

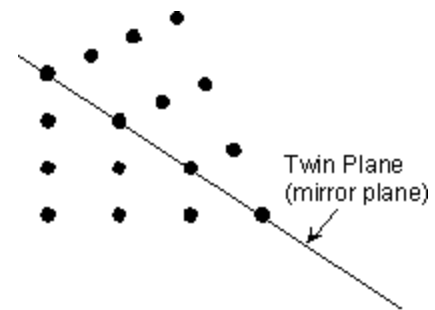
EENS 2110	Mineralogy
Tulane University	Prof. Stephen A. Nelson
<b>Twinning, Polymorphism, Polytypism, Pseudomorphism</b>	

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## 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 fashion. 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.

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.



### Symmetry Operations that Define Twinning

Because symmetry is added to a crystal by twinning, twinning 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*.

### Twin Laws

Twin laws are expressed as either form symbols to define twin planes (i.e.  $\{hkl\}$ ) or zone symbols to define the direction of twin axes (i.e.  $[hkl]$ ).

The surface along which the lattice points are shared in twinned crystals is called a *composition surface*.

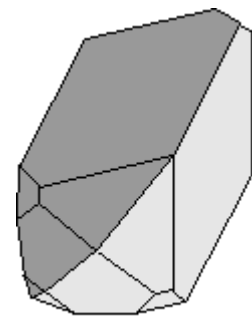
If the twin law can be defined by a simple planar composition surface, the twin plane is **always** parallel to a possible crystal face and **never** parallel to an existing plane of symmetry (remember that twinning adds symmetry).

If the twin law is a rotation axis, the composition surface will be irregular, the twin axis will be perpendicular to a lattice plane, but will never be an even-fold rotation axis of the existing symmetry. For example twinning cannot occur on a new 2 fold axis that is parallel to an existing 4-fold axis.

## Types of Twinning

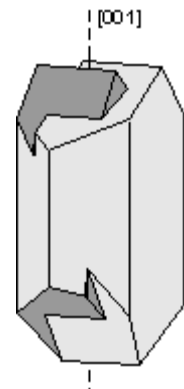
Another way of defining twinning breaks twins into two separate types.

1. **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). An example shown here is a crystal of orthoclase twinned on the Braveno Law, with  $\{021\}$  as the twin plane.



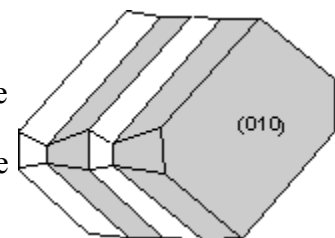
Twin Plane  $\{021\}$

2. **Penetration Twins** - have an irregular composition surface separating 2 individual crystals. These are defined by a twin center or twin axis. Shown here is a twinned crystal of orthoclase twinned on the Carlsbad Law with  $[001]$  as the twin axis.

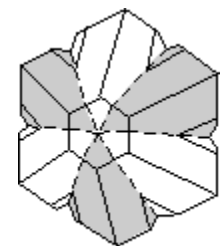


Contact twins can also occur as repeated or multiple twins.

- If the composition surfaces are parallel to one another, they are called **polysynthetic twins**. Plagioclase commonly shows this type of twinning, called the Albite Twin Law, with  $\{010\}$  as the twin plane. Such twinning is one of the most diagnostic features of plagioclase.



- If the composition surfaces are not parallel to one another, they are called **cyclical twins**. Shown here is the cyclical twin that occurs in chrysoberyl along a  $\{031\}$  plane.

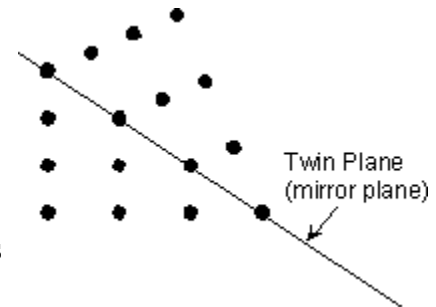


$\{031\}$

## Origin of Twinning

Twinning can originate in 3 different ways, as growth twins, transformation twins, and glide or deformation twins.

