

# Ceramics

Materials that are neither organic nor metallic are ceramics. Clay, graphite, sapphire and glass are all ceramics.

## *General Properties*

In general, most ceramics are

Hard (*chalk??*)

Wear resistant (but *chalk* or *graphite??*)

Brittle

Refractory

Thermally insulating (but diamond has the highest  $\lambda$ )

Electrically insulating (But *superconductors* are also *ceramics*)

Chemically stable/insensitive

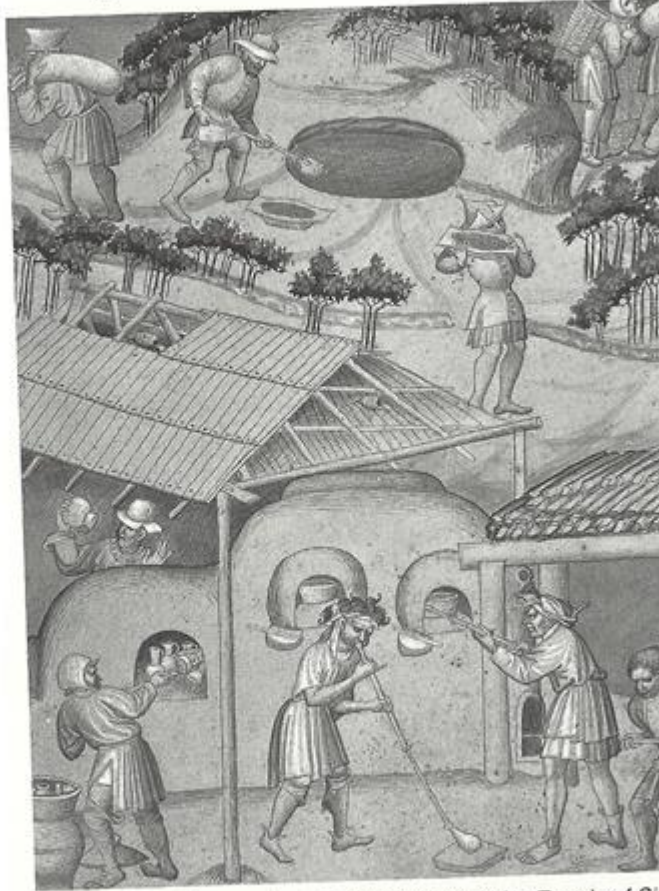
Oxidation resistant

Prone to thermal shock (*but silica or borosilicate glasses!!*)

Transparent

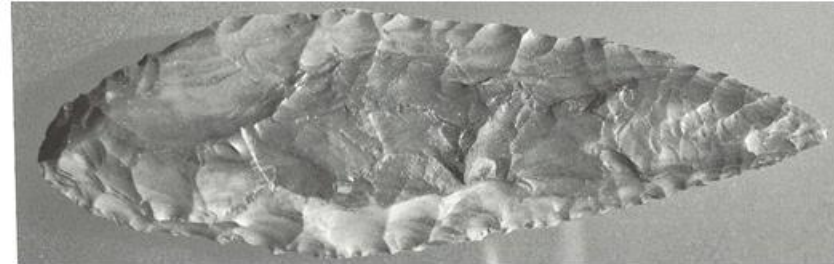
Property	Ceramic	Metal	Polymer
Hardness	Very high	Low	Very low
Elastic modulus	Very high	High	Low
High temperature strength			
Thermal expansion	High	Low	Very low
Ductility	Low	High	High
Corrosion resistance	High	Low	Low
Wear resistance	High	Low	Low
Electrical conductivity	Depends on material	High	Low
Density	Low	High	Very low
Thermal conductivity	Depends on material	High	Low
Magnetic	Depends on material	High	Very low

First Ceramic<sup>1</sup> pieces (man-made) date back to 24000 B.C. found in **Tczechoslovakia**.  
First glass, which dates back to 8000 BC and in the form of **glaze**, is found in **Upper Egypt**.  
It was CaO-based. First hollow glass item dates back to 1500 BC again in Egypt.



**FIGURE 2.11** Glass workers in Bohemia, from the *Travels of Sir John Mandeville*, ink and tempera on parchment, Flemish, early fifteenth century.





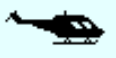



However glass-making is a newer art. The first ceramic objects used were actually weapons made out of flint ( a polycrystalline form of quartz ( $\text{SiO}_2$ ))



A pre-historic weapon made out of flint stone...25000 BC?

Nowadays many uses of ceramics from aerospace to building industries exist.

Ceramics encompass such a vast array of materials that a concise definition is almost impossible. However, one workable definition of ceramics is a refractory, inorganic, and nonmetallic material. Ceramics can be divided into two classes: traditional and advanced. Traditional ceramics include clay products, silicate glass and cement; while advanced ceramics consist of carbides (SiC), pure oxides ( $Al_2O_3$ ), nitrides ( $Si_3N_4$ ), non-silicate glasses and many others. Ceramics offer many advantages compared to other materials. They are harder and stiffer than steel; more heat and corrosion resistant than metals or polymers; less dense than most metals and their alloys; and their raw materials are both plentiful and inexpensive. Ceramic materials display a wide range of properties, which facilitate their use in many different product areas.

<i>Product Area</i>	Product
<b>Aerospace</b> 	space shuttle tiles, thermal barriers, high temperature glass windows, fuel cells
<b>Consumer Uses</b> 	glassware, windows, pottery, Coming <sup>®</sup> ware, magnets, dinnerware, ceramic tiles, lenses, home electronics, microwave transducers
<b>Automotive</b> 	catalytic converters, ceramic filters, airbag sensors, ceramic rotors, valves, spark plugs, pressure sensors, thermistors, vibration sensors, oxygen sensors, safety glass windshields, piston rings
<b>Medical (Bioceramics)</b> 	orthopedic joint replacement, prosthesis, dental restoration, bone implants
<b>Military</b> 	structural components for ground, air and naval vehicles, missiles, sensors
<b>Computers</b> 	insulators, resistors, superconductors, capacitors, ferroelectric components, microelectronic packaging
<b>Other Industries</b> 	bricks, cement, membranes and filters, lab equipment
<b>Communications</b> 	fiber optic/laser communications, TV and radio components, microphones

Humans have found applications for ceramics for the past 30,000 years; every day new and different applications are being discovered. This truly makes ceramics a Stone Age material, with space age qualities.



Atomic structure of the ceramics can be crystalline or amorphous. Amorphous ceramics have a liquid-like structural arrangement of their atoms. Difference between the structures stems from the forces that hold atoms or ions together. These forces are usually ionic, covalent or Van der Waals type forces. Many ceramics will have a combination of these forces. It is hard to find purely ionic (NaCl, LiF, MgO) or purely covalent (SiC) ceramics<sup>2</sup>.

Traditionally ceramic industry was based on three main classes of ceramics: **Clay**, **silica** and **cement**. Even today these are the materials that are used in largest tonnage in the world. The historical reason for this is because they are found in the nature as minerals: Did you know that the antic theater Aspendos is made from a natural cement stones found in the region and it is cemented together?



[Aspendos Amphitheater, Antalya Turkey](#)

So, ancient Anatolia was very closely related to the history of ceramics.

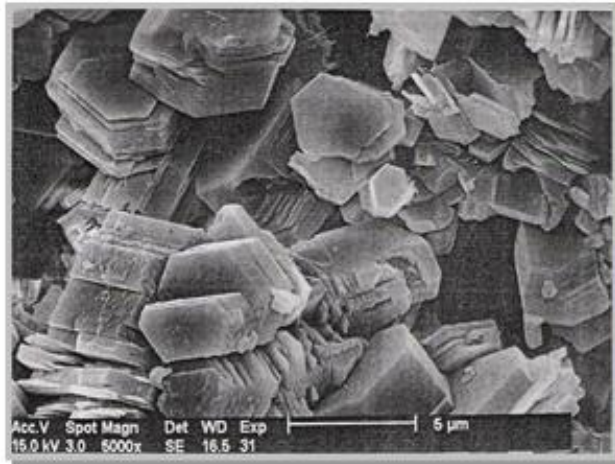
## CLAY

Clay is a layered or sheet silicate mineral with grain sizes  $< 2\mu\text{m}$ . They are basically aluminosilicates with Mg, Fe, Na, and/or in its structure. It exists almost everywhere on the earth crust. Most important characteristics of clay is that water molecules can get inbetween the layers and separate them giving them plasticity (ability to slide over each other) so that they can be shaped very easily. When dried clay retains its shape and can be fired at  $950\text{-}1000^{\circ}\text{C}$  to make a solid sintered piece out of it.



Aspendos Amphitheater, Antalya Turkey





SEM image of kaolinite platelets.

Depending on the composition the traditional ceramic pottery are called differently, e.g. earthenware, stoneware, porcelain, bone-china, ... the usual constituents are clay (sometimes kaolin) quartz (sand) and feldspar. Bone china has animal bone ash (calcium phosphate) in it.



## CEMENT:

The largest quantity of any material used on earth is cement. Cement is basically a hydraulic ceramic, i.e. it reacts with water to form a solid which is stable under water. It is a mixture of calcium oxide, silica, alumina, and iron oxide...in a reacted form!!

Today's modern cements are based either on calcium silicates or calcium aluminates. The so-called Portland cement is a mixture of

Dicalcium silicate,  $\text{Ca}_2\text{SiO}_4$  (C2S)

Tricalcium silicate,  $\text{Ca}_3\text{SiO}_5$  (C3S)

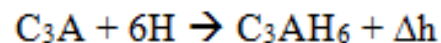
Tricalcium aluminate,  $\text{Ca}_3\text{Al}_2\text{O}_6$  (C3A)

Tricalcium aluminoferrite,  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  (C4AF)

And

Gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Portland cement hydration reactions start with the reaction of water with the Ca-rich phases, i.e. C3A, C3S, C2S. The more calcium there is the more reactive is the phase



In the presence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ) forms.

# Raw Materials

From the earth's crust → minerals containing Mg, Fe, Al, Ca, SiO<sub>2</sub> mined and beneficiated

Physical beneficiation → crushing, grinding

Chemical beneficiation → dissolution in a proper solvent and filtration

## Silica

Silica is an important raw material for ceramics. Mainly used in cement and glass industry.

There are also lots of production method and application area of Silica, such as;

- Fumed Silica (colloidal silica from SiCl<sub>4</sub>)

- Silica Fume (nanosized and amorphous silica as by product of Si and ferrosilicon alloys)

- Silica in microelectronics (thermal oxidation on Si layers)

- Silica Gel (acidification of sodium silicate)

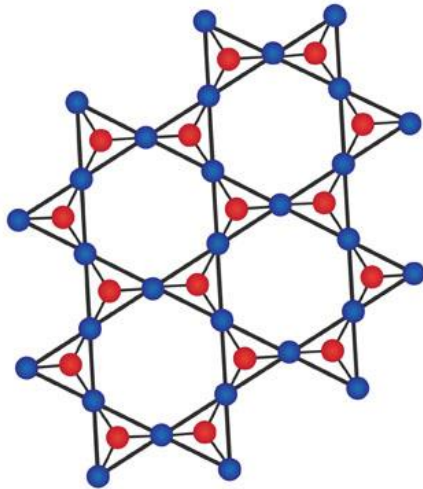


# Silica

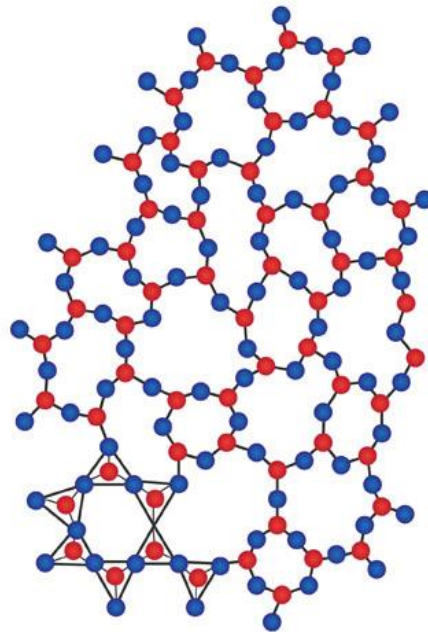
Major Silica source for glass industry is silica sand, quartz.

