

## Silica (Quartz):

Silica,  $\text{SiO}_2$ , occurs in a number of different forms in the Earth and is the second most abundant mineral in the Earth's crust.

Polymorphic in nature ( $>10$ ).

Quartz, or  $\alpha$ -quartz is the stable form of  $\text{SiO}_2$  at atmospheric temperature and pressure.

It occurs in igneous, sedimentary, metamorphic, and hydrothermal mineral environments, particularly in continental regions. It is, however, rare in oceanic rocks. It is usually nearly pure and accepts only very limited amounts of other elements in substitution. Some polymorphs include  $\beta$ -quartz, tridymite, cristobalite, coesite, stishovite, and keatite.

The high-pressure forms of silica are coesite, stable in the deep crust of the Earth, and stishovite which is thought to be stable in the Earth's mantle.

In low temperature environments at the Earth's surface and on the ocean floor, silica also occurs in amorphous and partly crystalline forms.

### Structure:

The structure of quartz consists of corner-sharing  $\text{SiO}_4$  tetrahedra so that each Si is bonded to four oxygens, and each oxygen is bonded to two silicon atoms. The resulting structure forms an open three-dimensional framework, so that quartz is classified as a framework silicate.

### Occurrence:

Quartz may crystallize from magmas, silica saturated groundwaters, or hydrothermal solutions.

Essential component of silicic and intermediate igneous rocks, many sediments, and many metamorphic rocks.

In some sedimentary rocks, such as chert or sandstone, it may be the only mineral present. In silicic and intermediate igneous rocks, quartz is commonly found with K-feldspar. Both are Si-rich minerals that form at relatively low temperature.

### Non-Occurrence:

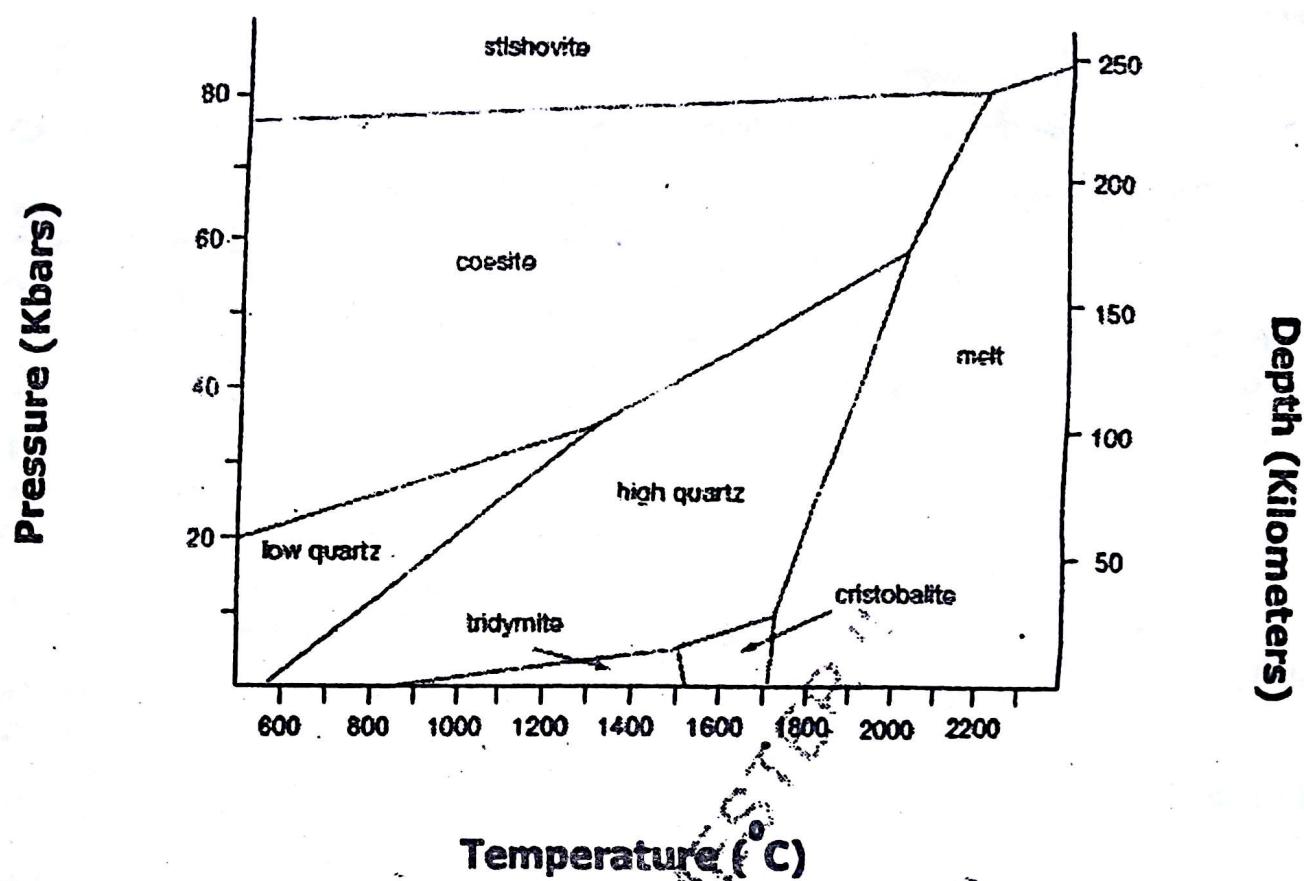
Quartz is not normally found in mafic igneous rocks;  $\text{SiO}_2$  is too scarce to remain after crystallization of mafic minerals such as olivine or pyroxene.

