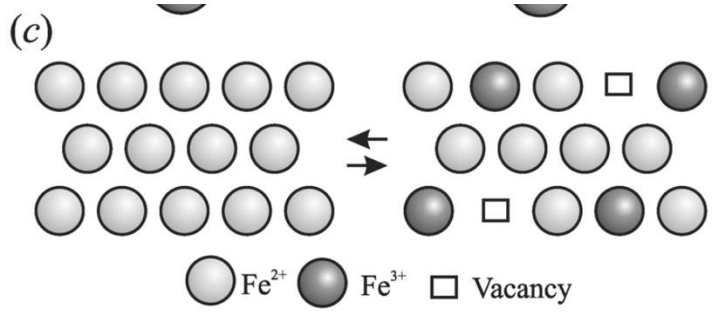
$KAlSi_3O_8$

$NaAlSi_3O_8$ $CaAl_2Si_2O_8$

Ref: Chapter 4. Introduction to Mineralogy, William D. Nesse

Compositional variation in minerals

- ***Ommision substitution***



$$(n+1)M^{n+} \Leftrightarrow nM^{(n+1)+} + \square$$

$$3Fe^{2+} \Leftrightarrow 2Fe^{3+} + \square$$

(Pyrrhotite FeS)

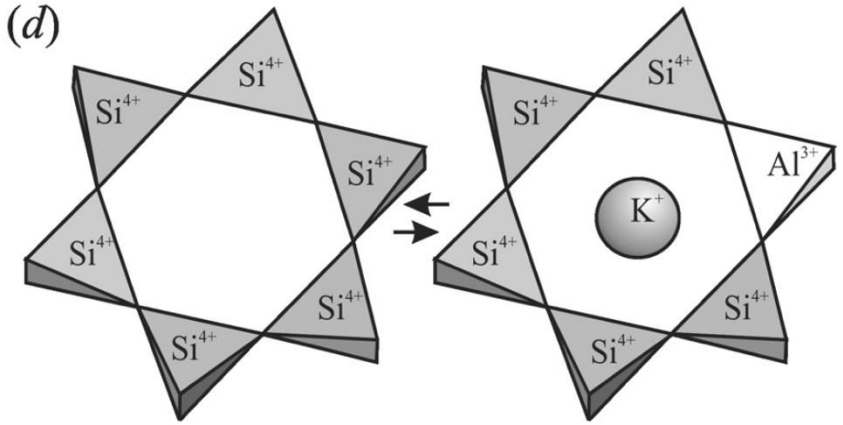
Upto 13% of the sites may be vacant in Pyrrhotite

M^{n+} and $M^{(n+1)+}$: two different cations substituting for each other,

n : the charge of lower charged cation,

[] : a vacant site that normally would be occupied by M^{n+}

- ***Interstitial substitution***



$$\square + Si^{4+} \Leftrightarrow Al^{3+} + (K^+, Rb^+, Cs^+) \quad \text{or}$$
$$\square + Si^{4+} \Leftrightarrow Be^{2+} + 2(K^+, Rb^+, Cs^+)$$

Mineral formula

- Cations are written first, followed by the anion(s) or anionic group.
- Charges must balance. The total charge of cations must equal the total charge of anions.
- Cations in the same structural site are grouped together.
- Cations in different structural sites are listed in order of decreasing coordination number.

Diopside ($CaMgSi_2O_6$)

Cation	Charge	Stoichiometric Coefficient	Total Charge[a]
Ca	2+	1	+2
Mg	2+	1	+2
Si	4+	2	+8
O	2–	6	–12
Total			0

Coordination	Common Cations
12	K^+, Ca^{2+}, Na^+
8	Fe^{2+}, Ca^{2+}, Na^+, Mg^{2+}
6	Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}
4	Si^{4+}, Al^{3+}, S^{6+}, P^{5+}
3	C^{4+} [a]
2	None

$^{VIII}Ca^{VI}Mg^{IV}Si_2O_6$

Diopside (End member composition)