Quartz is the general name of the crystal  $\text{SiO}_2$ , and also RT crystal structure name of  $\text{SiO}_2$ . (The other polymorph names are tridymite and cristobalite)

Crystalline  $\text{SiO}_2$   
(Quartz)

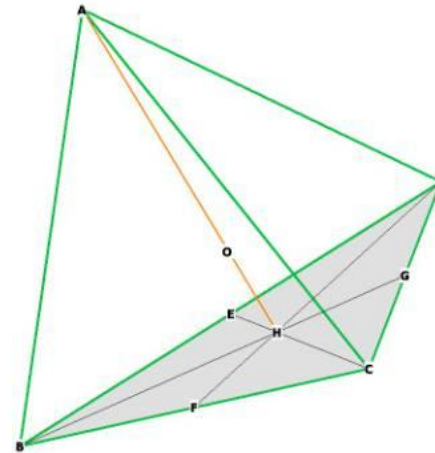
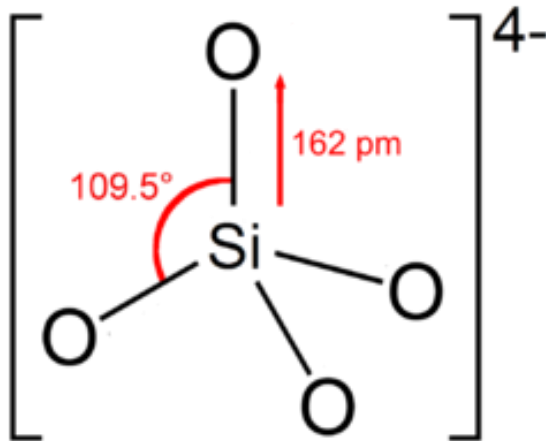


Amorphous  $\text{SiO}_2$   
(Glass)



# Silicates




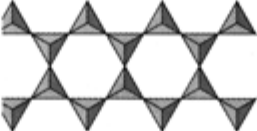
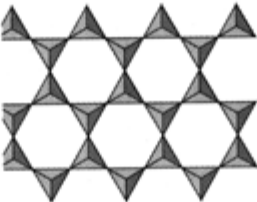

Silicates that we will examine are Feldspar, kaolin, mica and mullite. They all have tetrahedrons of Si at the center and oxygens at the corners.



These tetrahedra sometimes occur as isolated  $\text{SiO}_4^{4-}$  centres, but most commonly, the tetrahedra are joined together in various ways, such as pairs ( $\text{Si}_2\text{O}_7^{6-}$ ) and rings ( $\text{Si}_6\text{O}_{18}^{12-}$ ). Commonly the silicate anions are chains, double chains, sheets, and three-dimensional frameworks.

**TABLE 2.2**

**Major Silicate Structures**

GEOMETRY OF LINKAGE OF $\text{SiO}_4$ TETRAHEDRA		EXAMPLE MINERAL	CHEMICAL COMPOSITION
<i>Isolated tetrahedra:</i> No sharing of oxygens between tetrahedra; individual tetrahedra linked to each other by bonding to cation between them		Olivine	Magnesium-iron silicate
<i>Rings of tetrahedra:</i> Joined by shared oxygens in three-, four-, or six-membered rings		Cordierite	Magnesium-iron-aluminum silicate
<i>Single chains:</i> Each tetrahedron linked to two others by shared oxygens; chains bonded by cations		Pyroxene	Magnesium-iron silicate
<i>Double chains:</i> Two parallel chains joined by shared oxygens between every other pair of tetrahedra; the other pairs of tetrahedra bond to cations that lie between the chains		Amphibole	Calcium-magnesium-iron silicate
<i>Sheets:</i> Each tetrahedron linked to three others by shared oxygens; sheets bonded by cations		Kaolinite Mica (muscovite)	Aluminum silicate Potassium-aluminum silicate
<i>Frameworks:</i> Each tetrahedron shares all its oxygens with other $\text{SiO}_4$ tetrahedra (in quartz) or $\text{AlO}_4$ tetrahedra		Feldspar (orthoclase) Quartz	Potassium-aluminum silicate Silicon dioxide



# Silicate Structures

$R_{Si} / R_O = 0.29 \Leftrightarrow$  tetrahedral coordination of oxygens around Si.

In  $(SiO_4)^{4-}$  tetrahedra  
With  $3sp^3$  hybridized orbitals  
&  
high degree of covalency

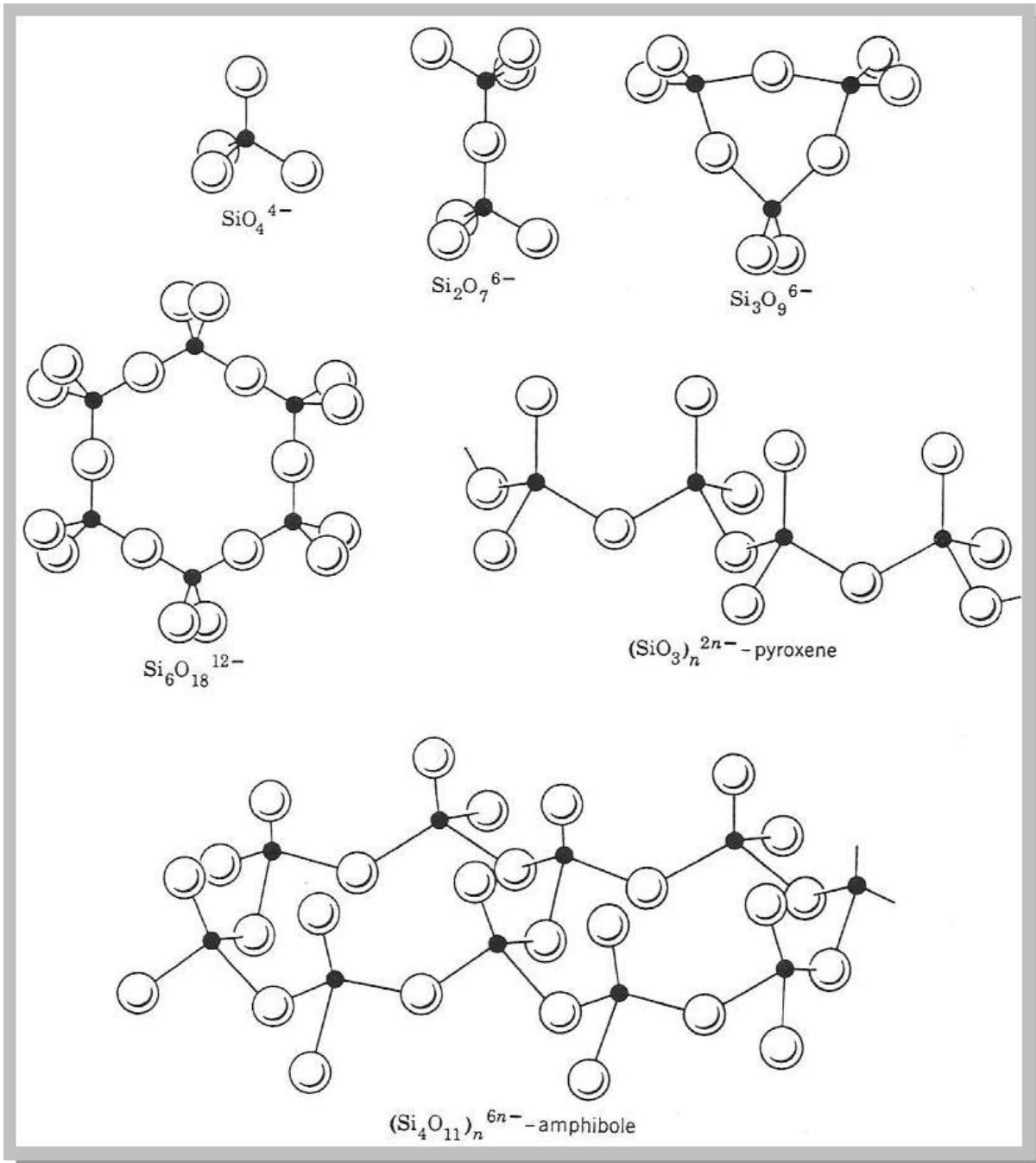


Tetrahedral Coordination

Oxygen ions coordinate with 2 Si ions in Silica. So,  $(SiO_4)^{4-}$  tetrahedra can be linked only by corner sharing in crystalline  $SiO_2$ , silicate minerals and silicate glasses.

Low coordination number of oxygen occurs if and only if there is a corner sharing of  $(SiO_4)^{4-}$  tetrahedra. That makes impossible to have close-packed structures. In other words, silicates generally have open structures.

Crystalline silicates, silicate minerals are usually classified according to several ways of sharing corners between  $(SiO_4)^{4-}$  tetrahedra.



Some silicate ions and chain structures

In orthosilicates,  $(\text{SiO}_4)^{-4}$  tetrahedra are independent of each other with charge compensation cations in between, like in forsterite  $\text{Mg}_2\text{SiO}_4$  and olivine  $\text{Fe}_2\text{SiO}_4$  or zircon  $\text{ZrSiO}_4$ .

In orthosilicates, the O / Si ratio is maximum at 4. O / Si ratio is a good indicator of connectivity between silica tetrahedral in silicate structures.

In pyrosilicates  $\text{Si}_2\text{O}_7^{-6}$  "ions" are composed of two tetrahedral with one corner shared, where the O / Si ratio is at 3,5.

When two corners are shared between silica tetrahedra (like in metasilicates)  $(\text{SiO}_3)^{-2}$  or  $(\text{SiO}_3)_n^{-2n}$  a variety of ring and chain structures can be formed. Chain structures with O/Si ratio between 2,75 and 3 may have fibrous habit. Pyroxenes like enstatite ( $\text{MgSiO}_3$ ) and jadeite are made up of single chains of  $(\text{SiO}_3)_n^{-2n}$ .

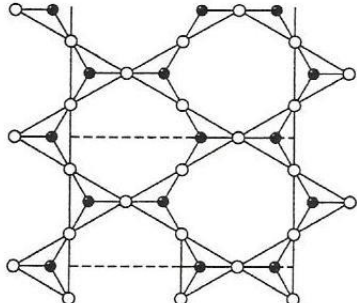
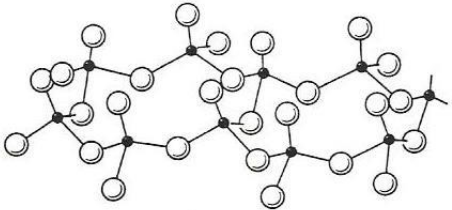
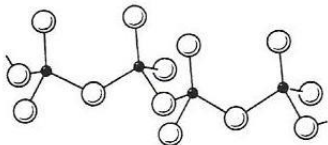
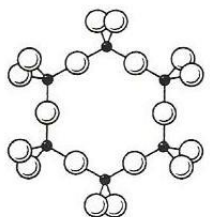
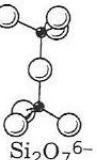


Jadeite mineral

The amphiboles like asbestos minerals have double silicate chains with  $(\text{Si}_4\text{O}_{11})_n^{-6n}$ . Some other double-corner-sharing structures form rings of isolated tetrahedral rings like beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , the basis of emerald) with six tetrahedral  $(\text{Si}_6\text{O}_{18})^{-12}$  or like wollastonite ( $\text{CaSiO}_3$ ) with three tetrahedral  $(\text{Si}_3\text{O}_9)^{-6}$  rings.

