

# TECNOLOGIA DOS MATERIAIS CERÂMICOS

## I - CERAMIC RAW MATERIALS

# 1.1 Ceramic Products: Traditional

Table ware



<http://www.construindominhacasaclean.com>

Sanitary ware



Bricks

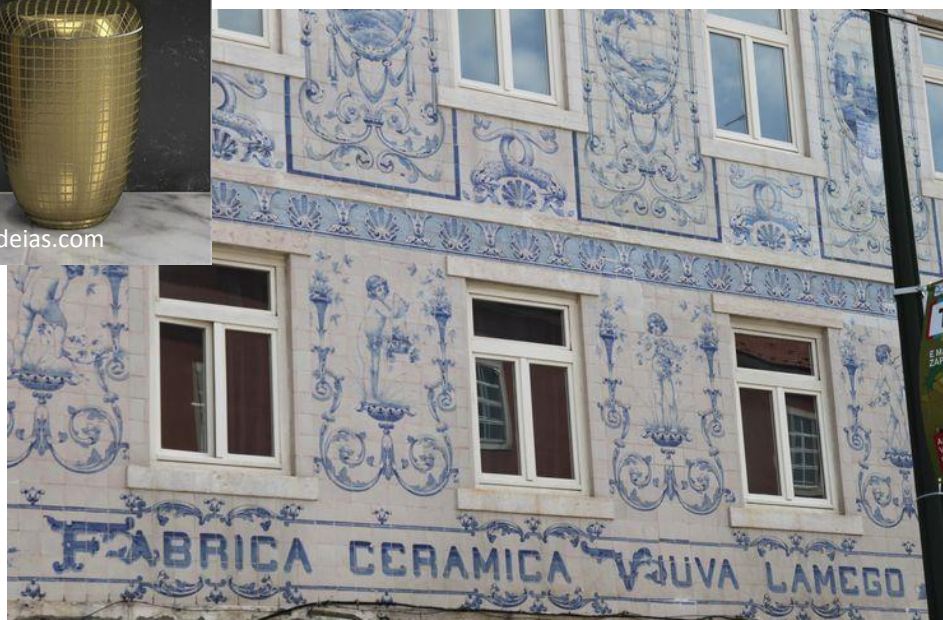


<http://www.nexus.globalquakemodel.org>



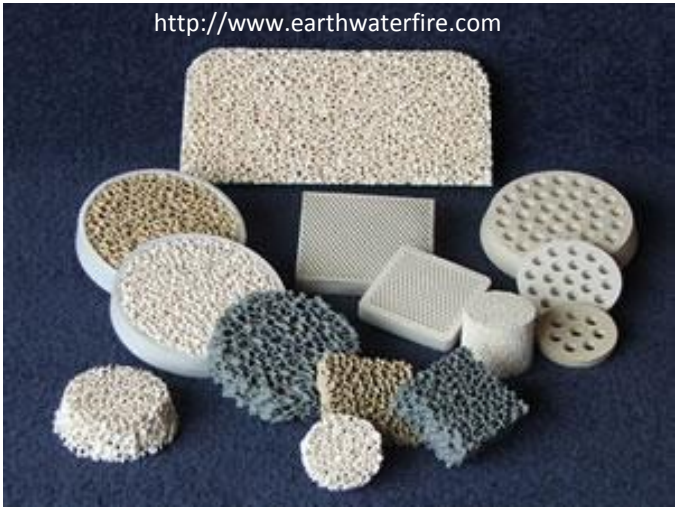
<http://www.decoracaoeideias.com>

Tiles



FABRICA CERAMICA VJUA LAMEGO

# 1.1 Ceramic Products: Refractory



**Membranes and filters**



**Crucibles and other lab artifacts**



**Kiln and furnaces**



**Ball (for ballmill)**



# 1.1 Ceramic Products: Mechanical and *Cutting-tools*



**Mechanical tools**



**Mechanical tools**



**Cutting tools**



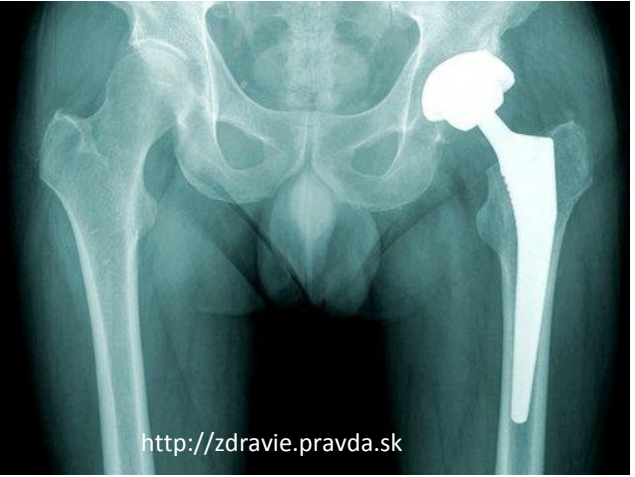
**Cutting tools**

# 1.1 Ceramic Products: Medical and Healthcare



<http://dentaltech.hu>

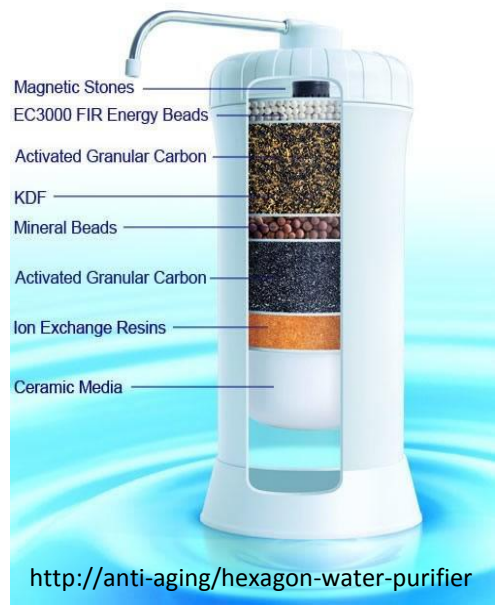
**Ceramic teeth**



<http://zdravie.pravda.sk>

**Ceramic hip implant**

## 8-Stage Water Filtration System



<http://anti-aging/hexagon-water-purifier>

**Water filter**

# 1.1 Ceramic Products: Bulletproof



Ceramic bulletproof plate ,  
Bulletproof protects armor , Ballistic helmet

**Bulletproof plate, armor and helmet**



<http://www.defensereview.com/prototype-mini-battle-shieldmini-combat-shield-gets-shoot-tested-pics/>

**Bulletproof shield**



# 1.1 Ceramic Products: na old history....



29000 b.C. - 25000 b.C.  
Věstonice, Tcheck Republic



Chan Chan – Pre-Coulombian, South America’s  
Mud-Brick City



750 b.C.  
Dipylon Cemetery, Athens

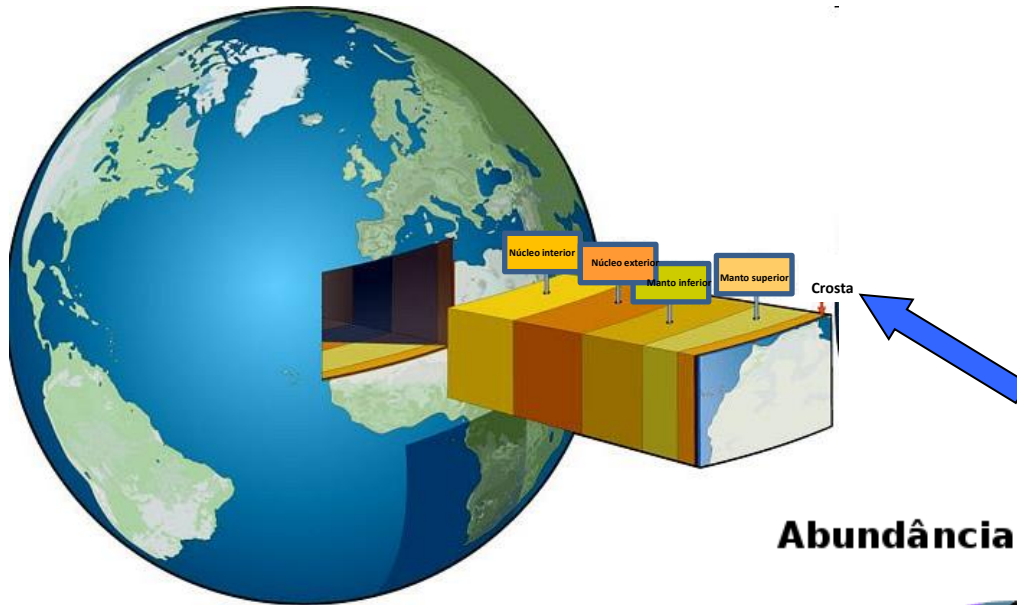


Dinasty Ming (1368-1644)  
French embassy, Lisboa

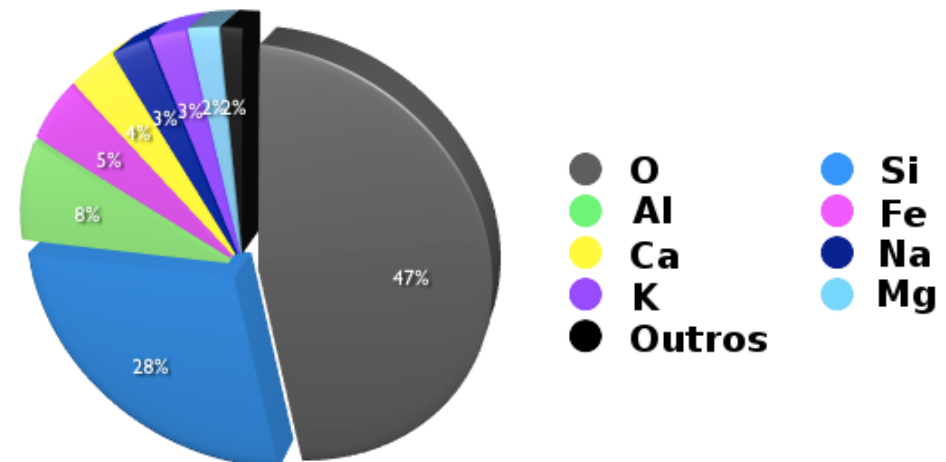
209-210 b.C.  
The Terracotta Warriors and Horses  
of Qin Shi Huangin, China.  
Terracotta Army held more than  
8,000 soldiers, 130 chariots with 520  
horses and 150 cavalry horses.



# Silica in earth crust



## Abundância dos elementos na crosta terrestre



Ref: Lutgens and Tarbuck, *Essentials of Geology* (2000)



**CERAMICS COMPOSITIONS**

**1.2 1950...**

**PROPERTIES**

**COMPOSITION**

**ELECTRICAL**

ISOLATION  
FERROELECTRIC  
PIEZOELECTRIC  
SUPERCONDUTOR

$\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgO, porcelain  
BaTiO<sub>3</sub>, SrTiO<sub>3</sub>  
PbZr<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>  
Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7-x</sub>

**FERRITES**

Mn<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2</sub>O<sub>4</sub>, BaFe<sub>12</sub>O<sub>19</sub>, SrFe<sub>12</sub>O<sub>19</sub>

**MAGNETIC**

STRUCTURAL REFRACTORY  
MECHANICAL RESISTANCE  
CUTTING/ABRASION  
CIVIL CONSTRUCTION (BRICK, ROOF TILE, CEMENT)

$\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgO, SiC, Si<sub>3</sub>N<sub>4</sub>, Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>  
 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>  
 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiC, TiC, Si<sub>3</sub>N<sub>4</sub>, SIALON  
Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

**MECHANICAL**

**FAIENCE / PORCELAIN**

FAIENCE,  
PORCELAIN  
CaO-SiO<sub>2</sub>-H<sub>2</sub>O

**FUNCTIONAL**

# 1.2 2015...

## CERAMICS COMPOSITION

### PROPERTIES

### COMPOSITION

#### ELECTRICAL

ISOLATION  
FERROELECTRIC  
PIEZOELECTRIC  
SUPERCONDUTOR

$\alpha\text{-Al}_2\text{O}_3$ , MgO, porcelain  
BaTiO<sub>3</sub>, SrTiO<sub>3</sub>  
PbZr<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>  
Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7-x</sub>

#### FERRITE

Mn<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2</sub>O<sub>4</sub>, BaFe<sub>12</sub>O<sub>19</sub>, SrFe<sub>12</sub>O<sub>19</sub>

#### MAGNETIC

#### NUCLEAR

FUEL  
COATING/ SHIELD

UO<sub>2</sub>, UO<sub>2</sub>- PuO<sub>2</sub>  
SiC, B<sub>4</sub>C

#### OPTICAL

TRANSPARENCY  
COLOR  
MEMORY

$\alpha\text{-Al}_2\text{O}_3$ , MgAl<sub>2</sub>O<sub>4</sub>  
ZrSiO<sub>4</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> dopados  
PbZr<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>

STRUCTURAL REFRACTORY  
MECHANICAL RESISTANCE  
CUTTING/ABRASION  
CIVIL CONSTRUCTION (BRICK, ROOF TILE, CEMENT)

$\alpha\text{-Al}_2\text{O}_3$ , MgO, SiC, Si<sub>3</sub>N<sub>4</sub>, Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>  
 $\alpha\text{-Al}_2\text{O}_3$ , ZrO<sub>2</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>  
 $\alpha\text{-Al}_2\text{O}_3$ , ZrO<sub>2</sub>, SiC, TiC, Si<sub>3</sub>N<sub>4</sub>, SIALON  
Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

#### MECHANICAL

#### ISOLATION

$\alpha\text{-Al}_2\text{O}_3$ , ZrO<sub>2</sub>, Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>, SiO<sub>2</sub>

#### THERMAL

#### CHEMICAL

RADIATOR  
GAS SENSOR  
CATALITIC CARRIER  
ELECTROD  
FILTER  
COATING

ZrO<sub>2</sub>, TiO<sub>2</sub>  
ZnO, ZrO<sub>2</sub>, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>  
Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>, Al<sub>2</sub>O<sub>3</sub>  
TiO<sub>2</sub>, TiB<sub>2</sub>, SnO<sub>2</sub>, ZnO  
SiO<sub>2</sub>,  $\alpha\text{-Al}_2\text{O}_3$   
NaO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

#### BIOLOGICAL

PROSTHESIS  
CEMENT

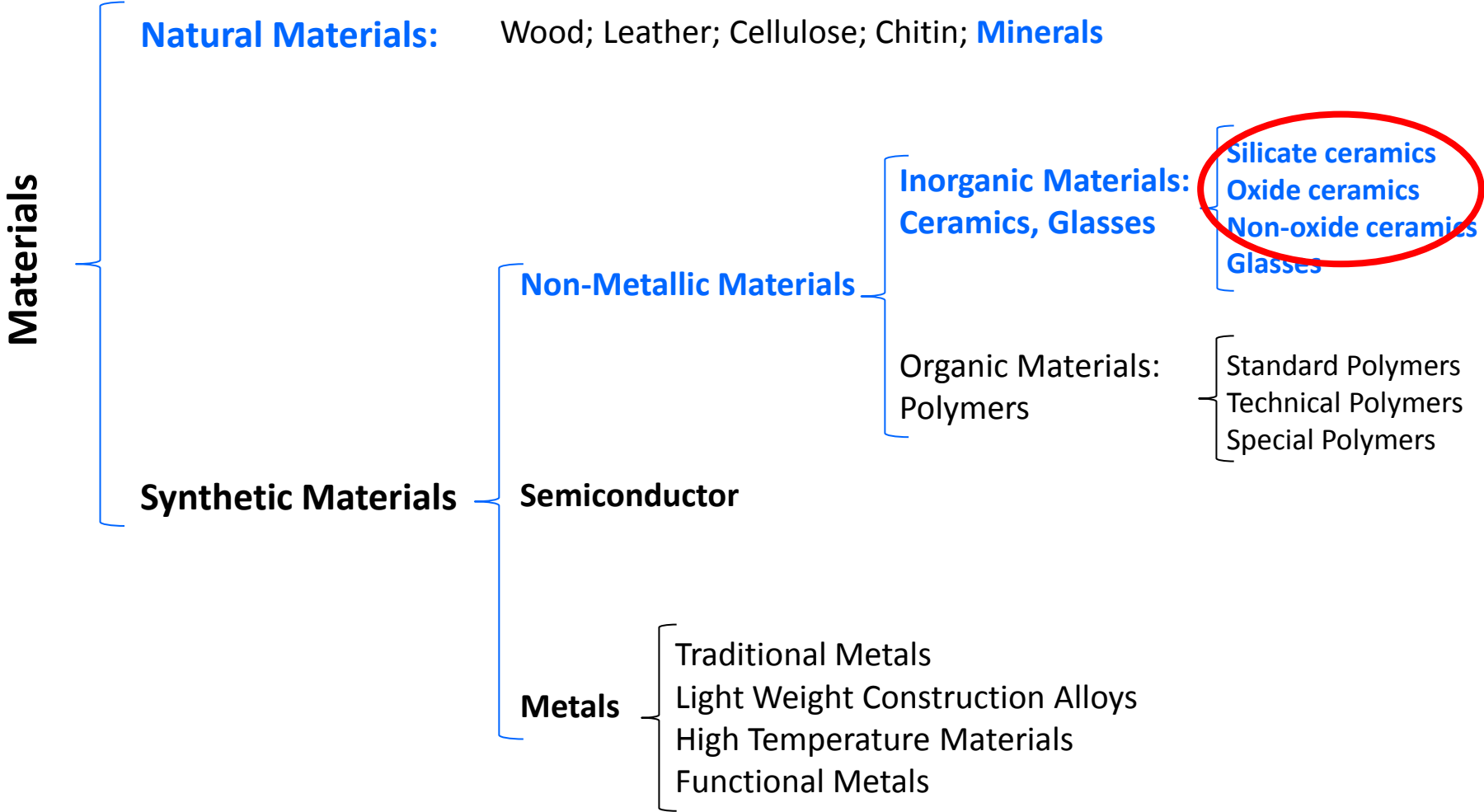
$\alpha\text{-Al}_2\text{O}_3$ , PORCELAIN  
CaHPO<sub>4</sub>·2H<sub>2</sub>O