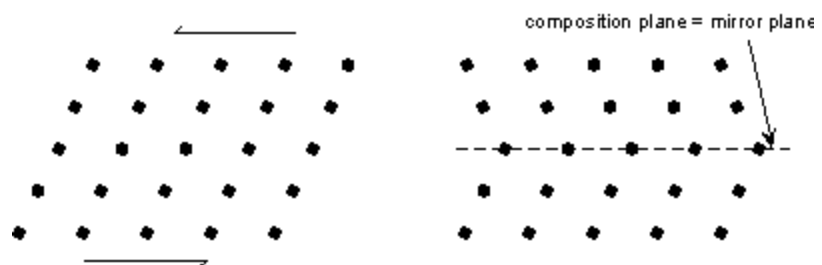
1. Growth Twins - When accidents occur during crystal growth and a new crystal is added to the face of an already existing crystal, twinning can occur if the new crystal shares lattice points on the face of the existing crystal, but has an orientation different from the original crystal. Such growth twins can be contact twins, as illustrated here, or can be penetration twins. All of twins discussed so far are growth twins.



2. Transformation Twins - Transformation twinning occurs when a preexisting crystal undergoes a transformation due to a change in pressure or temperature. This commonly occurs in minerals that have different crystal structures and different symmetry at different temperatures or pressures. When the temperature or pressure is changed to that where a new crystal structure and symmetry is stable, different parts of the crystal become arranged in different symmetrical orientations, and thus form an intergrowth of one or more crystals. Dauphiné and Brazil twinning in quartz commonly forms this way during a decrease in temperature.

Similarly the combination of albite twinning and pericline twinning in alkali feldspar results when high temperature sanidine (monoclinic) transforms to low temperature microcline (triclinic). This type of twinning is only observed using the polarizing microscope, and results in a "tartan" twinning pattern as shown in your text book on page 231, figure 10.18. When this twinning pattern is observed with the microscope it is one of the most characteristic diagnostic properties for the identification of microcline.

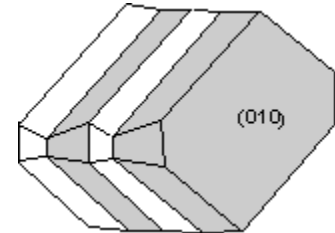
3. Deformation Twins - During deformation atoms can be pushed out of place. If this happens to produce a symmetrical arrangement, it produces deformation twins. The mineral calcite can be easily twinned in this way, producing polysynthetic twins on  $\{01\bar{1}2\}$ .



## Common Twin Laws

- **Triclinic System** - The feldspar minerals plagioclase and microcline are the most common triclinic minerals that show twinning. Two common twin laws are observed in these feldspars.

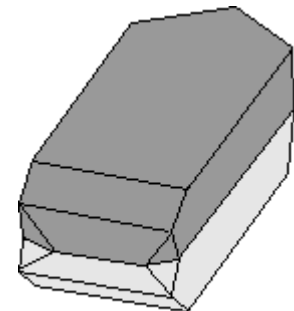
- Albite Law - As described above, plagioclase ( $\text{NaAlSi}_3\text{O}_8$  -  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) very commonly shows albite polysynthetic twinning. The twin law -  $\{010\}$  indicates that the twinning occurs perpendicular to the **b** crystallographic axis. Albite twinning is so common in plagioclase, that it's presence is a diagnostic property for identification of plagioclase.



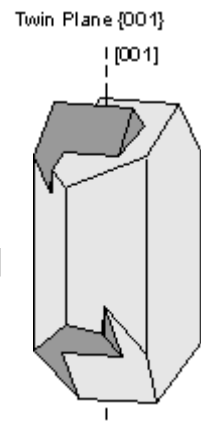
- Pericline Law - The pericline law has  $[010]$  as the twin axis. As stated above, pericline twinning occurs as the result of monoclinic orthoclase or sanidine transforming to microcline (all have the same chemical formula -  $\text{KAlSi}_3\text{O}_8$ ). Pericline twinning usually occurs in combination with albite twinning in microcline, but is only observable with the polarizing microscope. The combination of pericline and albite twinning produce a cross-hatched pattern, called tartan twinning, as discussed above, that easily distinguishes microcline from the other feldspars under the microscope.

