L7: Crystal defects and twinning

Thursday, July 30, 2020 16:55

Time on task: 3 hours (material posted on Sept 21st, Office hours: Monday Oct 5th and Wednesday Oct 7th)

Goals:

Upon completion of this lecture, you should be able to:

1. Recognize twinning in minerals
2. Recognize crystal defects in crystal structures
3. Describe the various polymorphic transformations
4. Understand isomorphism and the rules for substitution

1. Twinning in crystals

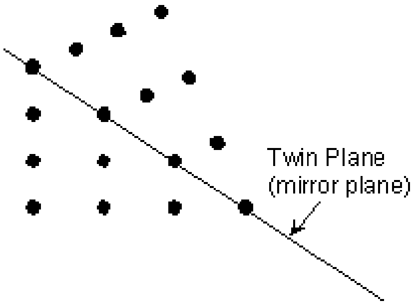
Sometimes during the growth of a crystal, or if the crystal is subjected to stress or temperature/pressure conditions different from those under which it originally formed, two or more intergrown crystals are formed in a symmetrical way. These **symmetrical intergrowths** of crystals are called **twinned crystals**. Twinning is important to recognize, because when it occurs, it is often one of the most **diagnostic features** enabling identification of the mineral.

Pyrite

Staurolite

Twinning is a situation that occur in a lot of minerals.

What happens is that lattice points in one crystal are shared as lattice points in another crystal **adding apparent symmetry** to the crystal pairs.
Twinning, because it adds symmetry, never occurs in relation to the existing symmetry of the crystal.



1.1. Symmetry Operations that Define Twinning

Because symmetry is added to a crystal by twinning, twining can be defined by the symmetry operations that are involved. These include:

- **Reflection** across a mirror plane. The added mirror plane would then be called a **twin plane.**

- **Rotation** about an axis or line in the crystal. The added rotation axis would then be called a **twin axis.**
- **Inversion** through a point. The added center of symmetry would then be called a **twin center**.

Each one of these three twins can result to a twin that is unique to a mineral, a class or to a specimen.
Some minerals tends to be more twinned than "untwinned". Ex.: **Feldspars**

Twin laws: There are specifics laws called the **twin laws** that add elements of symmetry above that provided by normal symmetry operations of the crystal (i.e., crystal class).

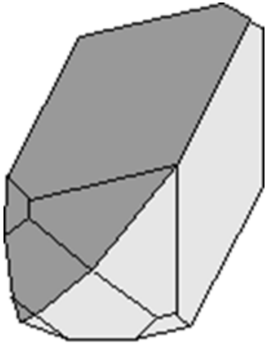
For example, you can get a monoclinic crystal in which you will see 2 mirrors plans. The second mirror plan is not part of the crystal class, it is due to the twin.

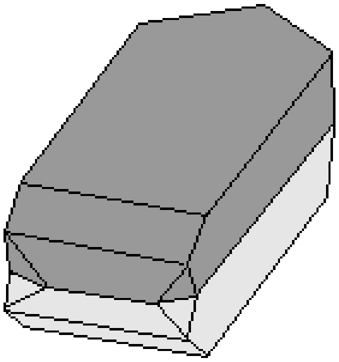
We are not going to look at these laws in details in this class, but just be aware that they exists.

1.2. Type of twinning

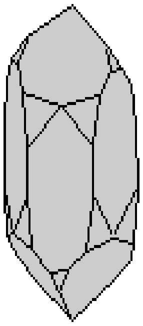
They are two separate types of twinning:

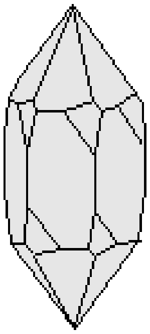
- **Contact Twins:** have a planar composition surface separating 2 individual crystals.
  These are usually defined by a twin law that expresses **a twin plane**
  (i.e. an added mirror plane).

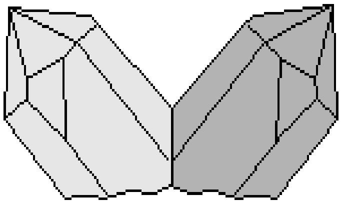

Twin Plane {021}


Twin Plane {001}

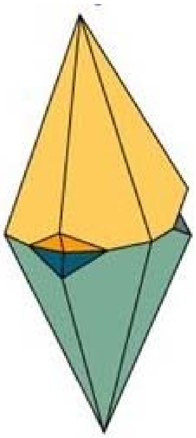
Ex.: orthoclase (monoclinic system): right: diagnostic of orthoclase when it occurs). *Credits: Tulane University*


Brazil Twin
{11$\bar{2}$0}

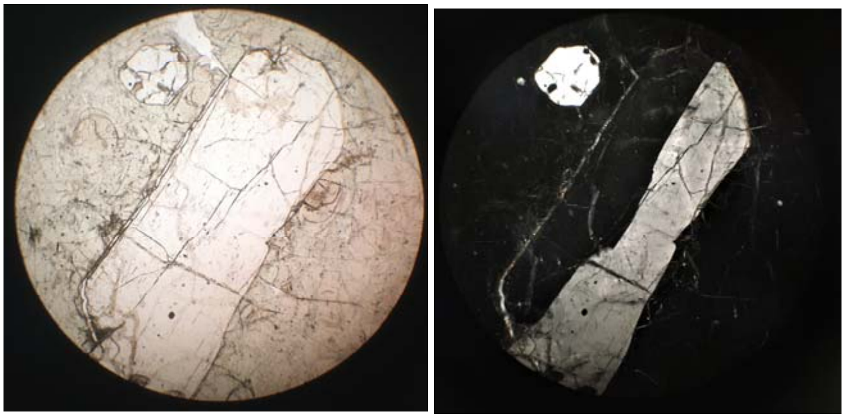

Dauphine Twin
[0001]


Japanese Twin
{11$\bar{2}$2}

Ex.: quartz (hexagonal system): *Credits: Tulane University*

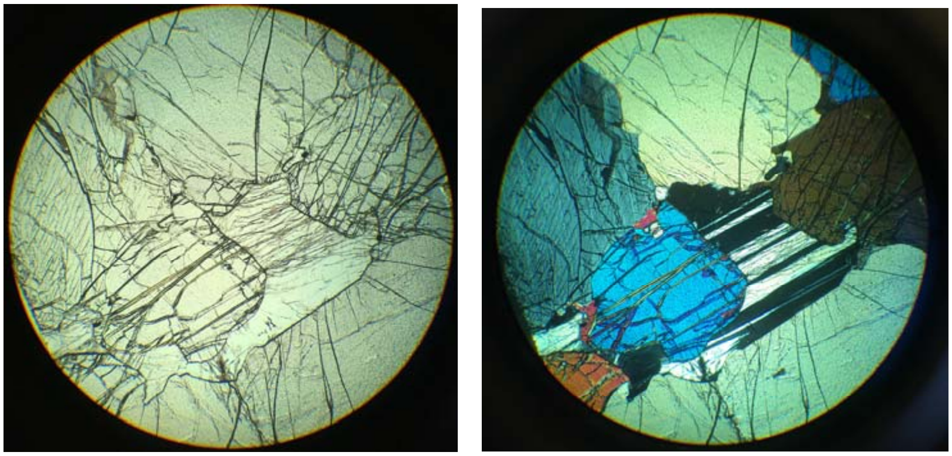

Ex.: calcite (trigonal system)

This type of twin might be difficult to identify in hand sample but are easy to see under crossed polarizers with a petrographic microscope.