FAIENCE / PORCELAIN

FAIENCE,  
PORCELAIN  
CaO-SiO<sub>2</sub>-H<sub>2</sub>O

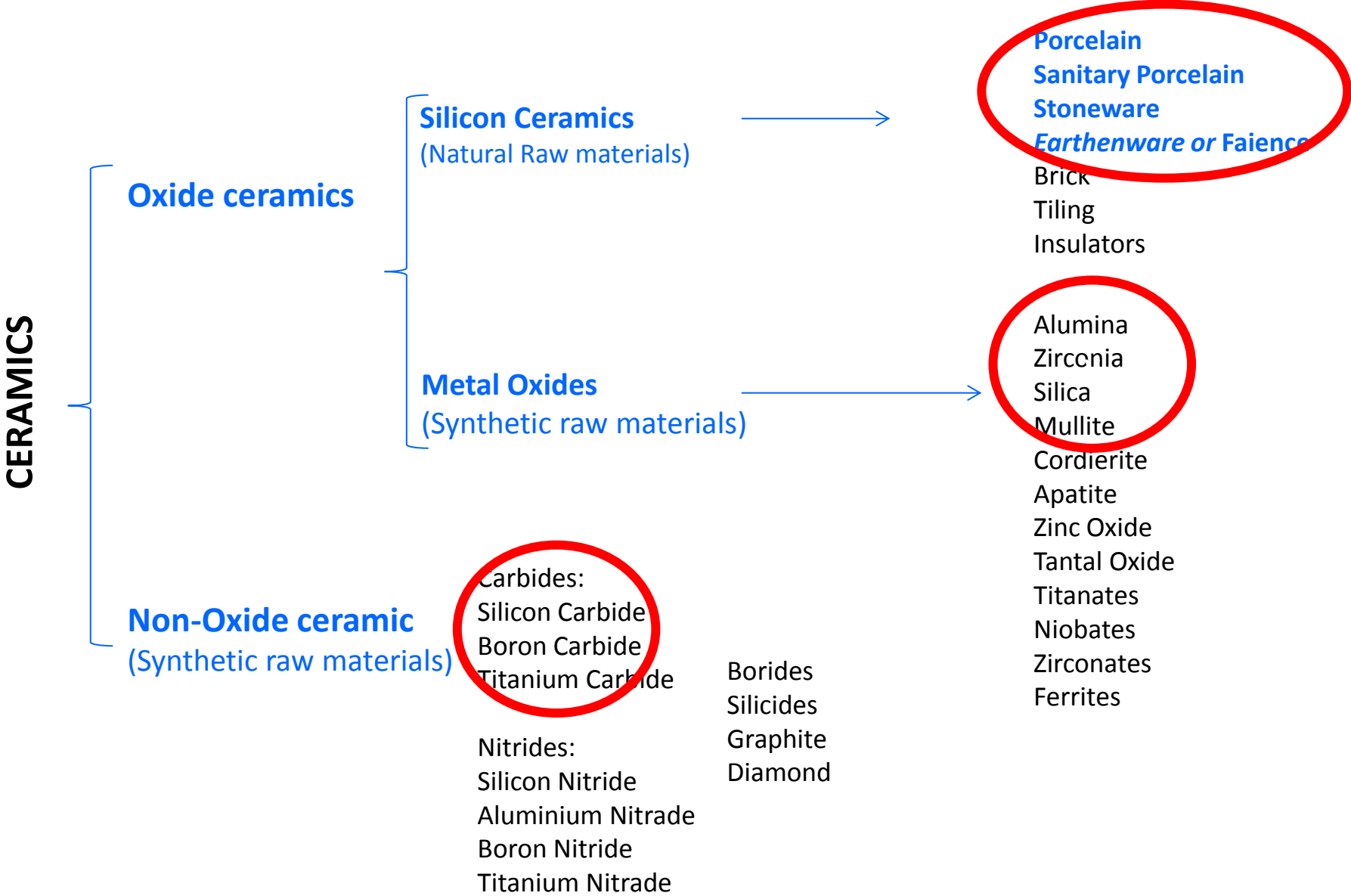
#### FUNCTIONAL

# 1.3 Classification of the main materials groups

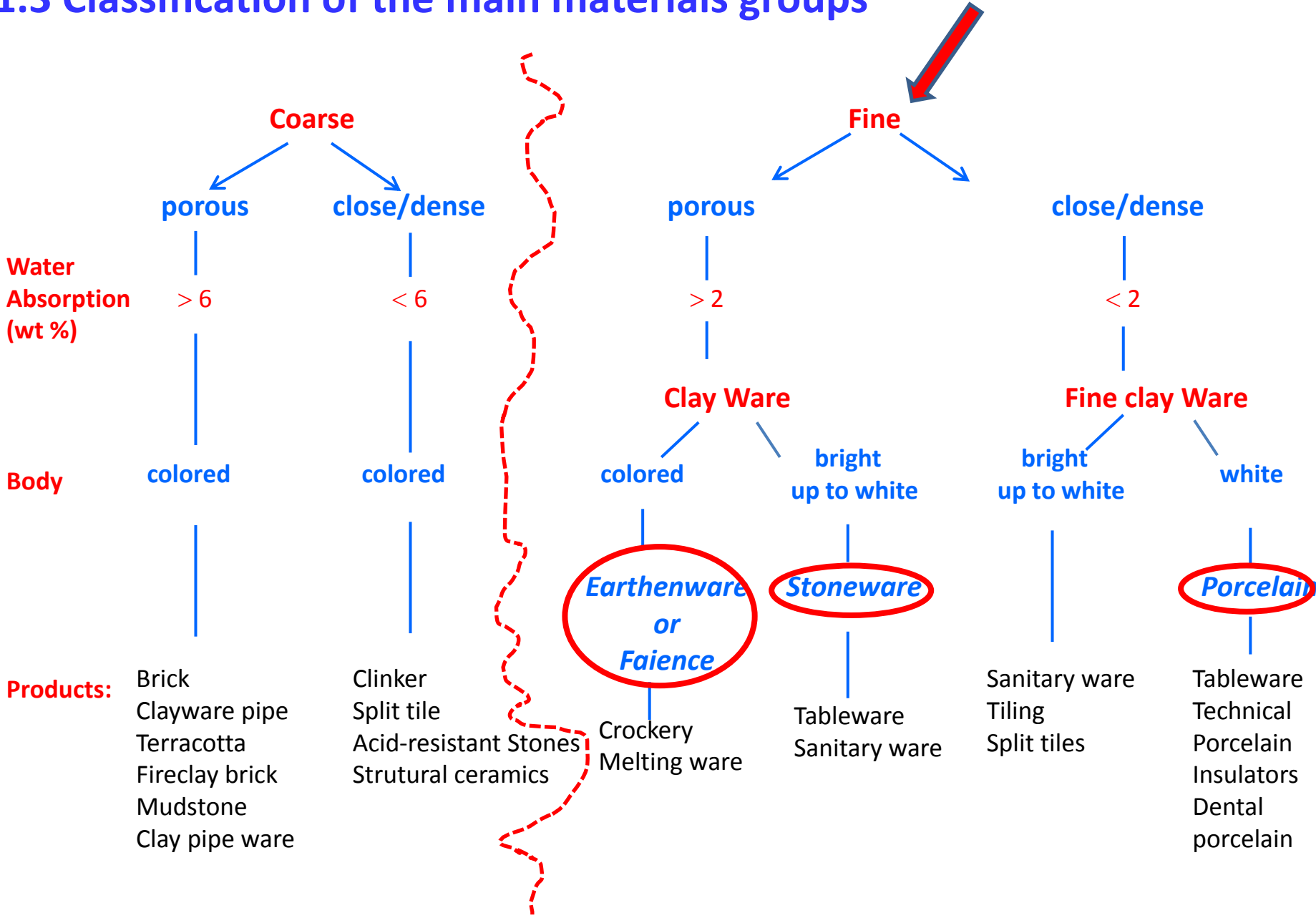




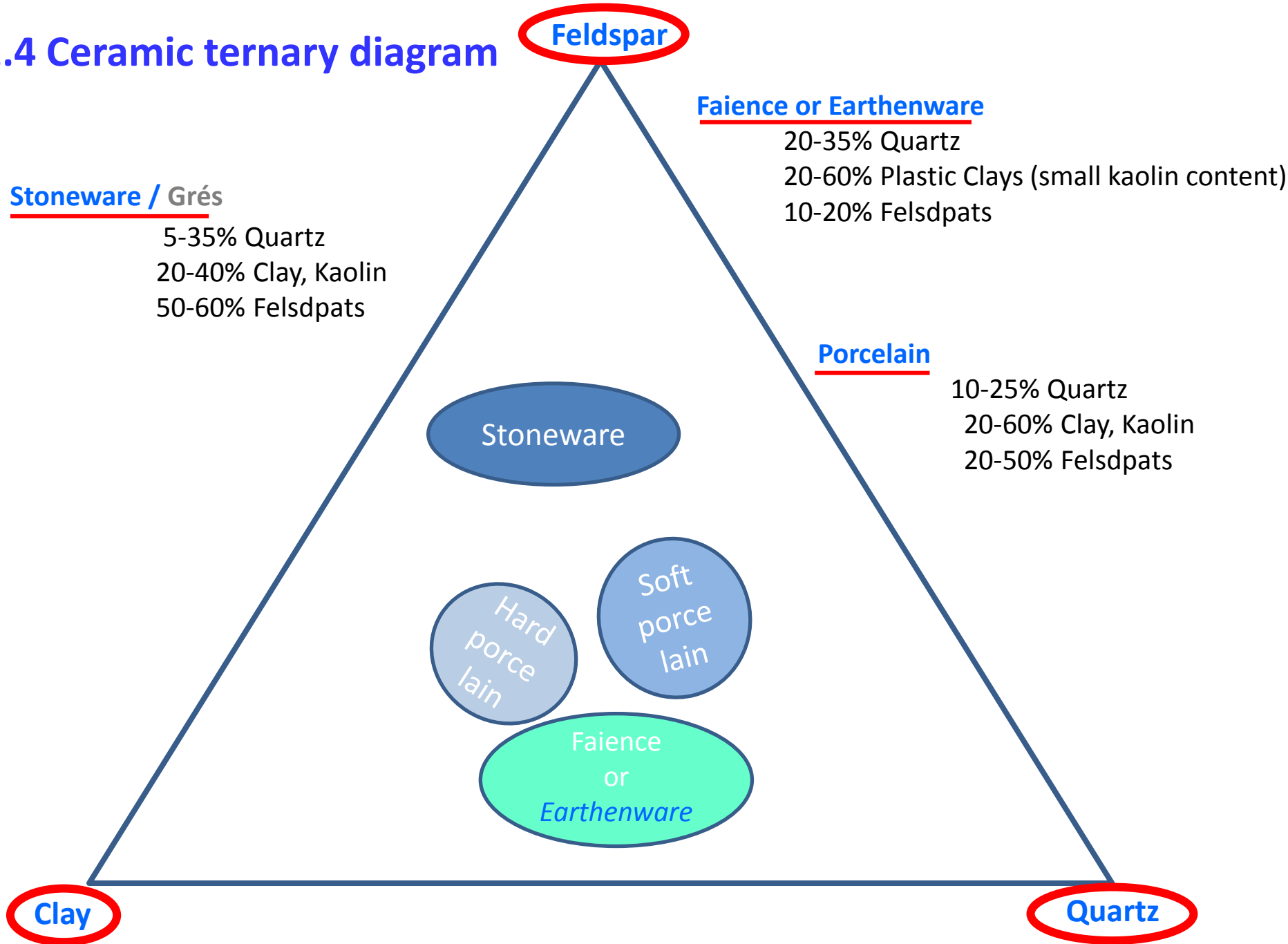
# 1.3 Classification of the main materials groups



# 1.3 Classification of the main materials groups



# 1.4 Ceramic ternary diagram



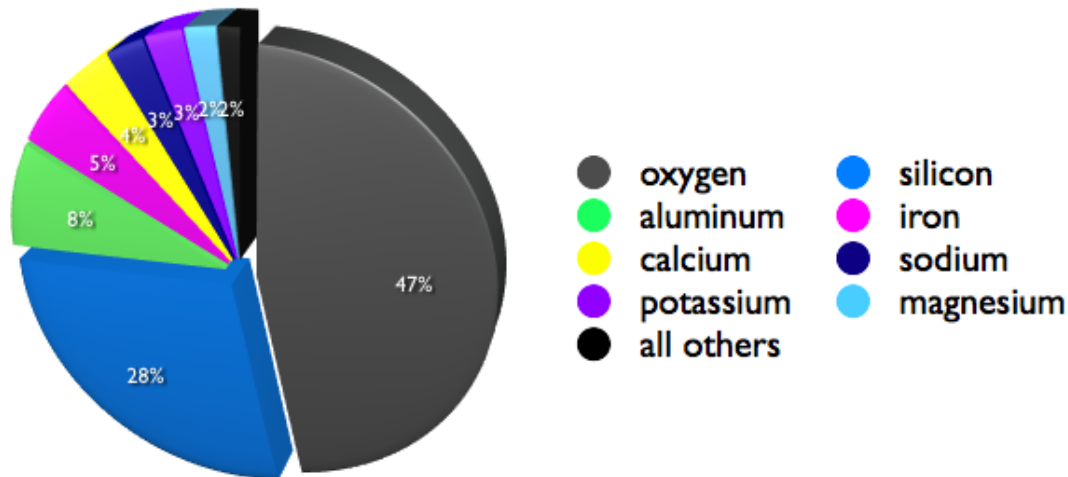


# *CLAYS and Quartz*

# 1.5 Ceramic raw materials

## Silica Abundance

abundances of the elements in the earth's crust



Ref: Lutgens and Tarbuck, *Essentials of Geology* (2000)

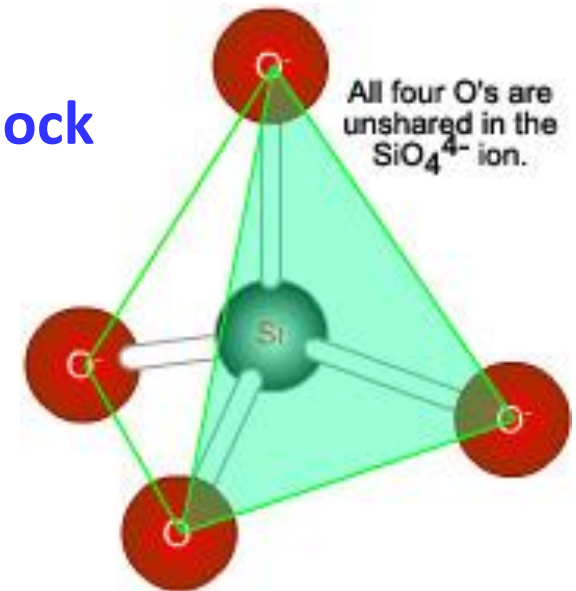
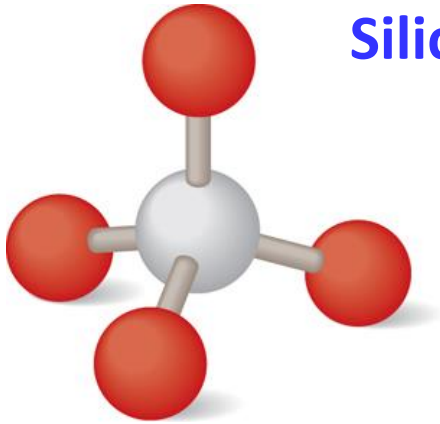
<https://fundamateria.wordpress.com/category/seed/>

→ Silicon is one of **the most abundant elements in the earth's crust**, but it occurs chiefly in combination with oxygen as silica, **SiO<sub>2</sub>**, and with oxygen and other elements as **silicates**.

→ **Silica** is a **polymorphic substance**, capable of existing in several different forms, all having the same empirical formula but differing in the arrangement of the structural units – **quartz**, **tridimite** and **crystalite** are the most abundant forms in earth's crust.

## 1.5 Ceramic raw materials

### Silica Tetrahedron – the building block

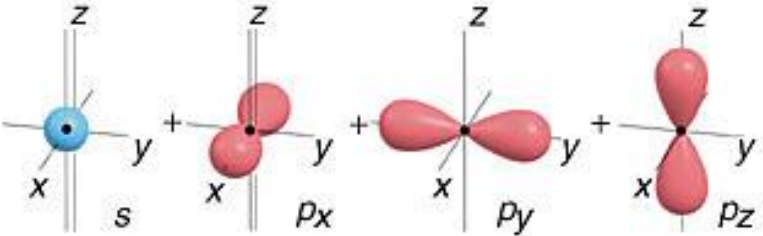


- The Si-O bond has sufficient **ionic character** to enable us to regard all forms of SiO<sub>2</sub> as being composed of **Si<sup>4+</sup>** and **O<sup>2-</sup>** ions.
- The **radius ratio of silicon to oxygen is 0.28** corresponding to a predicted **coordination number of 4**, which agrees with the observed value for the majority of crystalline and amorphous forms of silica.
- Each **Si<sup>4+</sup> ion** in silica is surrounded by **four oxygen ions**, forming a **tetrahedron**, having a triangular base and three triangular sides meeting at an apex.

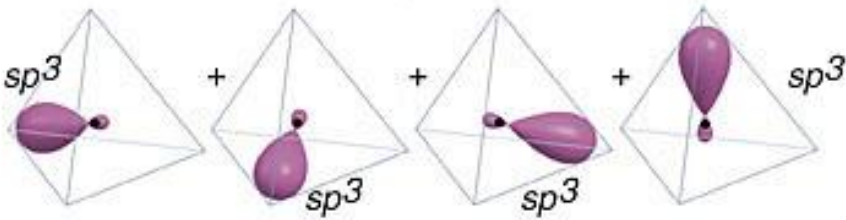


# 1.5 Ceramic raw materials

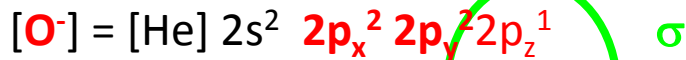
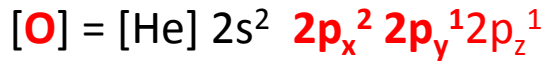
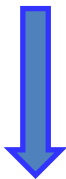
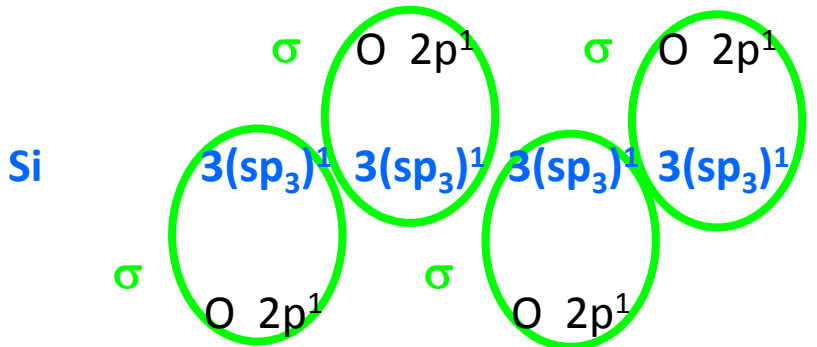
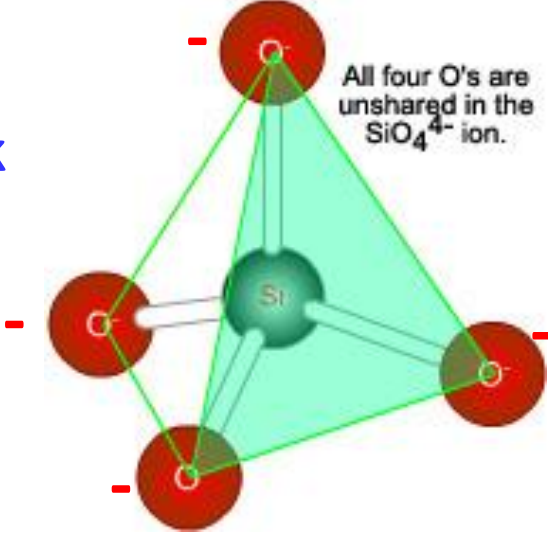
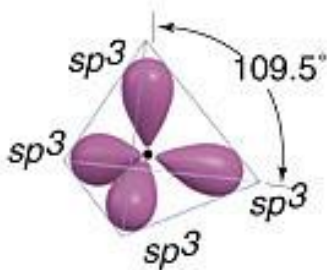
## Silica Tetrahedron – the building block



Hybridize to form four  $sp^3$  hybrid orbitals

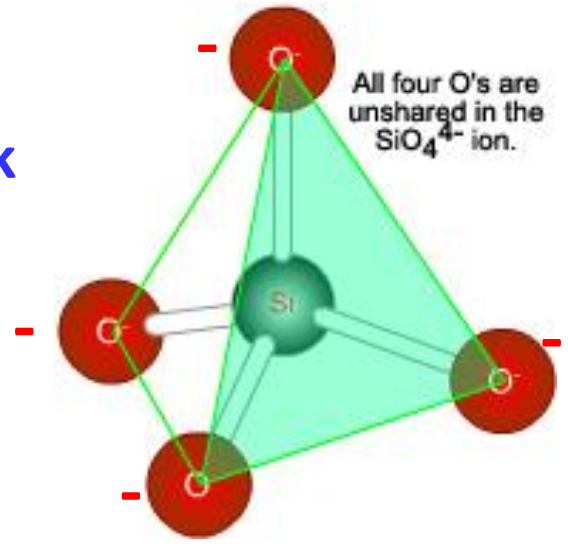
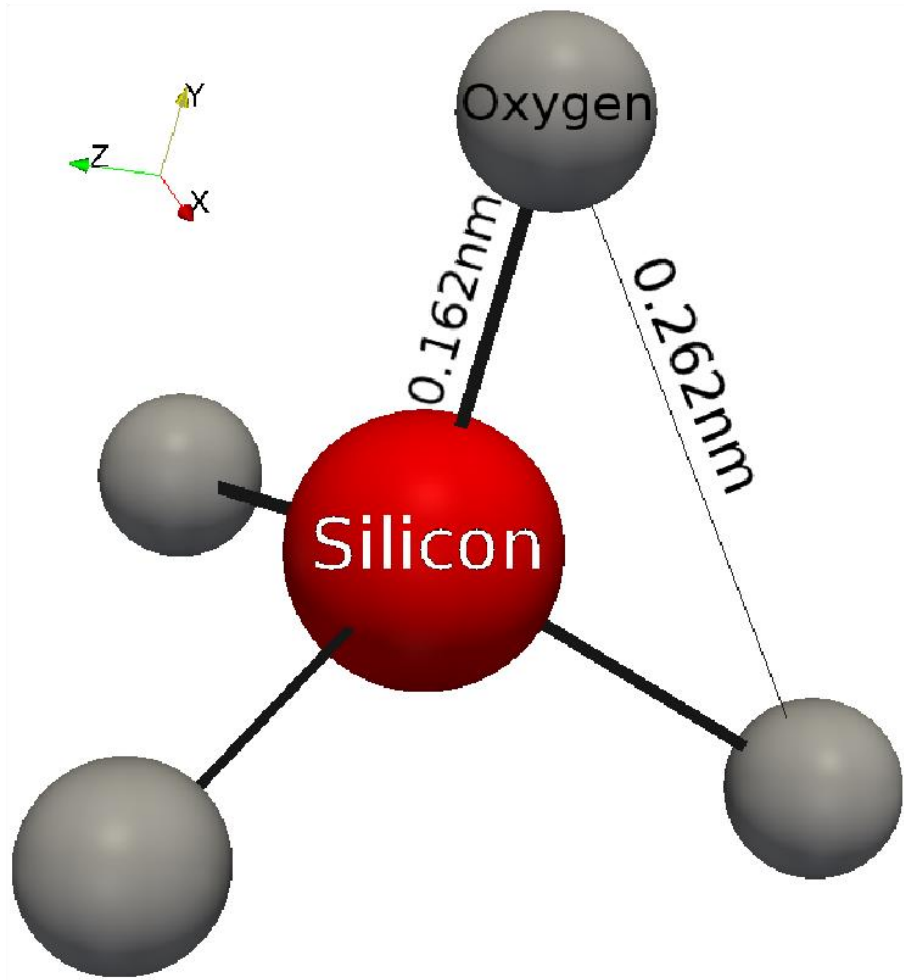


Shown together (large lobes only)



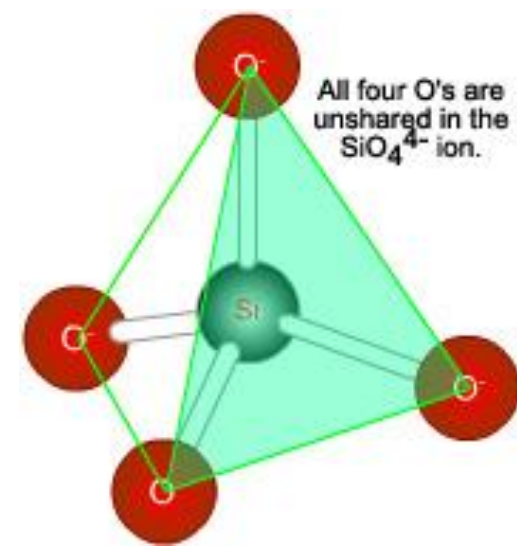
# 1.5 Ceramic raw materials

## Silica Tetrahedron – the building block



## 1.5 Ceramic raw materials

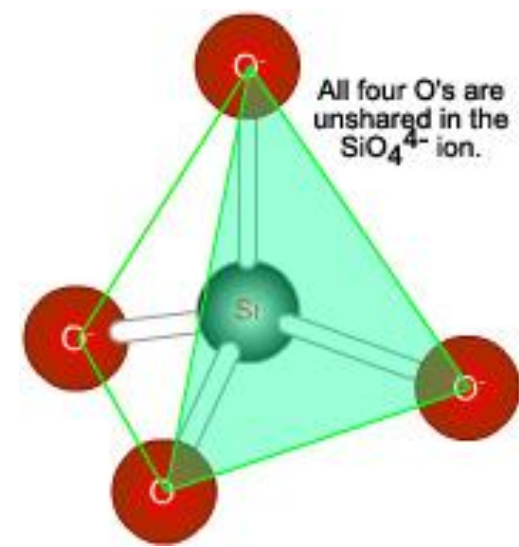
### Silica Tetrahedron – the building block



- The  $[\text{SiO}_4]^{4-}$  group is of course **incapable of independent existence** and **requires four positively charged units to balance the negative charges**; these groups may be other  $\text{SiO}_2$  groups, as in **silica**, or other **cations**, as in **silicates**.
- This fundamental unit is **repeated**, **linked** and **joined** in different ways giving rise to **different types of silicate structures**.

## 1.5 Ceramic raw materials

### Silica Tetrahedron – the building block



**AND NOW LET'S PLAY WITH THE  
SILICA TETRAHEDRON!**



Silicates

<https://www.youtube.com/watch?v=8q-Hzq0WXXw>



# 1.5 Ceramic raw materials

## Silica Tetrahedron – the building block

→ Silicon is located in the center of the tetrahedron and surrounded by 4 oxygens at the corners. This group is electrically unbalanced  $((\text{SiO}_4)^{4-})$ , so that the oxygen atoms are combined with other cations to compensate their negative charges. The number of vertices shared by each tetrahedron may be 0, 1, 2, 3 or 4.