Quartz cannot exist in rocks containing corundum ( $\text{Al}_2\text{O}_3$ ), because the two would react to form the mineral  $(\text{Al}_2\text{SiO}_5) / (\text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$



It cannot exist in rocks containing feldspathoids (leucite, nepheline, or analcime) because quartz and feldspathoids react to give feldspars. For similar reasons, quartz is absent or minor in many alkali-rich igneous rocks and in rocks containing the oxide mineral spinel  $\text{MgAl}_2\text{O}_4$ .

### Pressure-Temperature $P$ - $T$ stability of $\text{SiO}_2$ polymorphs:



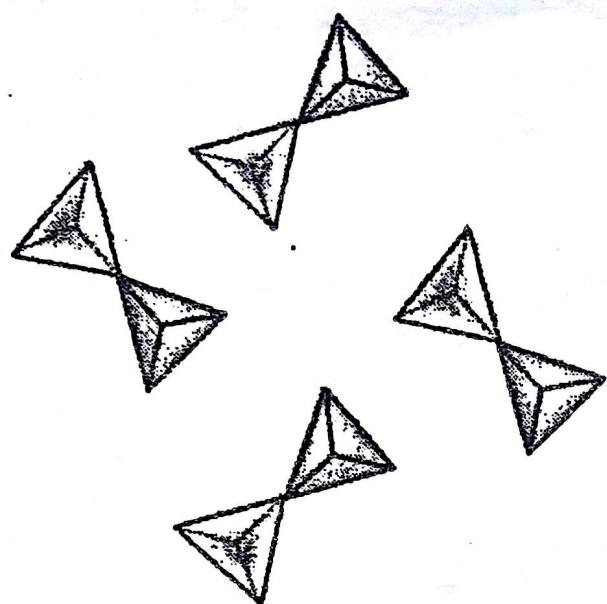
$P$ - $T$  diagram showing the stability fields of some of the  $\text{SiO}_2$  polymorphs, and the melting field at high temperature. Individual polymorphs (e.g., stishovite, coesite, or high quartz) are stable in the regions indicated. Two polymorphs may coexist at pressure-temperature conditions that fall on a line. Three polymorphs may coexist if conditions fall on a point where lines intersect. Most of this diagram is space between lines. So, only one polymorph is stable under most pressure-temperature conditions.

#### Most common polymorph:

$\alpha$ -quartz (low quartz) is the stable phase over a wide range of  $P$ - $T$ , including normal Earth surface conditions. Stishovite and coesite are dense minerals, only stable at very high pressures—pressures not normally encountered in the Earth's crust. They are usually associated with meteorite impact craters. Tridymite and cristobalite only exist in certain high temperature silicic volcanic rocks. They require temperatures greater than to form.

