ISOMORPHISM AND POLYMORPHISM

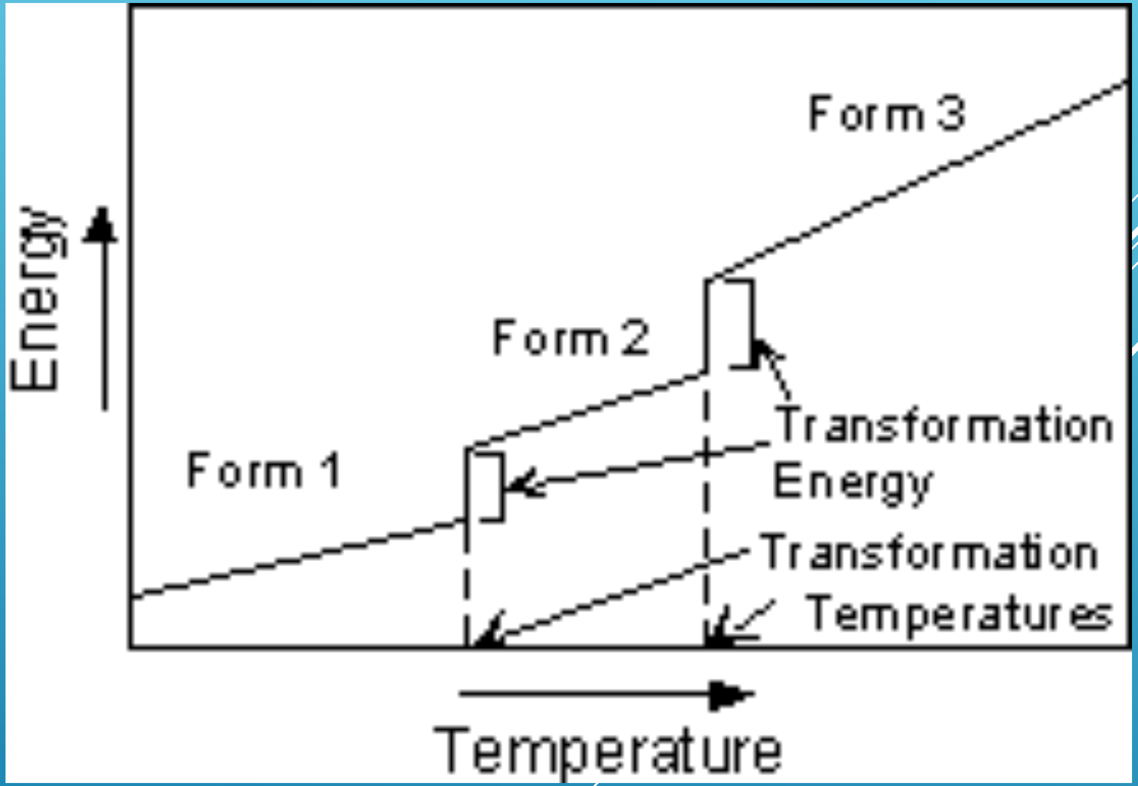
- **Polymorphism** = “many forms”: that a single chemical composition can exist with two or more different crystal structures.

- Change of structure = **polymorphic transformations:**
  - Reconstructive transformation
  - Displacive transformation
  - Order-disorder transformation