→ Tetrahedra may also join by their bases to form hexahedral molecules  $((\text{Si}_2\text{O}_4)_n^{2n-})$ . Depending on the number of oxygens that coordinate with other silicon cations, large groups of silicates may form in different shapes:

→  $Q^0$  no oxygens shared: isolated molecules (orthosilicates)

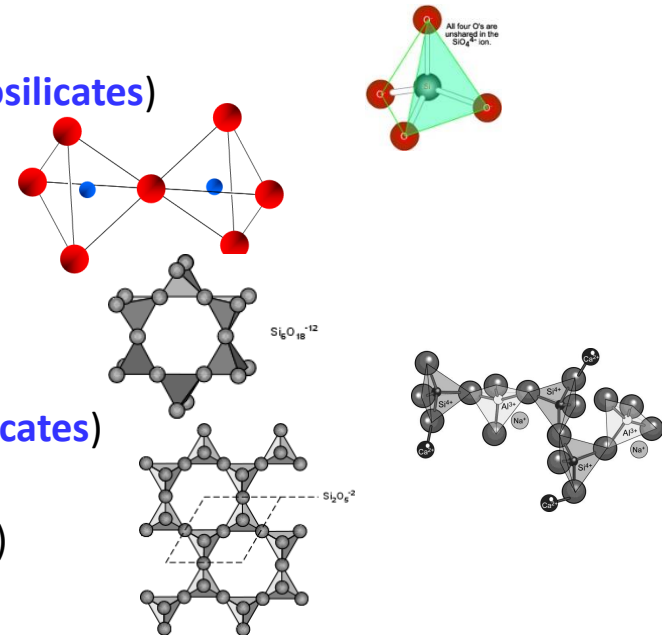
→  $Q^1$  one oxygen shared: pairs (sorosilicates)

→  $Q^2$  two oxygens shared: rings (cyclosilicates)

→  $Q^2$ - $Q^3$  two-three oxygens shared: chains (inosilicates)

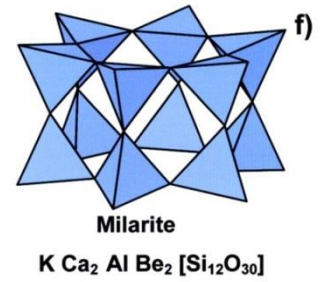
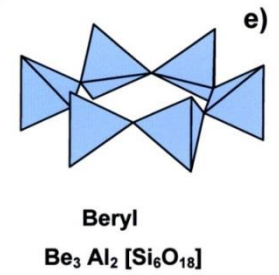
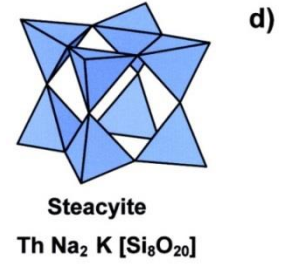
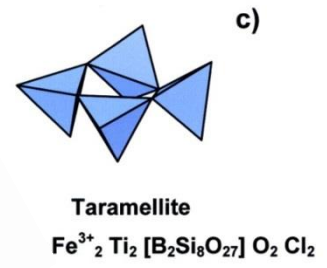
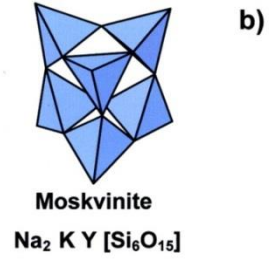
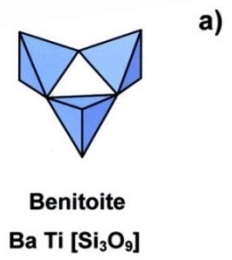
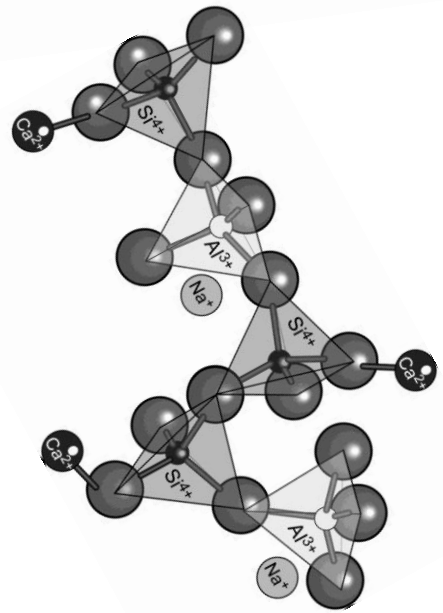
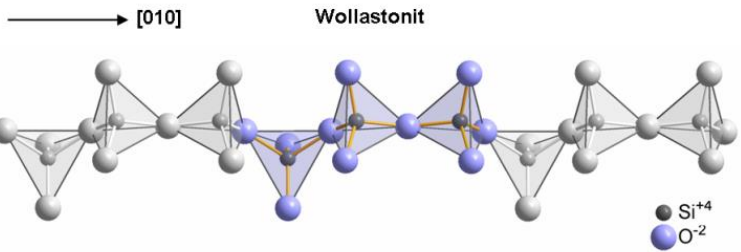
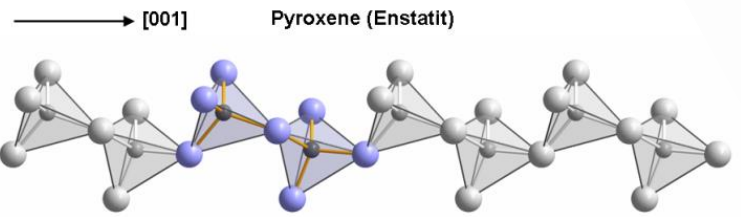
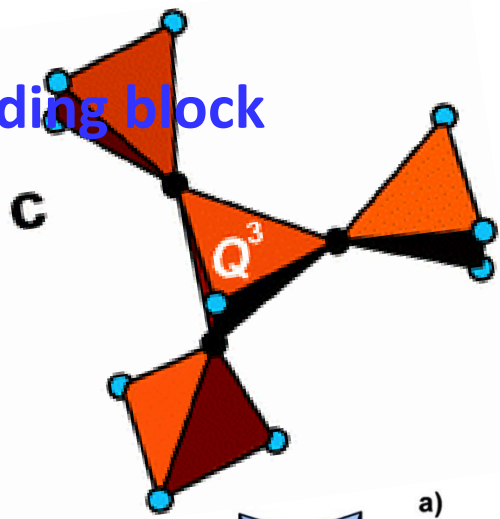
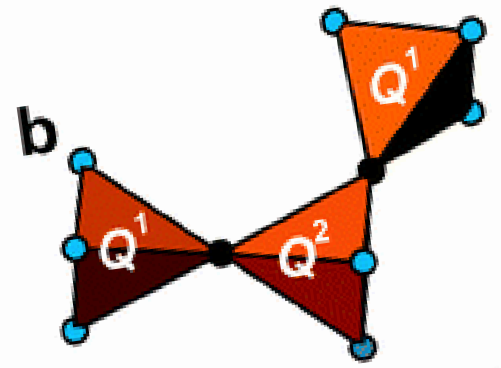
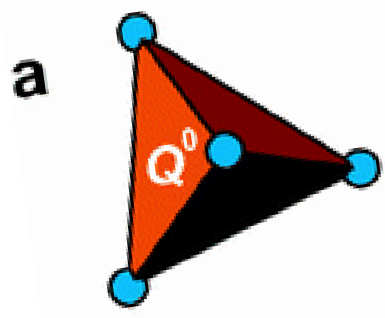
→  $Q^3$  three oxygens shared: planes (phyllosilicates)

→  $Q^4$  four oxygens shared: tridimensional structures (tectosilicates)



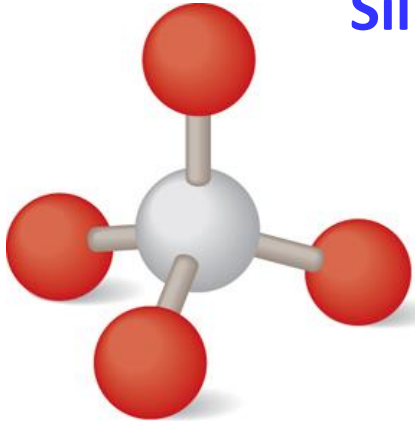
# 1.5 Ceramic raw materials

## Silica Tetrahedron – the building block



# 1.5 Ceramic raw materials

## Silica Tetrahedron – the building block



### Silicates

The basic building block of all silicates is the  $\text{SiO}_4$  tetrahedron.

4-

	$Q^0$		$Q^2$		$Q^2$		$Q^3$		$Q^3$		$Q^4$
Anionic unit	$\text{SiO}_4^{4-}$	$\text{Si}_2\text{O}_7^{6-}$	$\text{Si}_6\text{O}_{18}^{12-}$	$\text{Si}_2\text{O}_6^{4-}$	$\text{Si}_4\text{O}_{11}^{6-}$	$\text{Si}_2\text{O}_5^{2-}$	$\text{SiO}_2$				
Silicate subclass	Isolated tetrahedra	Paired tetrahedra	Ring	Chain	Double chain	Sheet	Framework				
NBO/T	4	3	2	2	1 or 2	1	0				
Approx. Raman band ( $\text{cm}^{-1}$ )	790-850	890-950	-	930-1000	-	1020-1100	1150-1200 1060-1070				
<ul style="list-style-type: none"> <li>○ NBO</li> <li>● BO</li> <li>▴ Silicon Tetrahedra</li> </ul>											

# 1.5 Ceramic raw materials

## Silica Tetrahedron – the building block

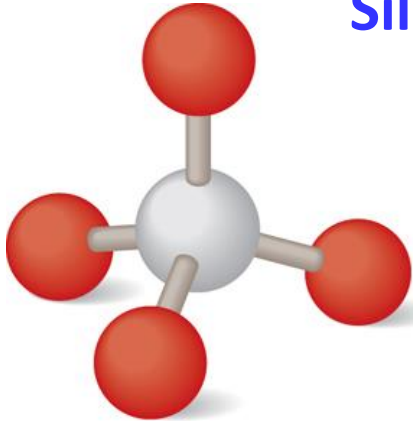

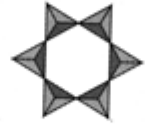

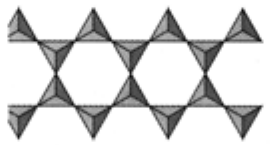
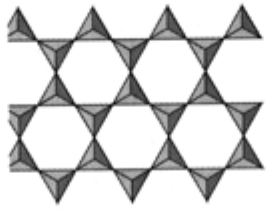

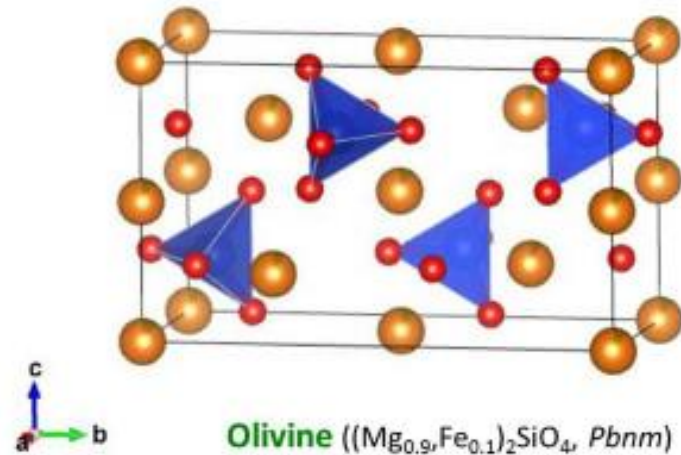


TABLE 2.2 Major Silicate Structures			
GEOMETRY OF LINKAGE OF SiO <sub>4</sub> TETRAHEDRA		EXAMPLE MINERAL	CHEMICAL COMPOSITION
<i>Isolated tetrahedra:</i> No sharing of oxygens between tetrahedra; individual tetrahedra linked to each other by bonding to cation between them		Olivine <b>Q<sup>0</sup></b>	Magnesium-iron silicate
<i>Rings of tetrahedra:</i> Joined by shared oxygens in three-, four-, or six-membered rings		Cordierite <b>Q<sup>2</sup></b>	Magnesium-iron-aluminum silicate
<i>Single chains:</i> Each tetrahedron linked to two others by shared oxygens; chains bonded by cations		Pyroxene <b>Q<sup>2</sup></b>	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 <b>Q<sup>3</sup></b>	Calcium-magnesium-iron silicate
<i>Sheets:</i> Each tetrahedron linked to three others by shared oxygens; sheets bonded by cations		Kaolinite Mica (muscovite) <b>Q<sup>3</sup></b>	Aluminum silicate Potassium-aluminum silicate
<i>Frameworks:</i> Each tetrahedron shares all its oxygens with other SiO <sub>4</sub> tetrahedra (in quartz) or AlO <sub>4</sub> tetrahedra		Feldspar (orthoclase) Quartz <b>Q<sup>4</sup></b>	Potassium-aluminum silicate Silicon dioxide

## 1.5 Ceramic raw materials

### Q<sup>0</sup>: Island Structures (orthosilicates)



→ A good example of this structure is **olivine**.

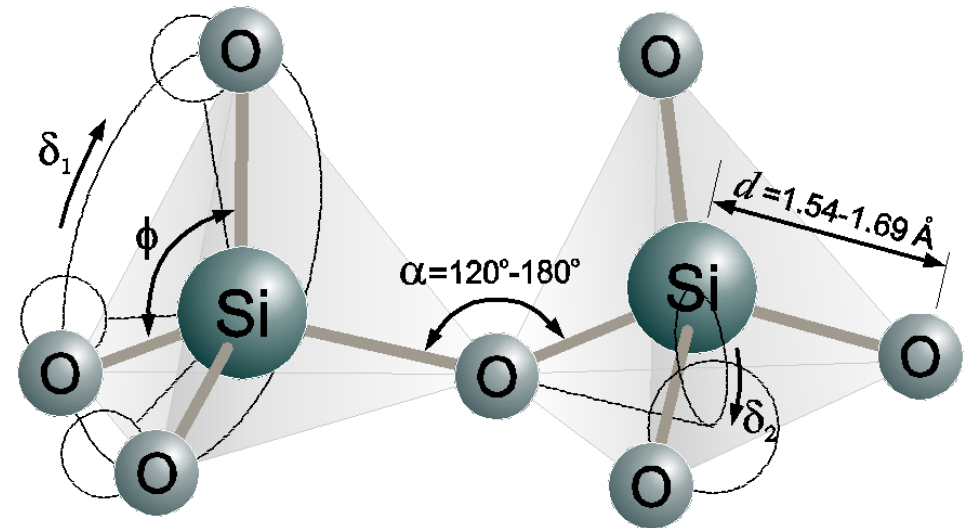
→ In **olivine**, **neutrality** is achieved by **metallic cations** (principally **Fe** and **Mg**) being attached to the four oxygen ions of the [SiO<sub>4</sub>]<sup>4-</sup>.

→ A complete crystal of olivine contains a very large number of SiO<sub>4</sub> units with their appropriate cations; it forms a **continuous network** because each atom is shared by two or more other atoms.



## 1.5 Ceramic raw materials

### Q<sup>1</sup>: Group Structures (sorosilicates)



### Beryl or emerald

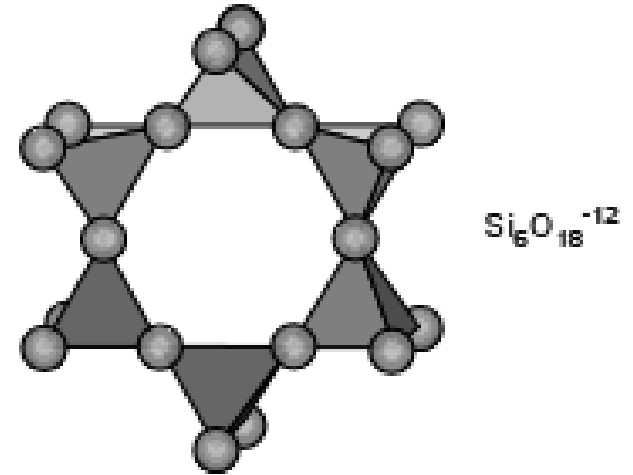
- Instead of all the free oxygen valencies being satisfied by metallic cations, **two or more silica tetrahedra** may be **joined, corner to corner**, to form a group structure.
- Joining two groups together gives the group **Si<sub>2</sub>O<sub>7</sub>**. Minerals of this type are rare (ex. **beryl** or **emerald**, with the formula **(Be<sub>3</sub>Al<sub>2</sub>)Si<sub>6</sub>O<sub>18</sub>**).

## 1.5 Ceramic raw materials

### Q<sup>2</sup>: Group Structures (cyclosilicates)



Cordierite



→ Instead of all the free oxygen valencies being satisfied by metallic cations, **two or more silica tetrahedra** may be **joined, corner to corner**, to form a group structure.

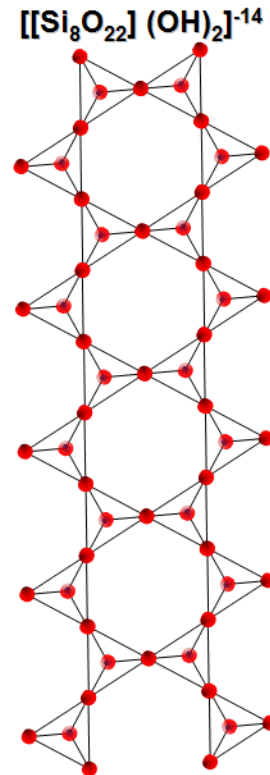
→ Six units can be linked to form a ring structure, where the basic structure is  $\text{Si}_6\text{O}_{18}^{12-}$ . An example is mineral **cordierite**,  $\text{Al}_3\text{Mg}_2(\text{Si}_5\text{Al})\text{O}_{18}$ , where one of the six silicons in the ring has been isomorphous substituted by an aluminium ion. The substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  upsets the charge balance, being the neutrality maintained by increasing the ratio of trivalent to divalent cations.

## 1.5 Ceramic raw materials

### Q<sup>2</sup>-Q<sup>3</sup> : Chain Structures (inosilicates)



**Pyroxenes** Q<sup>2</sup>



Q<sup>2</sup>-Q<sup>3</sup> **Amphiboles**

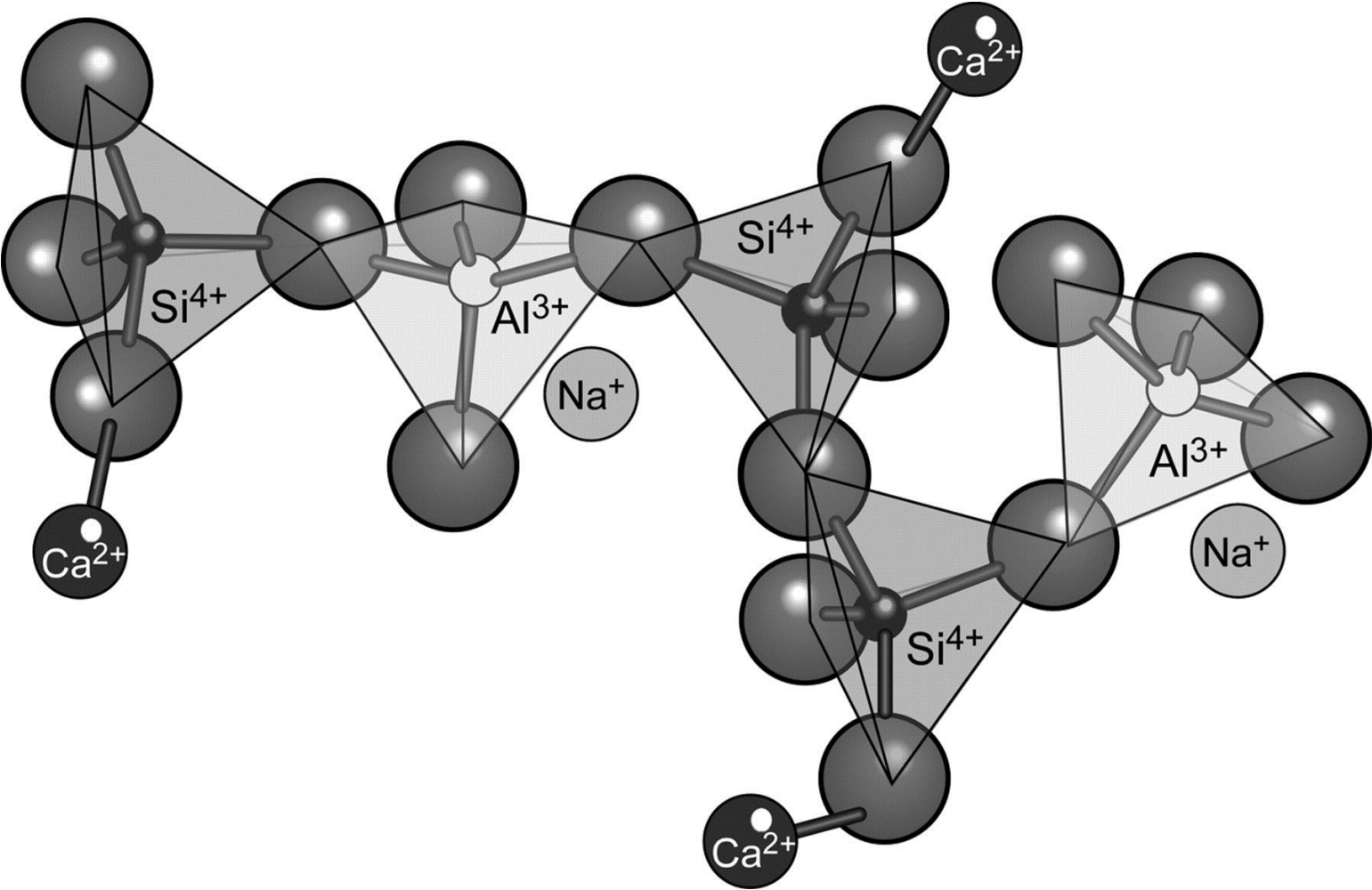
→ By joining an indefinitely large number of silica tetrahedra together, we arrive at a chain structure, which is common to two classes of minerals – the **pyroxenes** and the **amphiboles**.

→ **Pyroxenes** have SiO<sub>3</sub><sup>2-</sup> as the repeated group while **amphiboles** have the Si<sub>4</sub>O<sub>11</sub><sup>6-</sup> group.

→ Owing to their chain structure, the pyroxenes and amphiboles are fibrous, **asbestos like minerals**.