Crystal of sanidine in a basaltic glass. e.g., the presence of the contact twin is indetectable in plane polarized light (left) but clearly visible in crossed polarized light (right). FOV = 4mm; G&G teaching collection (UUOP65).

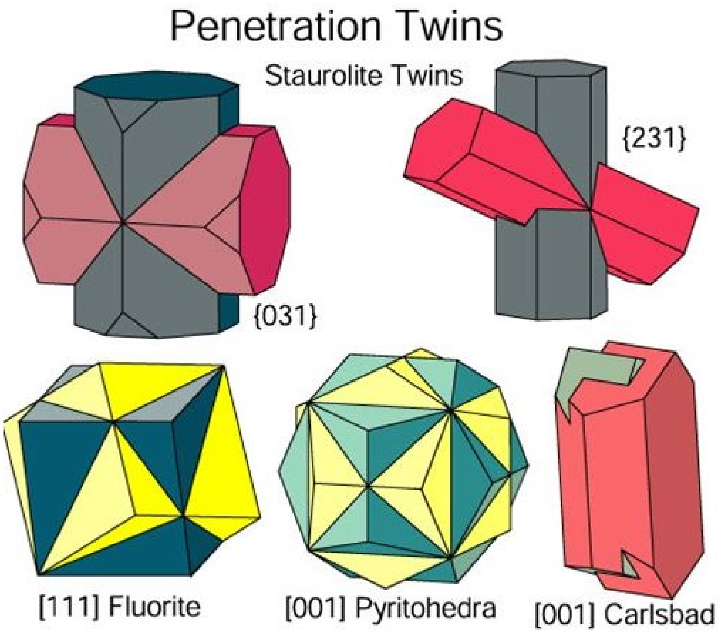
It is particularly easy to see in plagioclase because this type of twin is repeated numerous times. We called this repetition of twining: **polysynthetic twins**. This is a **diagnostic property** of plagioclase in thin section.



Peridotite thin section with, in the middle, a grain of plagioclase showing polysynthetic twins (alternance of black and white parallel bands) in XPL. FOV = 4mm; G&G teaching collection (R148).

- **Penetration Twins:** have an irregular composition surface separating 2 individual crystals. These are defined by a **twin center or twin axis**.

These are the one easy to see on a hand specimen. And they are the easiest thing to identify.
Ex. Orthoclase (yes, orthoclase can produced both type of twinning, the Carlsbad twin is also a diagnostic property of orthoclase), staurolite, pyrite, fluorite

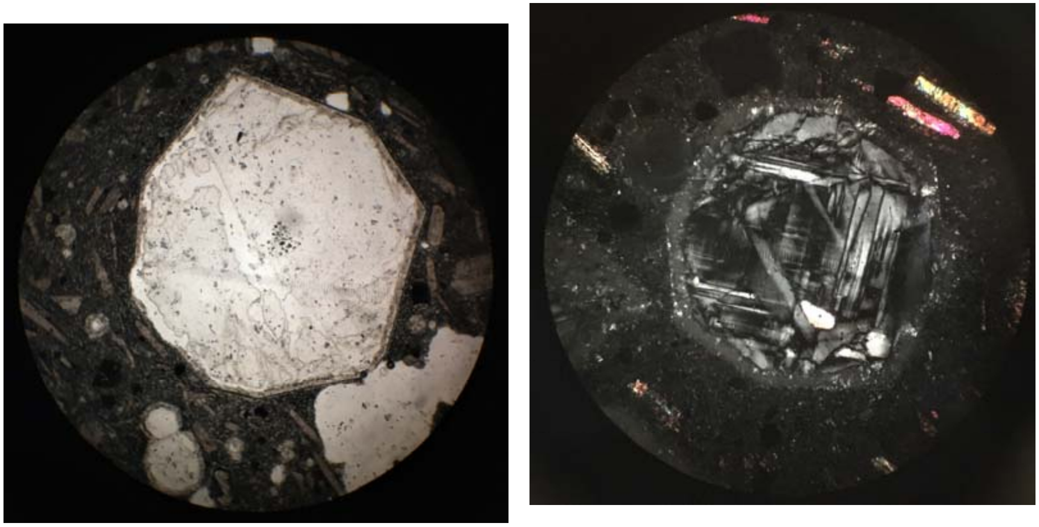


1.3. Causes of twinning

There are two major **<u>causes</u>** for twinning:

- **transformation twins:** are the result of a change in crystal system

  Ex.: Leucite: presence of polysynthetic twins due to the change of the crystal system. From cubic at high temperature to orthorhombic at low temperature



Euhedral grain of leucite (left: PPL, right: XPL) showing lamellar twins in XPL. FOV = 4mm; G&G teaching collection (UUOP9).

Quartz: Quartz-β (hexagonal) at High-T to Quartz-α (rhombohedral) at low-T. Notice that almost all quartz crystals are twinned but it is not detectable with optical microscopy because they keep the same optical properties.

- **Growth twins:** are the result of an interruption or change in the lattice of the crystal, **i.e., a crystal defect.**

  Ex.: alkali Feldspar and plagioclase

L7: Crystal defects

Monday, August 3, 2020 9:38

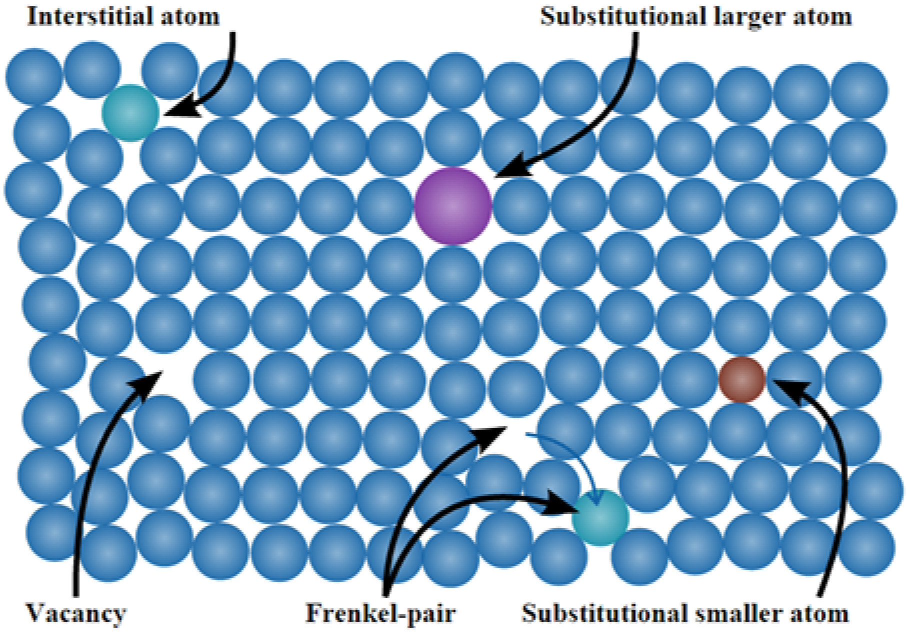
2. Crystal defects

There are four types of crystal defects:

- Point defects
- Linear defects (or dislocation)
- Plane defects
- Inclusions.