## Melilites

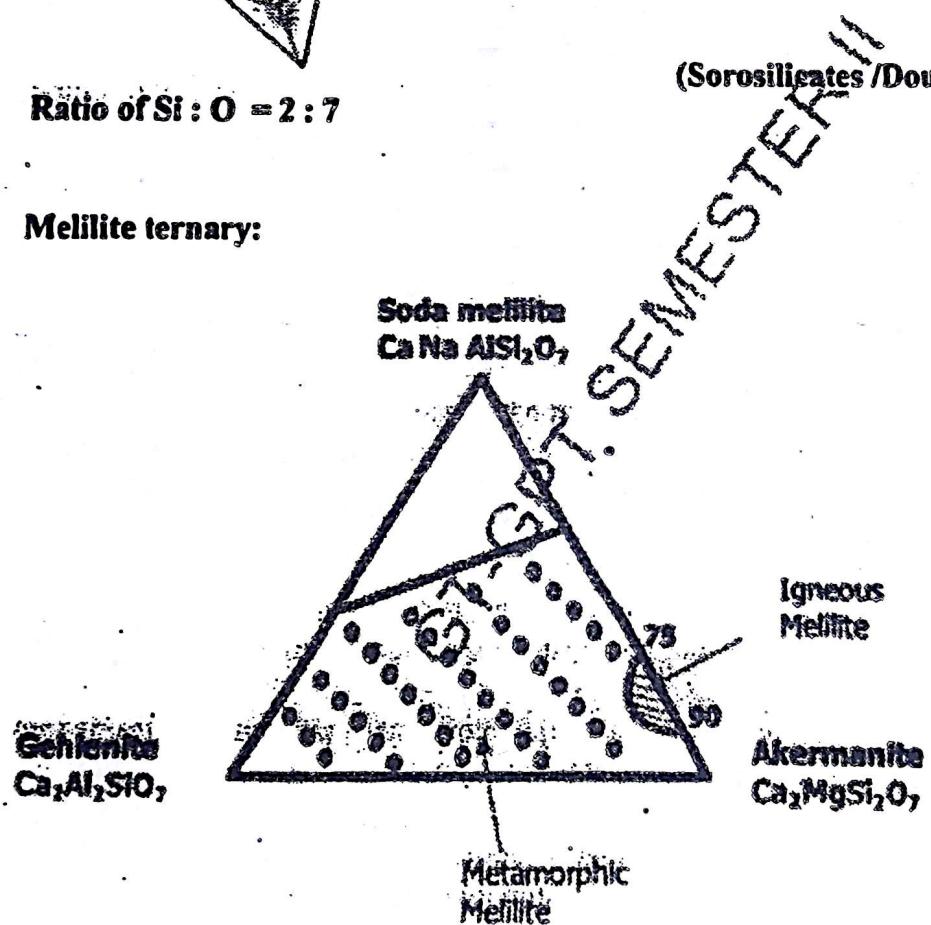
Structure:



Ratio of Si : O = 2 : 7

(Sorosilicates / Double island silicates)

Melilite ternary:



### Occurrence:

#### Igneous rocks

Melilite is the dominant constituent of the plutonic ultramafic rock 'pyroxene melilitonite', and has also been reported from carbonatites. Extrusive ultramafic melilite-bearing rocks, or melilitites contain melilites in the groundmass and occasionally also as phenocrysts. In igneous rocks in general, melilite is apparently incompatible with plagioclase and amphiboles (may coexist with plagioclase in 'hybrid rocks'). Melilite has been reported in 'chondrules' in several chondritic meteorites.

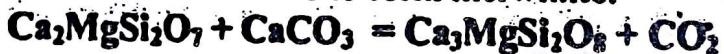
#### Metamorphic rocks

Melilite are characteristics of high-temperature mineral associations in thermally metamorphosed impure limestones.

Formation of akermanite during progressive metamorphism of siliceous limestones and dolomites is due to the reaction:



At higher temperatures Akermanite becomes unstable in the presence of calcite and reacts with carbonate to form merwinite:



## Garnet:

Garnets are diverse compositionally, physically, and in mode of occurrence. The garnet structure accommodates cations with a wide range of sizes and valence states. These nesosilicates crystallize in the isometric system. They make excellent candidates for gemstones. Garnets are stable phases in a wide range of pressures, temperatures, and chemical environments.

**General formula:**  $X_3Y_2Z_3O_{12}$

### Garnet End-Members

## Ugrandite Series

Uvarovite  $Ca_3Cr_2(SiO_4)_3$   
Grossular  $Ca_3Al_2(SiO_4)_3$   
Andradite  $Ca_3Al_2(SiO_4)_3$

## Pyralspite Series

Pyrope  $Mg_3Al_2(SiO_4)_3$   
Almandine  $Fe_3Al_2(SiO_4)_3$   
Spessartine  $Mn_3Al_2(SiO_4)_3$

### Occurrence:

**Pyrope** - mineral of the upper mantle - ultra-basic rocks

**Almandine** - common garnet in metamorphic rocks  
- regional metamorphism of argillaceous sediments

**Spessartine** - occurs in skarn deposits and Mn-rich deposits

**Grossular** - contact or regional metamorphism of impure limestones

**Andradite** - may be the result of metamorphism of impure siliceous environments similar to that of grossular

**Uvarovite** - rarest of garnets  
- found in serpentine associated with chromite

## **Polymorphism**

For minerals: this implies that a single chemical composition can exist with two or more different crystal structures.