- **Monoclinic System** - The most common twins in the monoclinic system occur on the planes  $\{100\}$  and  $\{001\}$ . The feldspars - orthoclase and sanidine - are the most commonly twinned minerals in the monoclinic system. Both contact twins and penetration twins occur, and both types result from accidents during growth.

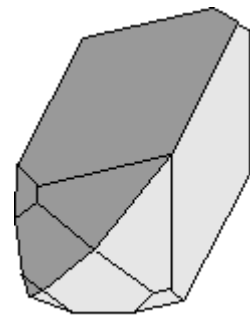
- Manebach Law -  $\{001\}$  - forms a contact twin commonly observed in the mineral orthoclase. This twinning is very diagnostic of orthoclase when it occurs.



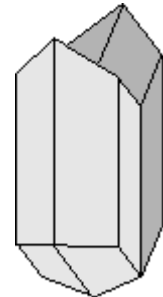
- Carlsbad Law -  $[001]$  - forms a penetration twin in the mineral orthoclase. Crystals twinned under the Carlsbad Law show two intergrown crystals, one rotated  $180^\circ$  from the other about the  $[001]$  axis. Carlsbad twinning is the most common type of twinning in orthoclase, and is thus very diagnostic of orthoclase when it occurs.



- Braveno Law -  $\{021\}$  - forms a contact twin in the mineral orthoclase.

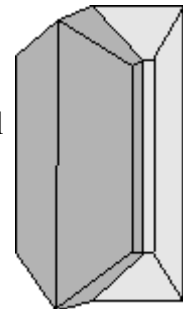
Twin Plane  $\{021\}$ 

- Swallow Tail Twins -  $\{100\}$ - are commonly observed in the mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

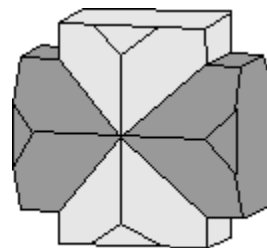
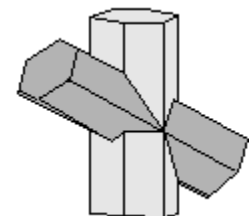
 $\{100\}$ 

- **Orthorhombic System** - Orthorhombic crystals commonly twin on planes parallel to a prism face. The most common is a  $\{110\}$  twin that results in many orthorhombic minerals having cyclical twins.

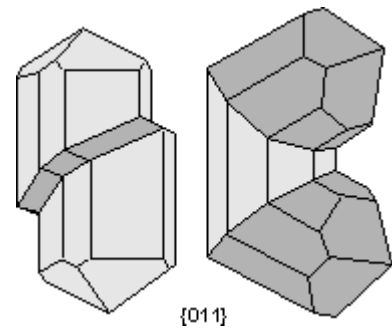
- $\{110\}$  Cyclical Twins - The mineral aragonite ( $\text{CaCO}_3$ ), chrysoberyl ( $\text{BeAl}_2\text{O}_4$ ), and cerrusite ( $\text{PbCO}_3$ ) commonly develop twinning on  $\{110\}$ . This results in a cyclical twin which gives these minerals a pseudo-hexagonal appearance.

 $\{110\}$ 

- Staurolite Law - The mineral staurolite is really monoclinic, but it has a  $\beta$  angle very close to  $90^\circ$  so it has the appearance of an orthorhombic mineral. Two types of interpenetration twins occur in staurolite the  $\{031\}$  twins from a right-angled cross and the  $\{231\}$  twins form a cross at about  $60^\circ$ .

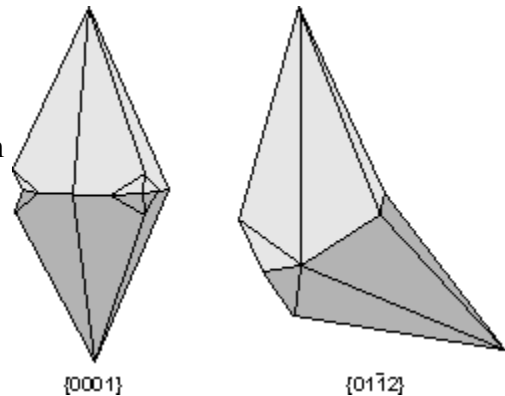
 $\{031\}$  $\{231\}$

- **Tetragonal System** - Twinning in the tetragonal system usually occurs on  $\{011\}$  forming cyclical contact twins. The minerals rutile ( $\text{TiO}_2$ ) and cassiterite ( $\text{SnO}_2$ ) commonly show this type of twinning.