POLYMORPHISM

Example: carbon - Diamond to graphite

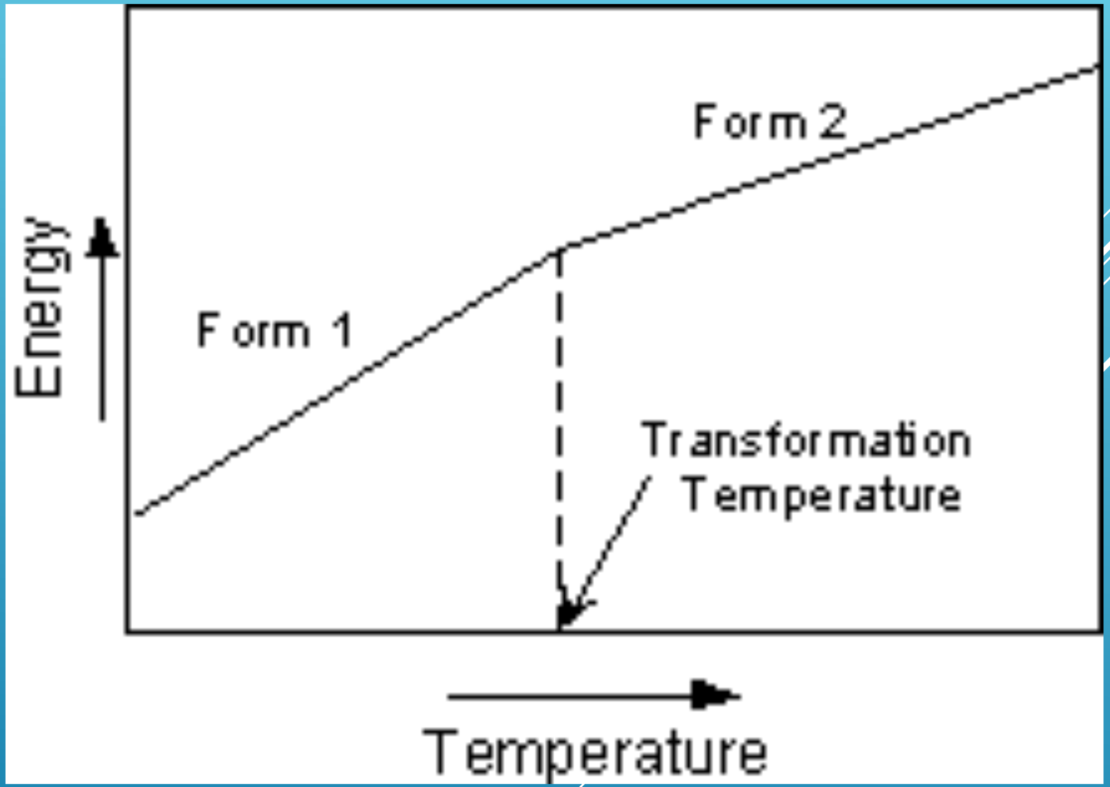
- **Reconstructive transformations:**
  - extensive rearrangement of the crystal structure (breaking of chemical bonds and reassembling the atoms into a different crystal structure)
  - a large change in energy of the structure
  - very slow rate ⇒ presence of metastable polymorphs



POLYMORPHISM

Example: quartz-
α -quartz at T> 580°C
β -quartz at T<580°C

- **Displacive transformations:**
  - Small rearrangement of the crystal structure (no broken bonds)
  - no change of energy
  - Instantaneous and reversible ⇒ no metastable polymorph



POLYMORPHISM

Example: $KAlSi_3O_8$ -
HT: sanidine (2/m)

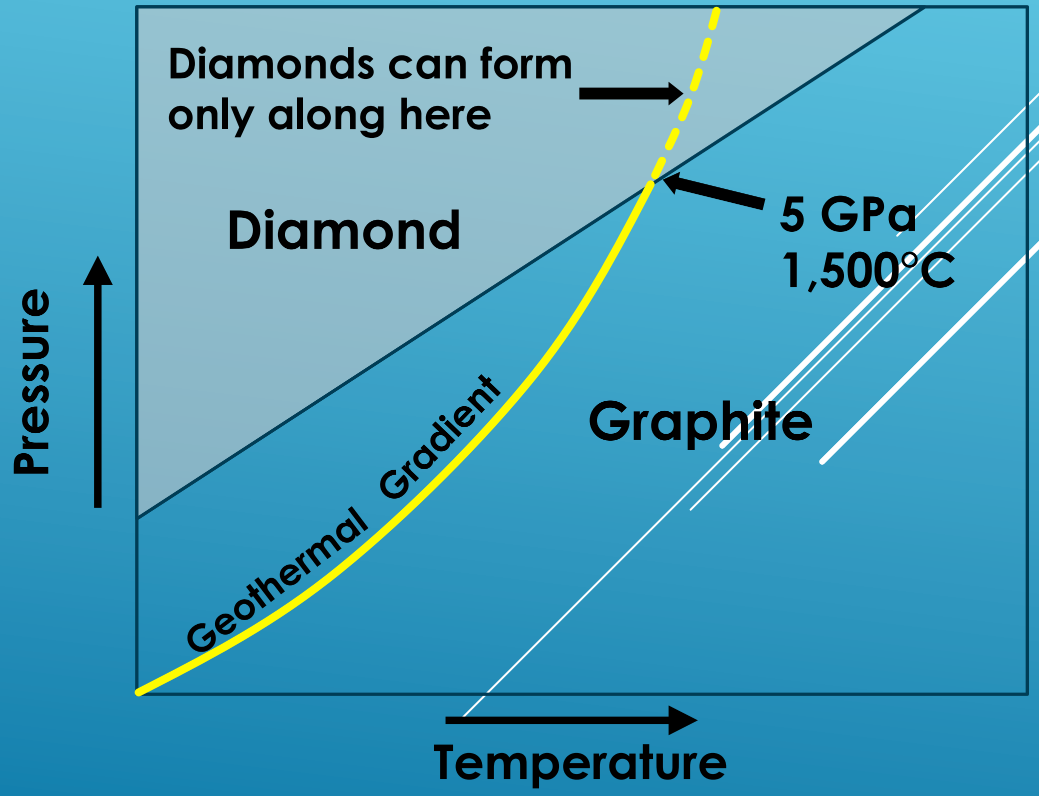
MT: orthoclase (2/m)