In layered structures with O / Si ratio at 2,5 layers are made up of 3 tetrahedra with shared corners, with  $(\text{Si}_2\text{O}_5)_n^{-2n}$  layers. As O / Si ratio decreases, number of shared corners increases. Three dimensionally connected crystalline  $\text{SiO}_2$  has all four corners shared, and has O / Si ratio of 2.

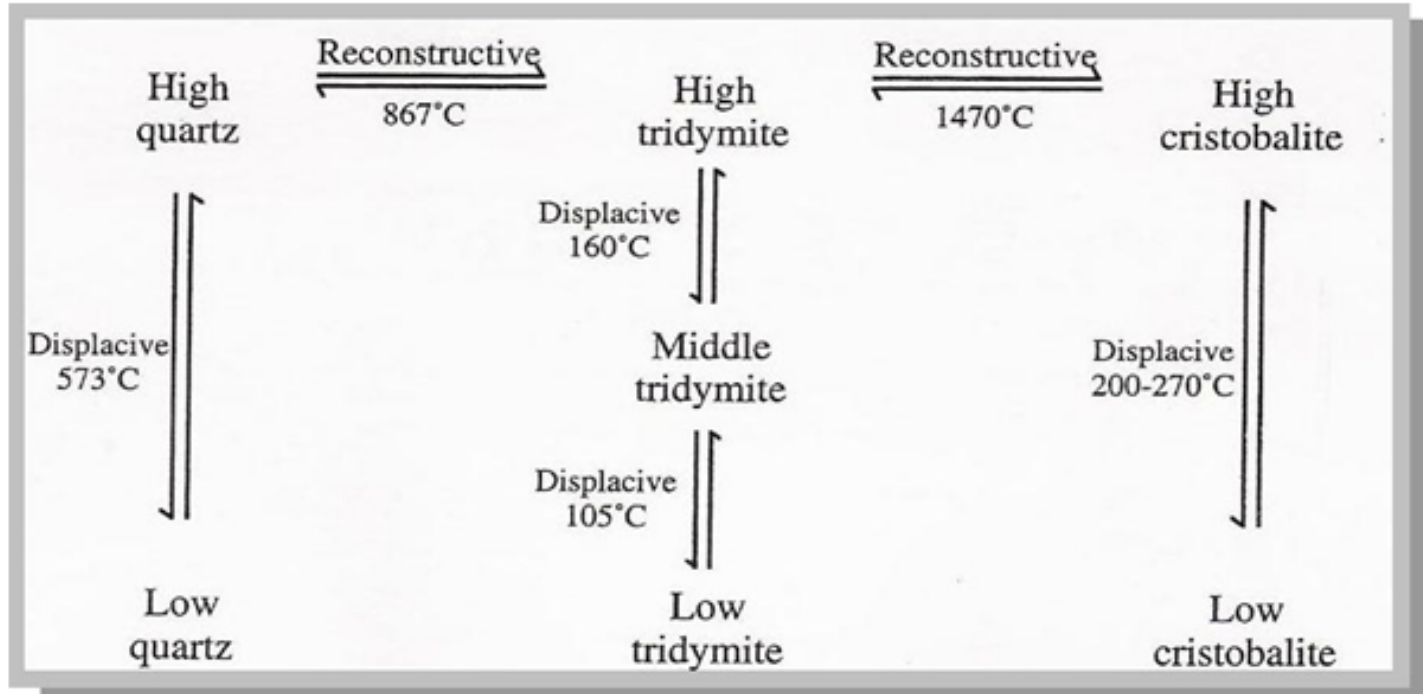


O/Si Ratio	Silicon-Oxygen groups	Silicate structure	Examples
2		$\text{SiO}_2$ (completely interconnected tetrahedra)	Quartz, tridymite, cristobalite
2.5		$\text{Si}_4\text{O}_{10}$ (sheets)	Talc, mica, kaolinite, montmorillonite clays, vermiculite
2.75		$\text{Si}_4\text{O}_{11}$ (chains)	Amphiboles (asbestos minerals)
3		$\text{SiO}_3$ (chains or rings)	Pyroxenes (chains), beryl (rings)
3.5		$\text{Si}_2\text{O}_7$ (tetrahedra sharing one oxygen ion)	Pyrosilicates
4	 $\text{SiO}_4^{4-}$	$\text{SiO}_4$ (isolated tetrahedra)	Orthosilicates (forsterite, olivine, zircon)

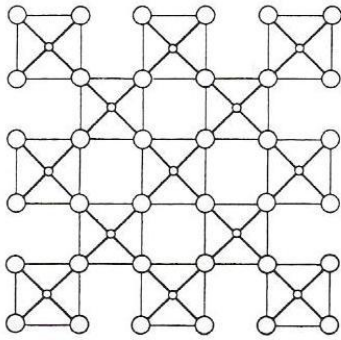
## Effect of oxygen-Silicon ratio on structure in silicates

Crystalline SiO<sub>2</sub> exists in many different polymorphic forms with three basic structures: Quartz, Trydymite and Cristobalite. Each exists in two or three modifications. Phase transformations between three structures are reconstructive (and sluggish) requiring diffusion. Whereas transformations within each basic form (i.e. high and low forms, tridimite also has a middle form) are displacive in nature

**Table 2.4 Polymorphic forms of silica**

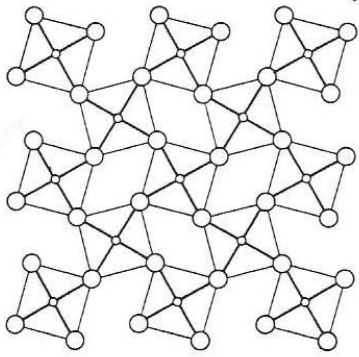


The most stable form at RT is low quartz up to 573 C. Between 573 C to 867 C is high quartz. High trydymite is stable between 867 – 1470 C. High crystabalite exists between high tridymite and liquid at 1710 C. Low temperature modifications are distorted (less symmetric) structures of high temperature forms.



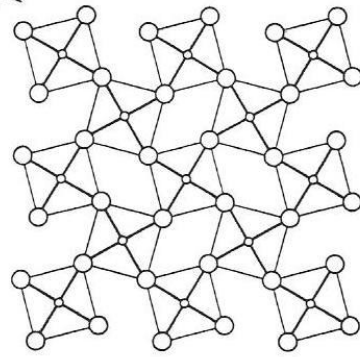
(a)

Displacive transformation

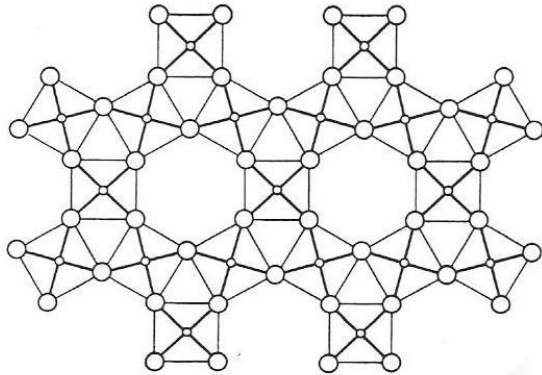


(b)

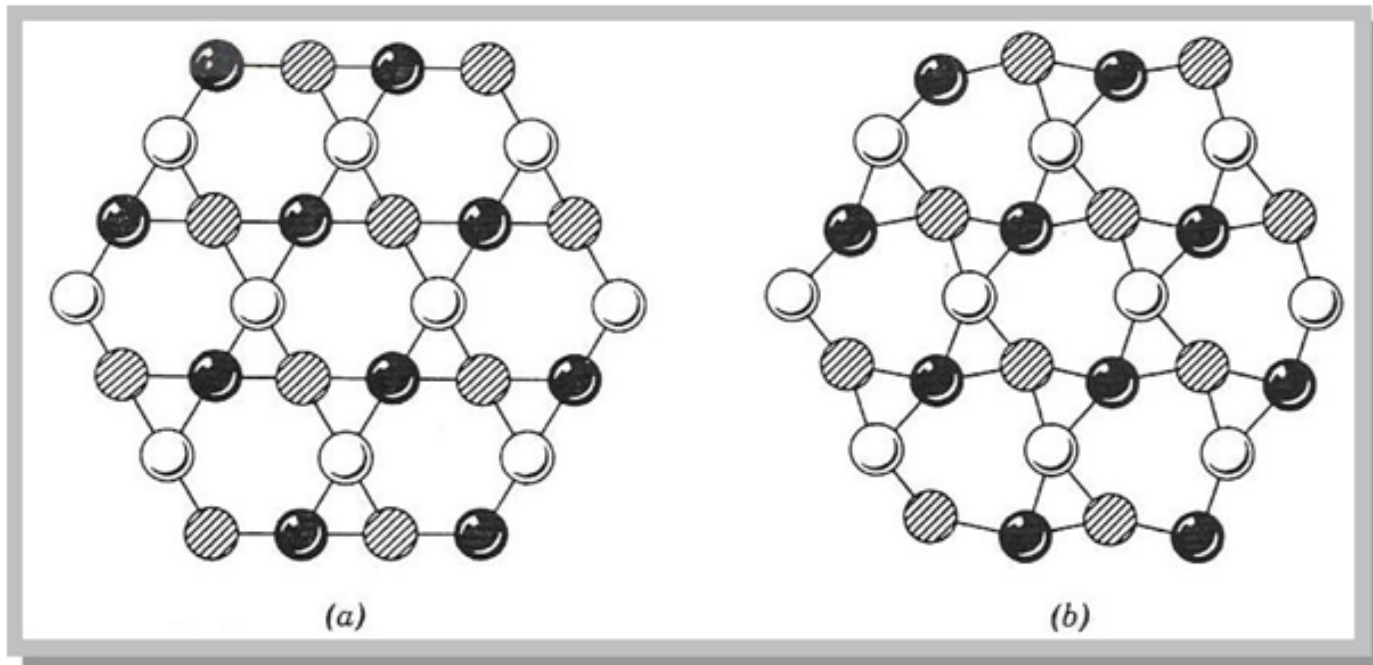
Reconstructive transformation



(c)

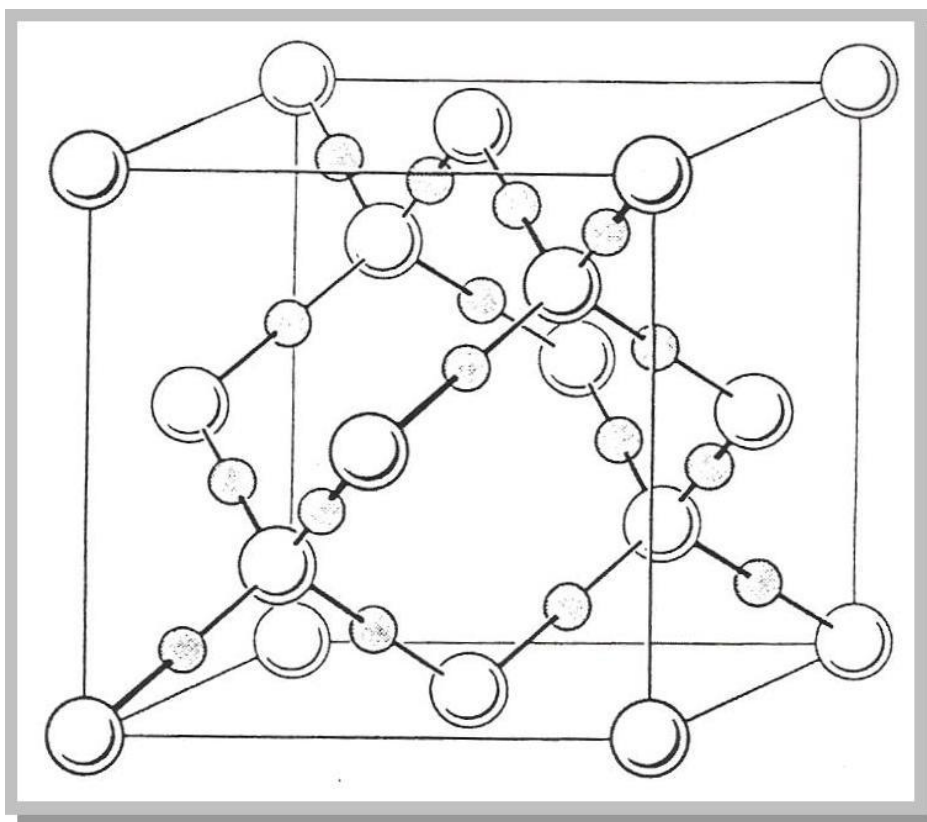






**Figure 2.38** Schematic illustration of relationship between (a) high temperature and (b) low temperature forms of quartz.