2.1. Point defects

Point defects are where an atom is missing or is in an irregular place in the lattice structure. We distinguish between:



- **Interstitial atom:** an extra atom into an interstitial void in the crystal structure. Interstitial atoms occur only in low concentrations because they distort and highly stress the tightly packed lattice structure.
- **Vacancy:** empty spaces where an atom should be, but is missing. They are common, especially at high temperature where atoms frequently change their positions leaving behind empty lattice sites. In most cases, diffusion can only occur because of vacancies.
- **Frankel pair:** Vacancy and interstitial atom due to the migration of an atom through successive steps and eventually settles at the crystal surface
- **Substitution:** an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. This atom can be bigger or smaller than the bulk atoms.

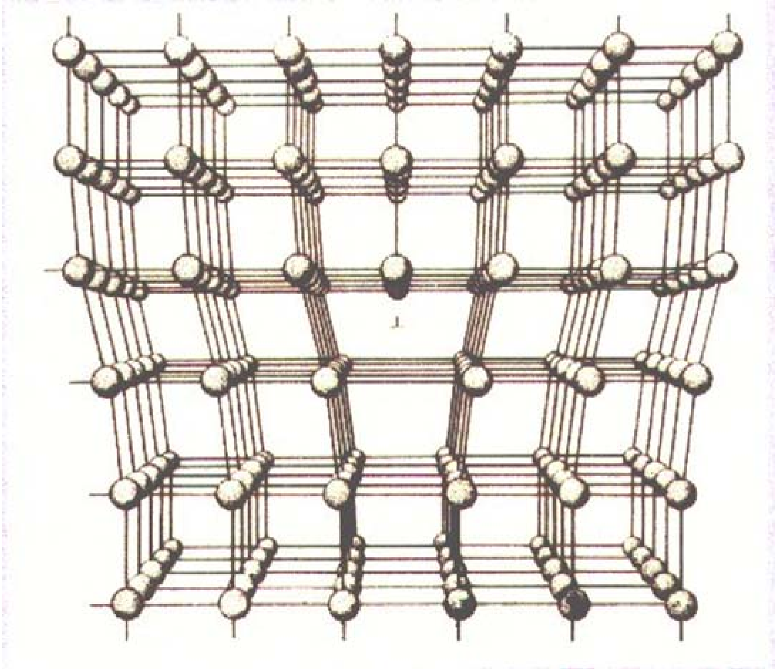
All crystals contain point defects (even crystal in equilibrium).

2.2. Linear defects

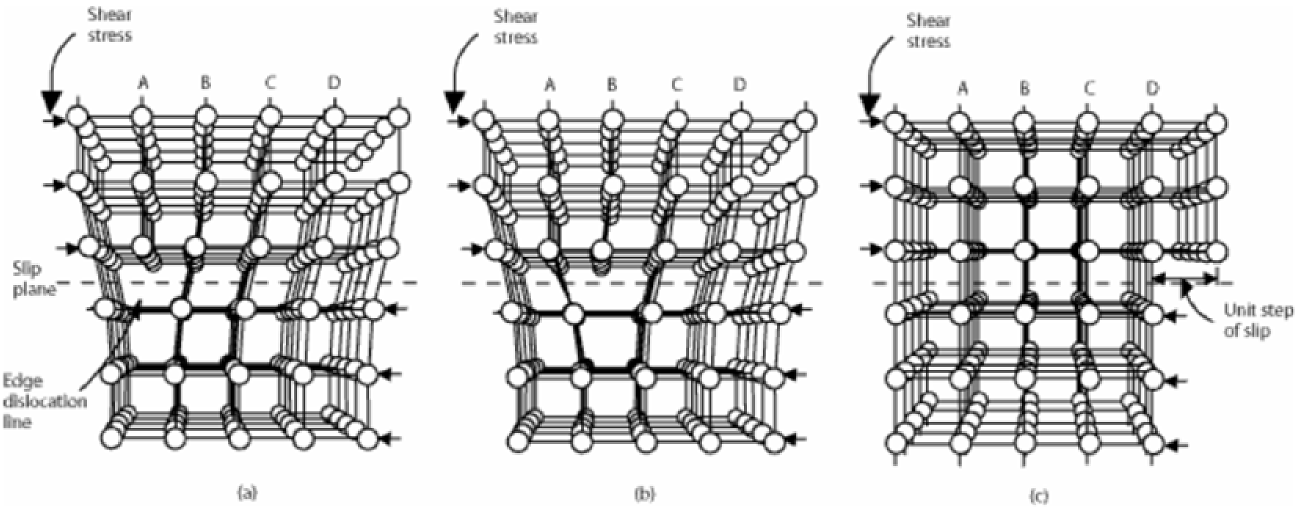
Linear defects are called **dislocations**. In the case of a dislocation, the distortion is centered only along a line and therefore the imperfection can be considered as the boundary between two regions of a surface which are perfect themselves.

There is two types of dislocations.

- **Edge dislocations:** The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. It occurs when an extra half-plane of atoms is introduced in the crystal, distorting nearby planes of atoms.

- 

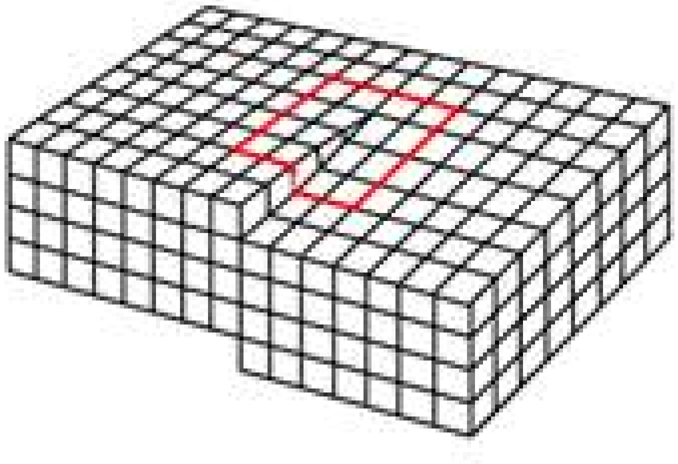
When a stress is applied on the crystal, the dislocation can migrate and potentially reach the side of the crystal.



Edge dislocations control the deformation in solids: there is an elastic deformation around the dislocation.

- **Screw dislocations**: is much harder to visualize. Imagine cutting a crystal along a plane and slipping one half across the other by a lattice vector, the halves fitting back together without leaving a defect.

Screw dislocation favor the crystal growth (see lecture 9).