# 1.5 Ceramic raw materials

## Q<sup>2</sup>-Q<sup>3</sup>: Chain Structures (inosilicates)



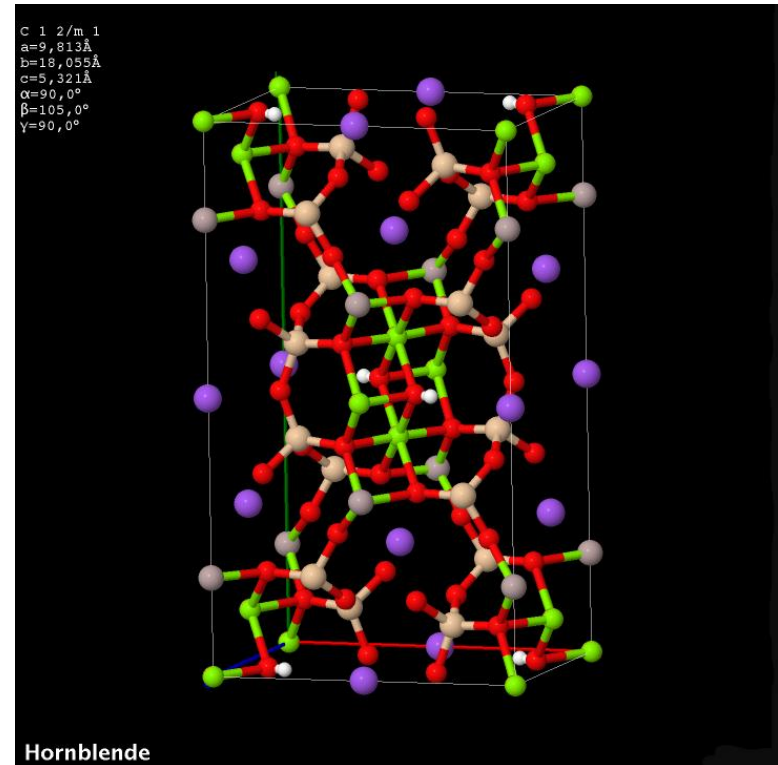


## 1.5 Ceramic raw materials

### Q<sup>2</sup>-Q<sup>3</sup>: Chain Structures (inosilicates)



**Hornblende**

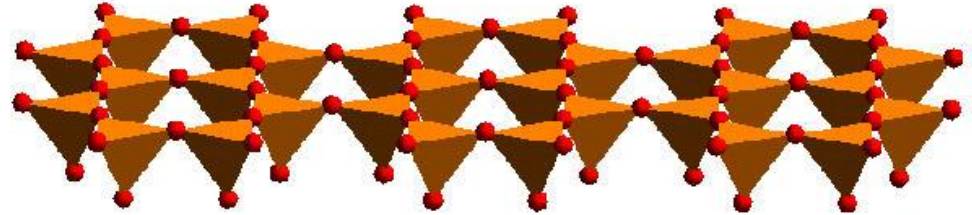
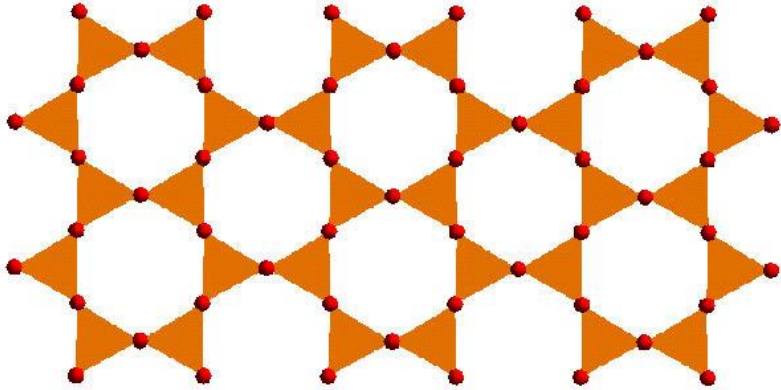


→ **Hornblende**, a naturally occurring amphibole found in igneous rocks, has the general formula  $(\text{Ca}, \text{Na}, \text{K})_{2-3}(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_2\text{Si}_6\text{O}_{22}(\text{OH})_2$ . As the formula implies, many varieties and degrees of substitution occur in this mineral.



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Sheet Structures (**phyllosilicates**)



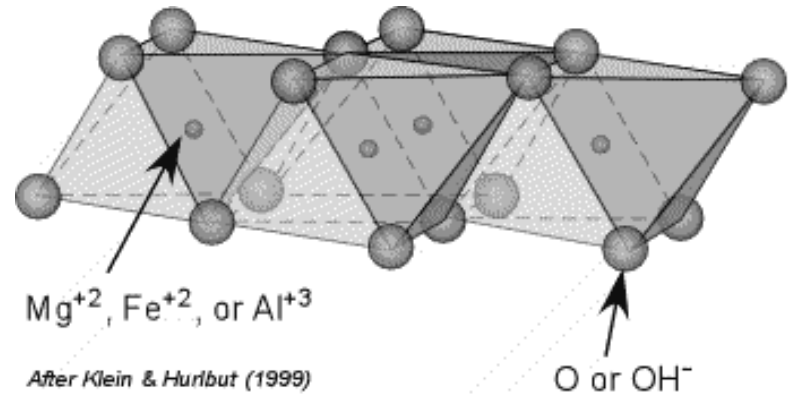
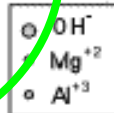
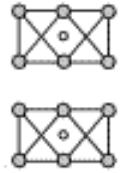
- Carrying the notion of linking silica tetrahedra a stage further, a **complete sheet of silicon-oxygen six-membered rings** is formed just by condensing a number of pyroxene or amphibole units.
- Such sheets, with a repeat formula **Si<sub>2</sub>O<sub>5</sub><sup>2-</sup>** are capable of **indefinite extension in two dimensions**; this is because the oxygen valencies within the plane are themselves satisfied by being joined to two silicons, except for those at the boundaries, which are available for linking to other similar units.
- The only **free oxygen valencies** are those **at the apices** of the silica tetrahedra, shown immediately above each silicon atom in the diagram; **these oxygens can not form sheets but may serve to link one sheet to another**.

## 1.5 Ceramic raw materials

### Other Sheet Structures: **Brucite**



Trioctahedral  
Brucite  $Mg(OH)_2$



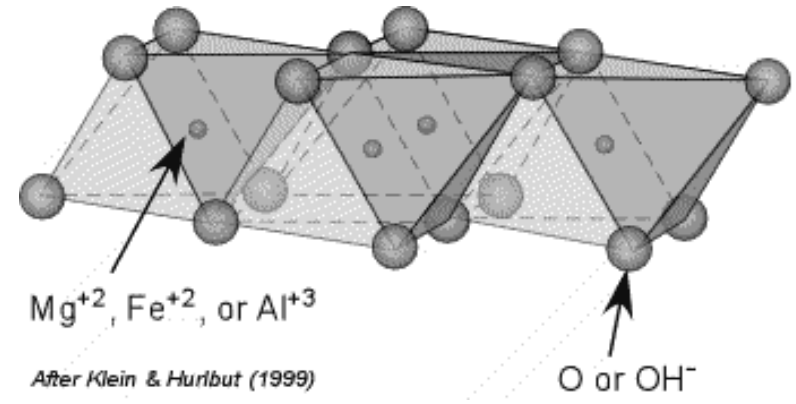
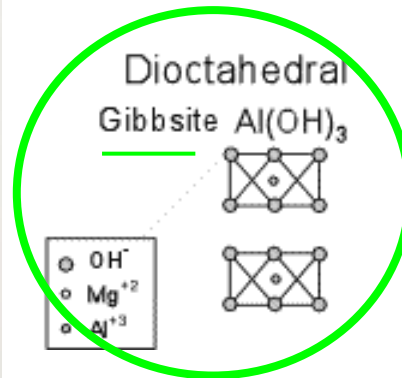
→ **Brucite** is the mineral form of **magnesium hydroxide**, with the chemical formula  **$Mg(OH)_2$** .

→ The basic structure forms **stacked sheets of octahedrons of magnesium hydroxide**. The octahedrons are composed of **magnesium ions** with a **+2 charge bonded to six octahedrally coordinated hydroxides** with a **-1 charge**. Each hydroxide is bonded to three magnesiums. The result is a **neutral sheet** since  $+2/6 = +1/3$  (+2 charge on the magnesiums divided among six hydroxide bonds) and  $-1/3 = -1/3$  (-1 charge on the hydroxides divided among three magnesiums); thus the charges cancel.

→ The lack of a charge on the **brucite** sheets means that there is no charge to retain ions between the sheets and act as a "glue" to keep the sheets together. The **sheets** are only held together **by weak residual bonds** and this results in a **very soft easily cleaved mineral**.

## 1.5 Ceramic raw materials

### Other Sheet Structures: **Gibbsite**



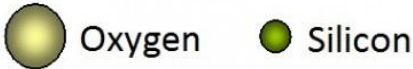
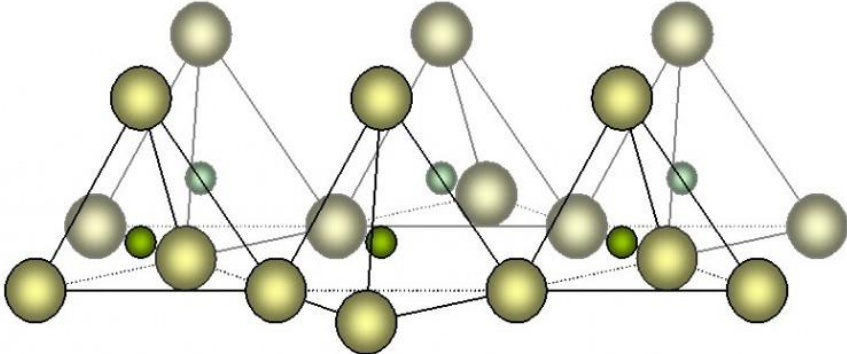
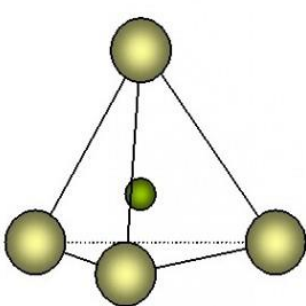
→ Brucite is closely related to **gibbsite**,  $\text{Al}(\text{OH})_3$ . However the extra charge in gibbsite's aluminum (+3) as opposed to brucite's magnesium (+2) requires that **one third of the octahedrons to be vacant of a central ion in order to maintain a neutral sheet**.

→ The octahedral layers take on the structure of either **Brucite** [ $\text{Mg}(\text{OH})_3$ ], if the cations are +2 ions like  $\text{Mg}^{+2}$  or  $\text{Fe}^{+2}$ , or **Gibbsite** [ $\text{Al}(\text{OH})_3$ ], if the cations are +3 like  $\text{Al}^{+3}$ . In the **brucite structure**, **all octahedral sites are occupied and all anions are  $\text{OH}^-$** . In the **gibbsite** structure **every 3<sup>rd</sup> cation site is unoccupied and all anions are  $\text{OH}^-$** .

# 1.5 Ceramic raw materials

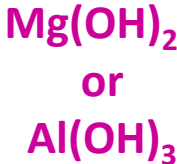
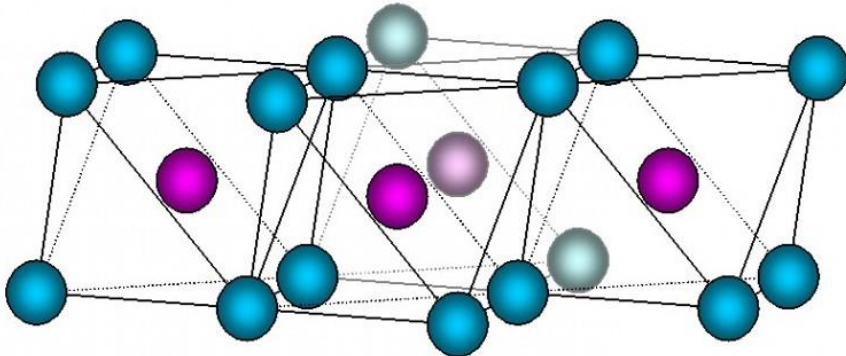
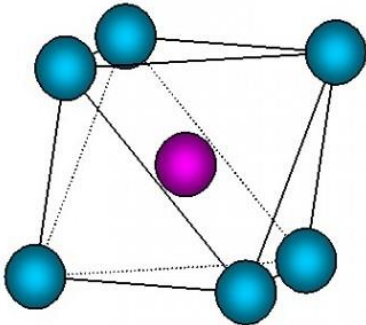
## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

→ In the synthesis of natural clay minerals, the first step is the production of sheet minerals like  $\text{Si}_2\text{O}_5^{2-}$  (silica-like) plus  $\text{Mg}(\text{OH})_2$  (brucite) or  $\text{Al}(\text{OH})_3$  (gibbsite).

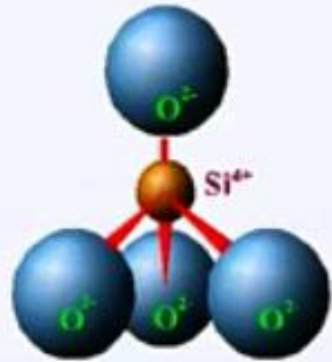


Layer of tetrahedra

<http://blogs.egu.eu/divisions/sss/tag/clay-mineralogy/>



Layer of octahedra

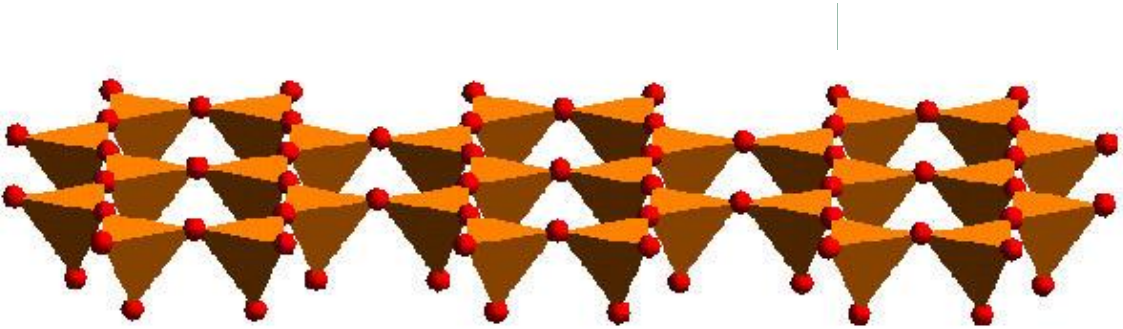




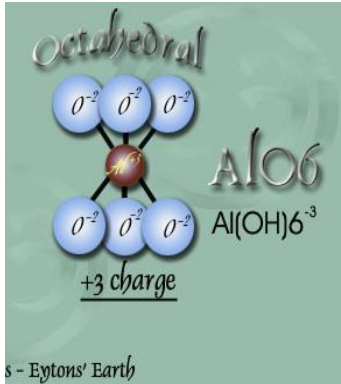
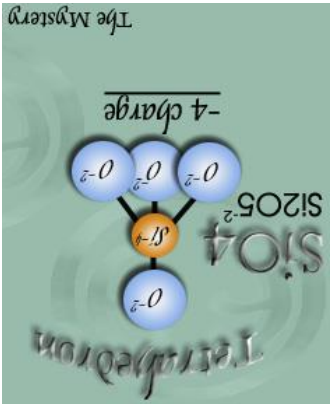
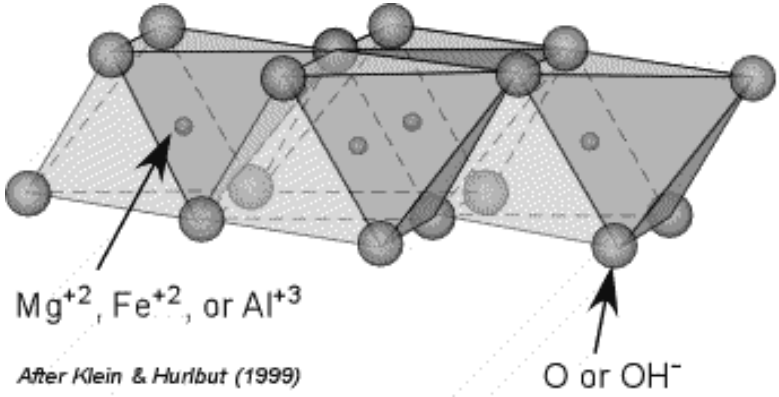
# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

→ We can build the structures of **sheet silicates** by adding **octahedral layers** similar to the structures of **gibbsite** or **brucite** to **silicate layers**.



+



<http://www.eytonsearth.org/clay-chemistry.php>

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

- **Clays** are one of the **major mineral components of the soil**, with a wide diversity of chemical and physical properties.
- The study of soil clay minerals allows a general idea of composition and genesis of soils. **Clays** are a group of **secondary minerals** (minerals formed by the subsolidus alteration of a pre-existing primary mineral; maybe a mineral in an igneous rock or another clay mineral after chemical weathering).
- Clay mineral are **aluminosilicates**. These are **basically constituted** by **Si**, **Al** and **O**, as well as other elements such as **Na**, **K**, **Ca**, **Mg** or **Fe** in variable proportion.
- **Clays** have a **colloidal size** (**bellow 2 μm**), with a well defined **crystal structure** and a **large surface/volume ratio**.
- From the chemical point of view, **clays are the most important component of the soil**, as it is constituted by **charged colloidal particles able to interact with the soil solutions**.

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

- **Phyllosilicates** are the most important group of soil. Phyllosilicates form by **silica tetrahedron (T) sharing three vertices**; **the fourth vertex binds to the central cation of an octahedron (apical O)**, usually **magnesium** or **aluminum** (gibbsite or brucite).
- The structure of **phyllosilicate** minerals is composed of a **stack of layers of tetrahedron and octahedron**, forming **lamellar structures**. Layers are linked by shared oxygens, being consequently **strongly covalently bonded** and are very difficult to separate.
- According to the repeating pattern, two types of structures are formed:
  - **1:1 structure** (with a tetrahedral layer and another octahedral T:O)
  - **2:1 structure** (with two layers of tetrahedrons and another octahedral T:O:T)
- Although we have shown that the **octahedral layers** fit perfectly between the **tetrahedral layers**, this is an **oversimplification**. **If the tetrahedral layers were stacked perfectly so that apical oxygens were to occur vertically aligned**, then the structure would have hexagonal symmetry. But, because this is not the case, most of the **phyllosilicates are monoclinic**.

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

**1:1 structure** (with a tetrahedral layer and another octahedral T:O)

Gibbsite layer + silica layer

**Kaoline group**

brucite layer+silica layer

**Serpentine group**

**2:1 structure** (with two layers of tetrahedrons and another octahedral T:O:T)

Silica + Gibbsite + silica

**Pyrophyllite group**

silica+brucite +silica

**Talc group**

**Montmorillonite**

**Montmorillonite**

**Mica group**

**Chlorite group**



<http://scmwaterproofporous.blogspot.pt/2010/10/clay.html>

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (phyllosilicates)

#### The kaolin-type group (1:1)

- The **kaolin group** includes the clay minerals **nacrite**, **dickite**, **kaolinite** and **halloysite**. Their structure have one thing in common – **they are composed of silica sheets linked to modified gibbsite sheets**.
- Imagine a **gibbsite sheet** placed directly over a **silica sheet** in such a way that **one in three of the OH groups is removed and replaced by the unsaturated apical oxygens of the silica sheets**. These latter oxygens now form a bridge between the two sheets, forming a composite layer of kaolin type.
- If we write the modified gibbsite layer as  $[\text{Al}_2(\text{OH}_4)]^{2+}$  (i.e. **having removed two OH groups**) and the **silica sheet** as  $(\text{Si}_2\text{O}_5)^{2-}$ , we arrive at the composite formula  $\text{Si}_2\text{O}_5 \cdot \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , or  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , the **unit formula of the kaolin group**.
- A **crystal of kaolinite mineral** consists not of one composite layer but of a **very large number of such layers**, which may be linked to a book, where each page represents a single layer.



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

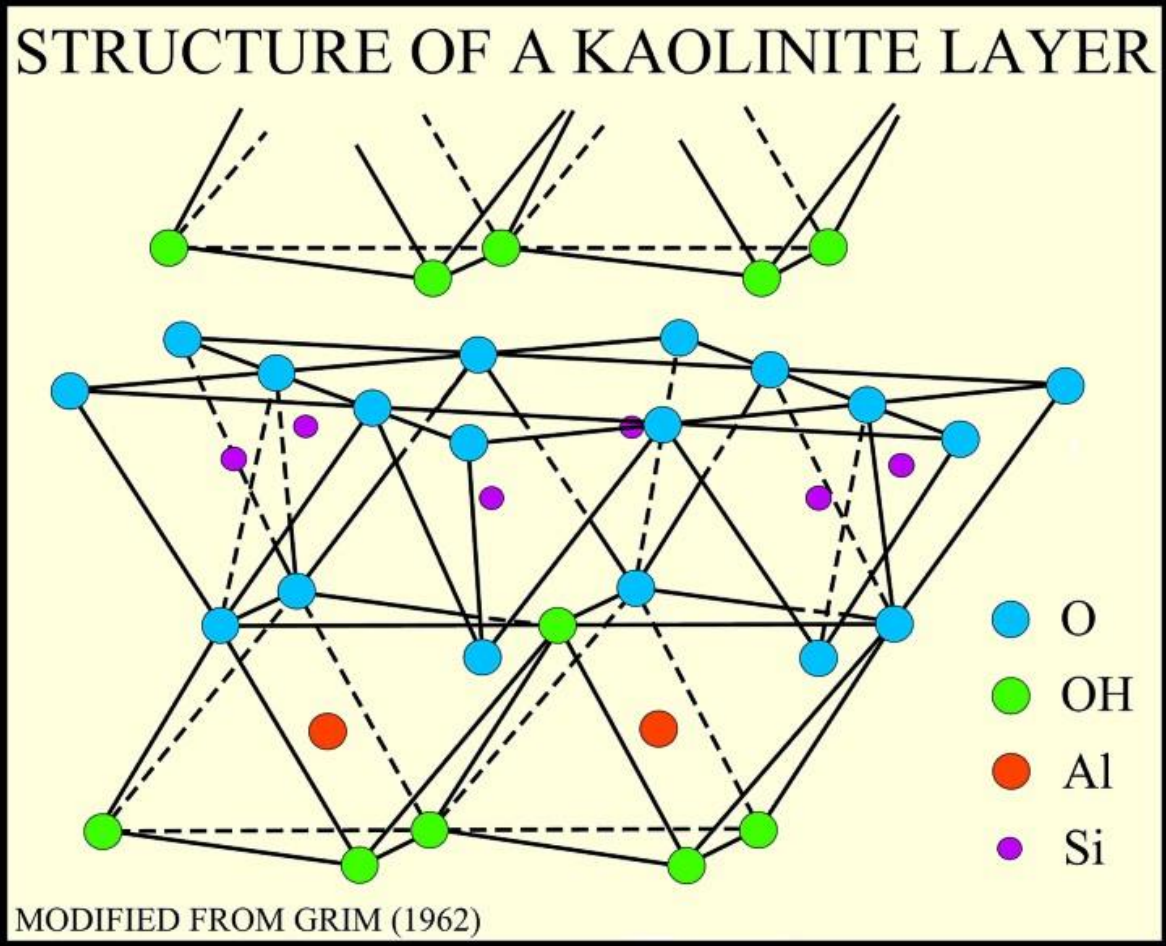
#### The kaolin-type group (**1:1**)

- One important feature of the octahedral layer in the **kaolins** is that only two out of three possible sites are occupied by aluminum ions, the remainder being vacant; such structures are therefore called **dioctahedral**.
- There are **three possible ways of filling three sites by two ions**, thus giving rise to **one source of variation in the unit layers**.
- Note that there is no ionic bonding between neighboring units; the whole **crystal is held together by hydrogen bonds**, acting between **OH groups of the gibbsite layers** and **oxygen atoms of adjacent silica layers**.
- For this relatively weak secondary bounds to be effective, the appropriate oxygens and OH groups must be closed together; there are several ways in which one unit can be stacked upon another to achieve this bonding and this give rise two four distinct minerals of kaolin type - **nacrite**, **dickite**, **kaolinite** and **halloysite**.