If a crystal is subjected to different pressures and temperatures, the arrangement of atoms depending upon the sizes of the atoms, changes with temperature and pressure.

With increase in pressure crystal volume 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.

With temperature increase, the atoms in 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.

### **Different types of Polymorphic Transformations in minerals:**

Stability of crystal structures is generally referred to in terms of the energy of the crystal structure. This may 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:

**Reconstructive Transformations**

**Displacive Transformations**

**Order - Disorder Transformations**

**Reconstructive Transformations:** There is 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 large-scale rearrangement involved, the rate at which this 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. 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.

**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 (α quartz) is the stable form of quartz above 580°C. When high quartz is brought to a temperature below 580°C, it is immediately transformed into low quartz (β quartz). Thus, high quartz is never seen in rocks at the surface of the Earth.

**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.

### Important Polymorphs:

#### Common minerals showing polymorphism:

1. Graphite-Diamond (Please refer to your class notes for more details)
2.  $\text{Al}_2\text{SiO}_5$  - 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.
3.  $\text{CaCO}_3$  - 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.
4.  $\text{SiO}_2$  (Please refer to the 'Pressure-Temperature P-T stability of  $\text{SiO}_2$  polymorphs' in the quartz lecture, and your class notes and for more details)

### 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.

Most common in micas and clay minerals.

Most important mica polytypes are: 1M (monoclinic), 2M<sub>1</sub> (also monoclinic), and 3T (Trigonal).

Other types are 2M<sub>2</sub>, 2O (orthorhombic) and 6H (hexagonal).

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

### 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:

Substitution

Encrustation

Alteration

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 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 ( $CaSO_4 \cdot 2H_2O$ ),

Encrustation: If during the alteration process a thin crust of a new mineral forms on the surface of a pre-existing mineral, then the pre-existing 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.

**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.

**For the following topics: Please refer to your class notes and the book 'Mineralogy' by Dexter Perkins as well.**

**Crystal imperfections (Defects)**

**Crystal imperfections (Zoning)**

**Crystal imperfections (Twining)**

**CRYSTALLIZATION OF MAGMAS**

**Equilibrium Between Crystals and Melt**

**Bowen's Reaction Series**

**Disequilibrium**

**Fractional Crystallization**

**Igneous minerals (We have covered this in great detail)**

**Optical Mineralogy**

# Coordination number:

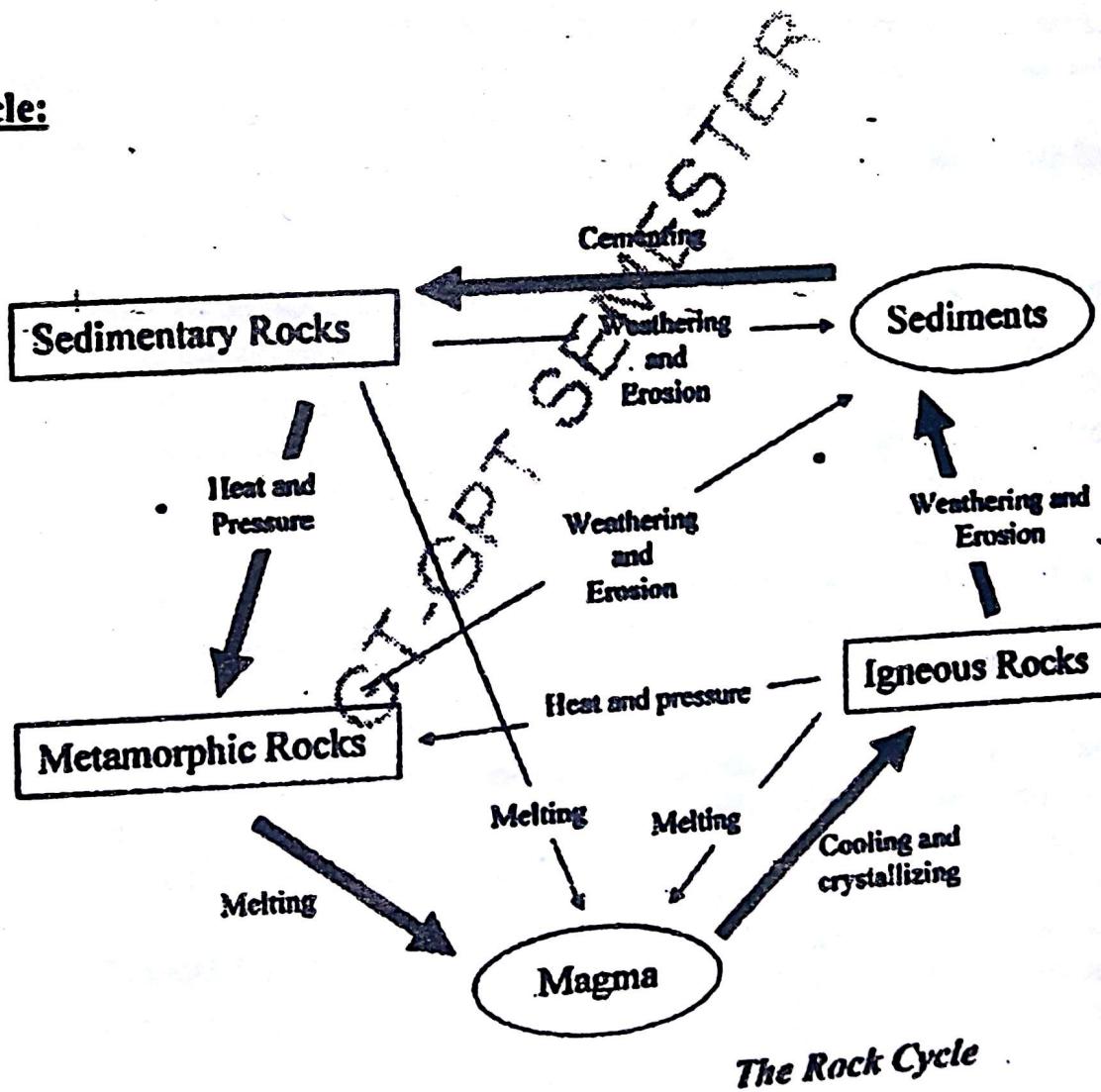
The number of anions surrounding a cation in a crystal structure is called the Coordination number of the cation.