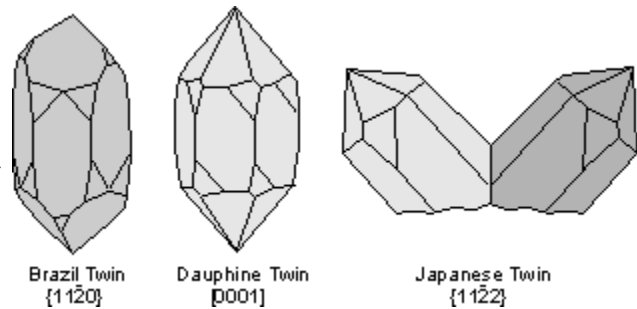
- **Hexagonal System** - The minerals calcite ( $\text{CaCO}_3$ ) and quartz ( $\text{SiO}_2$ ) are the most common hexagonal minerals and both show the types of twinning common in hexagonal minerals.

- Calcite Twins - The two most common twin laws that are observed in calcite crystals are  $\{0001\}$  and the rhombohedron  $\{01\bar{1}2\}$ . Both are contact twins, but the  $\{01\bar{1}2\}$  twins can also occur as polysynthetic twins that result from deformation.



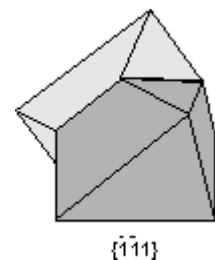
Quartz shows three other hexagonal twins.

- Brazil Law -  $\{11\bar{2}0\}$  - is a penetration twin that results from transformation.
- Dauphiné Law -  $[0001]$  - is also a penetration twin that results from transformation.
- Japanese Law -  $\{11\bar{2}2\}$  - is a contact twin that results from accidents during growth.

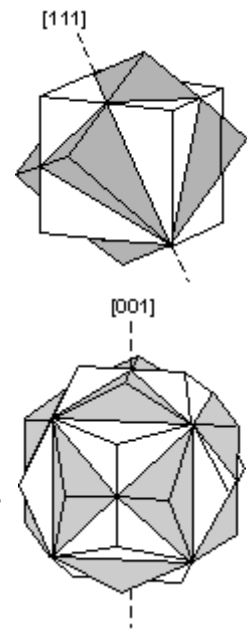


- **Isometric System** - Three types of twins are common in the isometric system.

- Spinel Law -  $\{\bar{1}\bar{1}1\}$  - is a twin plane, parallel to an octahedron. It occurs commonly in mineral spinel ( $\text{MgAl}_2\text{O}_4$ ).



- [111] - The twin axis perpendicular to an octahedral face adds three fold rotational symmetry.
- Iron Cross [001] - The mineral pyrite ( $\text{FeS}_2$ ) often shows the iron cross made of the interpenetration of two pyritohedrons. Since this occurs in the class  $2/m\bar{3}$ , with no 4-fold rotation axes, the [001] twin axis gives the mineral apparent 4-fold symmetry about 3 perpendicular axes.



## Polymorphism

Polymorphism means "many forms". In mineralogy it means that a single chemical composition can exist with two or more different crystal structures. As we will see when we look more closely at crystal structures, if a crystal is subjected to different pressures and temperatures, the arrangement of atoms depends on the sizes of the atoms, and the sizes change with temperature and pressure. In general, as pressure increases the volume of a crystal will decrease and a point may be reached where a more compact crystal structure is more stable. The crystal structure will then change to that of the more stable structure, and a different mineral will be in existence. Similarly, if the temperature is increased, the atoms on the crystal structure will tend to vibrate more and increase their effective size. In this case, a point may be reached where a less compact crystal structure is more stable. When the crystal structure changes to the more stable structure a different mineral will form.

The change that takes place between crystal structures of the same chemical compound are called ***polymorphic transformations***.