BT: microcline ($\bar{1}$)

- **Order – disorder transformations:**
  - Perfect order: Only at the absolute zero (0K or -273.15 °C)
  - High temperature forms ⇔ more disordered
  - Continuous transition (no specific transformation temperature)
  - Potential presence of metastable polymorphs (if the change of temperature is rapid)

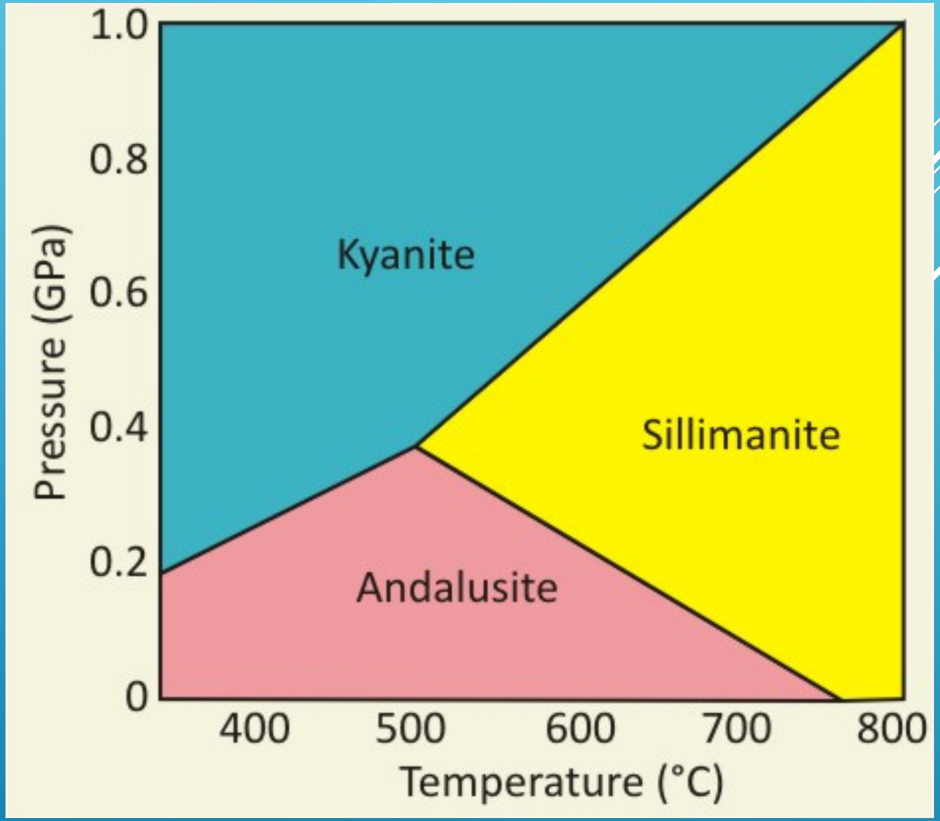
IMPORTANT POLYMORPHS

- **Carbon**
  - 2 polymorphs:
    - HP/HT: diamond (isometric)
    - LP/LT: graphite (hexagonal)
  - Reconstructive transformation
  - Require a lot of energy (from the hardest mineral to one of the softest one) ⇒ presence of diamond at the Earth's surface