High quartz (symmetric) appears as connected chains of silica tetrahedral with a very open structure (Density of quartz  $\sim 2.65 \text{ g/cm}^3$  that of alumina is  $3,96 \text{ g/cm}^3$ ). Tridymite and cristobalite have even lower density,  $\rho_{\text{tri}} = 2.26$  and  $\rho_{\text{cris}} = 2.32$ , respectively.



Structure of high cristobalite

Many silicates are based on an infinite dimensional silicate framework, like feldspars and zeolites.

Feldspars are framework silicates, where some  $\text{Si}^{+4}$  are replaced by  $\text{Al}^{+3}$  resulting in a structure with a net negative charge that must be balanced by large cations in interstitial positions, like in albite ( $\text{Na AlSi}_3\text{O}_8$ ) or anorthite ( $\text{Ca Al}_2\text{Si}_2\text{O}_8$ ), orthoclase ( $\text{KAlSi}_3\text{O}_8$ ), celsian ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ )... etc. The structure is similar to the one from cristobalite with alkali or alkaline earth ion fitting in the interstices. Only large positive cations form feldspars. Smaller ones that enjoy octahedral coordination will form chains or layered silicates.

Much more open alumina-silica frameworks with large channels in their structures occur in zeolites. These open channels are paths for ions to go in and out of the structure. Zeolites have very high base exchange capacity.

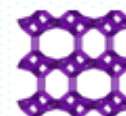
**Table 2.5 What Are Zeolites**

<http://www.bza.org/zeolites.html>

## What are Zeolites?

Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses, or produced by research scientists trying to understand more about their chemistry.

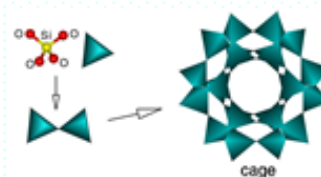
Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tonnes per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as *molecular sieves*.



## Framework Structure

A defining feature of zeolites is that their frameworks are made up of 4-connected networks of atoms. One way of thinking about this is in terms of tetrahedra, with a silicon atom in the middle and oxygen atoms at the corners. These tetrahedra can then link together by their corners (see illustration) to form a rich variety of beautiful structures. The framework structure may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter - i.e. the limiting pore sizes are roughly between 3 and 10 Å in diameter.

In all, over 130 different framework structures are now known. In addition to having silicon or aluminium as the tetrahedral atom, other compositions have also been synthesised, including the growing category of microporous aluminophosphates, known as ALPOs.



## Catalysis

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Examples are the use of titanium ZSM-5 in the production of caprolactam, and copper zeolites in NO<sub>x</sub> decomposition.

Underpinning all these types of reaction is the unique microporous nature of zeolites, where the shape and size of a particular pore system exerts a steric influence on the reaction, controlling the access of reactants and products. Thus zeolites are often said to act as *shape-selective catalysts*. Increasingly, attention has focused on fine-tuning the properties of zeolite catalysts in order to carry out very specific syntheses of high-value chemicals e.g. pharmaceuticals and cosmetics.



## Adsorption and Separation

The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of *para*-xylene by silicalite.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.



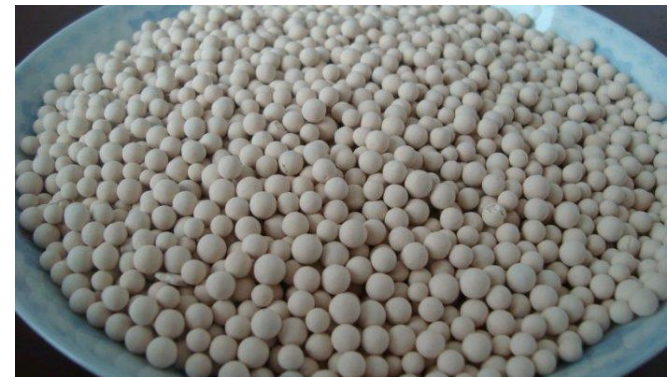
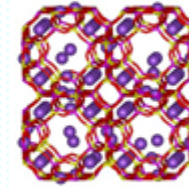
The shape of *para*-xylene means that it can diffuse freely in the channels of silicalite



## Ion Exchange

The loosely-bound nature of extra-framework metal ions (such as in zeolite NaA, right) means that they are often readily exchanged for other types of metal when in aqueous solution. This is exploited in a major way in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders thus contain substantial amounts of zeolite. Commercial waste water containing heavy metals, and nuclear effluents containing radioactive isotopes can also be cleaned up using such zeolites.

Sodium Zeolite A, used as a water softener in detergent powder



# Feldspar

Aluminium silicate of potassium, sodium, calcium, and/or lithium. Feldspars are important ingredients in clay bodies and glazes. In both applications, their primary function is to supply fluxes to the formulations, but they also provide additional alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ).

Feldspars are naturally occurring minerals and are generally classified as either potash (potassium) or soda (sodium) feldspars based upon the predominant alkali metal element (the flux) that is present. Present in volcanic and metamorphic rocks.

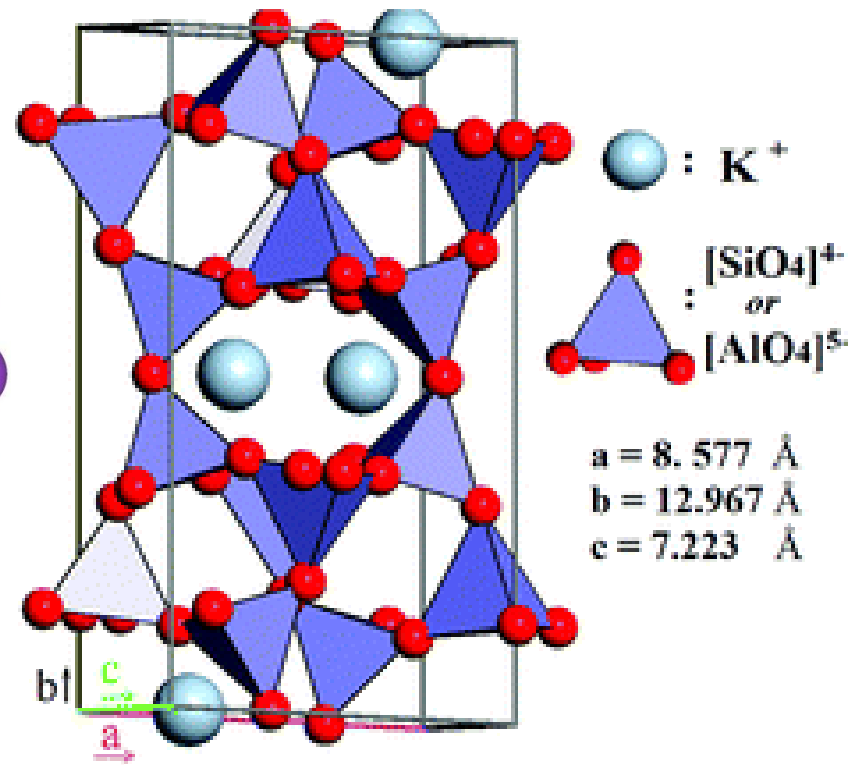
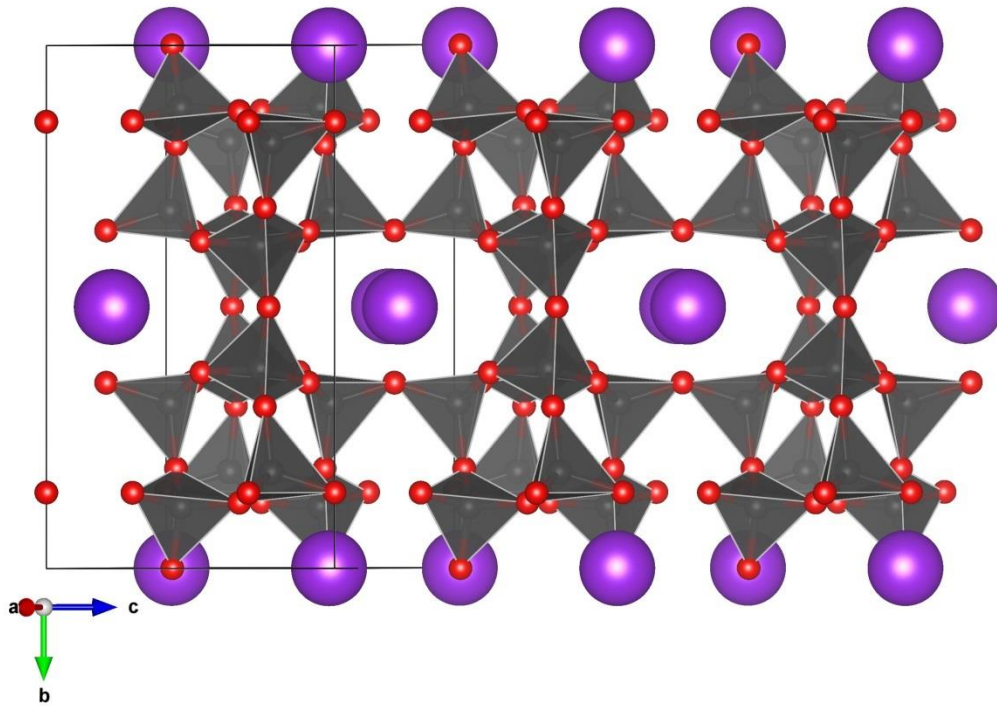


A **ceramic flux** functions by promoting partial liquification in clay bodies and glazes. Fluxes are used in glazes to lower the high melting point of the glass formers like silica