Most important anion in the Earth's crust: Oxygen (most abundant)

$$(\text{Radius}_{\text{cation}}) / (\text{Radius}_{\text{anion}}) = \text{Coordination number}$$

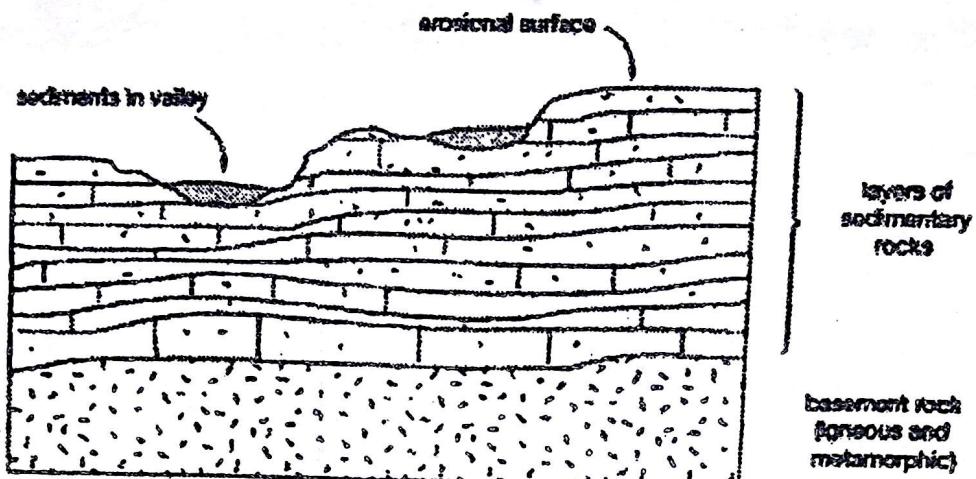
0.15 - 0.22	3
0.22 - 0.41	4
0.41 - 0.73	6
0.73 - 1	8
1	12

## Rock cycle:



## Sedimentary minerals:

Sediments and sedimentary rocks cover about 80% of all continental areas but are less than 1% of the volume of the Earth's crust. They are, in effect, a thin blanket on top of igneous and metamorphic basement rocks.



Sediments, and thus sedimentary rocks, are mostly recycled materials derived from preexisting igneous, metamorphic, or sedimentary rocks. Petrologists usually divide sedimentary rocks into two main groups:

### **Detrital rocks and Chemical rocks.**

**Detrital sedimentary rocks** are those for which the material has been transported as solid particles. The particles themselves may have derived from either physical weathering or chemical weathering. Sedimentation means settling from a fluid, either water or air. The texture of sedimentary rocks is described as "clastic", meaning that they are composed of discrete particles that are compacted and cemented together.

**Chemical sedimentary rocks** derive from material that is carried in solution to lakes and seas. If the solute precipitates out of the solution to form chemical sediments, rocks such as limestone can be formed.