IMPORTANT POLYMORPHS

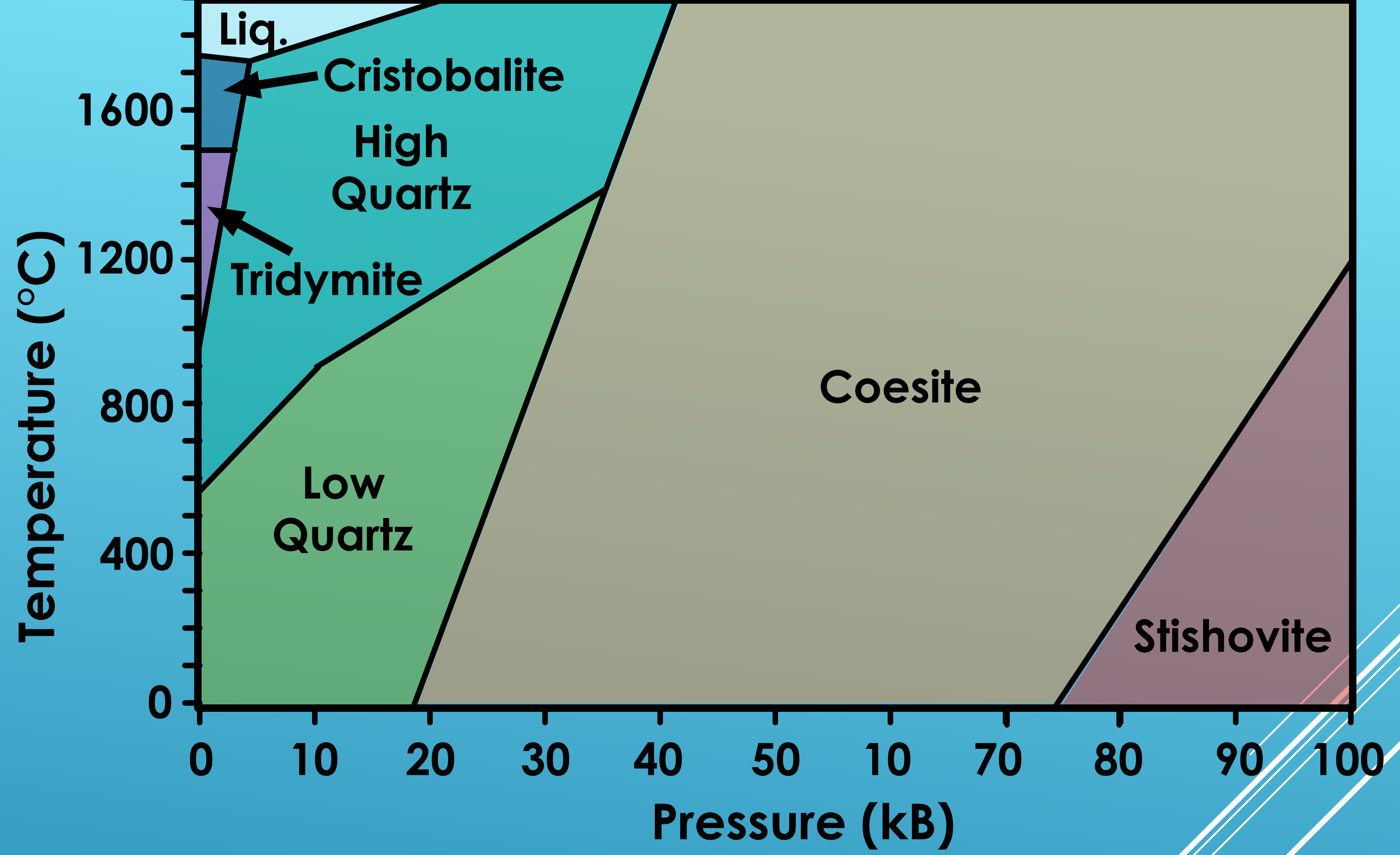
- **Al_2SiO_5**
  - 3 polymorphs:
    - HP: Kyanite (triclinic)
    - HT: sillimanite (orthorhombic)
    - LP/LT: Andalusite (orthorhombic)
  - Reconstructive transformations
  - Use to define metamorphic zones:
    - Andalusite: contact metamorphism
    - Sillimanite: Regional metamorphism