- **Representing mineral formula with solid solution**

If Fe^{2+} and Mg^{2+} can readily interchange in the octahedral site

$^{VIII}Ca^{VI}(Mg, Fe)^{IV}Si_2O_6$ or simply $Ca(Mg, Fe)Si_2O_6$

If the number Fe^{2+} of cations is x, then the formula can be written as:

$Ca(Mg_{1-x}, Fe_x)Si_2O_6$

If x=22%, i.e. x=0.22, then the formula will be written as:

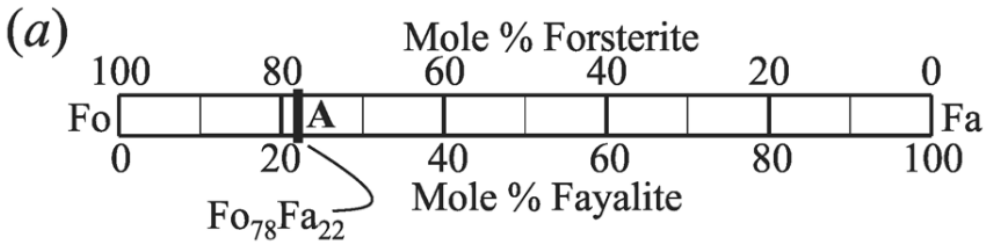
$Ca(Mg_{0.78}, Fe_{0.22})Si_2O_6$

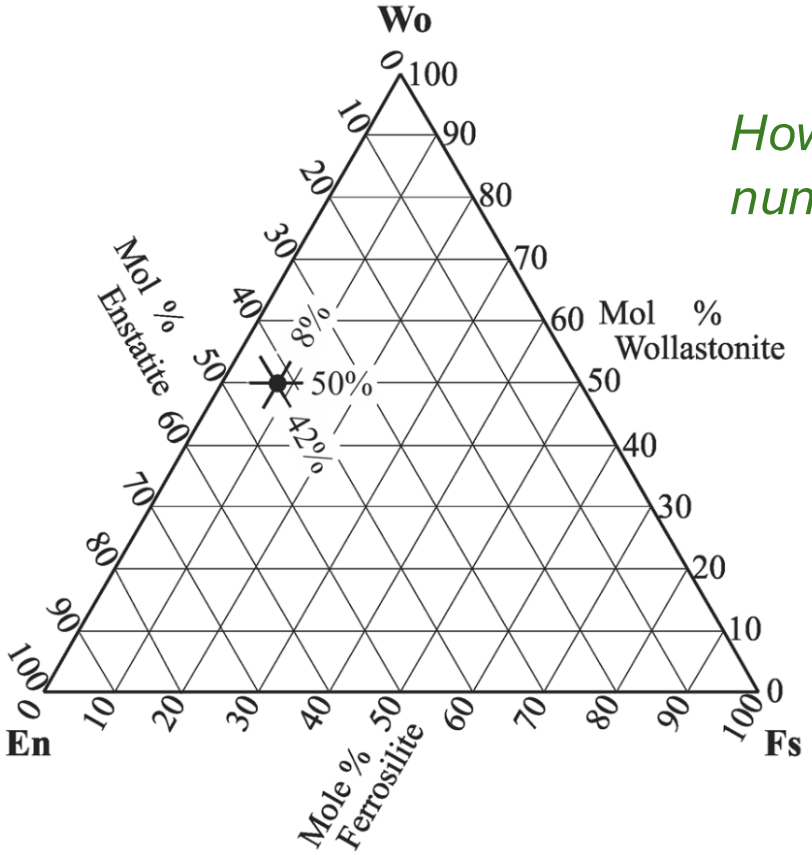
In minerals with just two end members this is sometimes shortened to report just one end member (e.g., Di_{78}) because the sum of both end members (diopside plus hedenbergide in clinopyroxene) must equal 100%.