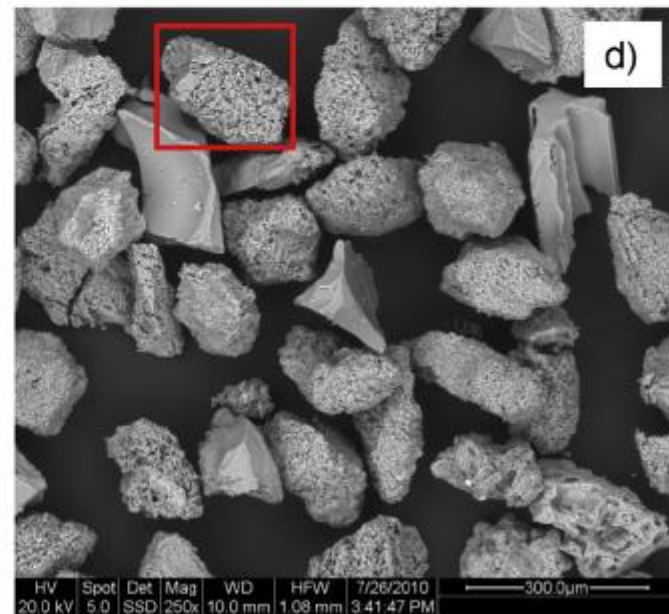
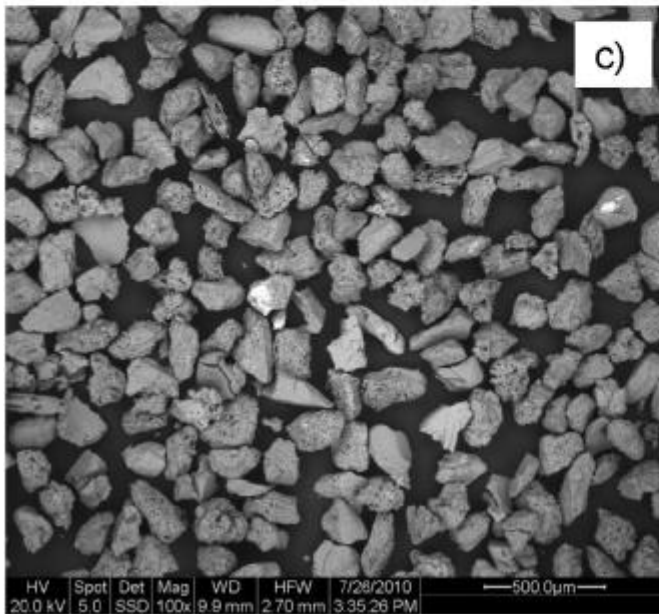
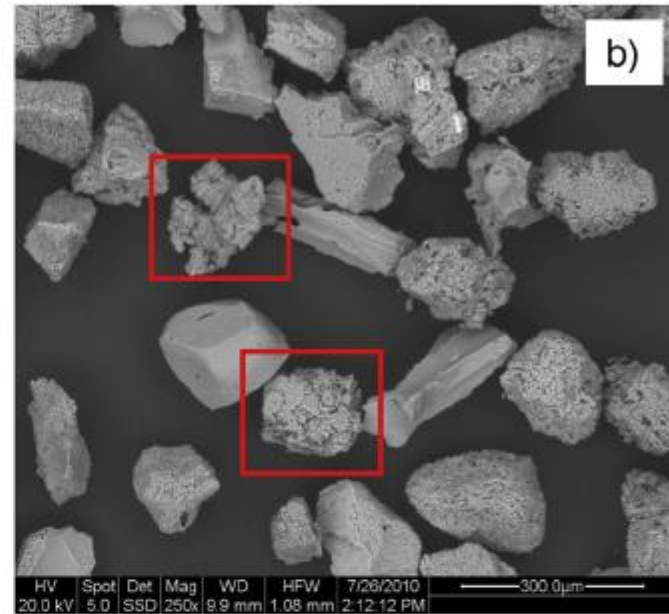
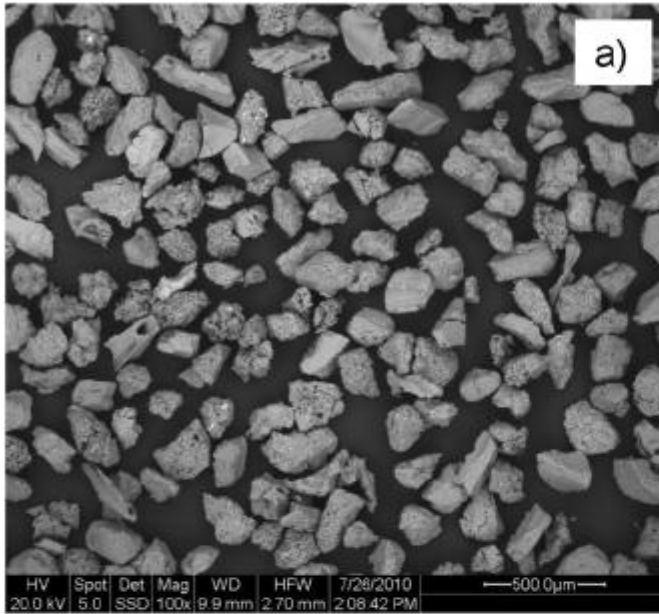
# Feldspar

Potash feldspars  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$

Soda feldspars  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$



# Feldspar





## Clay Minerals

Clay minerals are based hydrated aluminosilicate structures that are fine grained and with a platy habit. The crystal structure of clay minerals are formed from  $(\text{Si}_2\text{O}_5)_n$  sheets those are joined to  $\text{AlO}(\text{OH})_2$  layers containing octahedrally coordinated aluminum<sup>+3</sup>. The simplest clay mineral is kaolinite with one layer of  $(\text{Si}_2\text{O}_5)_n$  and one layer of  $\text{AlO}(\text{OH})_2$  where one (OH) group is replaced by this protruding oxygen from the silica layer below, giving the formula  $\text{Al}_2(\text{Si}_2\text{O}_5(\text{OH})_4$ .

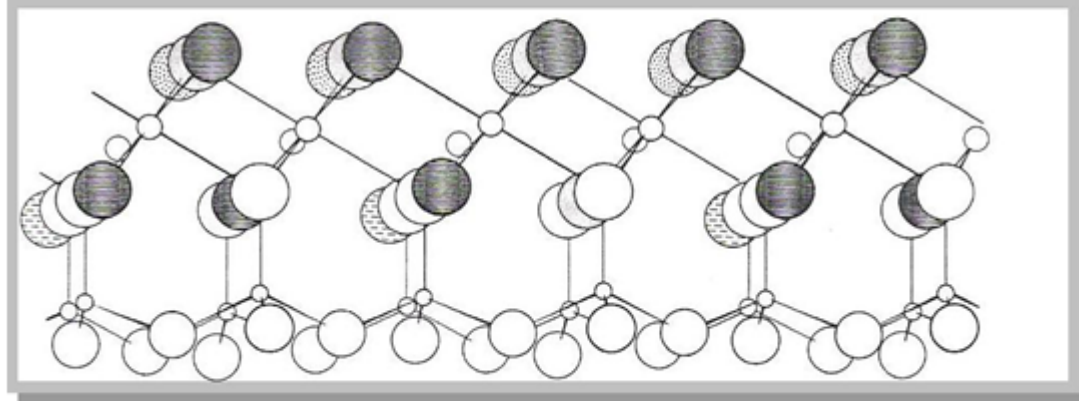


Figure 2.40 Perspective drawing of kaolinite,  $\text{Al}_2(\text{Si}_2\text{O}_5(\text{OH})_4$ , showing Si-O tetrahedral on the bottom half of the layer and Al-O,OH octahedral on the top half.

Kaolinite's platy appearance (a sheet silicate)

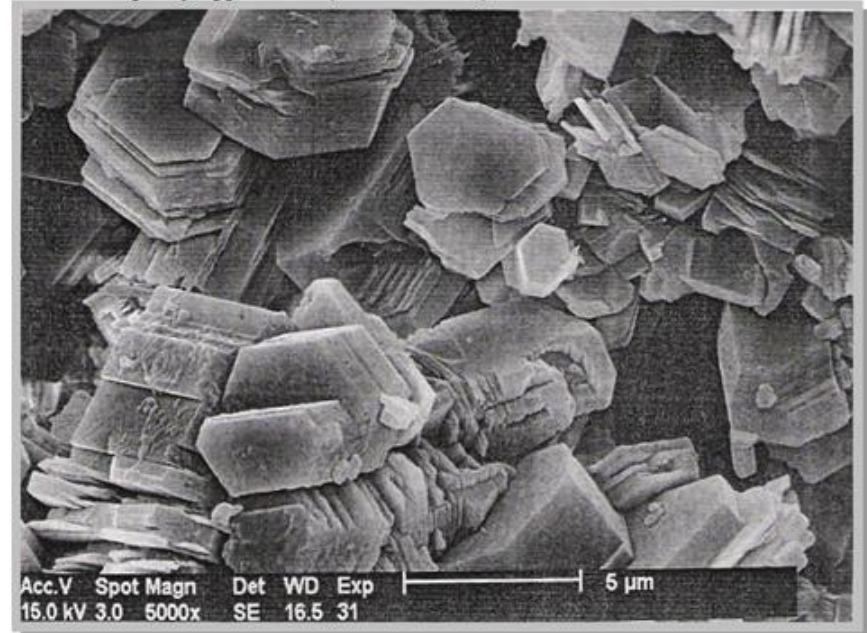
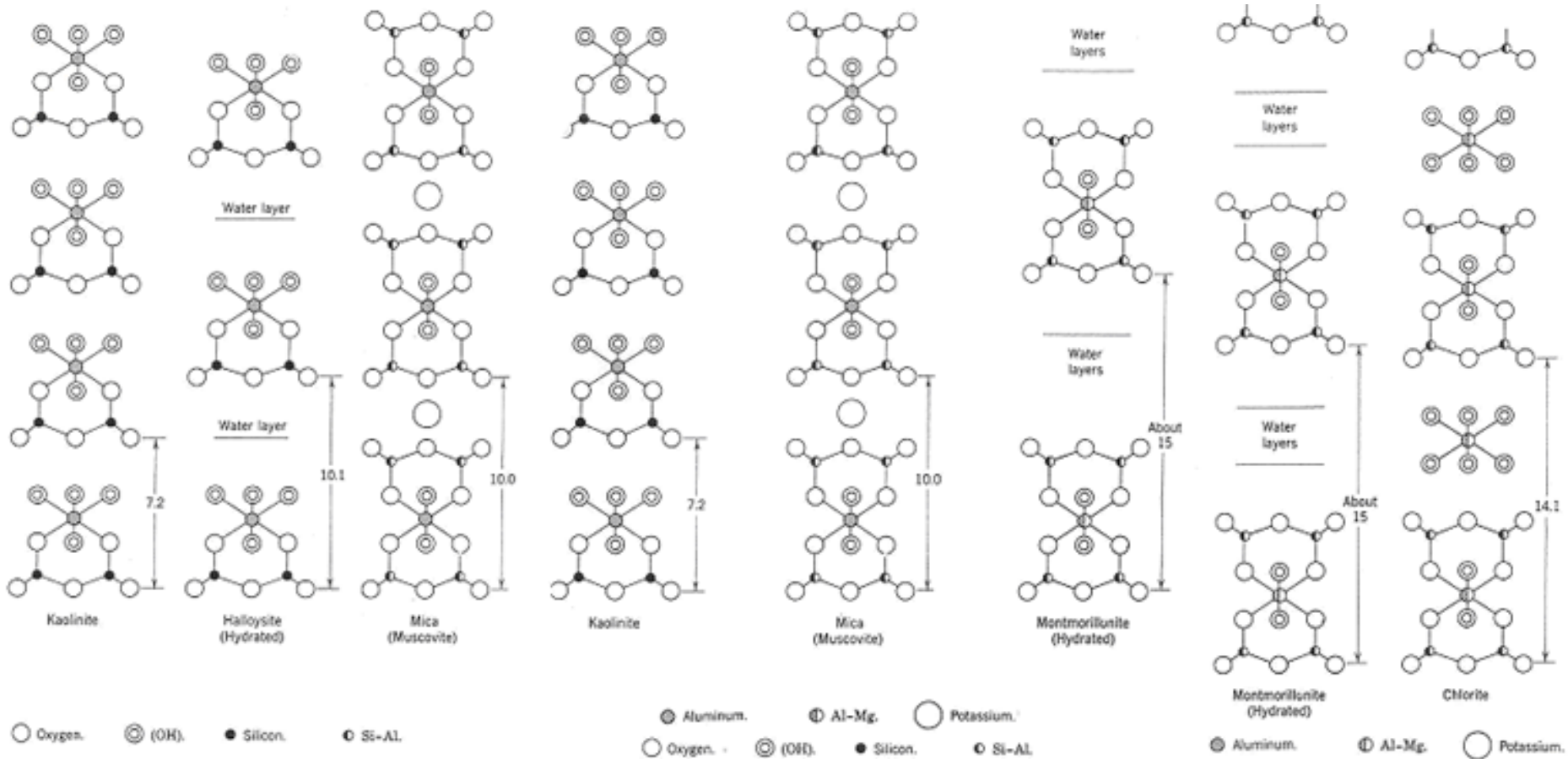