IMPORTANT POLYMORPHS

- **$CaCO_3$**
  - 3 polymorphs:
    - Aragonite (orthorhombic)and Vaterite (hexagonal): metastable at the Earth's surface conditions
    - Calcite (hexagonal): Stable at the Earth's surface conditions
  - Reconstructive transformations

IMPORTANT POLYMORPHS



- **SiO_2**
  - 6 polymorphs

Low pressure:

T

Cristobalite (isometric)

Tridymite (hexagonal) R

β -quartz (hexagonal)

D

α -quartz (trigonal) $\xrightarrow[P]{R}$ Coesite (monoclinic) $\xrightarrow[P]{R}$ Stishovite (tetra)

IMPORTANT POLYMORPHS

Fast cooling ⟷ slow cooling

- **KAl_2SiO_8**
  - 3 polymorphs
  - Order-disorder transformations
  - HT polymorph = sanidine (monoclinic): found in volcanic rocks that have cooled rapidly
  - Slower cooling: sanidine is transformed into orthoclase, then microcline
  - Sanidine & <u>orthoclase</u>: Carlsbad twinning:

PSEUDOMORPHISM

- **Pseudomorphism =** "false form": mineral that has the appearance of another mineral: internal structure and chemical composition are changed but its external form is preserved.
  - 3 mechanisms:
    - Substitution
    - Encrustation
    - Alteration

PSEUDOMORPHISM MECHANISMS

- **Substitution:**
  - Chemical constituents replaced by other chemical constituents
  - Examples:

Petrified forest: wood fibers replaced by quartz

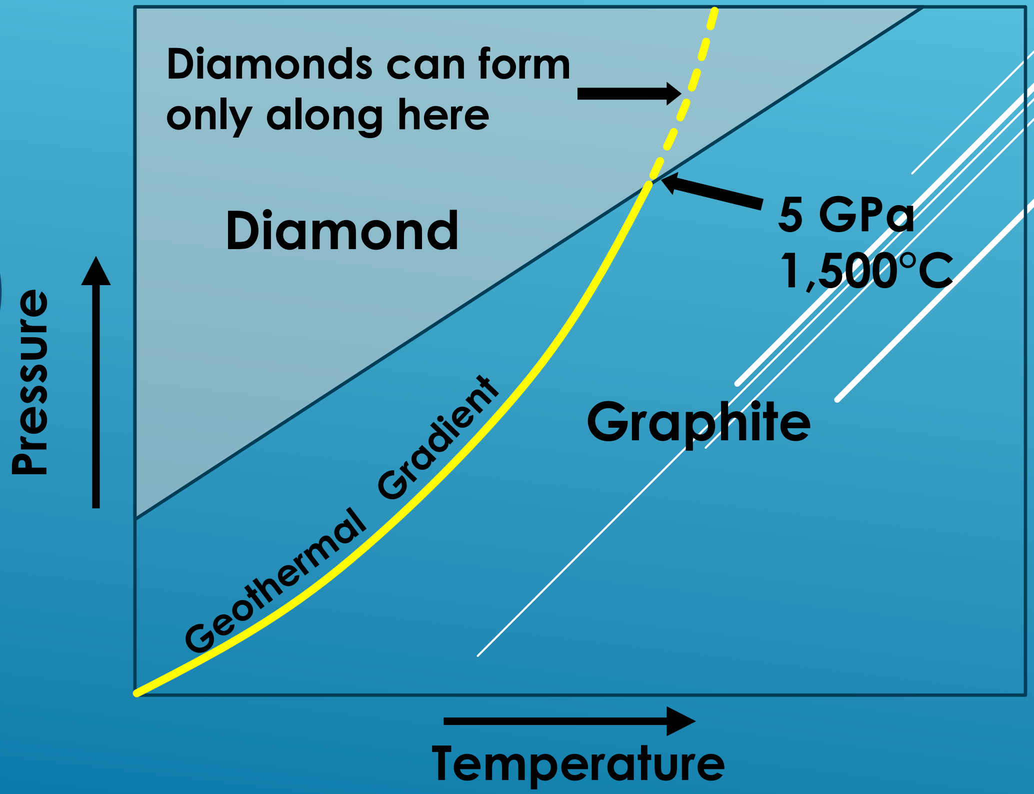
Fluorite alteration: fluorite replaced by quartz (trigonal) but looked isometric