In principle, silicate minerals could all exist in sediments and sedimentary rocks. In practice, most break down so quickly that they cannot be weathered or transported very much before completely decomposing. Quartz is the most resistant to weathering. It is also a common component of many igneous and metamorphic rocks found at the Earth's surface. So, quartz is the main component of many clastic sediments. Feldspars are also found in clastic sediment rocks. They are usually subordinate to quartz, and are rare in sediments transported long distances or weathered for long times.

Mafic silicate minerals occasionally exist in detrital rocks but are never major components. Besides quartz, the other common silicates in sedimentary rocks are clays and zeolites.

Important non-silicate minerals found in sedimentary rocks include carbonates, sulfates, and halide minerals.

**Zeolites:** The zeolite group includes more than 40 minerals. All are framework silicates containing open cavities capable of holding loosely bonded large cations and water. example, Natrolite,  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$

**Clay minerals:** Clays account for nearly half the volume of sedimentary rocks. They are usually very fine grained, often less than 1 micron in size, have complex chemistries, and are structurally variable, which makes identification of individual clay species difficult. In contrast with quartz and feldspar, clays do not form in igneous and metamorphic environments. Clays form in sedimentary environments and their compositions depend on the sources of the sediment. The clay mineral group includes many different minerals, all sheet silicates. They have layered atomic structures, similar in many respects to micas. Clays are hydrous, some containing as much as 15 to 20 wt%  $\text{H}_2\text{O}$ . Their layered structure and the weak bonding between layers give them a characteristic slippery feel when wet. Clays are common in shales and other sedimentary rocks. Although usually fine grained, they form thick beds or layers.

Talc, a secondary mineral that forms when Mg-silicates such as olivine or pyroxene are altered, and pyrophyllite, an uncommon metamorphic mineral, are often grouped with the clays. They are, however, less variable in their structure and composition and contain less  $\text{H}_2\text{O}$ . They are transitional between clays and micas in structure and, when seen in hand specimen or thin section, are typically easier to identify than clays.

The three most important kinds of clays are illite, montmorillonite, and the clays of the kaolinite group.

Clay	Chemical Formula
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Illite	$\text{K}_{1-2}\text{Al}_4(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_4$
Smectite group:	$(\text{Ca}, \text{Na})_{0.2-0.5}(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Montmorillonite	$(\text{Mg}, \text{Ca})_{0.3-0.4}(\text{Mg}, \text{Fe}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Vermiculite	

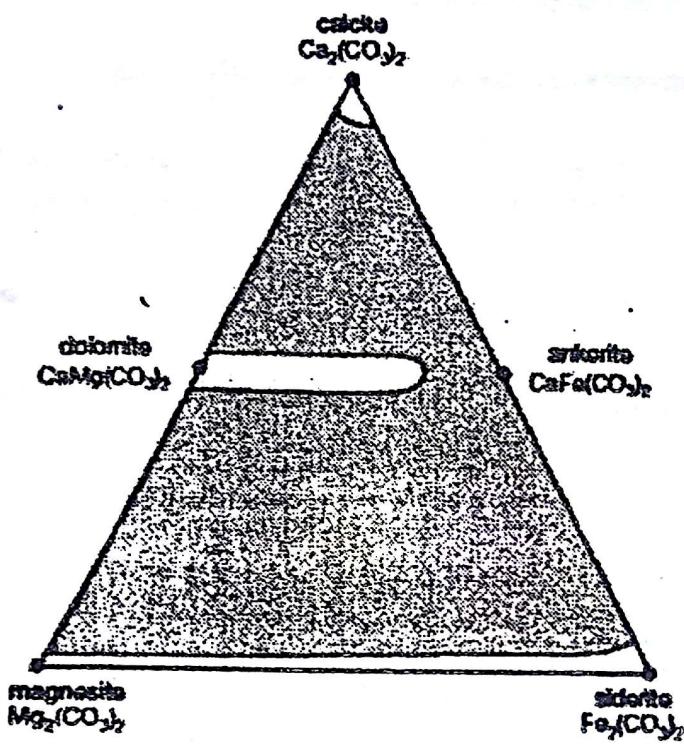
Kaolinites, also called kandites, vary less in composition and structure than other clays, although several kaolinite polymorphs are known. Kaolinite is the principal clay used to make ceramic ware.

Illite is similar to muscovite in some ways, but contains more Si and less K.

Montmorillonites, which belong to the smectite group, can take up extra water or other fluids between the layers of their atomic structure. In the process they expand; thus, we sometimes call them expandable or swelling clays. Because they absorb liquids so well, gas station operators use them to clean up spilled oil, and homeowners use them as kitty litter.