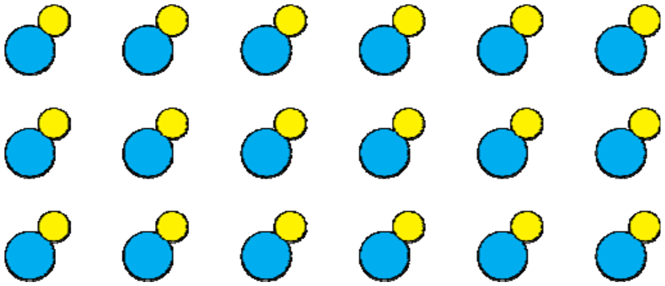
To visualize the two types of dislocation in 3D, open **edge_dislocation.html** and **screw_dislocation.html** associated with this lecture.

2.3. Planar defects

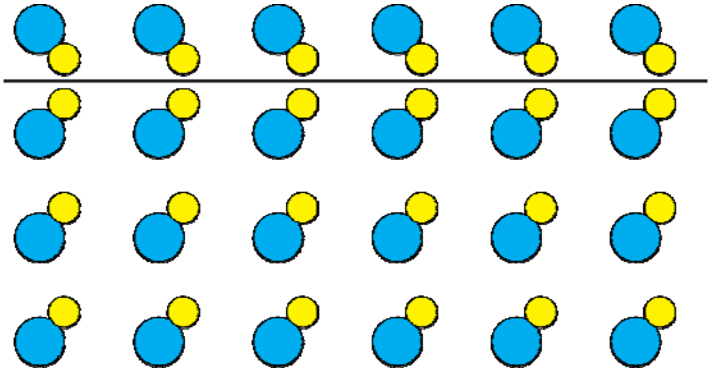
Planar defects are interfaces between homogeneous regions of the material. They are two types of planar defects:

Stacking Faults and Twin Boundaries. A change in the stacking sequence over a few atomic spacings produces a stacking fault whereas a change over many atomic spacings produces a twin region.

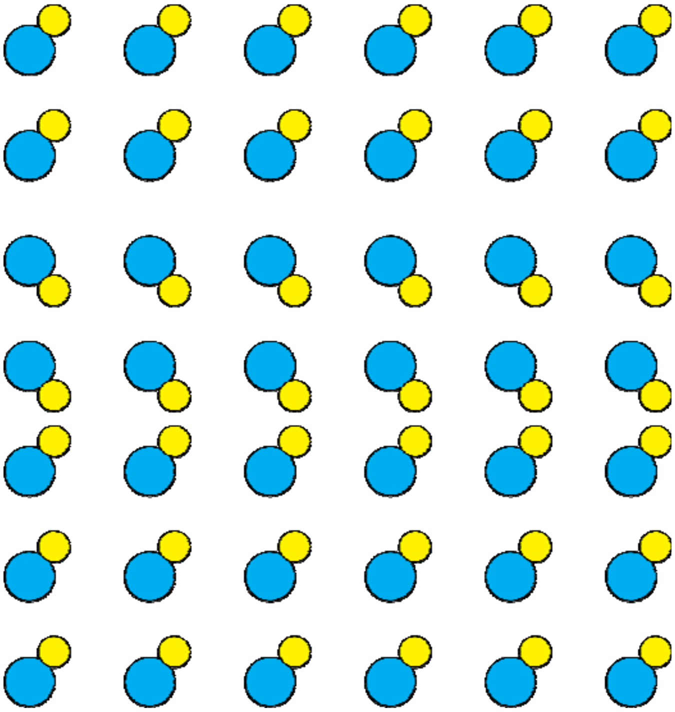
Here is an example of a lattice with periodic arrangement of atoms (the motif can be reproduced by translation).



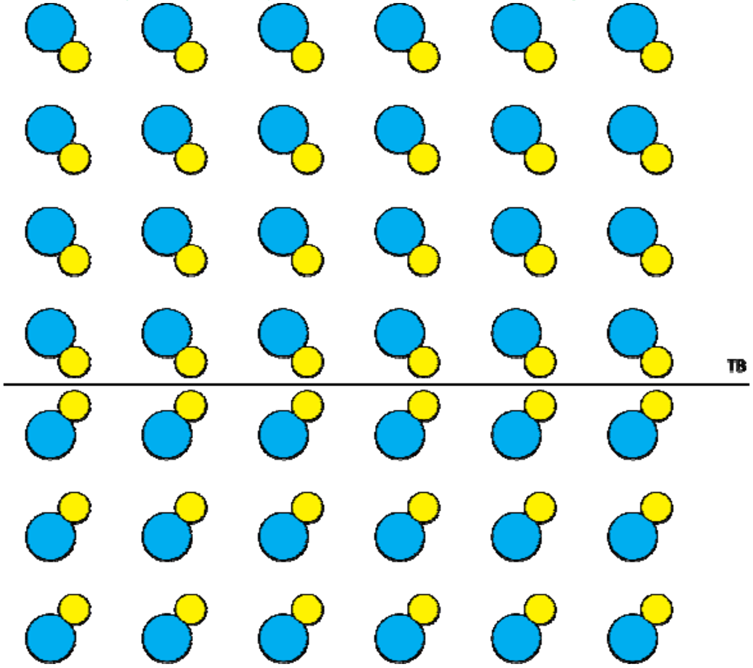
I now introduce a stacking fault, e.g. by adding the next layer in mirror-symmetry:



If, after a few atomic spacing, I'm back with the old sequence, this stays a stacking fault



However, if I continue with mirror-symmetric layers, I obtain the following structure:

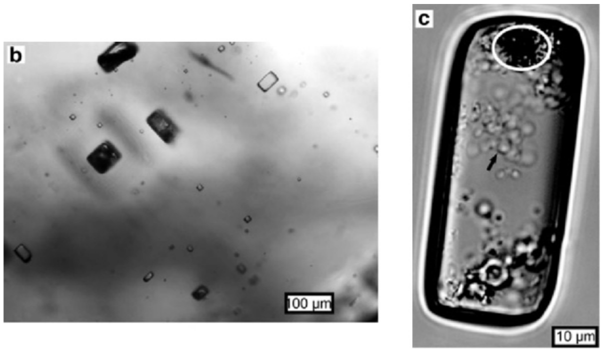


I generated a twin boundary!

2.4. Inclusions

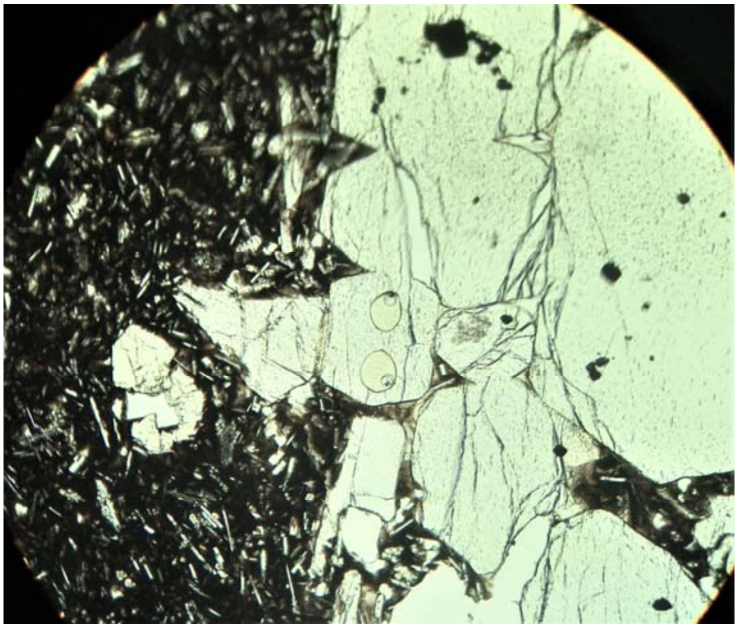
They can be solid, liquid or gaz.