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

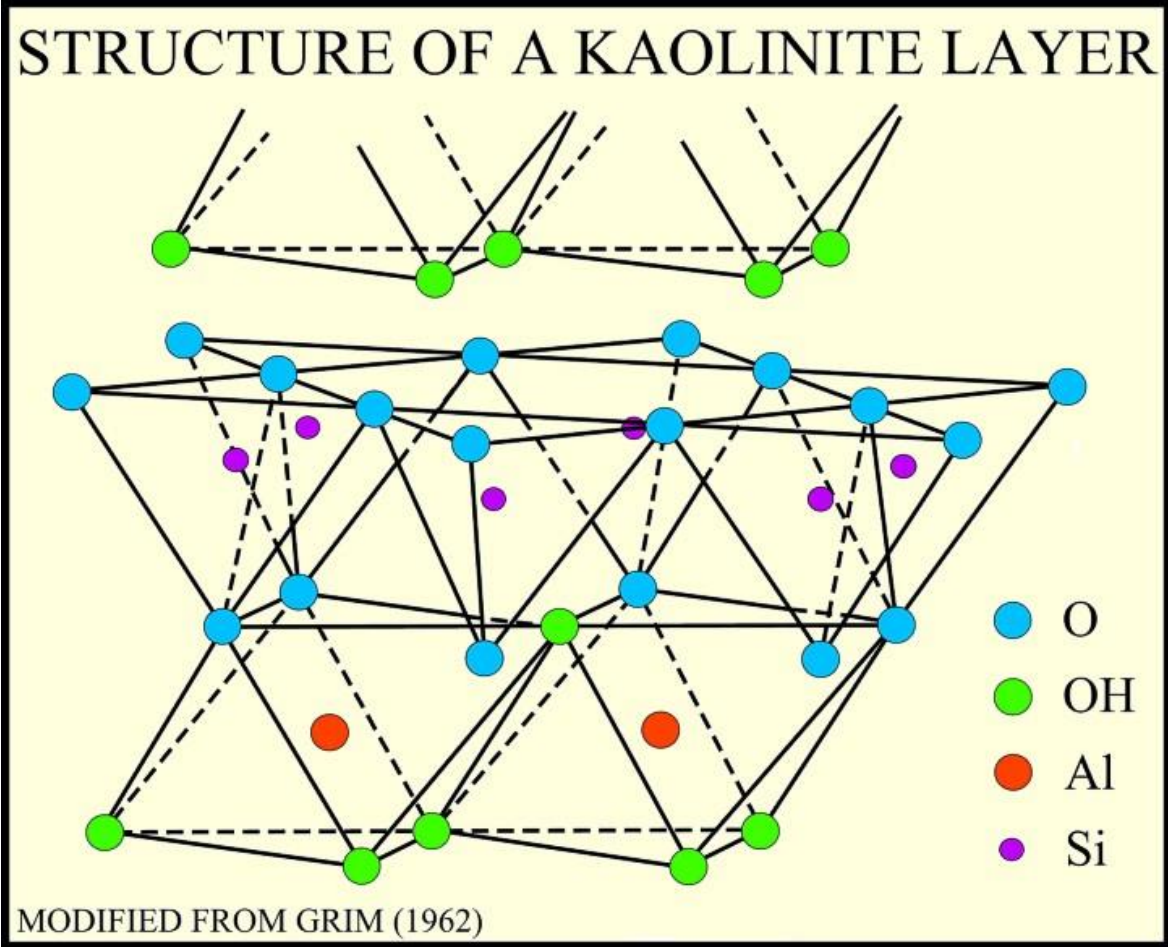
### The kaolin-type group (1:1)



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The kaolin-type group (1:1)



Kaolinite  
layer charge balance

6 O <sup>2-</sup> .....	-12
4 Si <sup>4+</sup> .....	+16
4 O <sup>2-</sup> , 2 OH <sup>-</sup> .....	-10
4 Al <sup>3+</sup> .....	+12
6OH <sup>-</sup> .....	-6
Charge Net.....	0

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

### The kaolin-type group (**1:1**)



<http://www.guptagrinding.com/kaolin-powder.htm>



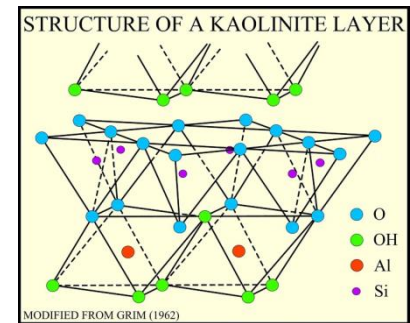
→ In **kaolin**, the unit are again displaced regularly along the a-axis, so that although  $\gamma=90^\circ$ , the  $\beta$ -angle is  $104.5^\circ$  and the  $\alpha$ -angle  $91.8^\circ$ .

→ The unit cell is **triclinic**, with  $a=5.15\text{\AA}$ ,  $b=8.95\text{\AA}$  and  $c=7.39\text{\AA}$ .

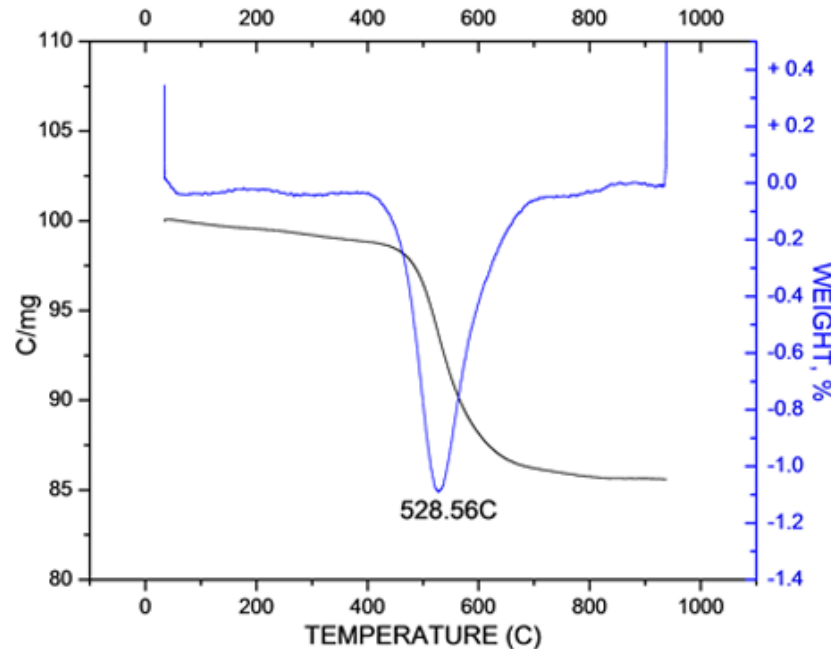
## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (phyllosilicates)

#### The kaolin-type group (1:1)



### Kaolinite DSC, TGA



<http://www.opticon1826.com/articles>

- A **small endothermic peak** occurs at about **100°C**, caused by the evolution of **adsorbed water**.
- At about **500°C** the **main endothermic peaks starts**, corresponding to the **decomposition of the mineral (structural breakage)**, with the **elimination of the hydroxyl groups as water**.
- A further peak, which is **exothermic**, occurs at about **1000°C**, and is associated with a **recrystallization** process.



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

#### The kaolin-type group (**1:1**)



### Halloysite

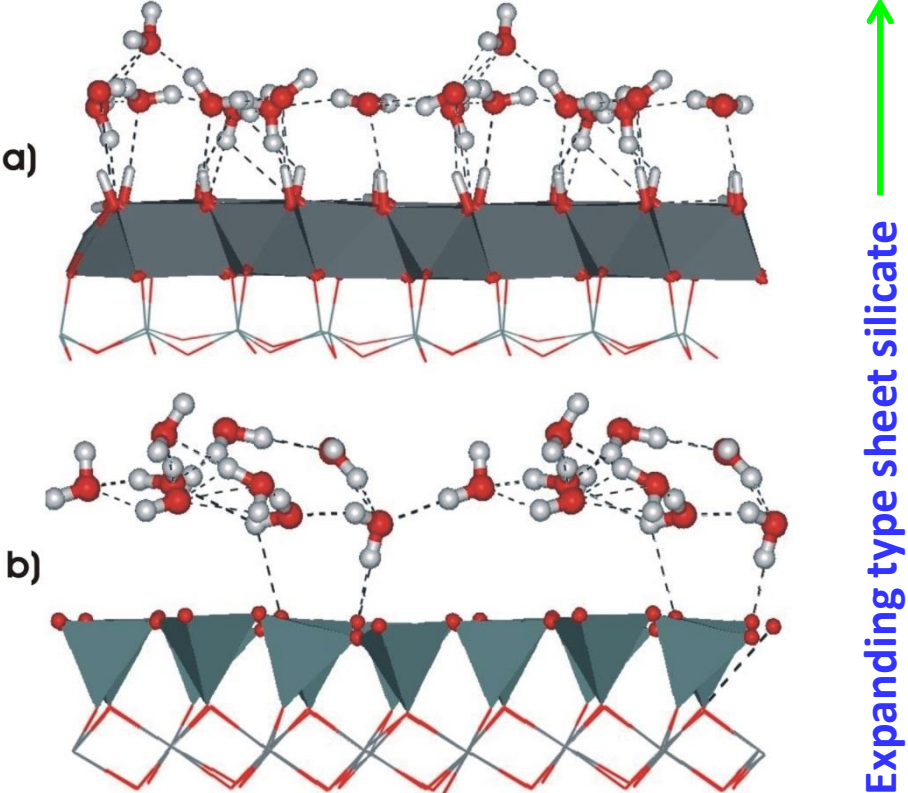
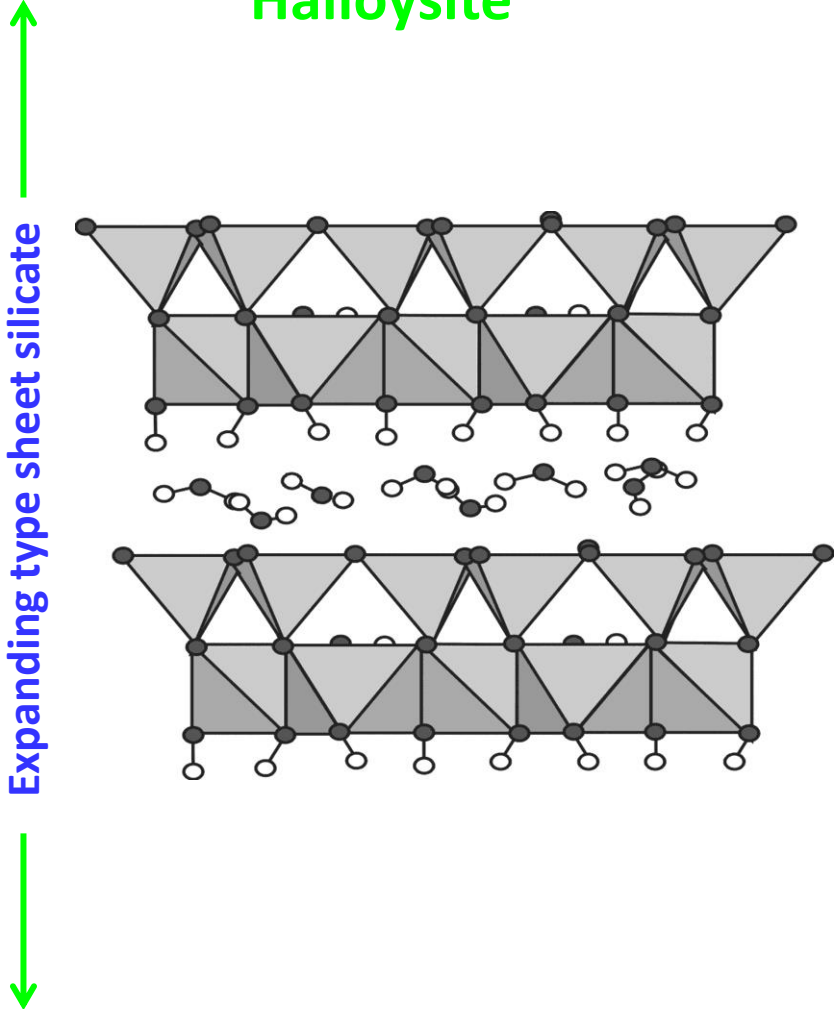
- In **halloysite**, unit kaolin layers are still present but are displaced along both **a-** and **b-axis** in a **random fashion**, so that no values can be assigned to the  $\alpha$ - and  $\beta$ -angles, though the  $\gamma$ -angle is still  $90^\circ$  and the unit cell dimensions for the meta-form are **similar to those of kaolin**.
- Owing to the **absence of hydrogen bonding between successive units**, the structure is **penetrable to water** and a hydrated form exists, with the formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot 2\text{H}_2\text{O}$ .
- The **extra  $2\text{H}_2\text{O}$**  in hydrated **halloysite** **increases the c-dimension** by about  **$2.9\text{\AA}$** .
- **Halloysite** is an **expanding type sheet silicates**; as the water is incorporated into the structure the mineral increases its volume.

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The kaolin-type group (1:1)

#### Halloysite



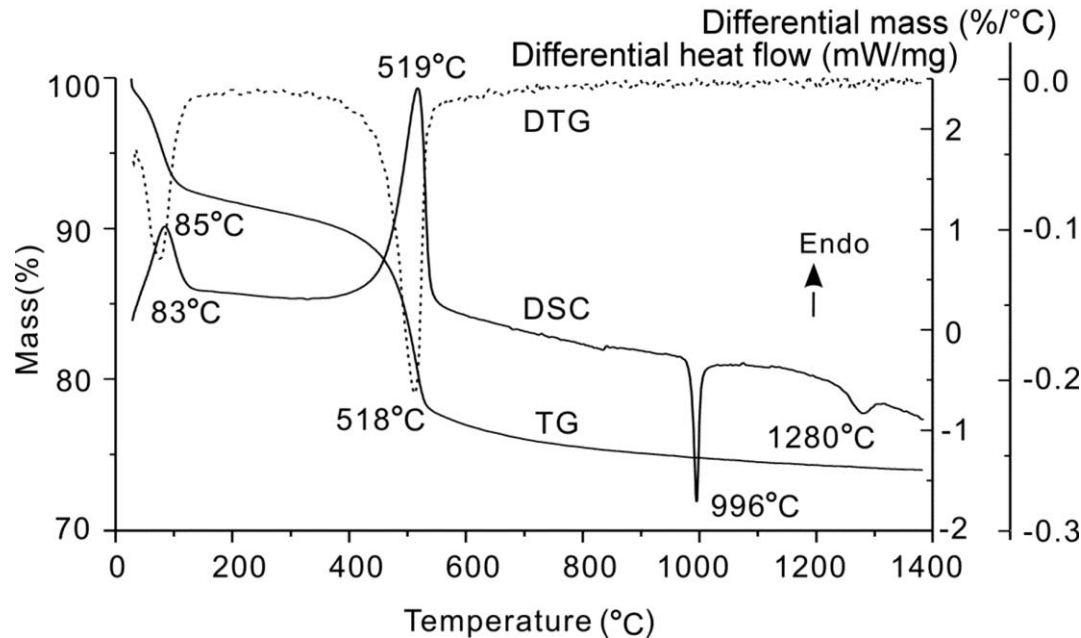
**Figure 1.** Distribution of the monomolecular water layer on the a) octahedral and b) tetrahedral surfaces of the kaolinite layer.

<http://www.univie.ac.at/qccd/hpsc/2003/Tunega/report2003.html>

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (phyllosilicates)

Halloysite  
DSC, TGA



- The **halloysite** starts **losing water at temperatures above 60 °C** and eventually is converted to the meta form.
- Compared to kaolinite, there is **an additional endothermic peak at 150 °C**, due to the **huge loss of water**.
- The **main endothermic peak** for halloysite occurs, as for kaolinite, at around **600 °C**.
- There is also the **exothermic peak**, as for kaolinite, at **1000 °C**.

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

#### The kaolin-type group (**1:1**)



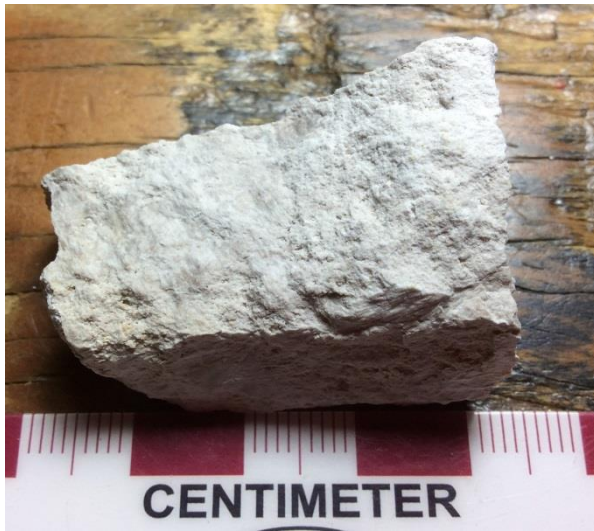
[https://commons.wikimedia.org/wiki/File:Nacrite\\_-\\_Mineralogisches\\_Museum\\_Bonn2.jpg](https://commons.wikimedia.org/wiki/File:Nacrite_-_Mineralogisches_Museum_Bonn2.jpg)

- In **nacrite**, the layers are stacked so that the atoms in one silica layer are directly above corresponding atoms in every other silica layer. Thus  **$\alpha$ - and  $\beta$ - angles (in addition to  $\gamma$ -angle) are very nearly equal to  $90^\circ$ .**
- Owing to the different ways of populating the octahedral positions, the structure only repeats after every sixth kaolin unit, making the **c-dimension of the unit cell** equal to **43 Å**.
- The **a-dimension** is **5.15 Å** and the **b-dimension 8.98 Å**, the unit cell as a whole being therefore practically **orthorhombic**.

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

#### The kaolin-type group (**1:1**)



<https://wgnhs.uwex.edu/minerals/dickite/>

- In **dickite**, the unit layers are displaced **regularly along the a-axis** (and possibly the b-axis) so that the **b-angle** is no longer  $90^\circ$  but is equal to  **$96.8^\circ$** .
- In the unit cell,  **$\alpha=\gamma=90^\circ$**  and  **$a=5.15 \text{ \AA}$** ,  **$b=8.95 \text{ \AA}$**  and  **$c=14.4 \text{ \AA}$** .
- There are thus two kaolin units in each unit cell, the latter being **monoclinic**.



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

#### The montmorillonite-type group (**2:1**)

- We can carry the process of layer condensation a stage further by condensing two silica layers (one each side) with one gibbsite or one brucite layer, giving us respectively the minerals **pyrophyllite**,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , and **talc**,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ . **Montmorillonite** may be considered as derived from them by the process of substitution.
- In **montmorillonite** a single crystal is composed of a large number of units approximating to one or other of the above formulas. Since **adjacent layers** in these units are now **silica layers**, there can be no outer hydroxyl bonds and **the units are bonded by van der Waals forces**. That is why the **montmorillonite** are **easily cleaved** and **feel soapy** when rubbed between fingers.

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

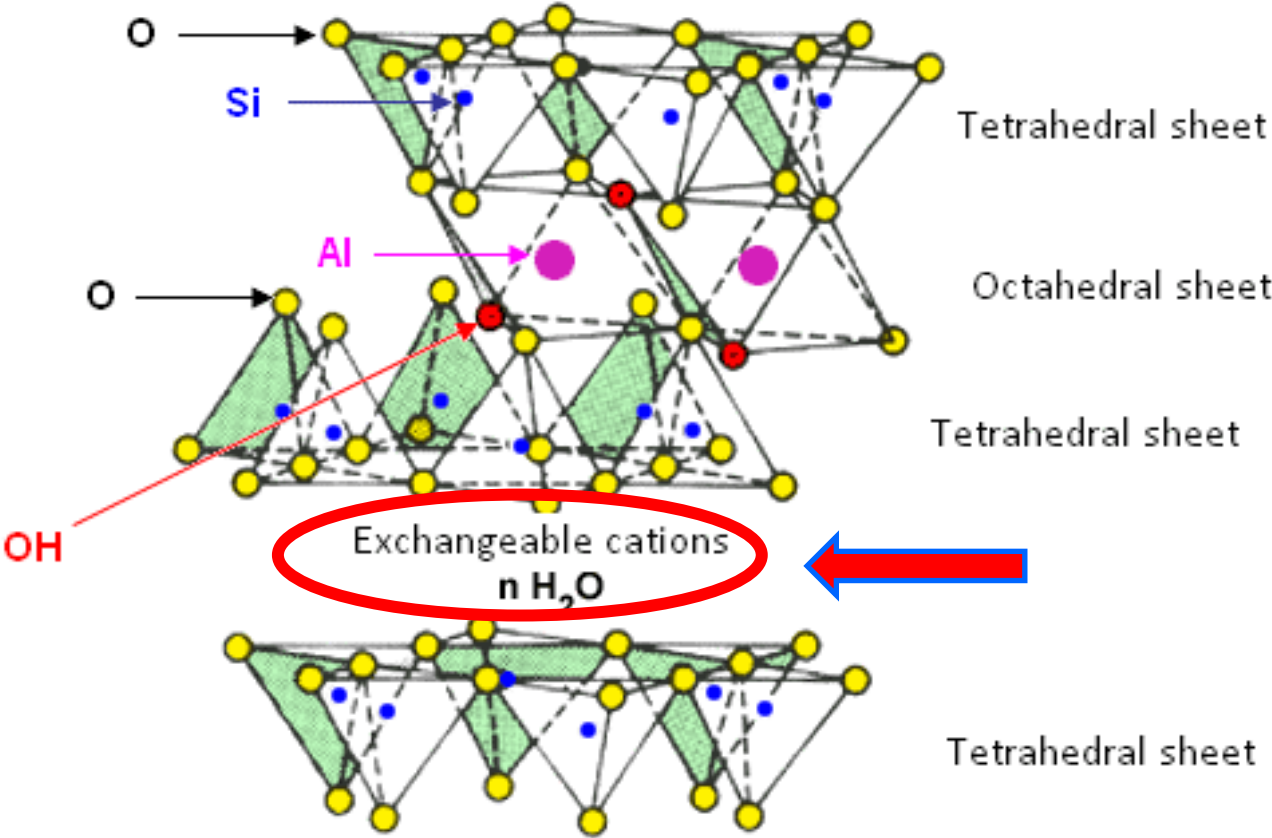
#### The montmorillonite-type group (**2:1**)

- Although X-ray diffraction may enable a montmorillonite-type mineral to be recognized, it cannot readily distinguish between members of the same group. The **Al atoms** in **pyrophyllite** are **partly substituted by magnesium, iron or lithium**; similarly, the **silicon atoms may be partly substituted by aluminium**, the only cation of similar radius.
- Since the replacement of trivalent aluminium by divalent magnesium, atom for atom, results in **an overall negative charge on the structure, electrical neutrality has to be maintained by other cations external to the lattice**; these **cations** are thus **exchangeable**. The very **high cation exchange capacity of montmorillonite** is thus adequately explained by the **high degree of substitution**.