**Carbonates:** More than 50 different carbonate species; all contain  $(\text{CO}_3)^{2-}$  but some also contain other anions or anionic groups.

examples: Calcite, Dolomite, Siderite, Magnesite etc.



The principal end members of carbonate minerals. Natural compositions falling in the shaded region are rare due to immiscibility.

**Sulfates:** More than 100 sulfate minerals are known. They fall into two main groups: those that contain no water (anhydrous sulfates) and those that do (hydrated sulfates). Examples in the first group include anhydrite, barite, celestite, and anglesite. The second group includes Gypsum and some other minerals. We have covered all these minerals in class lectures.

**Halides:** Halite and sylvite are common in sedimentary rocks.

## Metamorphic minerals

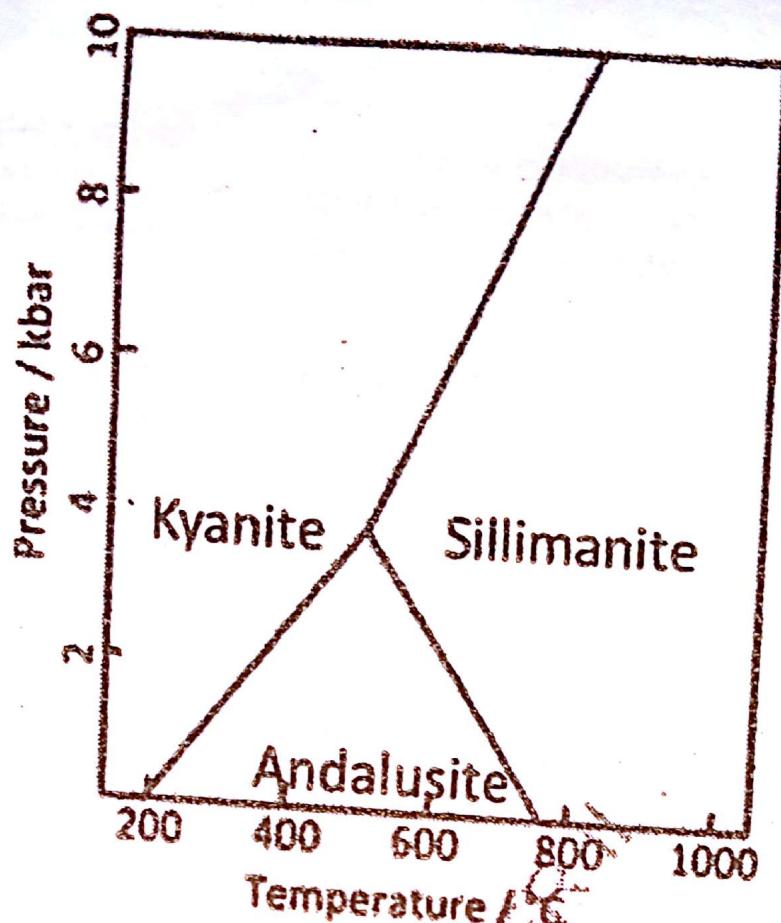
The term metamorphism describes a change in a rock's mineralogy, texture, or composition without melting. It occurs when minerals undergo metamorphic reactions, when texture changes due to recrystallization or realignment of minerals, or when a rock's chemistry is changed by flowing fluids.

The principal agents of metamorphism are heat, pressure, and fluids composed primarily of water and CO<sub>2</sub>.

All types of rocks can be metamorphosed. Some, such as clay-rich sediments, change greatly when metamorphosed; others, such as granite, change to a lesser extent. The nature of the changes depends on rock composition and the conditions at which metamorphism occurs.

Metamorphic rocks may contain all the minerals common in sedimentary and igneous rocks, as well as many minerals exclusive to metamorphic rocks. The two most important factors controlling mineralogy are the composition of the rock and the grade of metamorphism.

Common Kinds of Metamorphic Rocks	Essential Minerals	Unmetamorphosed Equivalents
slate	quartz	clay-rich sediments
phyllite	micas	
schist		
gneiss		
quartzite	quartz	sandstones
quartzofeldspathic gneiss		felspathic sandstones
greenstone		
amphibolite	amphiboles	basaltic rocks
anatic gneiss	plagioclase	
mafic granulite		
eclogite		
marble	carbonates	limestone dolomite
slate		
phyllite	micas	calcareous shale
schist	carbonates	shaly limestone
gneiss		
banded iron formation	quartz jasper magnetite hematite	iron-rich chemical sediments
serpentinite	serpentine talc Mg-rich amphiboles	ultramafic igneous rocks
granitic gneiss	K-feldspar	
granulite	quartz micas	granitic rocks



**Phase diagram.** The diagram shows the general P-T conditions under which kyanite, sillimanite and andalusite are stable. Kyanite is found in high-pressure pelitic rocks, andalusite is found in low-pressure pelitic rocks, and sillimanite is typical of high-grade pelitic rocks.