PSEUDOMORPHISM MECHANISMS

- **Encrustation:**
  - thin crust of a new mineral forms on the surface of a preexisting mineral
- **Alteration:**
  - only partial removal of the original mineral and only partial replacement by the new mineral has taken place
  - **Examples:**
  - serpentine pseudomorphed after olivine or pyroxene
  - anhydrite ($CaSO_4$) pseudomorphed after gypsum ($CaSO_4.2H_2O$)
  - limonite [$FeO.(OH).nH_2O$] after pyrite (FeS_2)

PSEUDOMORPHISM MECHANISMS

- **Paramorphism:**
  - Different external and internal structures
  - **Example:** Graphite after diamond in the Beni Bousera pyroxenites (Morocco)
  - P > 5 Gpa (asthenospheric depths)



ISOMORPHISM

- **Isomorphism = solid solutions**: mineral with the same crystal structure in which specific sites can be occupied by two or more elements, ions, or radicals.
- Example: olivine
  - Forsterite $Mg_2SiO_4 \rightleftharpoons$ Fayalite Fe_2SiO_4
  - Mg^{2+} can be substituted by Fe^{2+}: olivine = $(Mg,Fe)_2SiO_4$

- **⇒ compositional variations in the minerals**

ISOMORPHISM

- **Rules for substitution**
  - 1) Extent of substitution more enhanced at higher T
  - 2) Electrical neutrality has to be maintained (in most cases)

ISOMORPHISM

- 3) If difference in charge (Z) between substituting ions > 1: difficult substitution
- 4) The substitution should involve similar ion sizes:
  - Size difference < 15%: extensive substitution
  - Size difference: 15-30%: limited or incomplete
  - Size difference > 30%: almost impossible
- 5) If two ions are competing for the same site, the one with the highest charge (Z) and smaller radius (r) is favored (i.e. higher Z/r or ionic potential is favored).
- **Rules 3-5: Goldschmidt's rules for ionic substitution**

ISOMORPHISM

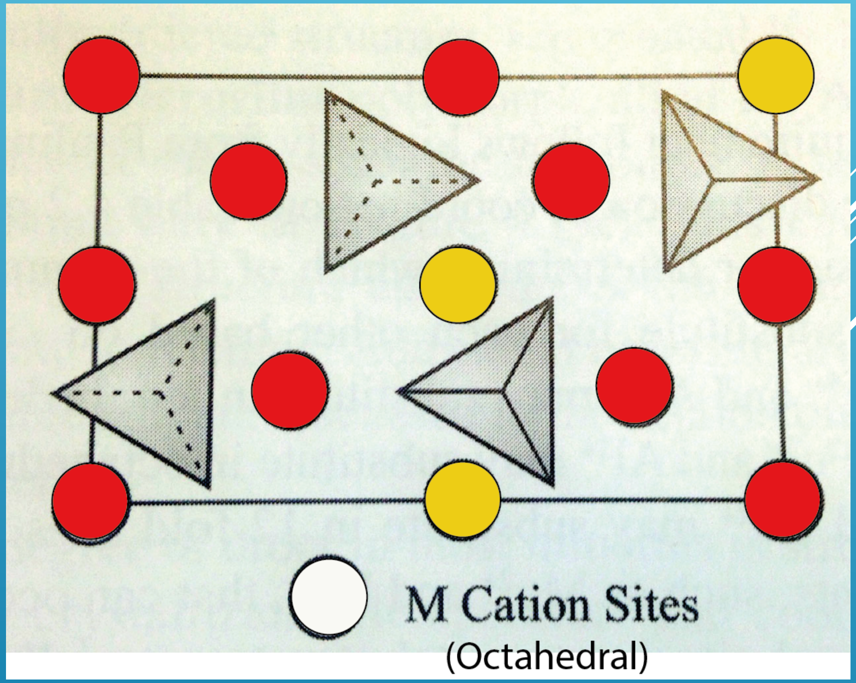
- **Type: of substitutions**
- **Simple substitution**: substitution of cations with the same charges

Ex.: Olivine $(Mg,Fe)_2SiO_4$

Tetrahedral sites are occupied by Si4+.