Inclusions are usually trapped during the growing of the crystal. Fluid and melt inclusion often contain a vapor bubble and can also contain small crystals. Sometimes, the form of the inclusion is controlled by the crystal system of the crystal. In geology, we use theses inclusions to constrain the pressure and temperature conditions of the crystal during its formation.



Source: Wang et al. (2016), Astrobiology, DOI: 10.1089/ast.2015.1397

DNA can be recovered from fluid inclusion to learn about ancient ecosystems in extreme environments.



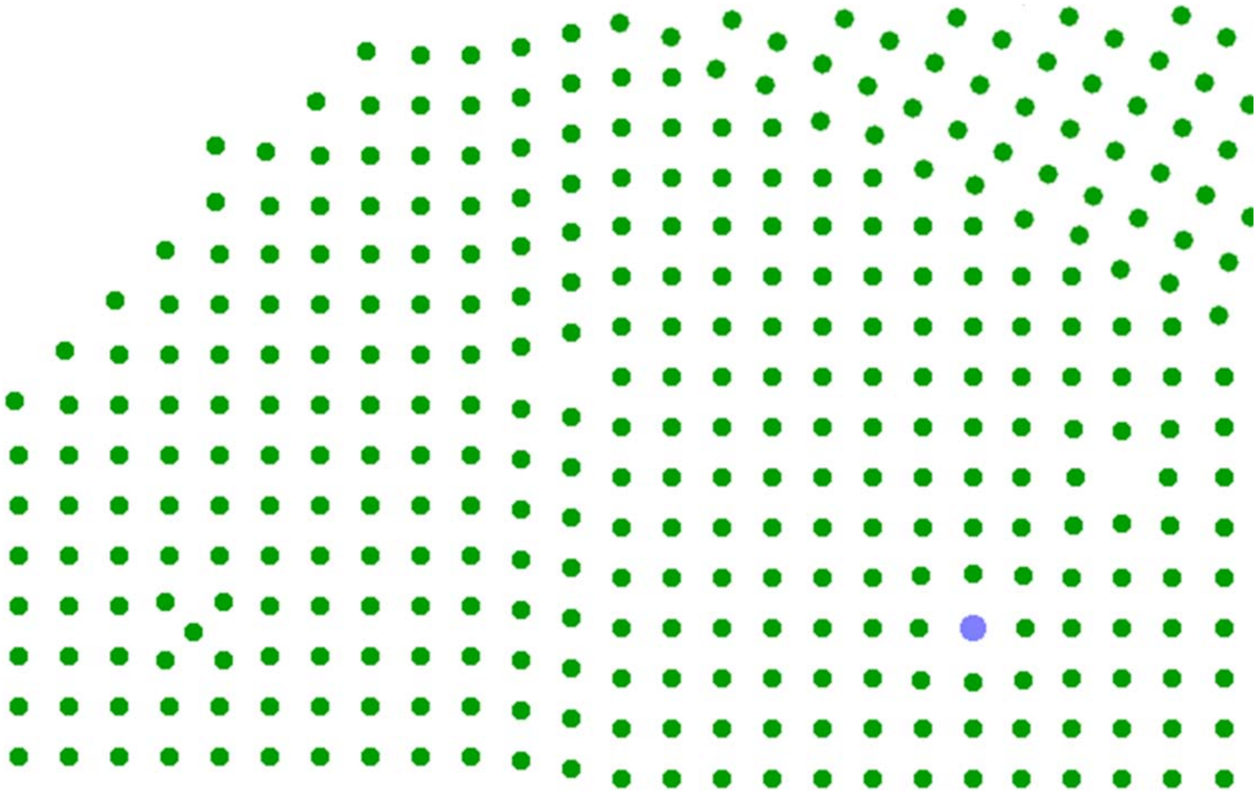
Melt inclusion in olivine grains from the lava erupted from Kilauea in 2018 (Fissure 8). FOV=4.5mm - H10

Melt inclusion in olivines have been used to constrain the composition of the primary magma: Olivine are the first mineral to crystallize and the inclusion will preserve information on the nature of the source and P and T conditions of magma formation.

Credits: Stephen Richardson, University of Cape Town, South Africa - Deep Carbon Observatory: A Decade of Discovery p. 12

Garnet inclusions in diamond have been used to constrain the onset of plate tectonic on Earth:
Eclogitic garnet appeared in inclusion around 3Ga and suggests that crustal material started to be recycled in the mantle at this time.

Practice: Find the defects in this figure (keys at the end of the assessment):



L7: Polymorphism

Monday, August 24, 2020 10:20

3. Polymorphism

Polymorphism = "many forms": a single chemical composiition can exist with two or more **different crystal structures**.

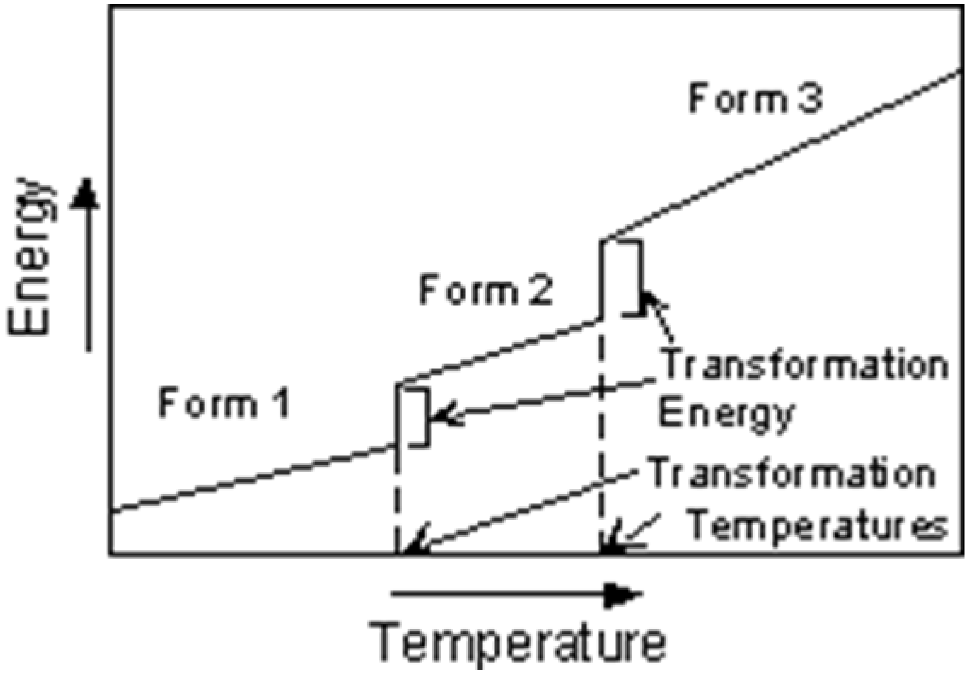
Change of structure = **polymorphic transformation.**