Pelite is a term applied to metamorphic rocks derived from a fine-grained ( $<1/16$  mm) sedimentary protolith. The term usually implies argillaceous, siliciclastic sediments as opposed to carbonate mudstones.

The original rock that has undergone metamorphism is called the *protolith*.

## Primary and Secondary minerals

Whether the mineral is primary or secondary depends on the mode of formation and not on the mineral composition.

Minerals that crystallize from cooling magma are called primary.

Examples (Important Primary minerals):

Quartz,  
Orthoclase, Plagioclase (Feldspars),  
Olivine,  
Pyroxene,  
Mica

Minerals that crystallize during the weathering of primary minerals are called secondary minerals.

Examples (Important Secondary minerals):

Clay minerals- kaolinite, montmorillonite  
Oxides – Hematite, Goethite, Gibbsite  
Carbonates – Calcite, Dolomite  
Sulfates – Gypsum

Accessory minerals:

Accessory mineral is <1 % of a rock by volume.

Generally Accessory minerals (in igneous rocks) are not essential to the naming of the rock. When it is present in small amounts, as is common, it is called a minor accessory. If the amount is greater or is of special significance, the mineral is called a varietal, or characterizing, accessory and may give a varietal name to the rock (e.g., the mineral biotite in biotite granite).

Accessory minerals characteristic are formed during the solidification of the rocks from the magma; in contrast are secondary minerals, which form at a later time through processes such as weathering by hydrothermal alteration.

Examples of common minor accessory minerals include topaz, zircon, corundum, fluorite, garnet, monazite, rutile, magnetite, and tourmaline. Typical varietal accessories include biotite, muscovite, amphibole, pyroxene, and olivine.

The following minerals have been extensively covered in class. Please refer to your class notes and the book 'Mineralogy' by Dexter Perkins as well.

### Non-silicate minerals:

**Metals (platinum, iridium, osmium, iron, zinc, tin, gold, silver, copper, mercury, lead, chromium);**

**Semimetals (bismuth, antimony, arsenic, tellurium, selenium); and**

**Nonmetals (sulfur; carbon: Graphite and Diamond)**

**Sulfides: Sphalerite ( $ZnS$ ); Chalcopyrite ( $CuFeS_2$ ); Galena ( $PbS$ ); Pyrrhotite ( $Fe_{1-x}S_x$ ); Pentlandite ( $FeNi_{1-x}S_x$ ); Pyrite ( $FeS_2$ );**

**Halides: halite  $NaCl$ ; sylvite  $KCl$ ; Flourite  $CaF_2$ ; Cryolite  $Na_3AlF_6$**

**Oxides: Periclase ( $MgO$ ); Hematite ( $Fe_2O_3$ ); Corundum ( $Al_2O_3$ ); Ilmenite ( $FeTiO_3$ ); Zincite ( $ZnO$ ); Rutile ( $TiO_2$ ); Cassiterite ( $SnO_2$ ); Pyrolusite ( $MnO_2$ ); Columbite-Tantalite ( $(Fe, Mn)(Nb, Ta)O_3$ ); Spinel ( $MgAl_2O_4$ ); Magnetite ( $Fe_3O_4$ ); Chromite ( $FeCr_2O_4$ ); Uraninite ( $UO_2$ ); Cuprite ( $Cu_2O$ )**

**Hydroxides: Gibbsite  $Al(OH)_3$ ; Brucite  $Mg(OH)_2$ ; Manganite  $MnO(OH)$ ; Goethite  $FeO(OH)$ ; Diaspore  $AlO(OH)$ ; Romanechite (Psilomelane)  $BaMnO_3(OH)_4$**

**Carbonates: Calcite  $CaCO_3$ ; Aragonite  $CaCO_3$ ; Magnesite  $MgCO_3$ ; Siderite  $Fe(CO_3)_2$ ; Rhodochrosite  $MnCO_3$ ; Dolomite  $CaMg(CO_3)_2$ ; Ankerite  $CaFe(CO_3)_2$**

For the following mineral groups, you already have the ppt (Mineralogy 20032017):

- Nitrates
- Borates
- Sulfates
- Tungstates, Molybdates and Chromates
- Phosphates, Arsenates and Vanadates