Octahedral sites are occupied by either Mg^{2+} or Fe^{2+}: 10 are occupied by Mg^{2+} (red) and 3 are occupied by Fe2+ (yellow): the olivine formula is

$(Mg_{70}Fe_{30})_2SiO_8$ (called "Forsterite seventy")



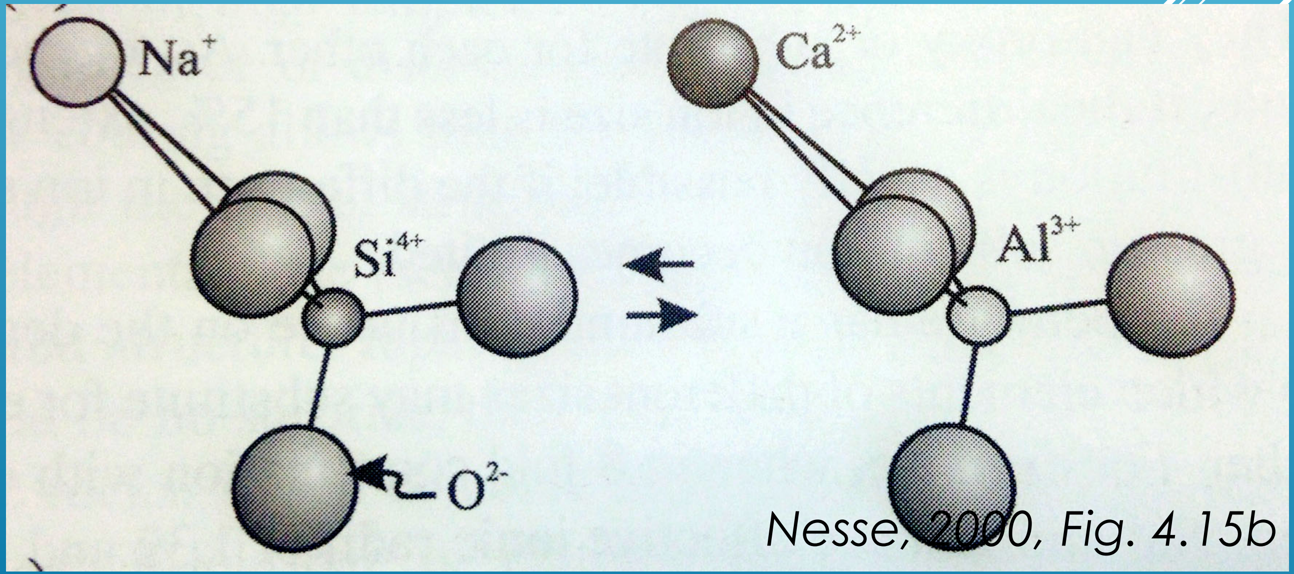
Modified from Nesse, 2000, Fig. 4.15a

ISOMORPHISM

- **Coupled substitution**: maintain charge balance by coupling one substitution that increases the charge with one that reduces the charge

Ex.: Plagioclase:
albite: ($NaAlSi_3O_8$) ↔ anorthite ($CaAl_2Si_2O_8$)

Substitution of Na^+ for Ca^{2+} is balanced by the substitution of Si^{4+} for Al^{3+}



Nesse, 2000, Fig. 4.15b

ISOMORPHISM

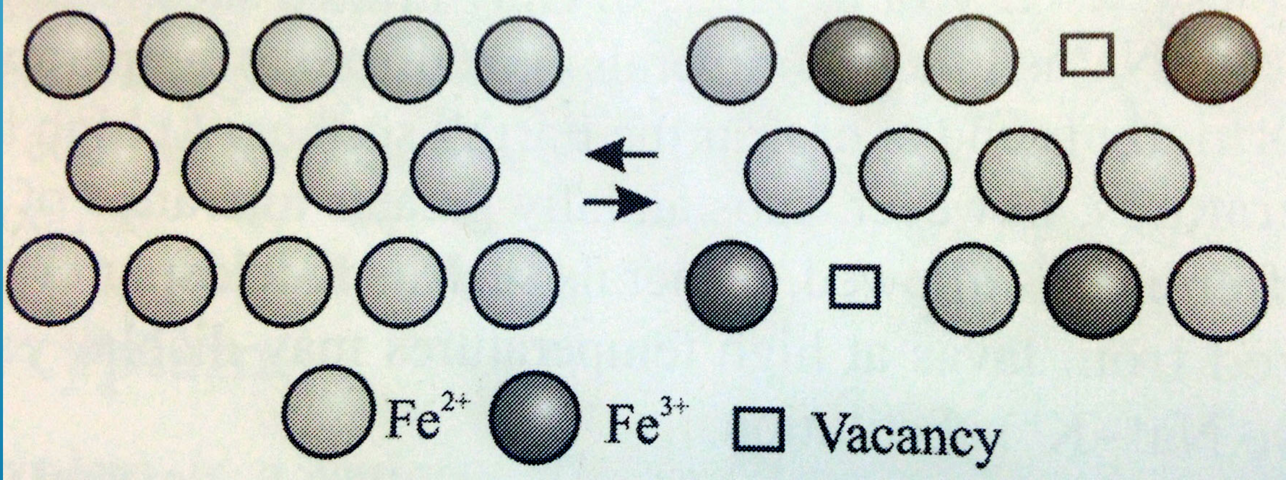
- **Omission substitution**: maintain charge balance by leaving structural sites vacant:

