## Polymorphism and Pseudomorphism:

There are three word **ploy** = many, **mor**= shape and **phism** = process,
An element or compound that can exist in more then one Crystal form is said to be polymorphous and the process that an element or compound that can change more then one crystal from this process is known as Polymorphism, which is internal structure is same and outer arrangment is different but chemical composition is same ...! Diamond and graphite is mainly composed by Carbon element but have cubic and orthorhombic respectivily.
**Pseudo**= false, **mor**= shape and **phism** = process,
A mineral can replaced by another mineral without any change in the external from, such replacement are called pseudomorhous and process is known as pesudomorpism. This process the cavity of mineral is present and filled with another mineral.....!

### 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.

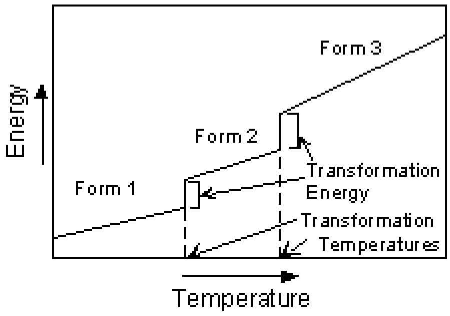
The change that takes place between crystal structures of the same chemical compound are called ***polymorphic transformations.***

### 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.

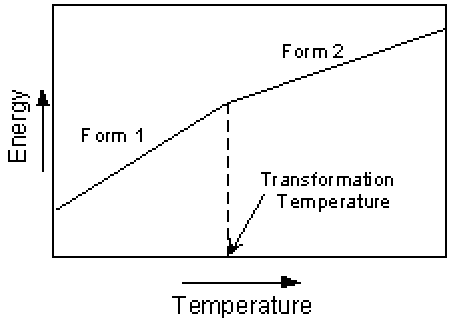
This results in three types of transformations.

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 (β quartz) is the stable form of quartz above 580°C. When high quartz is brought to a temperature below 580° it immediately is transformed into low quartz (α 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°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.

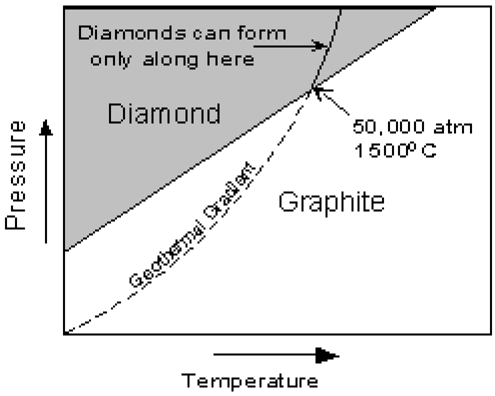
An example of polymorphic transformations that involve order-disorder is the compound $KAlSi_3O_8$. At high temperature the stable form is Sanidine (Monoclinic). At lower temperature the structure changes to one of orthoclase (also Monoclinic), and at even lower temperature the structure becomes that 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 a low temperature.

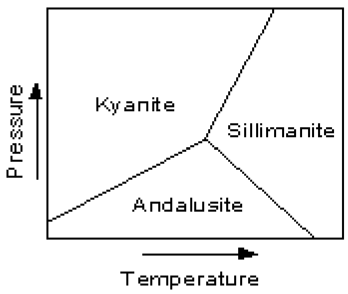
**Important Polymorphs**

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.

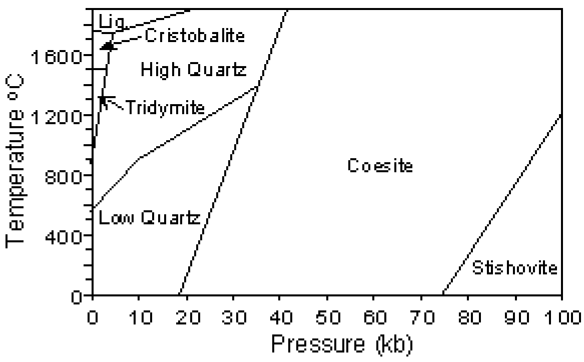



- $Al_2SiO_5$ - has three polymorphs. The high pressure form is kyanite (Triclinic), the high temperature form is sillimanite (orthorhombic), and the low temperature, and low pressure form is andalusite (orthorhombic). Transformations between all three polymorphs are reconstructive, thus all three forms can metastably exist at the Earth's surface. Transformation rates are somewhat faster, however, at higher temperatures in the Earth.



- $CaCO_3$ -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 exit.

- $SiO_2$- 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 displace 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.

- $KAlSi_3O_8$- 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 ($ZrSiO_4$) 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.

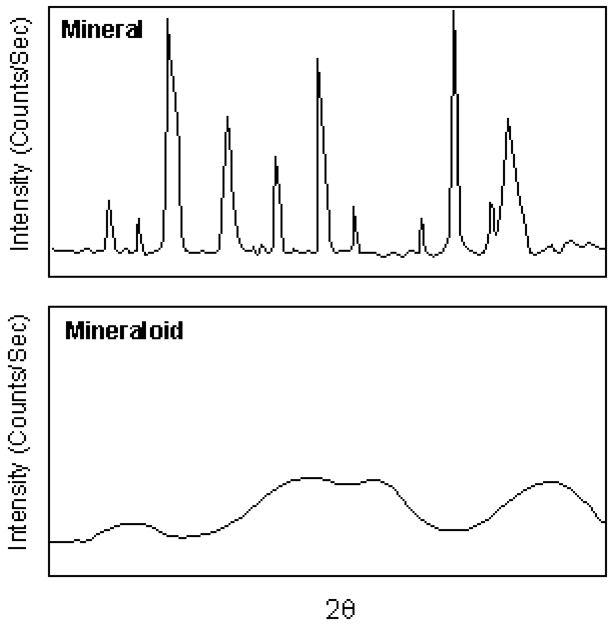
## Mineraloids

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 [$FeO\cdot(OH)\cdot nH_2O$] and allophane ( a hydrous aluminum silicate) are good examples.

Others like volcanic glass and opal ($SiO_2\cdot nH_2O$) 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 ($CaSO_4$) pseudomorphed after gypsum ($CaSO_4 \cdot 2H_2O$), limonite [$FeO \cdot (OH) \cdot nH_2O$] after pyrite ($FeS_2$), and anglesite ($PbSO_4$) after galena (PbS).