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

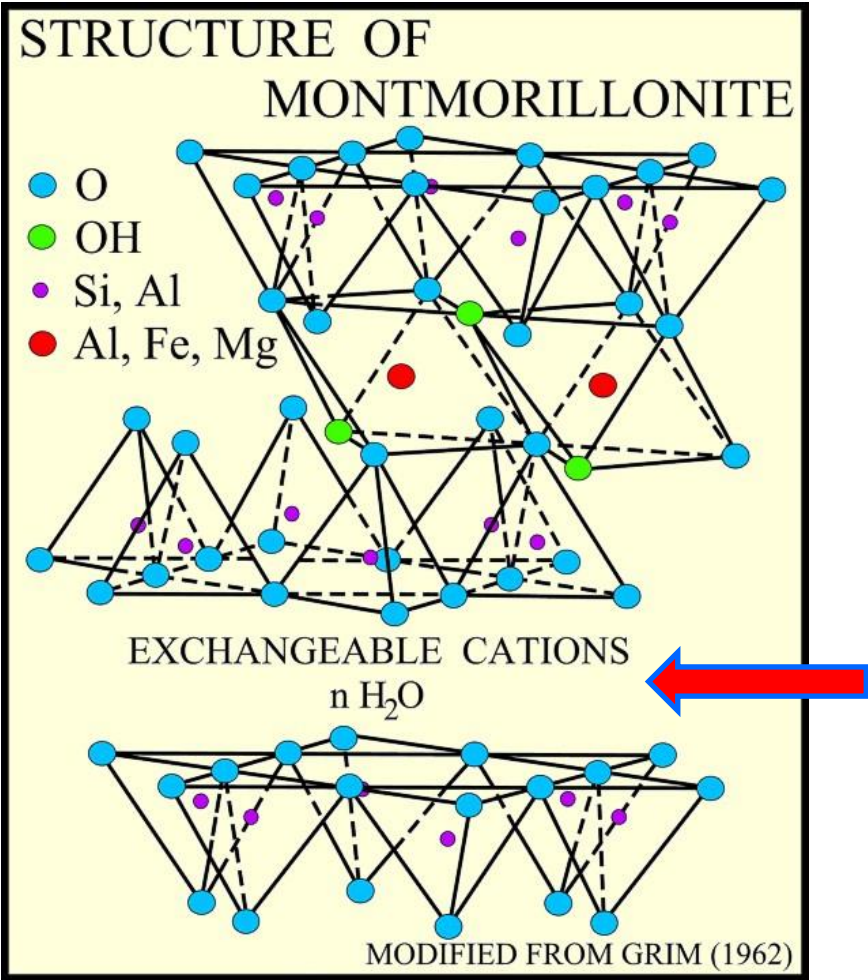
### The montmorillonite-type group (2:1)



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

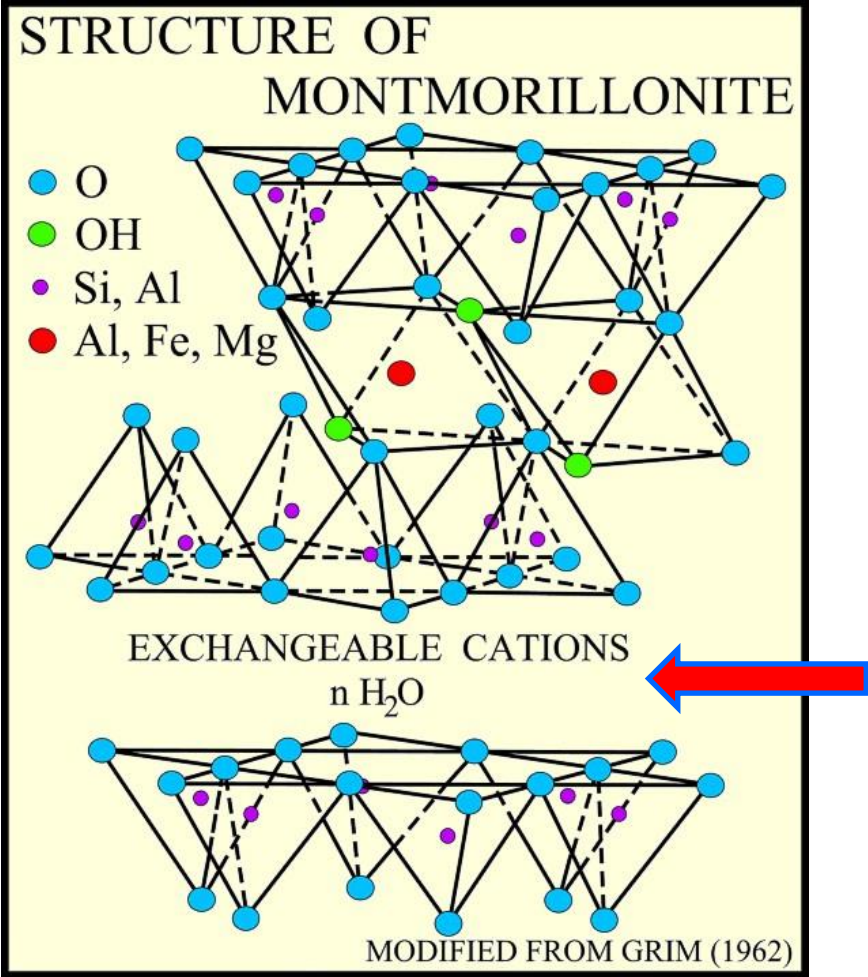
### The montmorillonite-type group (2:1)



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The montmorillonite-type group (2:1)



Montmorillonite layer charge balance

$$\begin{array}{r}
 6 \text{ O}^{2-} \dots\dots\dots -12 \\
 \cancel{4 \text{ Si}^{4+}, \text{ Al}^{3+}} \dots\dots\dots \cancel{+16}
 \end{array}$$

$$\begin{array}{r}
 4 \text{ O}^{2-}, 2 \text{ OH}^- \dots\dots\dots -10 \\
 \text{Al}^{3+}, \text{ Mg}^{2+}, \text{ Fe}^{2+}, \text{ Li}^+ \dots \text{vary} \\
 4 \text{ O}^{2-}, 2 \text{ OH}^- \dots\dots\dots -10
 \end{array}$$

$$\begin{array}{r}
 6 \text{ O}^{2-} \dots\dots\dots -12 \\
 \cancel{4 \text{ Si}^{4+}, \text{ Al}^{3+}} \dots\dots\dots \cancel{+16}
 \end{array}$$

Charge Net.....usually between **-0.6-0.25**



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (phyllosilicates)

#### The montmorillonite-type group (2:1)

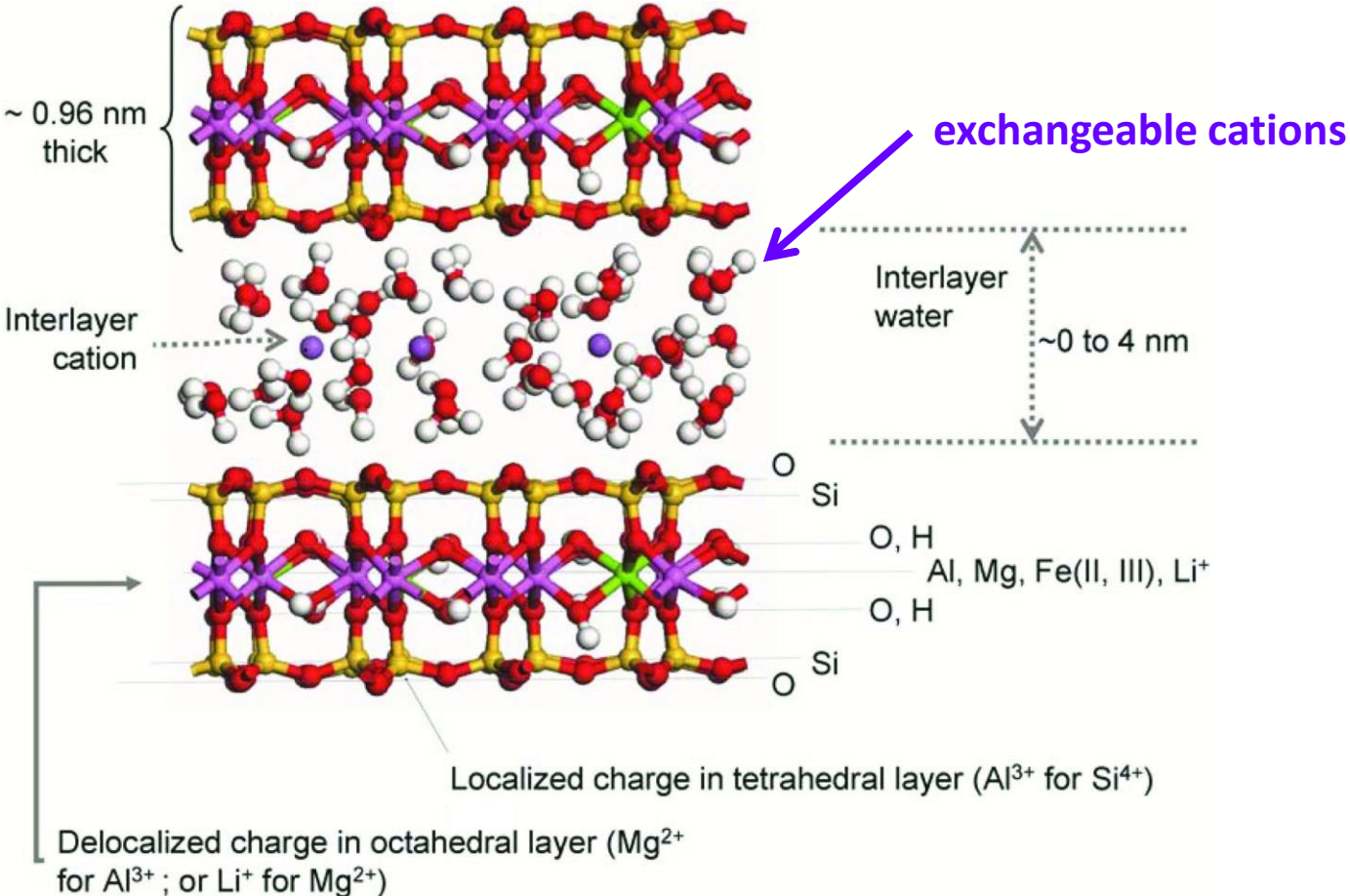
- It is generally accepted that the **unit layers in the montmorillonites** are superposed in a completely **random manner** due to the **relatively weak bonding between the layers**.
- Because of the great variety of substitutions possible, the unit cell dimensions vary from type to type, but are approximately: **a= 5.3 Å, b= 9.2 Å, b = 97°, the value of c being variable**.
- The unit layers can be forced apart by water and other polar liquids, causing the **basal spacing** (the perpendicular distance between equivalent planes) **to vary from about 10 to 15 Å for water**.
- The structural formula is **Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>**.

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The montmorillonite-type group (2:1)

Expanding type sheet silicate

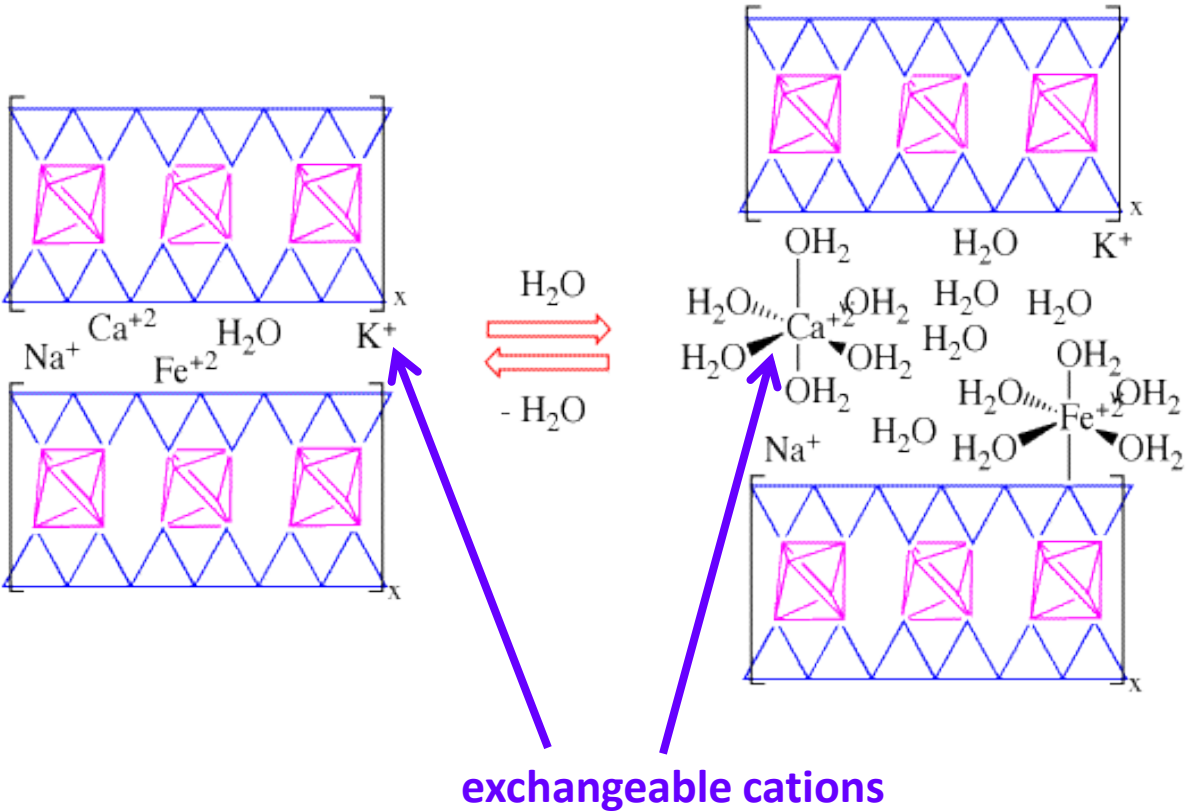


# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The montmorillonite-type group (2:1)

Expanding type sheet silicate



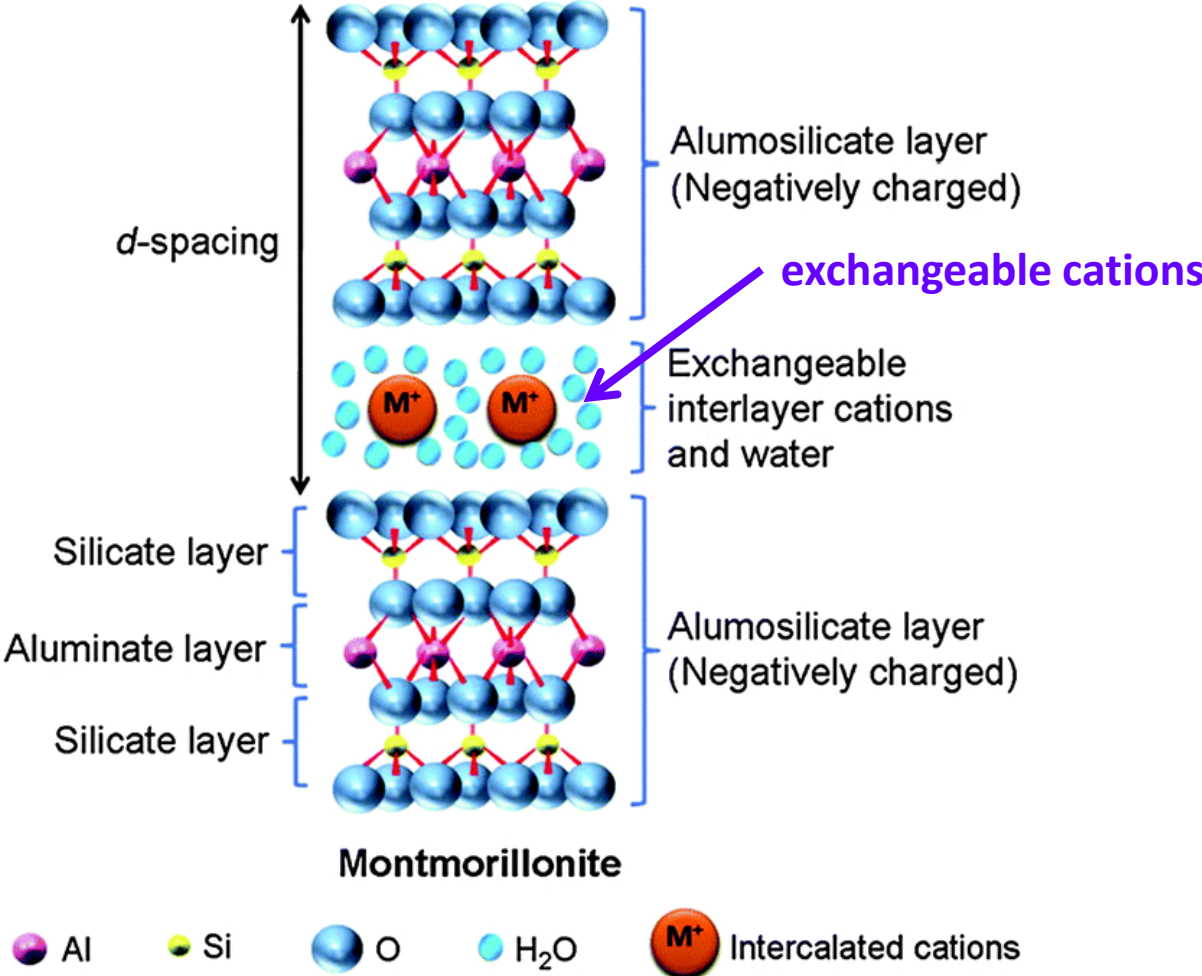
Expanding type sheet silicate

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The montmorillonite-type group (2:1)

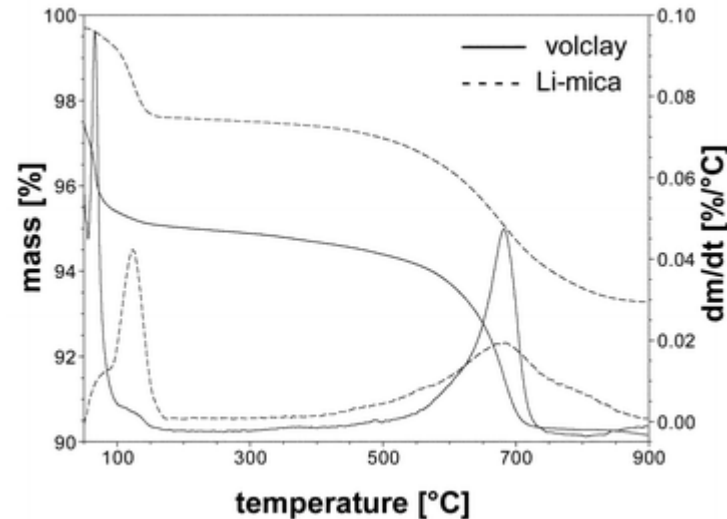
Expanding type sheet silicate



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (phyllosilicates)

#### The montmorillonite-type group (2:1)



DOI: 10.1039/B302331A

- The **montmorillonite** all have in common a **large endotherm** at about **150°C**, corresponding to the **evolution of inter-layer water and water associated with exchangeable cations**. The peaks varies in size and shape according to the nature of the cations and the lattice substitutions.
- The **main endotherm**, corresponding to the **thermal decomposition of the mineral**, occurs at about **700°C** and there is a **final exotherm** at about **1000°C** as for kaolinite.
- **Multiple low-temperature peaks** have also been reported around **150 to 200°C**, for montmorillonites saturated with various cations, corresponding to **partly hydration of the surface and partly to hydration of the cations**.



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

#### The serpentine-type group (**2:1**)

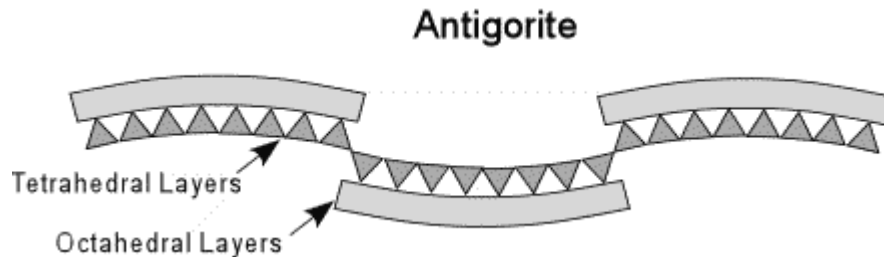
- The **serpentine group** of minerals have a structure consisting of a **silica sheet** condensed with a **brucite sheet**, with the unit formula  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . This group is clearly **trioctahedral**, this being possible because three atoms of divalent magnesium carry only the same charge as two atoms of trivalent aluminium.
- The best known minerals of this group are **antigorite** and **chrysotile**, but these latter are not generally classed as clay minerals.

## 1.5 Ceramic raw materials

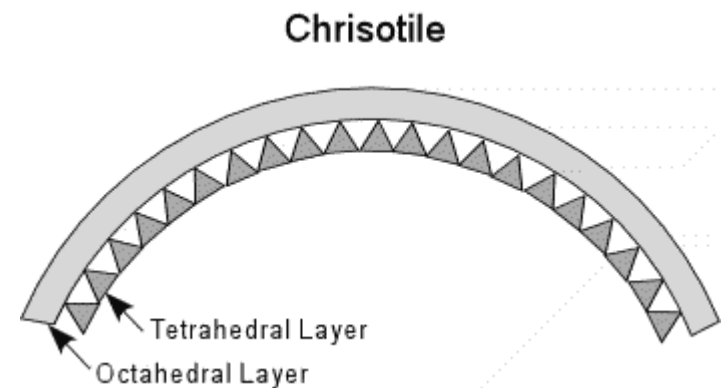
### Q<sup>3</sup>: Clay Minerals (phyllosilicates)

#### The serpentine-type group (2:1)

→ The **serpentine group** of minerals has the formula -  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . Three varieties of serpentine are known. Antigorite and **Lizardite** are usually massive and fine grained, while **Chrisotile** is fibrous. As discussed above, the imperfect fit of the octahedral layers and the tetrahedral layers causes the crystal structure to have to bend.