There are three types of polymorphic transformations:

- **Reconstructive** transformations
- **Displacive** transformation
- **Order-disorder** transformation

3.1. Reconstructive transformations

A reconstructive transformation involves the **extensive rearrangement** of the crystal structure (breaking of chemical bonds and reassembling the atoms into a different crystal structure). It results into a large change of energy in the crystal structure. e.g., diamond ↔ graphite

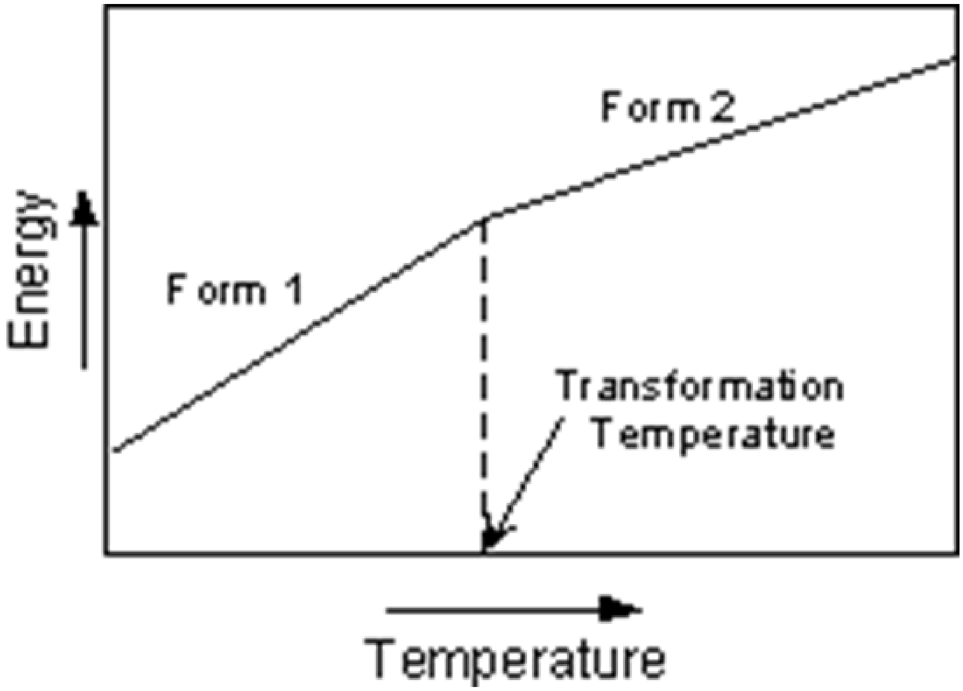


It also requires energy to happen and consequently happened at a very slow rate. Hence, it's responsible for the presence of **metastable polymorphs**.

e.g., diamond are mostly found in kimberlite, volcanic rock that is known to be formed at great depths and to travel very fast to the surface. Diamond is not stable at the surface of the Earth and should convert into graphite, but it's because it requires so much energy to transform the structure of diamond into graphite that we find diamond. Diamonds are metastable and if you give them enough time (geologically speaking), they will eventually convert into graphite. No diamond are not forever...

3.2. Displacive transformations

A displacive transformation involves a small rearrangement of the crystal structure (no broken bonds). There is no change of energy in the structure when the reaction occurs. e.g., α-quartz at T < 580 °C ↔ β-quartz at T > 580 °C



It's an instantaneous and reversible transformation. Hence, metastable polymorphs of displacive transformations can't be found because will immediately be transformed in the stable form of the polymorph.

3.3. Order-disorder transformations

Order-disorder transformation usually occurs with a change of temperature (i.e., a change of entropy).

At the absolute zero (0K or -273.15°C), a structure is in perfect order. When the temperature increases, the structure becomes more disordered.

An order-disorder transformation is a continuous transformation (no specific transformation temperature unlike the reconstructive and displacive transformations).

Metastable polymorphs can exist if the change of temperature is rapid enough (e.g., lava arriving at the surface)

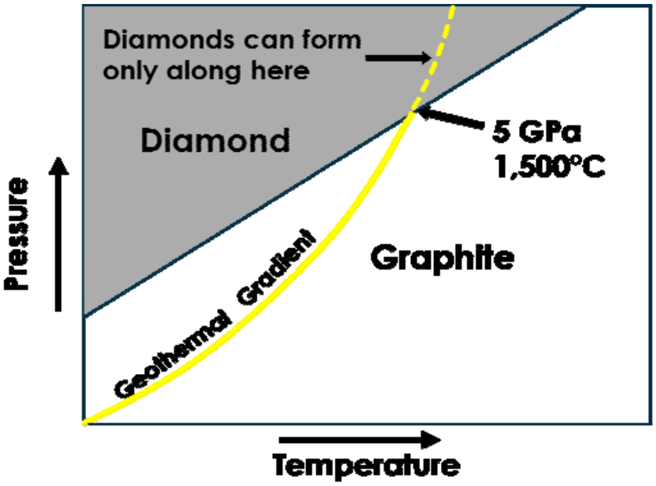
e.g., K-feldspar ($KAlSi_3O_8$):
 High Temperature: sanidine (2/m)
 Intermediate temperature : orthoclase (2/m)
 Low temperature: microcline ($\bar{1}$)

3.4. 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

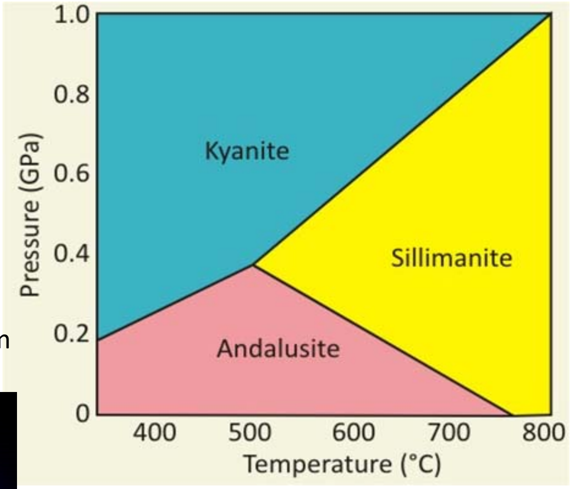


- ***Aluminum silicates (Al_2SiO_5): 3 polymorphs***

- HP: Kyanite (triclinic)
- HT: Sillimanite (orthorhombic)
- LP/LT: Andalusite (orthorhombic)

Reconstructive transformations

Use to define <u>metamorphic</u> zones:
Andalusite: contact metamorphism, Sillimanite: Regional metamorphism