Graphical representation of mineral formula

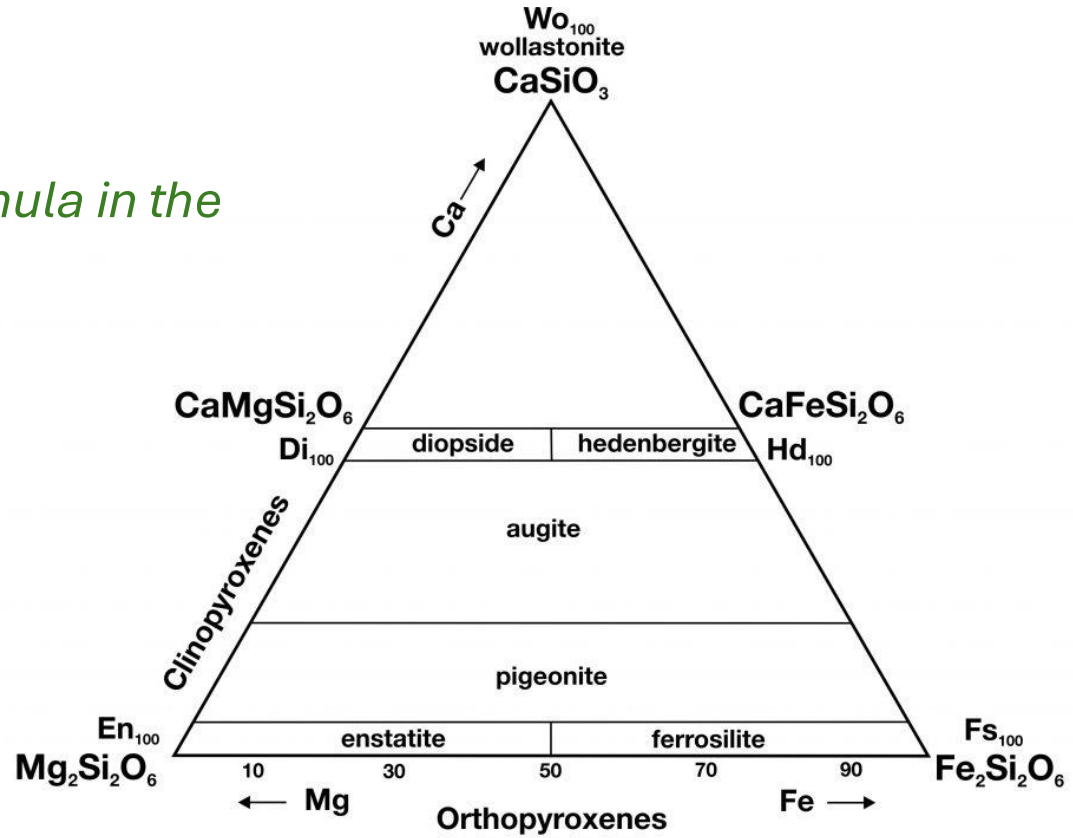
- ***Complete solid solution***

Trusted website for Mineral information:
https://www.mindat.org/
https://webmineral.com/





How do you write the formula in the number of cations?



Thank
You

Compositional variation in minerals

Minerals have a ***definite*** but ***not fixed*** chemical composition (as minerals are crystalline solids). Variation in composition takes place keeping the crystal structure constant.


Garnet (Fe rich)

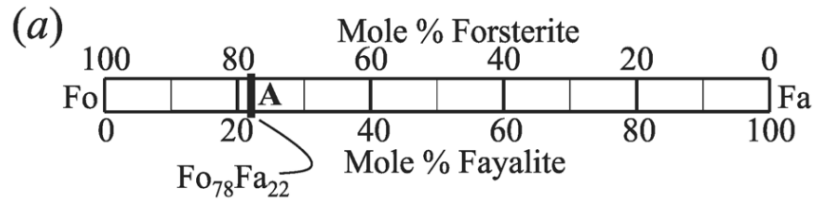

Garnet (Mg rich)

❑ Solid solution

- ✓ Compositional variation is not a matter of mixing various solutes into a solid solvent.
- ✓ Compositional variation is a consequence of the ability of different elements, mostly cations, to substitute for each other within the crystal structure.
- ✓ Compositional variation is possible because different cations can interchangeably occupy the various sites among the anions.