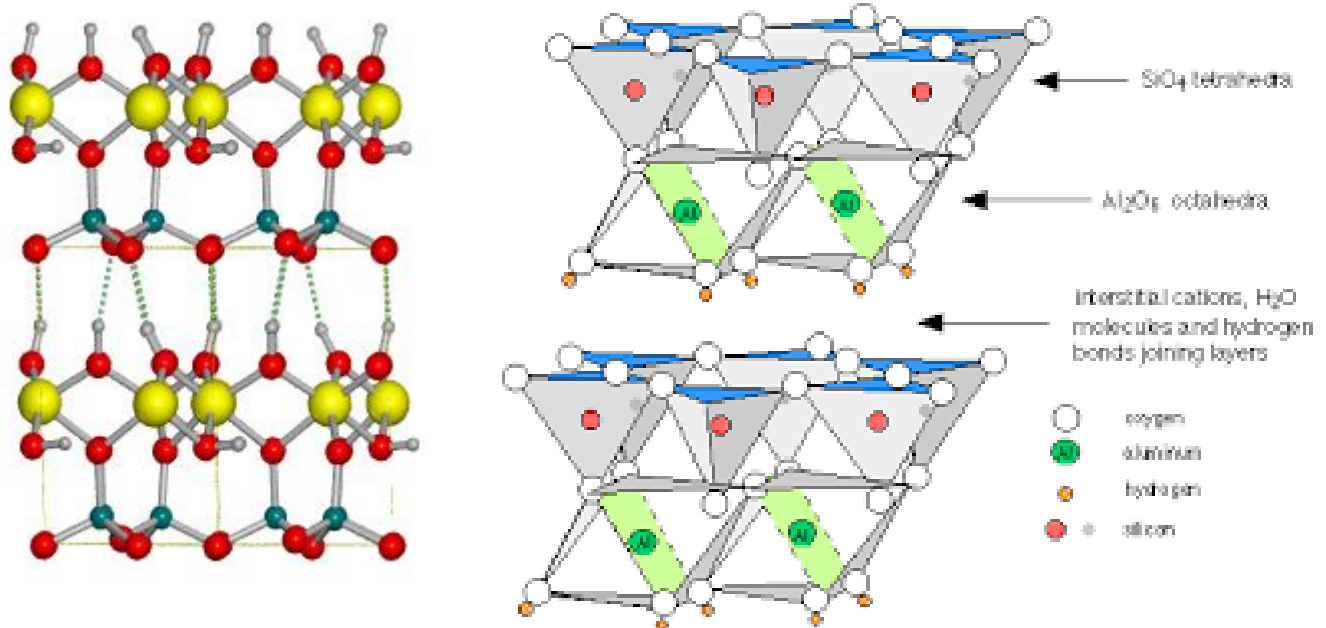
Figure 2.41 SEM image of kaolinite platelets.



**Layer structure of clays and similar materials.**

# Kaolin

Kaolin is a clay mineral. Clay minerals are layered silicates. Rocks that are rich in kaolinite are called as Kaolin or China Clay



# Mica

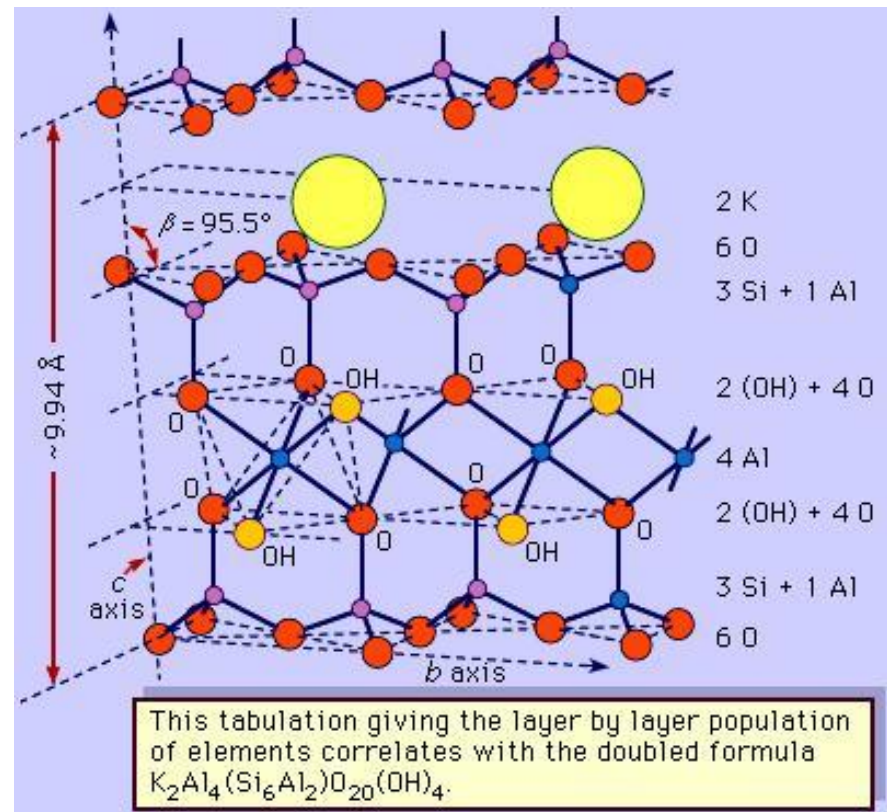
There are 2 classes of mica. True and Brittle.

True micas contain univalent cations ( $\text{Na}^+$  or  $\text{K}^+$ ) btw each pair of layers. These layers are separated under shear stress in cleavage/splitting manner.



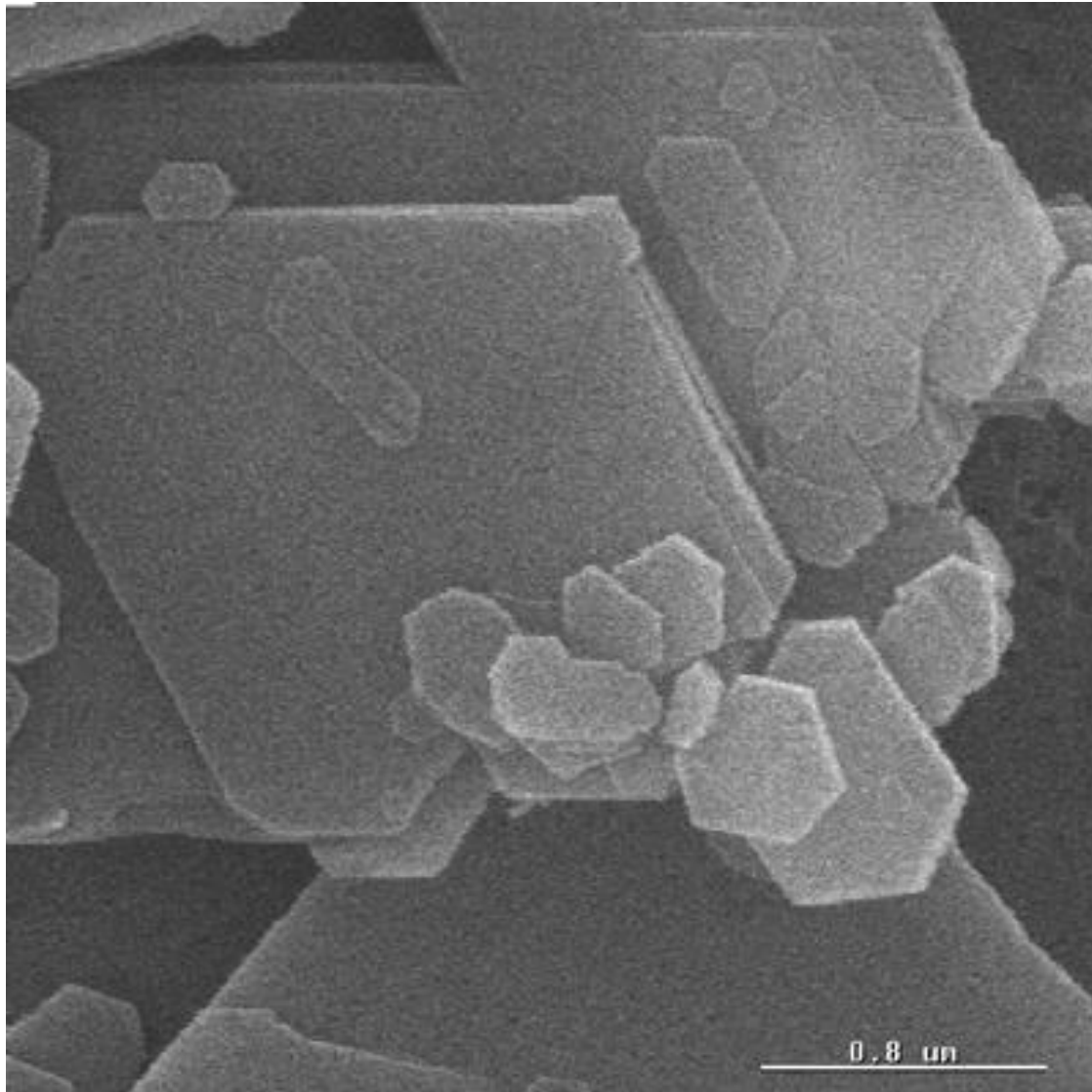
In brittle micas, interlayer ions are divalent, like  $\text{Ca}^{2+}$

Because of 2+ charge, they are stronger than True micas. These micas are rare.





# Mica



## Other Structures

### Mullite

Mullite has the formula of  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and exist in nature very rare.