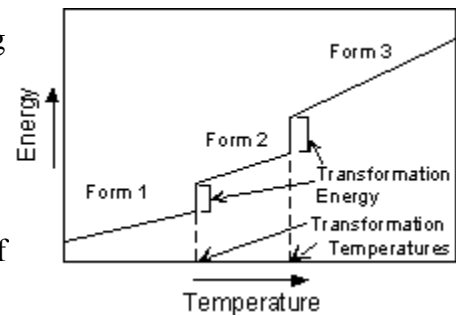
### Types of Polymorphic Transformations

Stability of crystal structures is generally referred to in terms of the energy of the crystal structure. In general terms this can be thought of as the bond strength (enthalpy), and entropy (degree of order or randomness) of the structure. In general, the structure with the lowest energy is the most stable at any given temperature and pressure.

This results in three types of transformations.

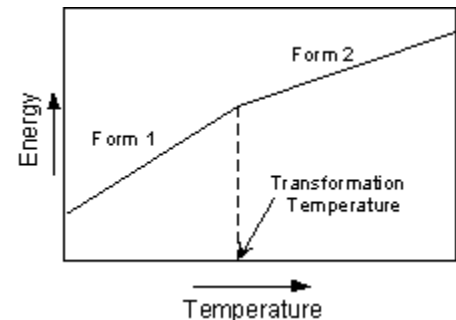
1. ***Reconstructive Transformations*** - these involve

extensive rearrangement of the crystal structure and requires breaking of chemical bonds and reassembling the atoms into a different crystal structure. This usually involves a large change in energy of the structure which must occur at the transformation temperature or pressure. 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.



For example, diamond is a metastable polymorph of Carbon at the pressures and temperatures present at the Earth's surface, yet, as the saying goes "diamonds are forever". Not really, it's just that the rate at which diamond can rearrange its crystal structure to become graphite, the polymorph stable at low P and T, is very slow at the low temperatures found near the Earth's surface.

2. **Displacive Transformations** - these involve only small adjustments to the crystal structure. Generally no bonds are broken, but the angles between the atoms may change slightly. Because there is little rearrangement, displacive transformations involve no change in energy at the transformation temperature or pressure, and the transformations are instantaneous and reversible. Thus, no unstable polymorphs will occur.



For example, at 1 atmosphere pressure high quartz ( $\alpha$  quartz) is the stable form of quartz above  $580^{\circ}\text{C}$ . When high quartz is brought to a temperature below  $580^{\circ}$  it immediately is transformed into low quartz ( $\beta$  quartz). Thus, high quartz is never seen in rocks at the surface of the Earth.

3. **Order - Disorder Transformations** - these involve the state of order or disorder in a crystal structure. Perfect order can only occur at a temperature of absolute zero ( $-273^{\circ}\text{C}$ ). As temperature increases, the degree of order or randomness of a crystal structure decreases, so that the higher temperature forms of minerals are more disordered than the lower temperature forms. Because the state of order-disorder changes gradually with increasing temperature, there is no definite temperature at which a transformation occurs.

An example of polymorphic transformations that involve order-disorder is the compound  $\text{KAlSi}_3\text{O}_8$ . At high temperature the stable form is Sanidine (Monoclinic). At lower temperature the structure changes to one of orthoclase (also Monoclinic), and at even lower temperature the structure becomes that of the more ordered structure of microcline



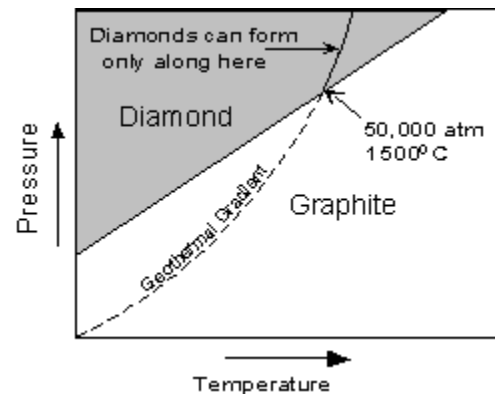
(also Triclinic).

There is no definite temperature at which Sanidine changes to orthoclase or orthoclase changes to Microcline, since the structure changes gradually as temperature decreases. If the temperature change is rapid, then unstable polymorphs can continue to exist at a low temperature.