- ***SiO_2: 6 polymorphs***

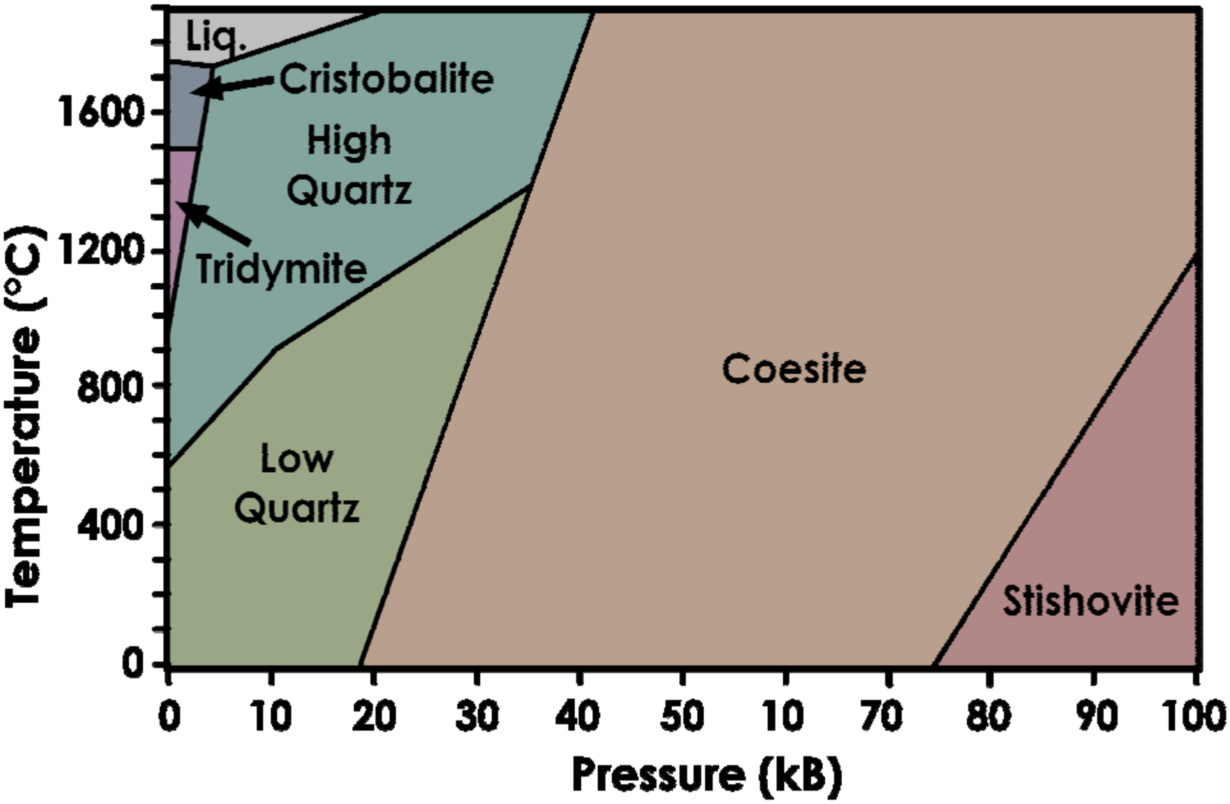
Low pressure → **High pressure**

T ↑
Cristobalite (isometric)
Tridymite (hexagonal)
β-quartz (hexagonal)
α-quartz (trigonal)

Coesite

Stichovite

The reactions are all reconstructive except for the transformation β-quartz↔α–quartz that is displacive.



Can we find β-quartz in a sample?
Can we find coesite in a sample?

- *K- feldspars (KAlSi3O8): 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 & orthoclase: Carlsbad twinning

Fast cooling → **Slow cooling**

3.5.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: Paramorphism, Encrustation, Alteration

- ***Paramorphism***

Chemical constituents replaced by other chemical constituents

Petrified tree: wood fiber replaced by silica

Fluorite replaced by quartz (trigonal) but looks isometric

- ***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
e.g., 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)

L7: Isomorphism

Tuesday, August 25, 2020 10:16 AM

4. 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.

In other words, solid solutions are minerals with defined but variable compositions.

e.g., olivine: The composition of the olivine $(Mg,Fe)_2SiO_4$ can vary between two end-members: Forsterite (Mg_2SiO_4) and Fayalite (Fe_2SiO_4)

4.1. Rules for substitution

1) **Extent of substitution more enhanced at higher temperature**
2) **Electrical neutrality has to be maintained (in most cases)**
3) **If difference in charge (Z) between substituting ions > 1: substitution is difficult**
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 1 to 3 are the Goldschmidt's rules for ionic substitution

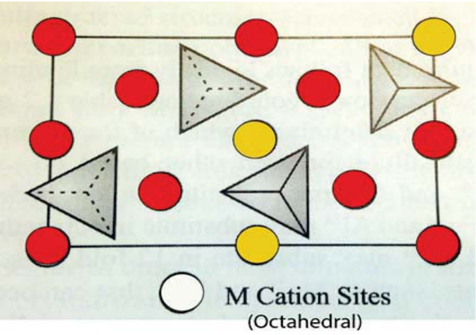
4.2. Type of substitutions

- ***Simple substitution***

Simple substitution are substitution of one cation with another.
Both cations have the same charge

e.g., olivine $(Mg,Fe)_2SiO_4$

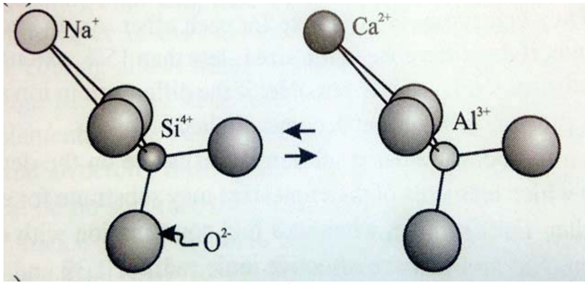
Tetrahedral sites are occupied by Si^{4+}.
Octahedral sites are occupied by either Mg^{2+} or Fe^{2+}:
In this example, 10 sites are occupied by Mg^{2+} (red) and 3 are occupied by Fe^{2+} (yellow): the olivine formula is $(Mg_{77}Fe_{23})SiO_4$ (called "Forsterite seventy seven"; Fo_{77})



Modified from Nesse, 2000, Fig. 4.15a

- ***Couple substitution***

Couple substitution maintains charge balance by coupling one substitution that increases the charge with one that reduces the charge



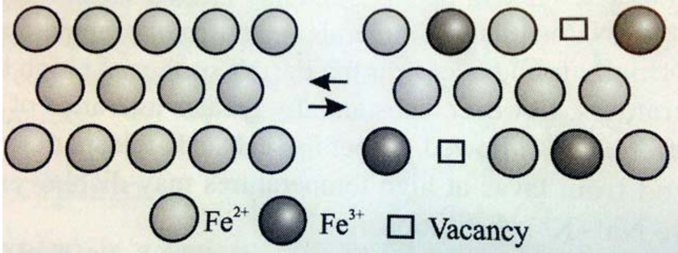
Nesse, 2000, Fig. 4.15b

e.g., plagioclase
albite: $(NaAlSi_3O8)$ ↔ anorthite $(CaAl_2Si_2O_8)$

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

- ***Omission substitution***

Omission substitution maintains charge balance by leaving structural sites vacant: $(n+1)M^{n+} \Leftrightarrow nM^{n+1} + \square$