<http://www.tulane.edu/~sanelson/eens211/phyllosilicates.htm>



## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (phyllosilicates)



### The mica-type group (2:1)

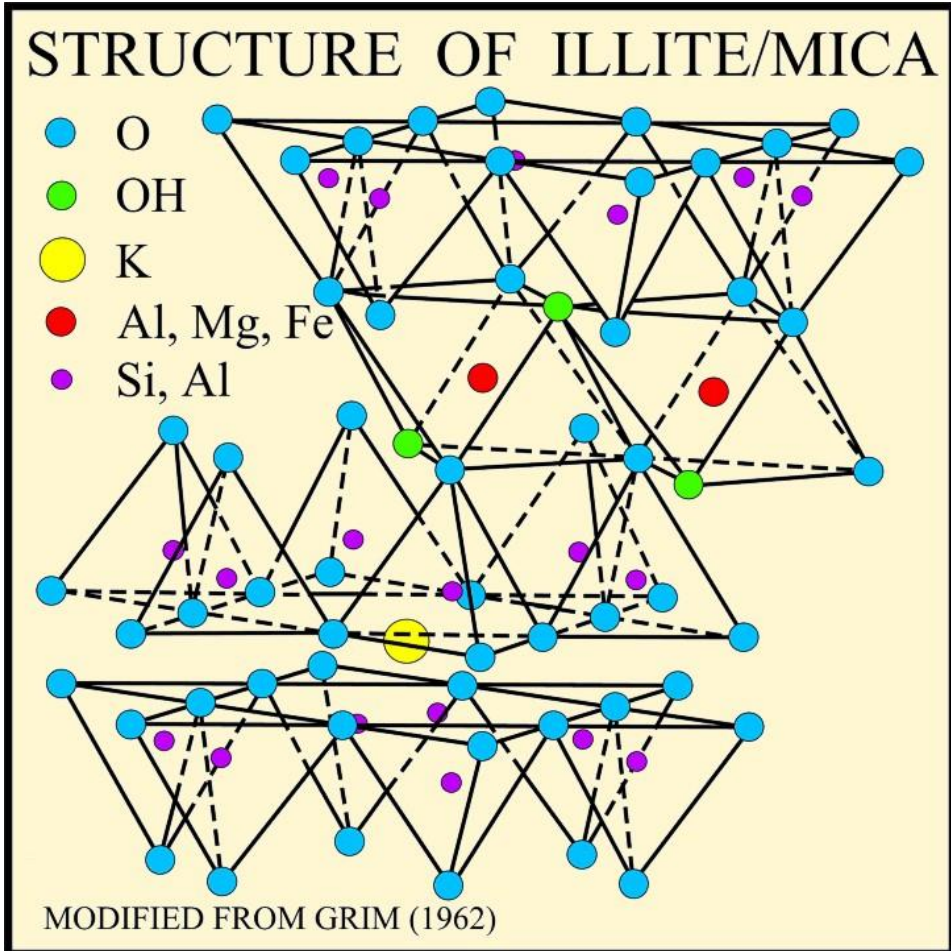
→ In **montmorillonite** the degree of substitution rarely exceeds one-third of an atom per unit formula in any one layer. Image that, starting with **pyrophyllite**  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , we substitute one whole atom of Al for a Si atom in the tetrahedral layer, to form the negatively charged unit  $\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_9^{2-}$ . Let the charge deficiency now be balanced by one atom of potassium, and we arrive at potash mica or muscovite,  $\text{K}.\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ , or as it frequently written  $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ .

→ The essential big difference between this structure and a montmorillonite is that in the **mica** there is a comparatively big charge, concentrated in one layer, so that **the balancing cation, K**, is very strongly held and therefore **not exchangeable**.

# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### The mica-type group (2:1)



Layer charge balance

-----

.....

-----

-----

.....

.....

.....

Charge Net

## 1.5 Ceramic raw materials

### Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

#### The chlorite-type group (**2:1**)



© geology.com

<http://www.realmagick.com/chlorite/>

→ **Chlorite** is another group of phyllosilicates minerals. Although chlorite is complex in that the amount of Al that can substitute Mg and Si is variable, it may be depicted as consisting of a brucite-like layer (with some Al) sandwiched between tetrahedral layers that are similar to phlogopite.



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

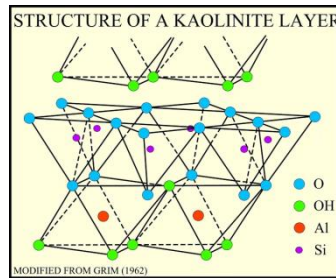
→ If we start with the **gibbsite** and **brucite** structures, and **replace 2 of the OH ions with O**, where the Oxygens are now the apical Oxygens of the SiO<sub>2</sub> tetrahedral sheets, then we get:

↓  
**dioctahedral layer, Al<sup>+3</sup>**

→ **Kaolinite**



**1:1**



↓  
**(trioctahedral layer, Mg<sup>+2</sup>)**

→ **Lizardite**

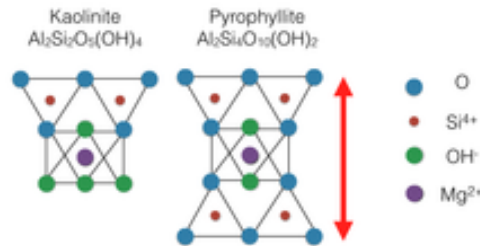


→ If we now **replace another 2 of the OH ions with O**, and these O become the apical Oxygens for another tetrahedral layer, then this builds up:

→ **Pyrophyllite**



**2:1**



→ **Talc**



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

↓  
dioctahedral layer, Al<sup>+3</sup>

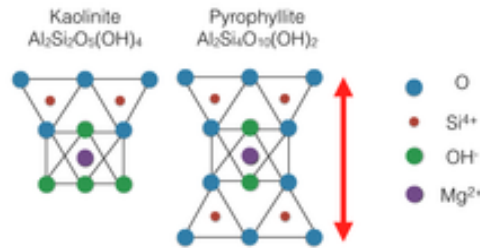
↓  
(trioctahedral layer, Mg<sup>+2</sup>)

→ If in the **pyrophyllite** or **talc** minerals, an Al<sup>+3</sup> is substituted for every 4<sup>th</sup> Si<sup>+4</sup> in the tetrahedral layer, this causes an excess -1 charge in each T-O-T layer. To satisfy the charge, K<sup>+1</sup> or Na<sup>+1</sup> can be bonded between 2 T-O-T sheets in 12-fold coordination.

→ **Muscovite**



2:1



→ **Phlogopite**



→ Replacing 2 more Si<sup>+4</sup> ions with Al<sup>+3</sup> ions in the tetrahedral layer results in an excess -2 charge on a T-O-T layer, which is satisfied by replacing the K<sup>+1</sup> with Ca<sup>+2</sup>.

→ **Margarite**



2:1

→ **Clintonite**



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

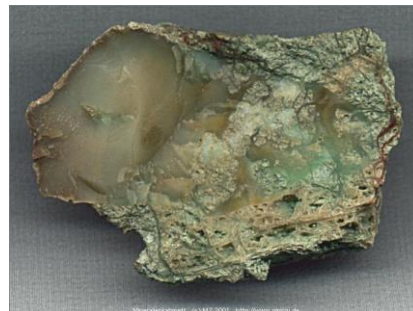
### Expanding type sheet silicate

- **Halloysite** is an **expanding type sheet silicates**; as the water is incorporated into the structure the mineral increases its volume.
- Another important sheet silicate structure is that of **vermiculite**. This is similar to the talc structure, discussed above, with layers of water molecules occurring between each T-O-T layer.
- Similarly, insertion of layers of water molecules between the T-O-T sheets of pyrophyllite produces the structure of **smectite** clays. The vermiculite and smectite groups are therefore **expanding type sheet silicates** and as the water is incorporated into the structure the mineral increases its volume. [http://fpsc.wisc.edu/growguide/covering\\_seeds.shtml](http://fpsc.wisc.edu/growguide/covering_seeds.shtml)

**Halloysite**



**smectite**



<http://www.gimizu.de>

**vermiculite**

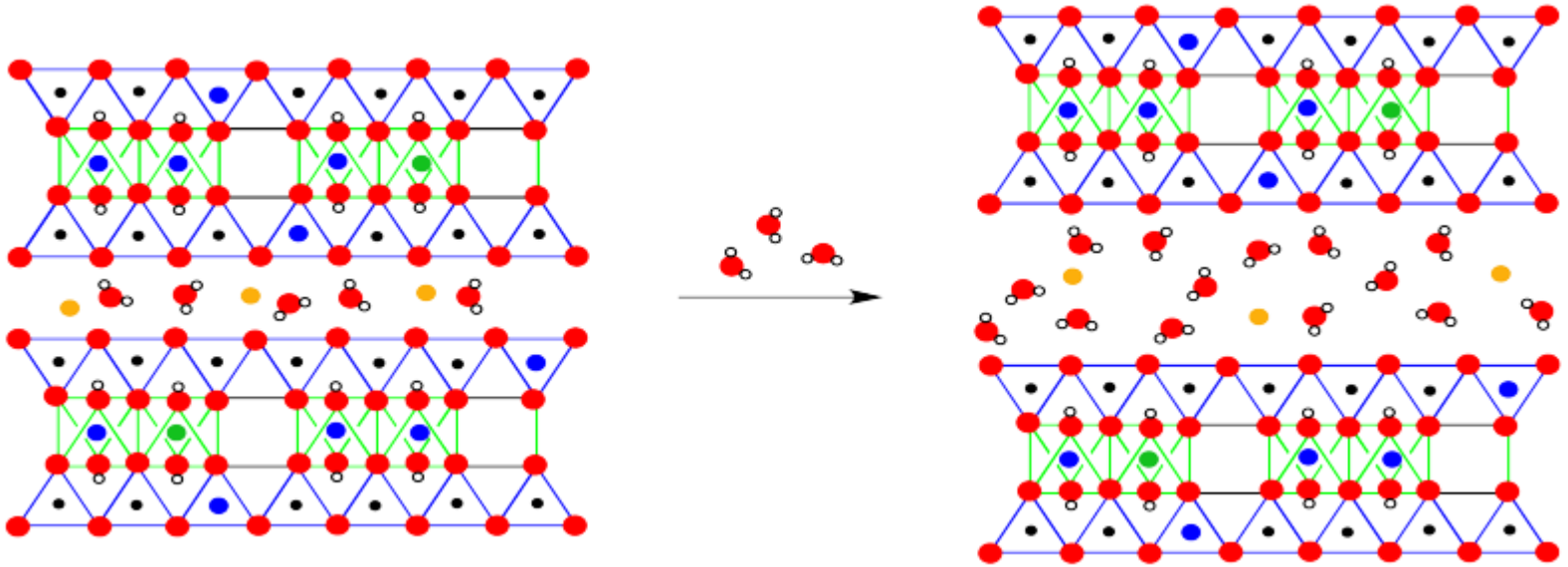


# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

### Expanding type sheet silicate

Expanding type sheet silicate



<https://www.youtube.com/watch?v=cKapahIjses>



1.5 Ceramic raw materials

Q<sup>3</sup>: Clay Minerals (**phyllosilicates**)

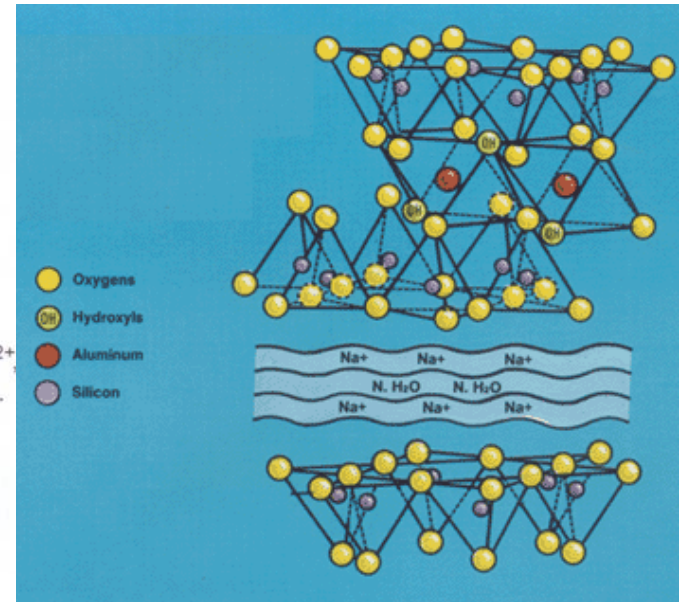
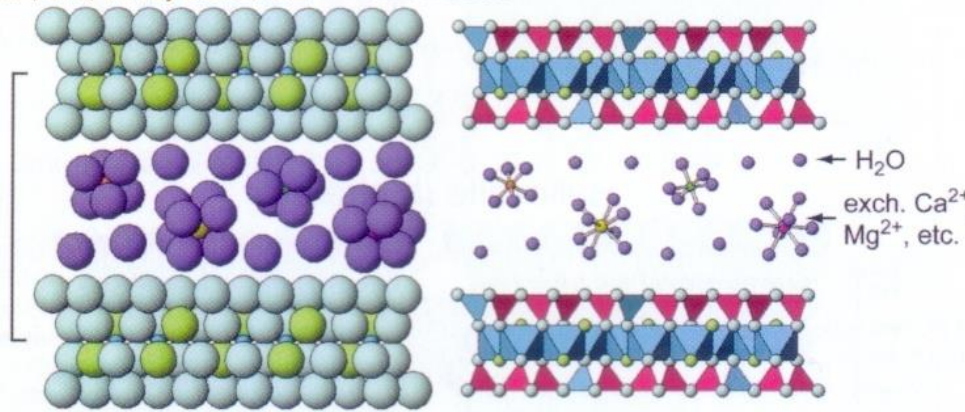
Expanding type sheet silicate

Expanding type sheet silicate

Expanding type sheet silicate

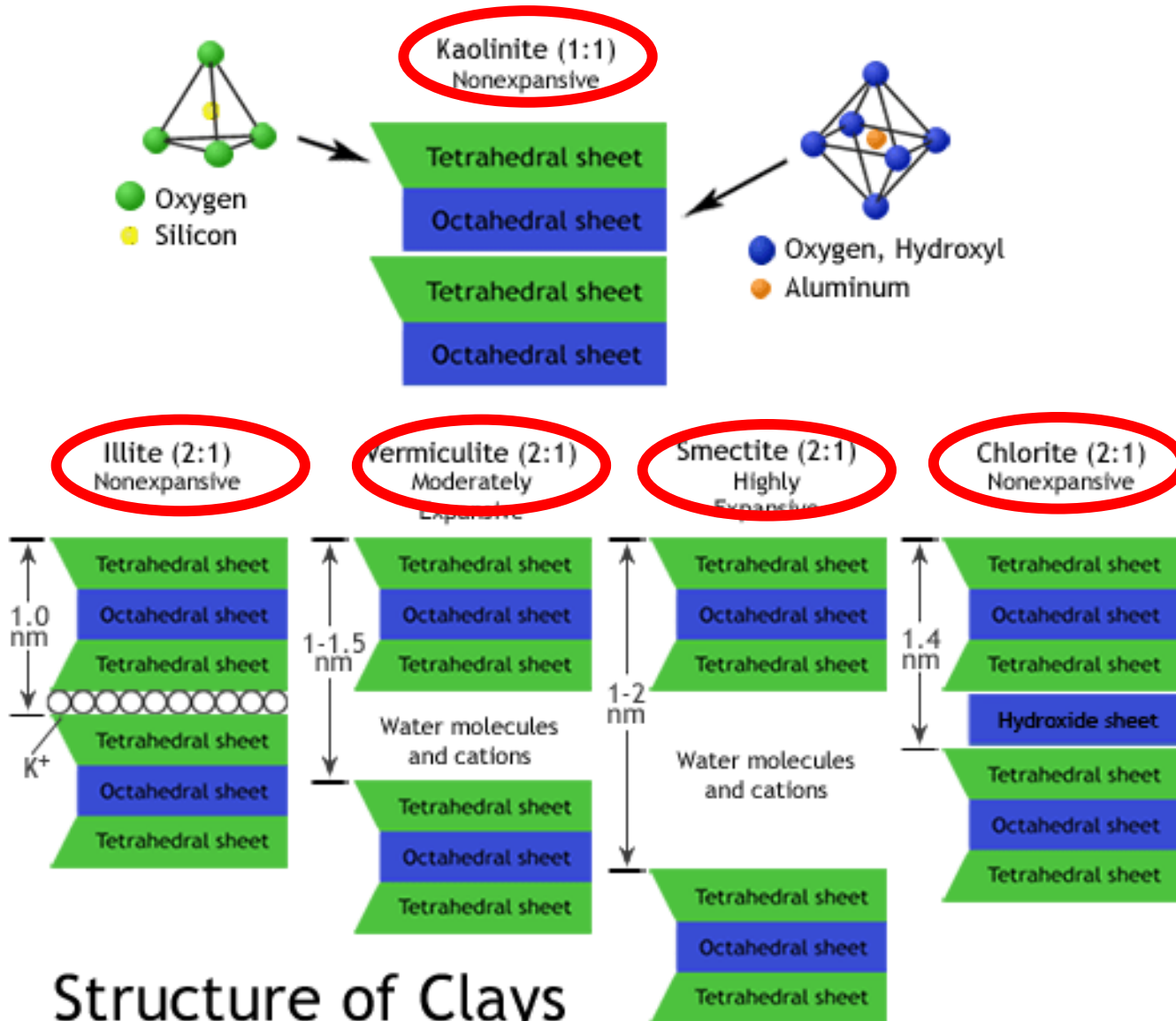
From "Soil Mineralogy with Environmental Applications", Ch 1; Ch 1 by D.G. Schultz

Smectite



# 1.5 Ceramic raw materials

## Q<sup>3</sup>: Clay Minerals (phyllosilicates)

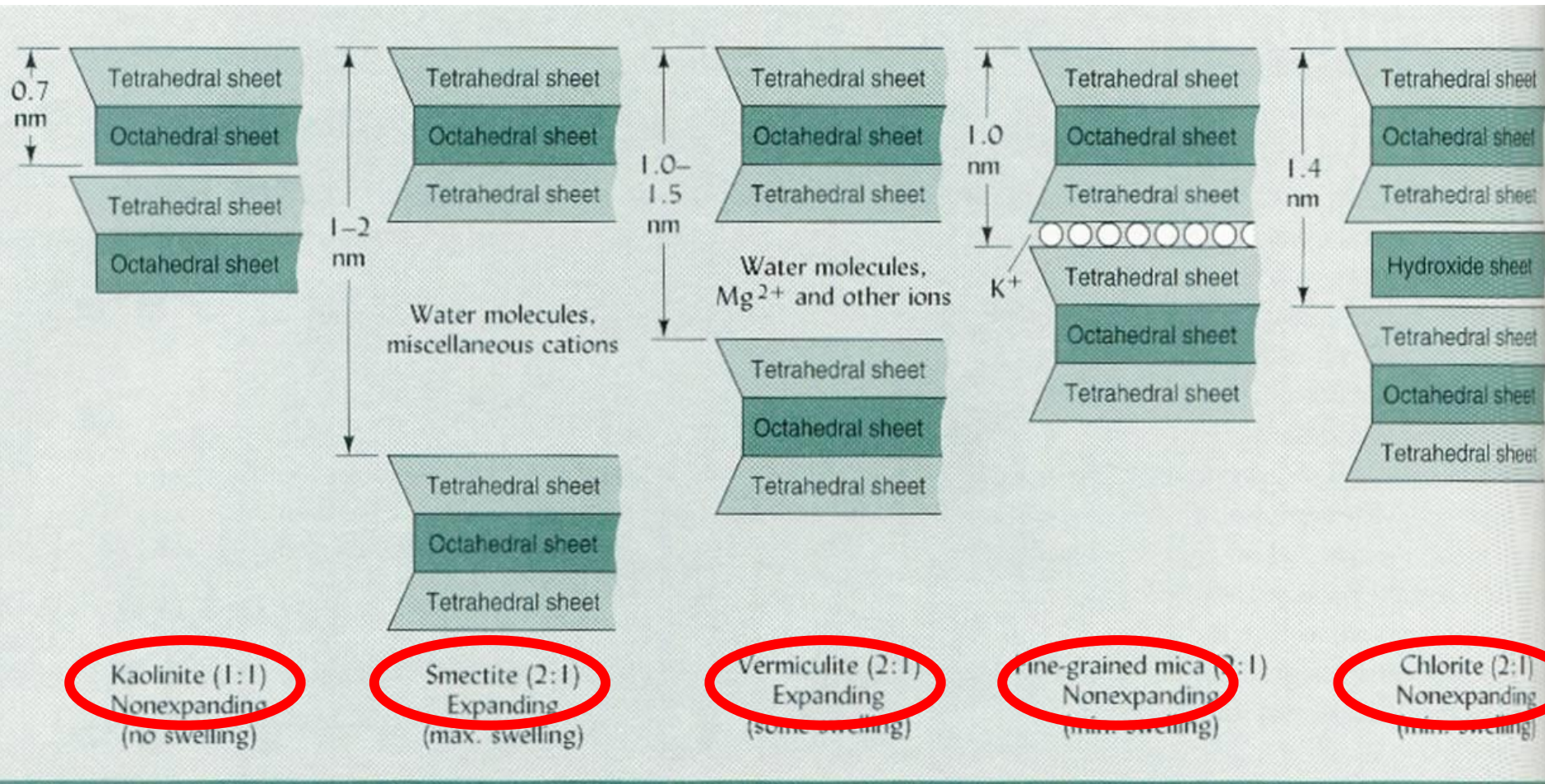


Structure of Clays

Created by Josh Lory for [www.soilsurvey.org](http://www.soilsurvey.org)