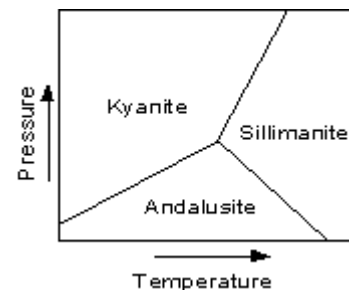
### Important Polymorphs

Many common minerals show polymorphism. We here look at some of the more common ones.

- **Carbon** - has two polymorphs. At high pressure carbon has an isometric crystal structure that is called diamond. As temperature and/or pressure are decreased diamond should undergo a reconstructive transformation to the hexagonal structure of graphite. Because this transformation involves a drastic rearrangement of atoms on the crystal structure, as evidenced by the fact that diamond is the hardest naturally occurring substance and graphite is one of the softest) diamond is found at the T & P conditions present at the Earth's surface, where it is therefore only metastable.

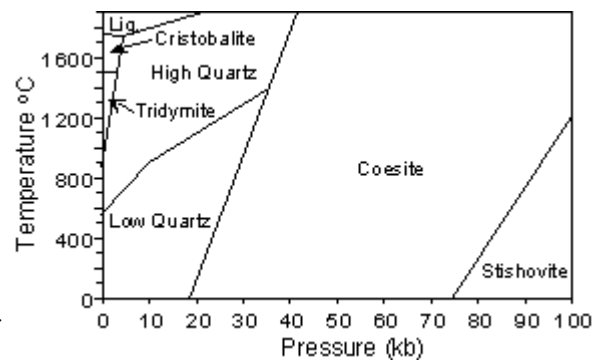


- $\text{Al}_2\text{SiO}_5$  - has three polymorphs. The high pressure form is kyanite (Triclinic), the high temperature form is sillimanite (orthorhombic), and the low temperature, low pressure form is andalusite (orthorhombic). Transformations between all three polymorphs are reconstructive, thus all three forms can metastably exist at the Earth's surface. Transformation rates are somewhat faster, however, at higher temperatures in the Earth.



- $\text{CaCO}_3$  - has two polymorphs. The high pressure form is aragonite (orthorhombic) and the low pressure form is calcite (hexagonal). The transformation between the two polymorphs is reconstructive, so metastable polymorphs can exist.

- $\text{SiO}_2$  - has 6 polymorphs. With decreasing temperature at low pressure, cristobalite (isometric) undergoes a reconstructive transformation to tridymite (hexagonal). Further lowering of temperature results in tridymite undergoing a reconstructive transformation to high quartz (also hexagonal). Lowering temperature further results in high quartz undergoing a



displacive transformation to low quartz.

Cristobalite and tridymite can exist metastably at the low temperatures near the Earth's surface, and thus are found in rocks. But high quartz will also transform to low quartz before it reaches temperatures present at the Earth's surface, so it is never found in rocks.

With increasing pressure, at low temperature low quartz undergoes a displacive transformation to coesite (Monoclinic), and coesite undergoes a reconstructive transformation to stishovite (tetragonal) at even higher pressures. Thus, coesite and stishovite have metastable polymorphs that can be found in rocks.

- $\text{KAlSi}_3\text{O}_8$  - As discussed above, this compound has three polymorphs that undergo order-disorder transformations with lowering of temperature. The high temperature polymorph is sanidine (monoclinic). It is usually only found in volcanic rocks that have cooled very rapidly so that a higher state of order is not achieved. With slower cooling, sanidine eventually undergoes a transformation to orthoclase (also monoclinic), and orthoclase eventually transforms to microcline (triclinic) with further slow cooling.

### Polytypism

**Polytypism** is a type of polymorphism wherein different polymorphs exist in different domains of the same crystal. It has to do with the way that individual layers are stacked within a crystal structure. Polytypism has little geologic consequence, and will thus not be discussed further here.

### Metamict Minerals

Metamict minerals are minerals whose crystal structure has been partially destroyed by radiation from contained radioactive elements. The breakdown of the crystal structure results from bombardment of a particles emitted by the decay of U and Th radioactive isotopes.

The mineral zircon ( $\text{ZrSiO}_4$ ) often has U and Th atoms substituting for Zr in the crystals structure. Since U and Th have radioactive isotopes, Zircon is often seen to occur in various stages of metamictization.