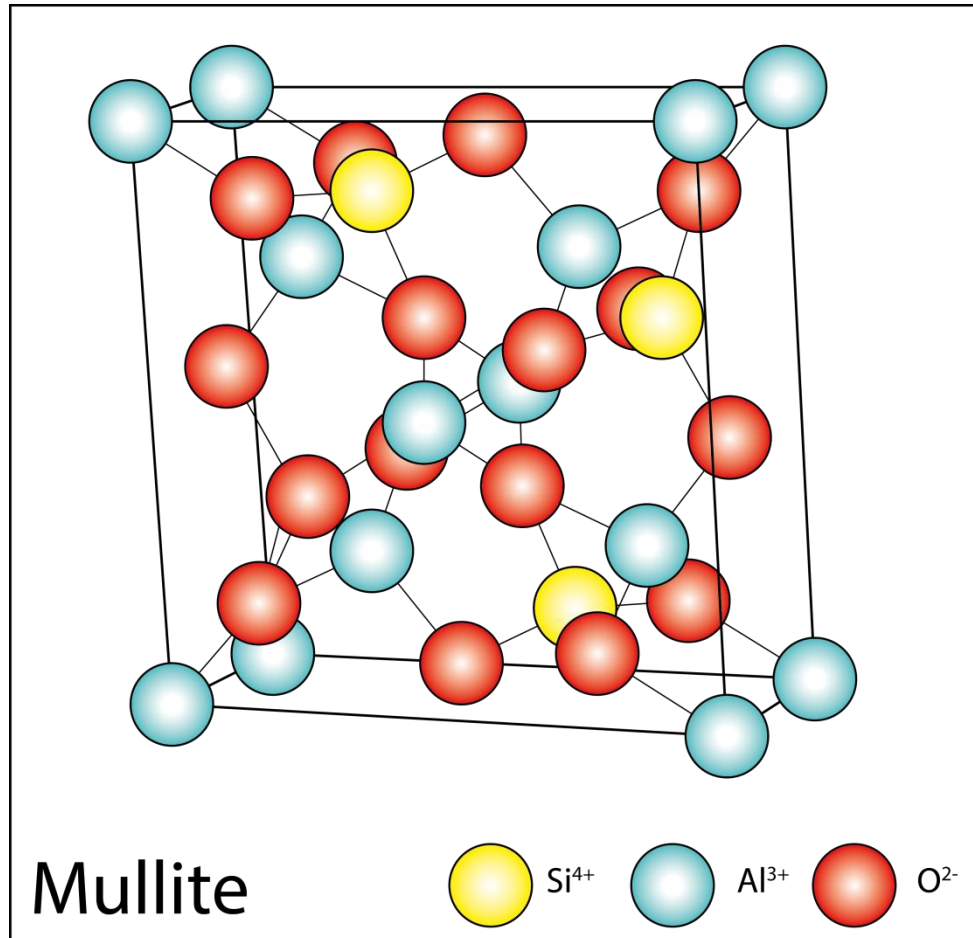
Mullite is suitable for high temperature applications. It is used in furnace lining, refractory applications in iron, steel and glass industries.

Can be produced;

- By sintering mixture of kyanite ( $\text{Al}_2\text{OSiO}_4$ ), bauxite ( $\text{Al}(\text{OH})_3$ ) and kaolin. Sintered at around  $1600^\circ\text{C}$  with correct proportions. Sintered product contains around 60-70% mullite. Rest will be silica based by products.
- By fusing in an electric arc furnace at about  $1750^\circ\text{C}$  of alumina and kaolin. This method gives higher purity mullite ( $>95\%$ )

It has a high melting point, around  $1840^\circ\text{C}$

# Mullite

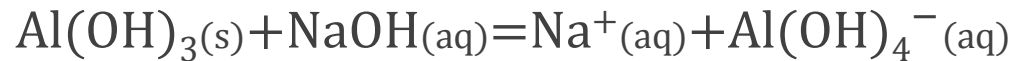


## Alumina, $\text{Al}_2\text{O}_3$

Alumina is known as corundum, which is the name of its crystal structure. It is produced mainly from Bauxite ( $\text{Al}(\text{OH})_3$ ) mineral by Bayer process. Bauxite has some impurities of iron, titanium and silicon oxide impurities in it.

A purity of 95% alumina, with main impurity of  $\text{Na}_2\text{O}$ , can be obtained by Bayer process.

1- Ground bauxite is treated with  $\text{NaOH}$  solution at  $\sim 150^\circ\text{C}$ . The impurities in bauxite do not dissolve.



2- By filtration, we get rid of impurities. To the filtered solution, gibbsite crystals are added as seeds for the ppt of Al-hydrate from the solution.



## Alumina, $\text{Al}_2\text{O}_3$

3- The ppts are separated from the solution by filtration. Then washed to get rid of residual sodium.

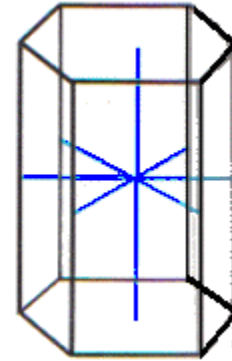
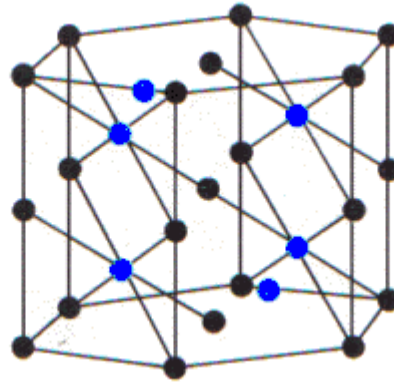
4- Calcination of aluminium hydroxide at around  $1100^\circ\text{C}$ - $1200^\circ\text{C}$ .



5- 5-10  $\mu\text{m}$  crystals produced. Further milling is done to decrease particle size. Purity is  $>99.5\%$ , main impurity is  $\text{Na}_2\text{O}$

# Alumina, $\text{Al}_2\text{O}_3$

Its crystal structure is corundum, in an hexagonal lattice.



Alumina has melting temperature of  $2072^{\circ}\text{C}$ .

# Magnesium Oxide, MgO

It is found in the form of periclase mineral. But, it is not used as MgO source, because it is rare in nature.

MgO sources are mainly magnesium hydroxide (Mg(OH)) or magnesite (MgCO<sub>3</sub>, magnesium carbonate). Impurities in magnesite mineral are quartz, talc (Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>), mica, and magnetite (Fe<sub>3</sub>O<sub>4</sub>)

Beneficiation is applied to get rid of impurities include crushing, screening, washing, magnetic separation, froth flotation. After that;

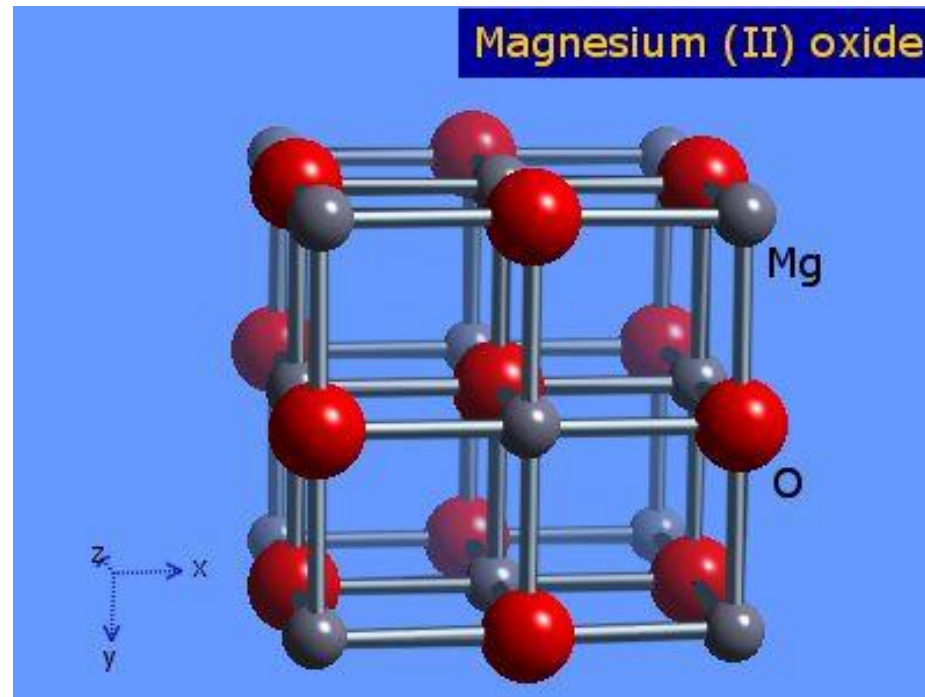


MgO is also produced from seawater. 1,3 gr MgO is present in 1 kg seawater.

Most of MgO is used as refractory linings in furnaces.

# Magnesium Oxide, MgO

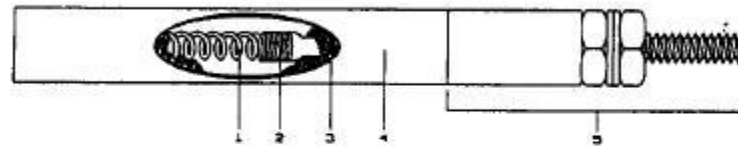
MgO has Rock Salt Structure



# Magnesium Oxide, MgO



TUBULAR ELEMENTS



- Where:
- 1 - Element Coil
  - 2 - Element Cold Junction
  - 3 - Magnesium Oxide (MgO)
  - 4 - Element Sheath
  - 5 - Element Terminal Post



# Zirconia, $ZrO_2$

Source of  $ZrO_2$  is Zircon ( $ZrSiO_4$ ), present in volcanic rocks.

Secondary source is beach-sands. Mainly in Australia and Brazil. In Turkey, Şile beach has also Zircon concentration around 3%.

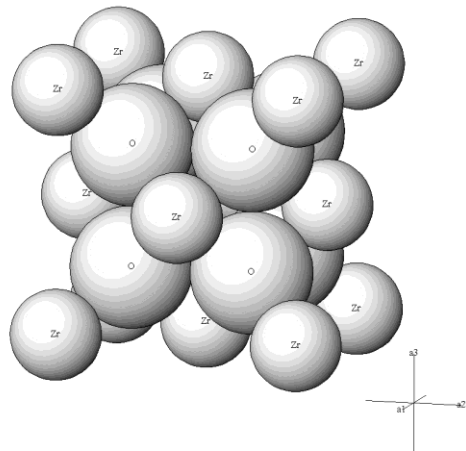
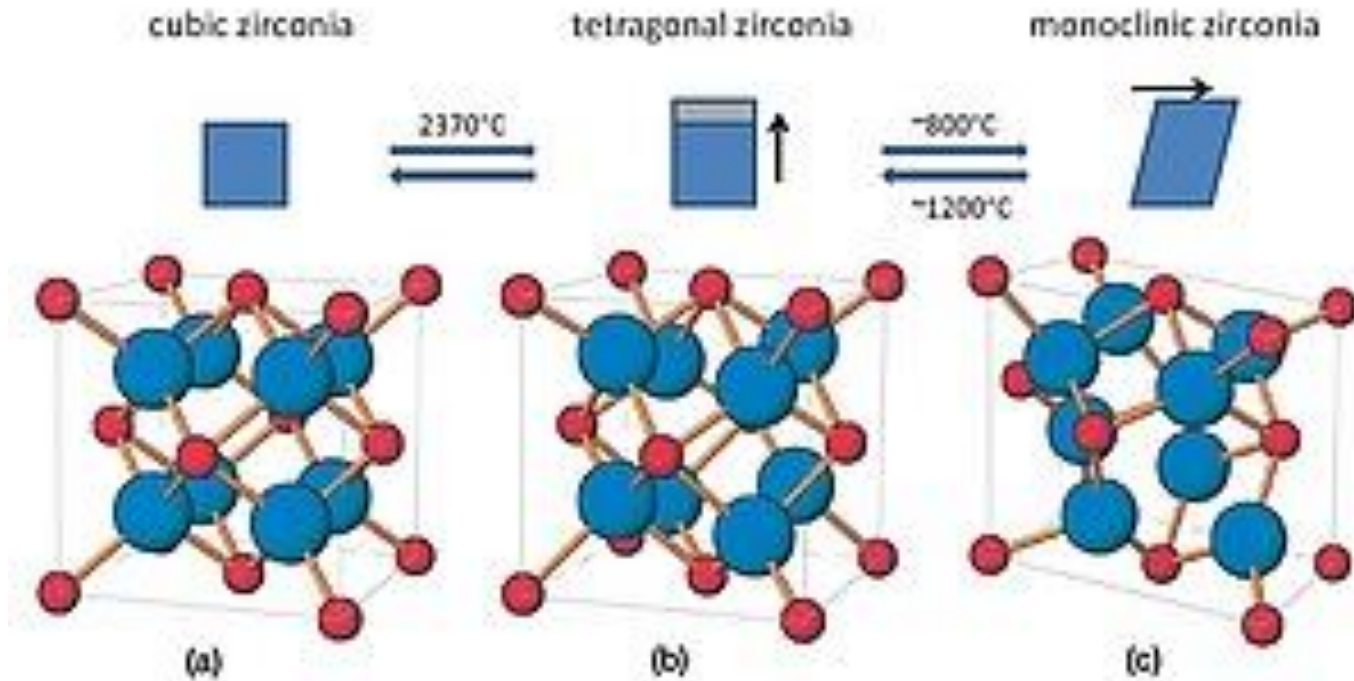
One way of Zirconia production is dissociating zircon above  $1750^{\circ}C$  with the help of plasma.