❖ *Some important terminologies related to compositional variation*

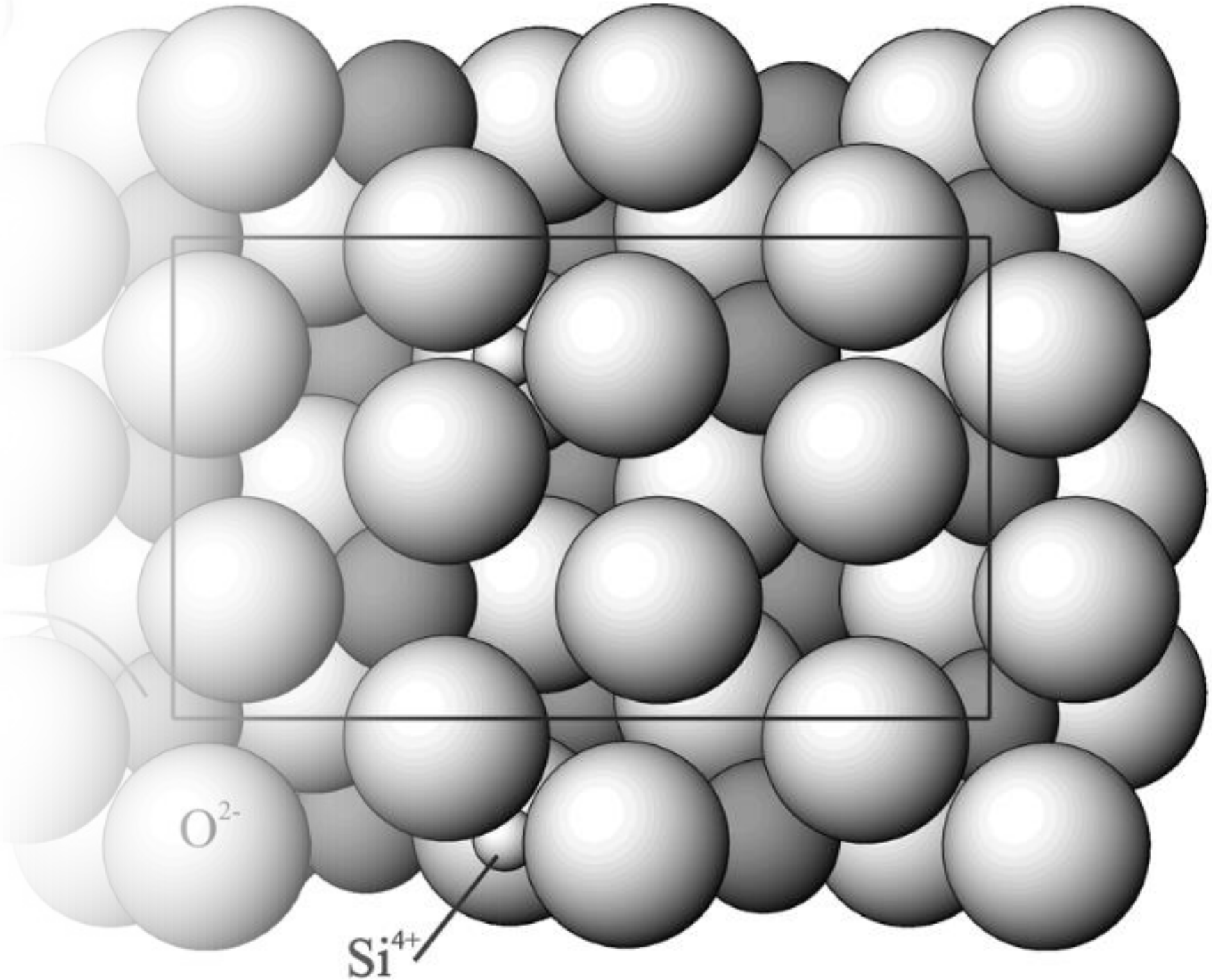
- ✓ ***Solid solution series:*** The range of compositions produced by solid solution in a given mineral
- ✓ ***End members:*** The compositional extremes of a substitution series



Mg_2SiO_4 Fe_2SiO_4

- ✓ A continuous or ***complete substitution*** series is one in which all intermediate compositions are possible.
- ✓ An incomplete or ***discontinuous substitution*** series is one in which only a restricted range of compositions between the end members is found.

Crystal structure



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