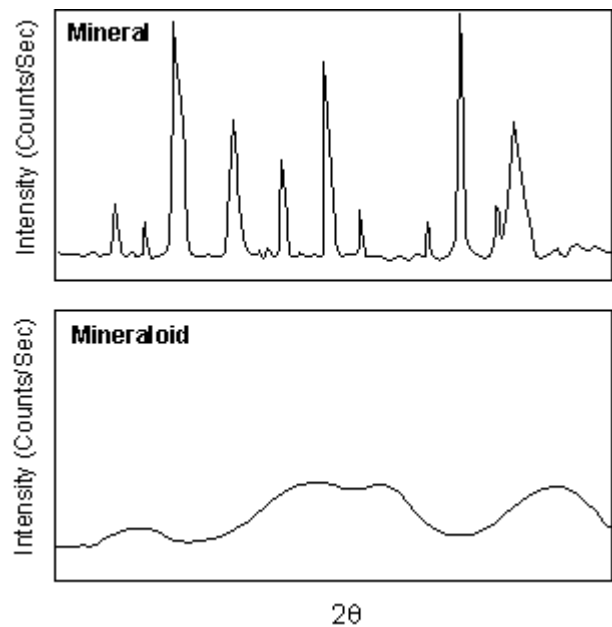
### Mineraloids

By definition, a mineral has to have an ordered atomic arrangement, or crystalline structure. There are some Earth materials that fit all other parts of the definition of a mineral, yet do not have a crystalline structure. Such compounds are termed **amorphous** (without form).

Some of these amorphous compounds are called mineraloids. These usually form at low temperatures and pressures during the process of chemical weathering and form mammillary, botryoidal, and stalactitic masses with widely varying chemical compositions. Limonite [ $\text{FeO} \cdot (\text{OH}) \cdot n\text{H}_2\text{O}$ ] and allophane ( a hydrous aluminum silicate) are good examples.

Others like volcanic glass and opal ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) have short-range order or domains wherein some crystalline-like order exists.

Unlike crystalline minerals that show sharp, well defined x-ray diffraction peaks, these mineraloids with short-range order show broad diffraction peaks that give evidence of the short-range order.



### Pseudomorphism

**Pseudomorphism** is the existence of a mineral that has the appearance of another mineral. Pseudomorph means false form. Pseudomorphism occurs when a mineral is altered in such a way that its internal structure and chemical composition is changed but its external form is preserved. Three mechanisms of pseudomorphism can be defined:

1. Substitution. In this mechanism chemical constituents are simultaneously removed and replaced by other chemical constituents during alteration. An example is the replacement of wood fibers by quartz to form petrified wood that has the outward appearance of the original wood, but is composed of quartz. Another example is the alteration of fluorite which forms isometric crystals and is sometimes replaced by quartz during alteration. The resulting quartz crystals look isometric, and are said to be pseudomorphed after fluorite.
2. Encrustation. If during the alteration process a thin crust of a new mineral forms on the surface of a preexisting mineral, then the preexisting mineral is removed, leaving the crust behind, we say that pseudomorphism has resulted from encrustation. In this case the thin crust of the new mineral will have casts of the form of the original mineral.
3. Alteration. If only partial removal of the original mineral and only partial replacement by the new mineral has taken place, then it is possible to have a the space once occupied entirely by the original mineral be partially composed of the new mineral. This results for example in serpentine pseudomorphed after olivine or pyroxene, anhydrite ( $\text{CaSO}_4$ ) pseudomorphed after gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), limonite [ $\text{FeO} \cdot (\text{OH}) \cdot n\text{H}_2\text{O}$ ] after pyrite ( $\text{FeS}_2$ ), and anglesite ( $\text{PbSO}_4$ ) after galena ( $\text{PbS}$ ).

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### Examples of questions on this material that could be asked on an exam

1. Define the following : (a) Twinning, (b) twin plane, (c) twin axis, (d) composition surface, (e) contact twin, (f) penetration twin.

2. What are three ways that twinning can originate?
  3. Why can't twinning occur parallel to axes or planes of existing symmetry in a crystal.
  4. Define polymorphism.
  5. Give several examples of minerals that show polymorphism, being sure to name all of the polymorphs.
  6. Describe that three different types of transformations that result in new polymorphs.
  7. Define the following: (a) metamict mineral, (b) pseudomorphism, (c) mineraloid.
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