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

Ex.: Pyrrhotite

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

The amount of Fe^{3+} that can replace Fe^{2+} is limited to less than 20%:
$Fe_{(x-1)}S$ with x = 0 to 0.2



Nesse, 2000, Fig. 4.15c

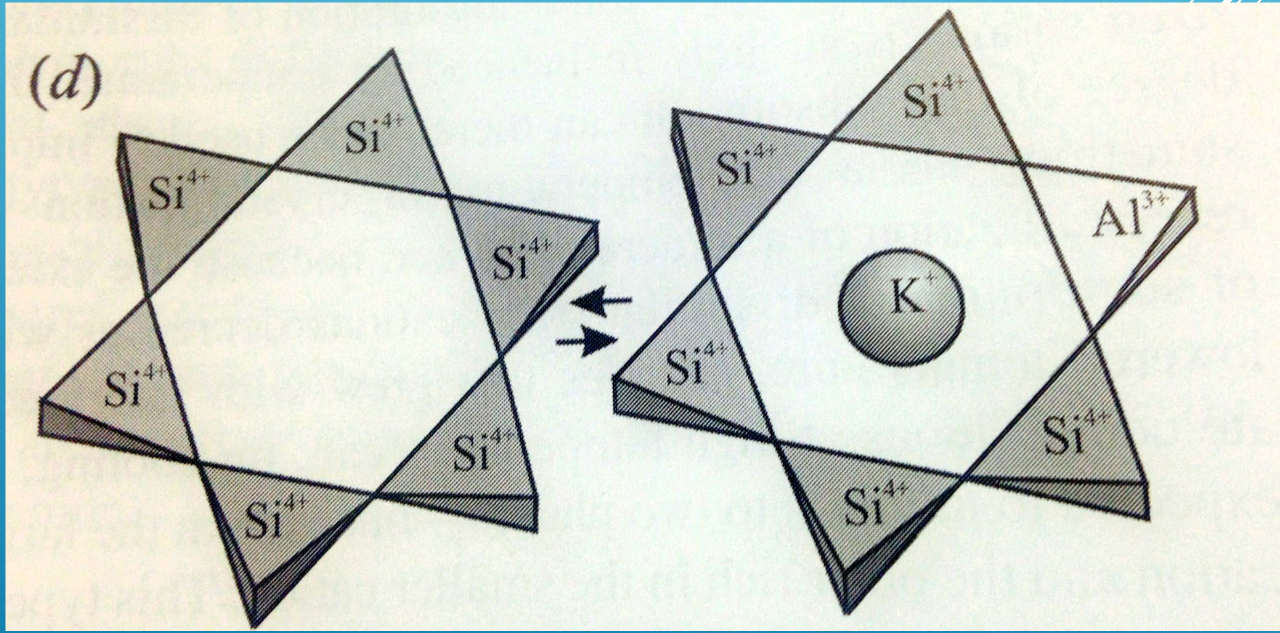
ISOMORPHISM

- **Interstitial substitution**: maintain charge balance by placing ions in sites that normally are vacant:

  Ex.: Beryl $Al_2Be_3SiO_6O_{18}$

  $\square + Si^{4+} \Leftrightarrow Al^{3+} + (K^+, Rb^+, Cs^+)$

Insertion of large cations in the open channel is balanced by the substitution of Si^{4+} by Al^{3+}



Nesse, 2000, Fig. 4.15d