During cooling, zirconia solidifies first. Later, silica solidifies and covers zirconia crystals. At high cooling rates, silica forms glass. This can be separated from zirconia by dissolving it in hot NaOH.

Another method is direct melting of zircon in electric arc furnace at  $2300^{\circ}C$ . At this T Silica melts and it can be separated from solid state zirconia.

# Zirconia, $\text{ZrO}_2$



Pure zirconium dioxide undergoes a phase transformation from monoclinic (stable at the room temperature) to tetragonal (at about 1173 °C) and then to cubic (at about 2370 °C)

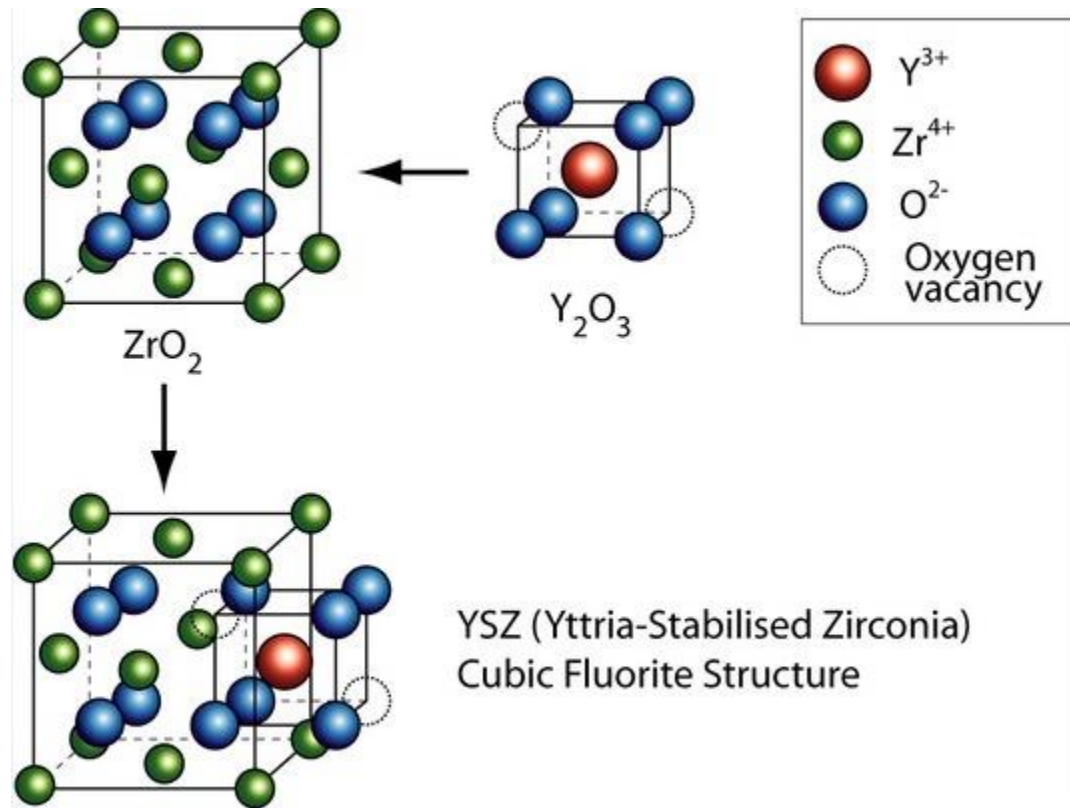
# Zirconia, $\text{ZrO}_2$

Pure zirconium dioxide undergoes a phase transformation from monoclinic (stable at the room temperature) to tetragonal (at about 1173 °C) and then to cubic (at about 2370 °C)

monoclinic (1173 °C)  $\leftrightarrow$  tetragonal (2370 °C)  $\leftrightarrow$  cubic (2690 °C)  $\leftrightarrow$  melt

Stable sintered zirconia ceramic products is difficult because of the large volume change from tetragonal to monoclinic ( $\sim 9\%$ ). Stabilization of the cubic polymorph of zirconia over wider range of temperatures is accomplished by substitution of some of the  $\text{Zr}^{4+}$  ions (ionic radius of 0.82 Å, too small for ideal lattice of fluorite characteristic for the tetragonal zirconia) in the crystal lattice with slightly larger ions, e.g., those of  $\text{Y}^{3+}$  (ionic radius of 0.96 Å). The resulting doped zirconia materials are termed *stabilized zirconia*

# Zirconia, $ZrO_2$



Stabilization with yttria, forms oxygen vacancy, which brings oxygen ion conductivity to material.

# Calcium Oxide, CaO

CaO – Calcium Oxide

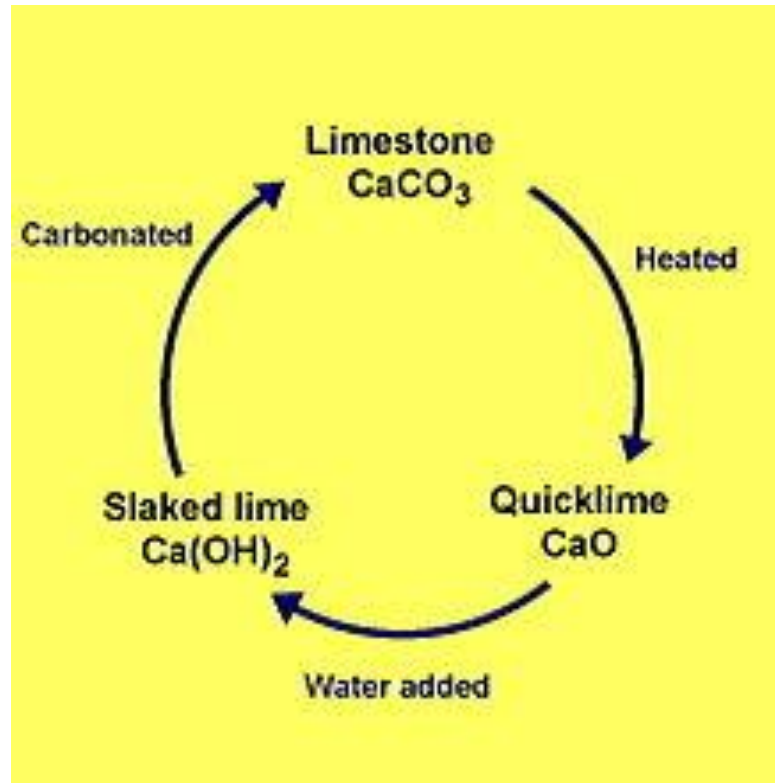
Ca(OH)<sub>2</sub> – Calcium Hydroxide

CaCO<sub>3</sub> – Calcium Carbonate

- Lime, Quicklime

- Lime, Slaked lime

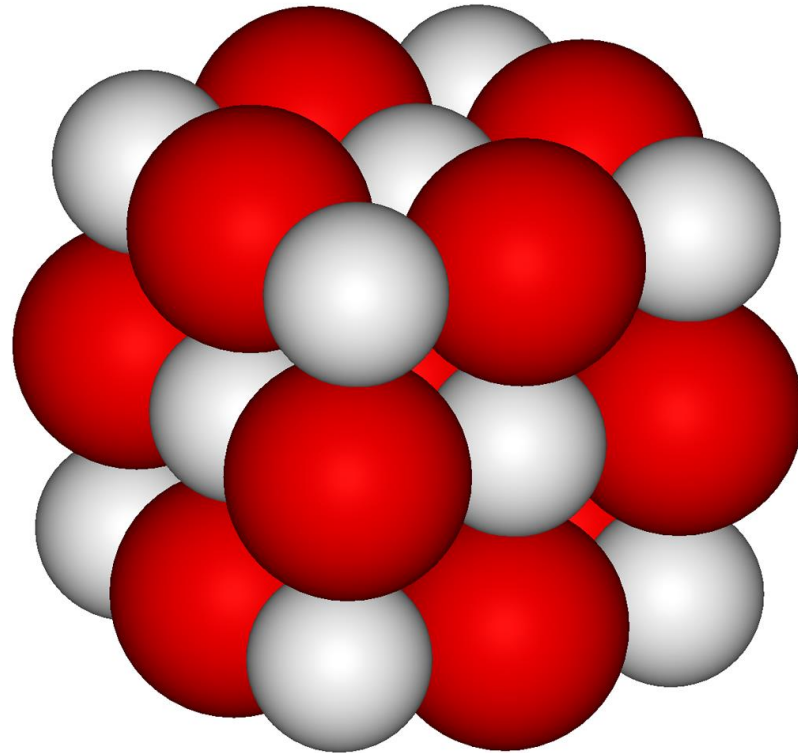
- Calcite, Limestone





# Calcium Oxide, CaO

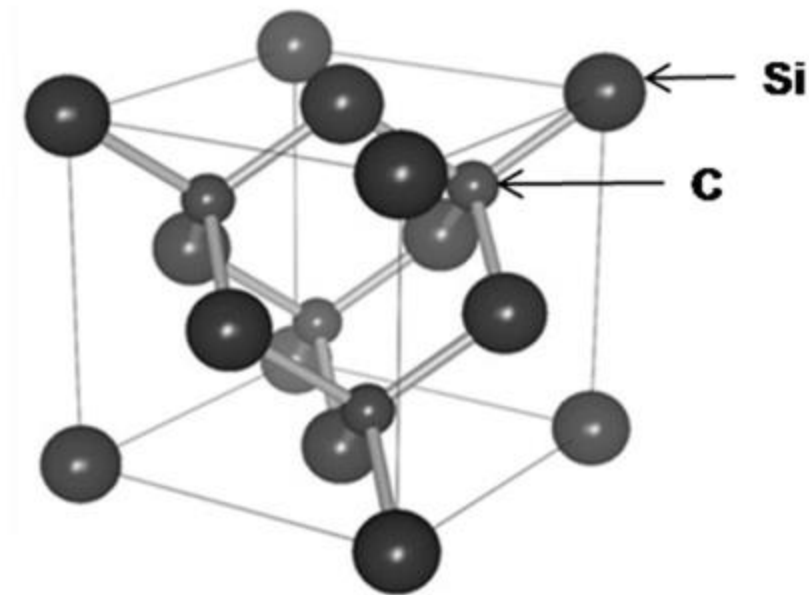
Rock Salt Structure, similar to MgO



# SiC

Silicon Carbide, one of the non-oxide ceramics.

- One of the hardest material (after diamond)
- Possess very high thermal conductivity
- High electrical conductivity
- Crystal structure is : Diamond Cubic



# Graphite

One of the crystalline forms of carbon.

Graphite has very high melting point ( $\sim 4000^{\circ}\text{C}$ ), but it burns out at  $600^{\circ}\text{C}$  in  $\text{O}_2$  atm.

- Extremely soft material because of the sheet-structure and van der Waals bonding btw sheets.
- Extremely high thermal conductivity in a-axis
- Very low thermal conductivity in c-axis
- High electrical conductivity in a-axis. Graphite electrodes used in arc furnaces.

Natural graphites are used as refractor

- Crystal structure is hexagonal