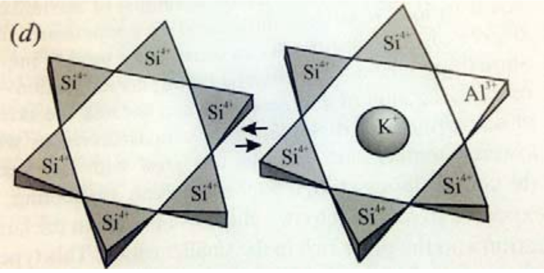


Nesse, 2000, Fig. 4.15c

e.g., 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

- ***Interstitial substitution***

Interstitial substitution maintains charge balance by placing ions in sites that normally are vacant:
E.g.: Beryl $Al_2Be_3SiO_6O_{18}$
$\square + Si^{4+} \Leftrightarrow Al^{3+} + (K^+, Rb^+, Cs^+)$



Nesse, 2000, Fig. 4.15d

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

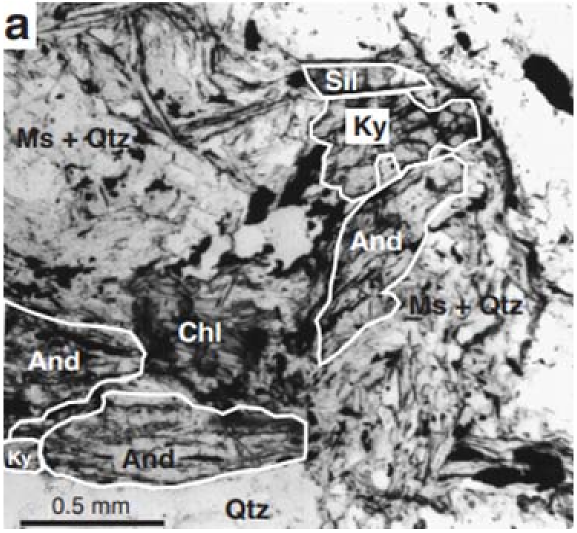
L7- Personal assessment

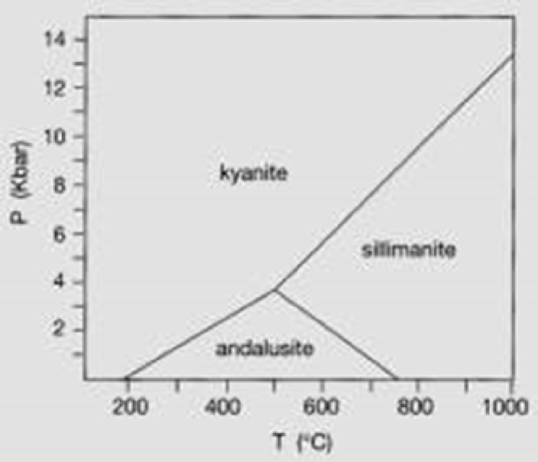
Tuesday, August 25, 2020 10:54 AM

After reviewing this material, you should be able to answer these questions:

****Multiple choices possible!****

1) **Whitney (2002, American Mineralogist) found a sample with kyanite, sillimanite and andalusite in a muscovite-bearing quartzite from Turkey. What is the most likely explanation?**

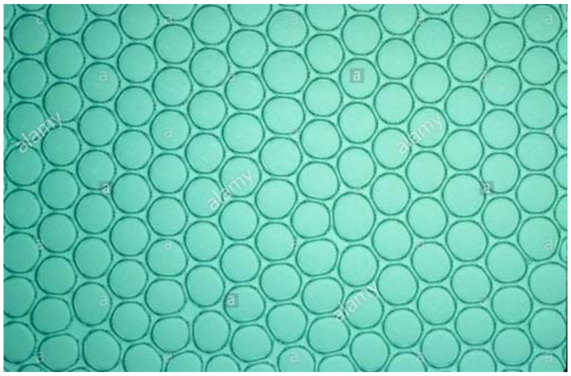




A - The rock was found at the pressure-temperature conditions of the triple point (i.e., where all three minerals are stable)?

B - 2 or more of these polymorphs are metastable?

2) **Which mineral is more likely to grow?**



A

B

3) **Finish these sentences:**

1. Point defects promote ________________
2. Planar defects promote _________________
3. Linear defects promote

A - twinning

B - crystal growth

C - diffusion

1. Point defects promote ________________
2. Planar defects promote _________________
3. Linear defects promote __________________

A - twinning
B - crystal growth
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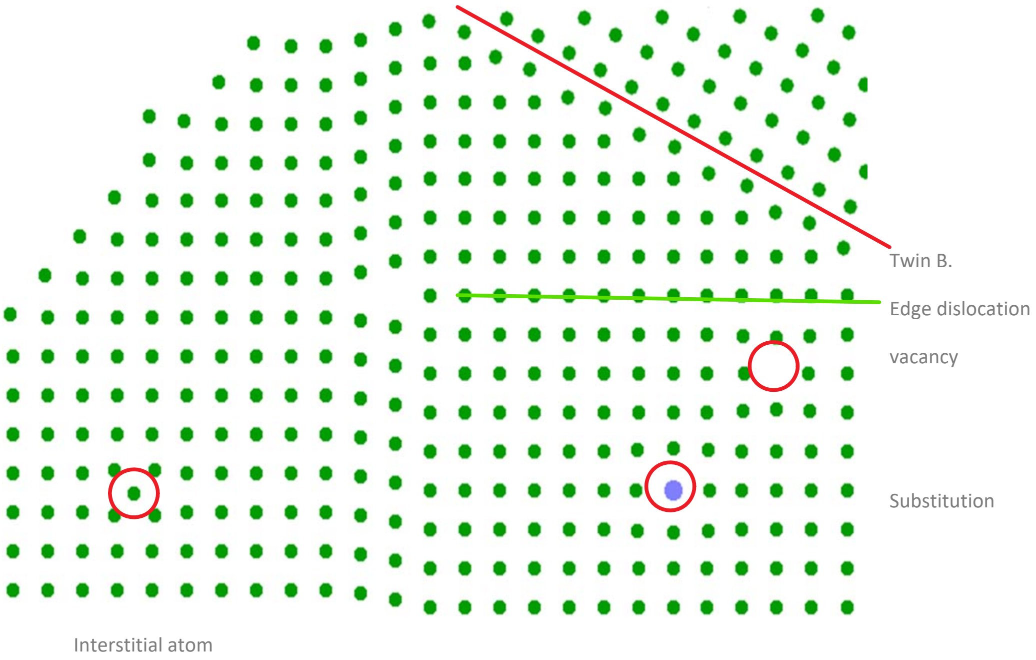
4) Plagioclase forms a complete solid solution because:

A – albite and anorthite are isomorphs
B – Na+ and Ca2+ have similar ionic radii
C – sodium and calcium are abundant on Earth
D – Na+ and K+ have similar ionic radii

5) Crystal twinning can be created:

A – During polymorphic phase transformation
B – During crystal growth
C – Thanks to the presence of a dislocation
D – By symmetry

Practice keys:



Can we find β-quartz in a sample? No because the transformation to α-quartz (the stable form of SiO2 at the surface of the Earth, is displace. Hence, β-quartz has only been observed in experiments. β-quartz is not a mineral.

Can we find coesite in a sample? Yes, because the transformation from coesite to quartz (α or β) is reconstructive. We can find metastable forms of coesite in samples.