# 1.5 Ceramic raw materials

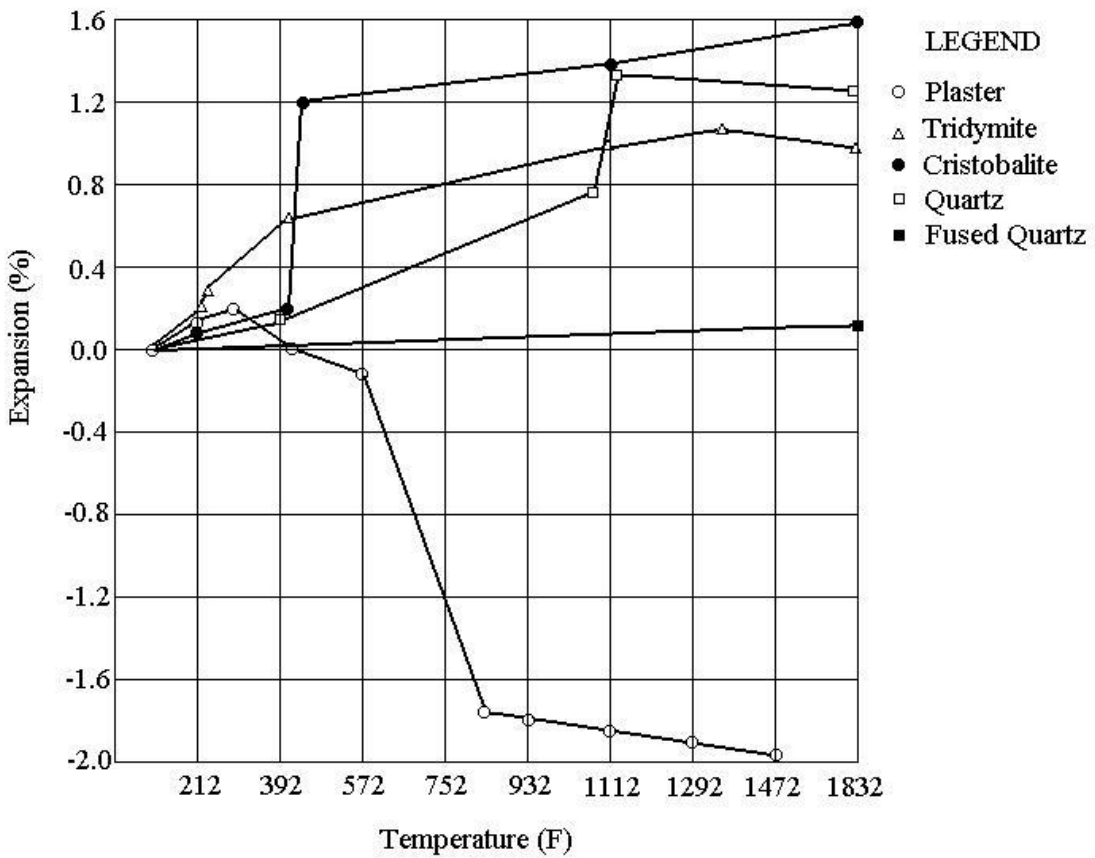
## Q<sup>3</sup>: Clay Minerals (phyllosilicates)





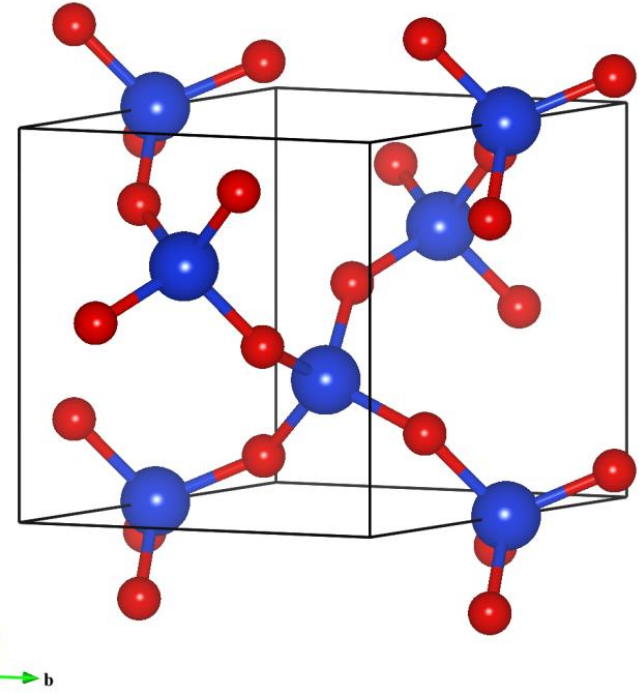
# 1.5 Ceramic raw materials

## Q<sup>4</sup>: Quartzites and Sands (tectosilicates)



## 1.5 Ceramic raw materials

### Q<sup>4</sup>: Quartz (tectosilicates)

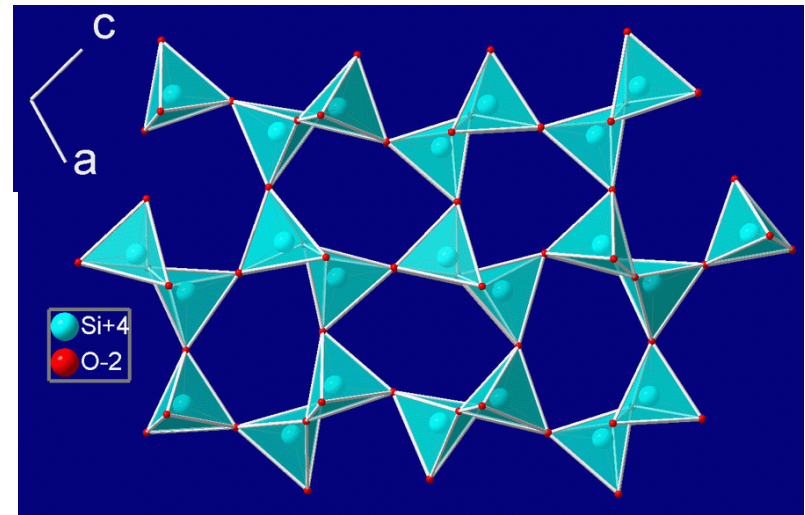
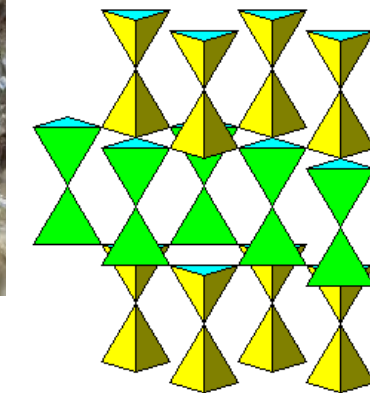


- In **quartz**, the best-known crystalline form of silica, the **Si-O-Si bonds joining neighbouring tetrahedra** do not form a straight line but are bent round to give **spiral chains**.
- Starting with any Si<sup>4+</sup> ion, passing through silicon and oxygen alternately, **spiral chains (Si<sub>3</sub>O<sub>3</sub>)** can be traced throughout the structure, all in the same direction.
- The entire structure is built up by the linking of many **spiral chains** through common silicon oxides.



## 1.5 Ceramic raw materials

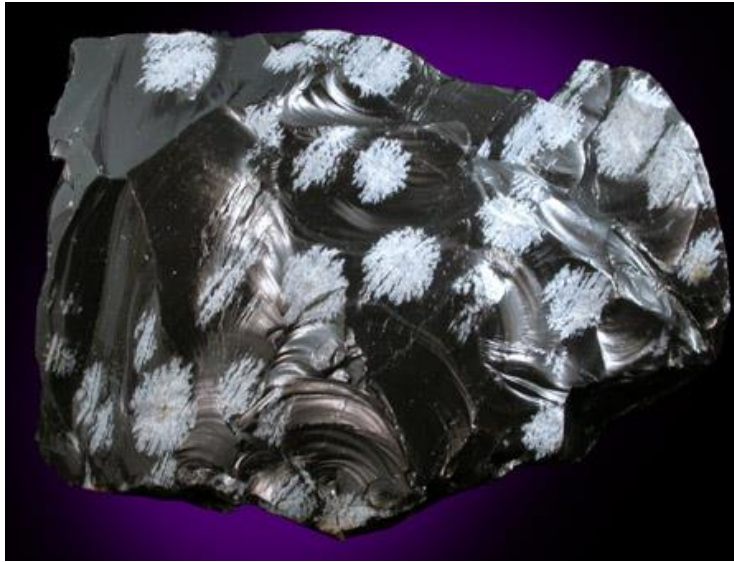
### Q<sup>4</sup>: Tridymite (tectosilicates)



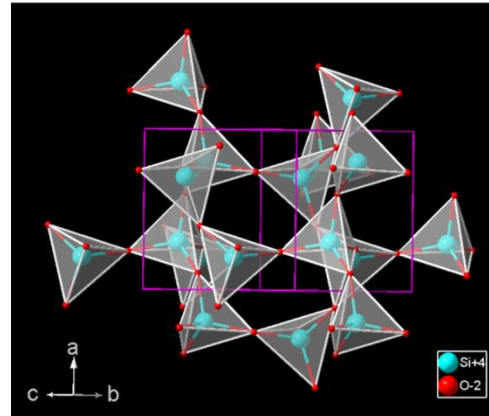
- In **tridymite** the silica tetrahedra are linked to form **rings**, each containing **six oxygen and six silicon ions**.
- These **Si<sub>6</sub>O<sub>6</sub>** rings are joined to form planes throughout the structures, each plane being linked to a neighbouring one by **bridging oxygen ions**.
- In **tridymite** has hexagonal close packing (**hc**) structure (of **oxygens**) i.e., in two linked silicon-oxygen tetrahedra, the three basal oxygens of the upper tetrahedron fall directly below the corresponding oxygens in the base of the lower tetrahedron.

## 1.5 Ceramic raw materials

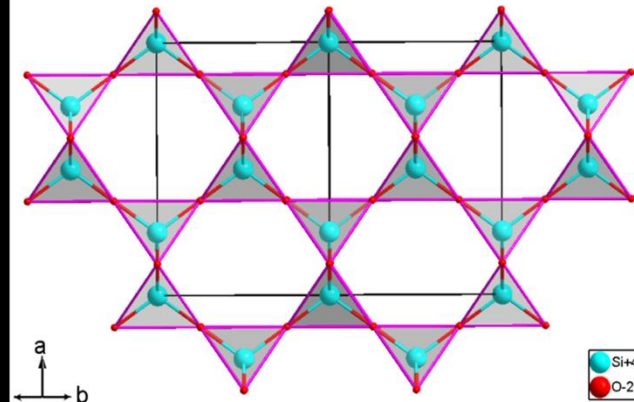
### Q<sup>4</sup>: Cristobalite (tectosilicates)



$\alpha$ -cristobalite



$\beta$ -cristobalite



- In **cristobalite** the silica tetrahedra are linked to form **rings**, each containing **six oxygen and six silicon ions**.
- These **Si<sub>6</sub>O<sub>6</sub>** rings are joined to form planes throughout the structures, each plane being linked to a neighbouring one by **bridging oxygen ions**.
- However, in **cristobalite** the **hc network** are much more distorted than in tridymite.

## 1.5 Ceramic raw materials

***Feldspats***

# Feldspar

- most common mineral



•

## 1.5 Ceramic raw materials

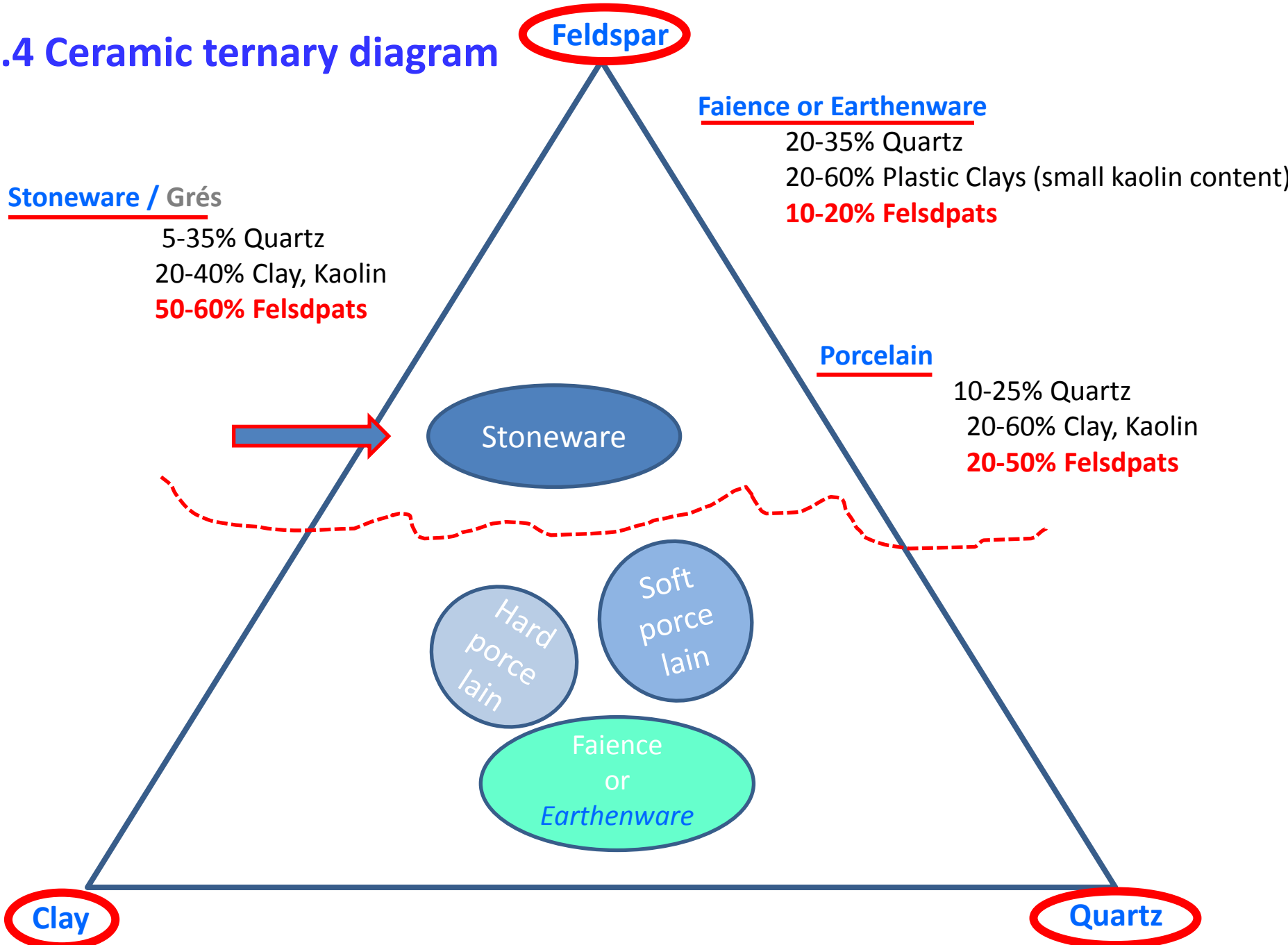
### Q<sup>4</sup>: Feldspar (tectosilicates)



**Feldspar** is a common raw material used in glassmaking, ceramics, and to some extent as a filler and extender in paint, plastics, and rubber. In glassmaking, alumina from feldspar improves product hardness, durability, and resistance to chemical corrosion.

In **ceramics**, **the alkalis in feldspar** (calcium oxide, potassium oxide and sodium oxide) act as a **flux**, **lowering the melting temperature** of a mixture. Fluxes melt at an early stage in the firing/sintering process, forming a **glassy matrix that bonds the other components of the system together**.

# 1.4 Ceramic ternary diagram





## 1.5 Ceramic raw materials

### Q<sup>4</sup>: Feldspat (tectosilicates)



If in **tectosilicates** the **SiO<sub>2</sub>** tetrahedra silicon atoms are replaced by aluminium ions, electrical neutrality is re-established by incorporation of **alkali** or **alkaline earth ions** on **interstitials**, resulting a **feldspar**.



Microcline



triclinic

Sanidine



monoclinic

Albite



triclinic

Analcite



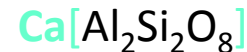
triclinic

Monalbite



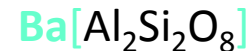
monoclinic

Anorthite



triclinic

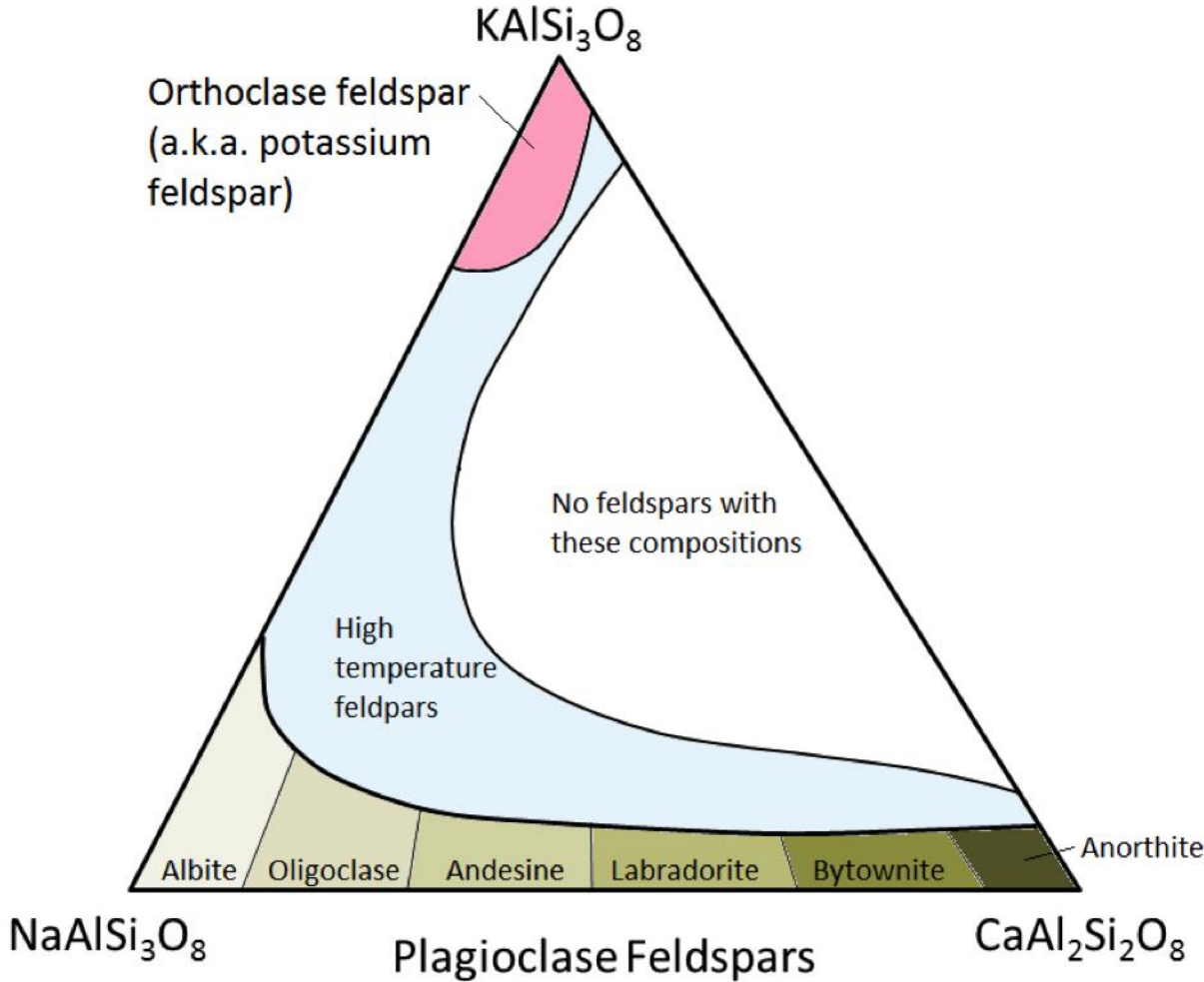
Celsian



monoclinic

# 1.5 Ceramic raw materials

## Q<sup>4</sup>: Feldspat (tectosilicates)



<http://opentextbc.ca/geology/chapter/2-4-silicate-minerals/>

## 1.5 Ceramic raw materials

# *Other oxides*

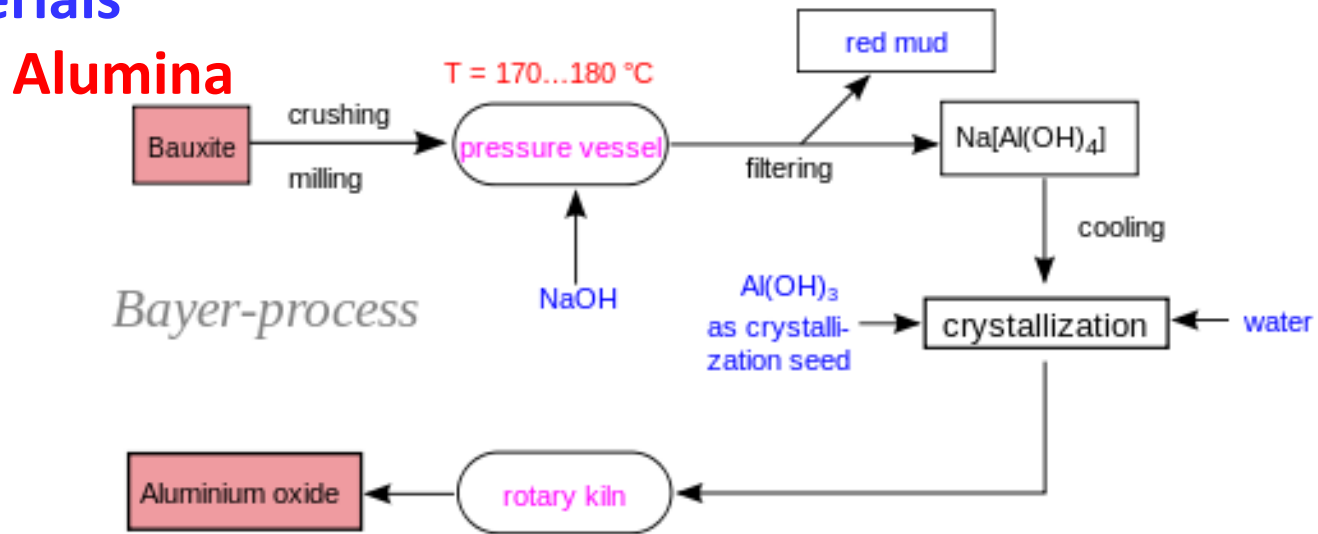
# 1.5 Ceramic raw materials

## Other oxides

Oxide	Density (g/cm <sup>3</sup> )	Melting Point (°C)	Resistivity 225°C	(Ω.cm) 1000°C
BeO	3.01	2570	10 <sup>14</sup>	10 <sup>8</sup>
MgO	3.57	2840	10 <sup>14</sup>	10 <sup>7</sup>
CaO	3.32	2580	10 <sup>14</sup>	10 <sup>6</sup>
Al <sub>2</sub> O <sub>3</sub>	3.99	2050	10 <sup>14</sup>	10 <sup>8</sup>
Y <sub>2</sub> O <sub>3</sub>	4.50	2450	-----	-----
ZrO <sub>2</sub>	5.56 Mon. 6.10 Tetr.	2680	10 <sup>11</sup>	10
HfO <sub>2</sub>	9.68 Mon. 10,0 Tetr.	2900	-----	-----



## 1.5 Ceramic raw materials



**Bauxite** is a mixture of different aluminum hydroxides, contaminated with iron hydroxides, silicates and titanium oxides. First the raw materials are grinded to a grain size of  $< 1\text{ mm}$ . Then they are processed with sodium hydroxide in an autoclave at a pressure of 40 bars and a temperature of about  $250^{\circ}\text{C}$ . A sodium solution is formed dissolving the alumina hydrates as aluminates. Iron oxide, titanium oxide and  $\text{SiO}_2$  remain undissolved. This so-called red-mud (red coloration caused by iron hydroxide) can be separated by filtration from the sodium aluminate.

Aluminium hydroxide seed crystals are now dispersed in the aluminate solution and aluminum hydroxide again crystallizes and can be separated by filtration from the sodium hydroxide.

This aluminum hydroxide is transformed into aluminum oxide by a thermal treatment in a rotary kiln.



## 1.5 Ceramic raw materials

### Zirconia

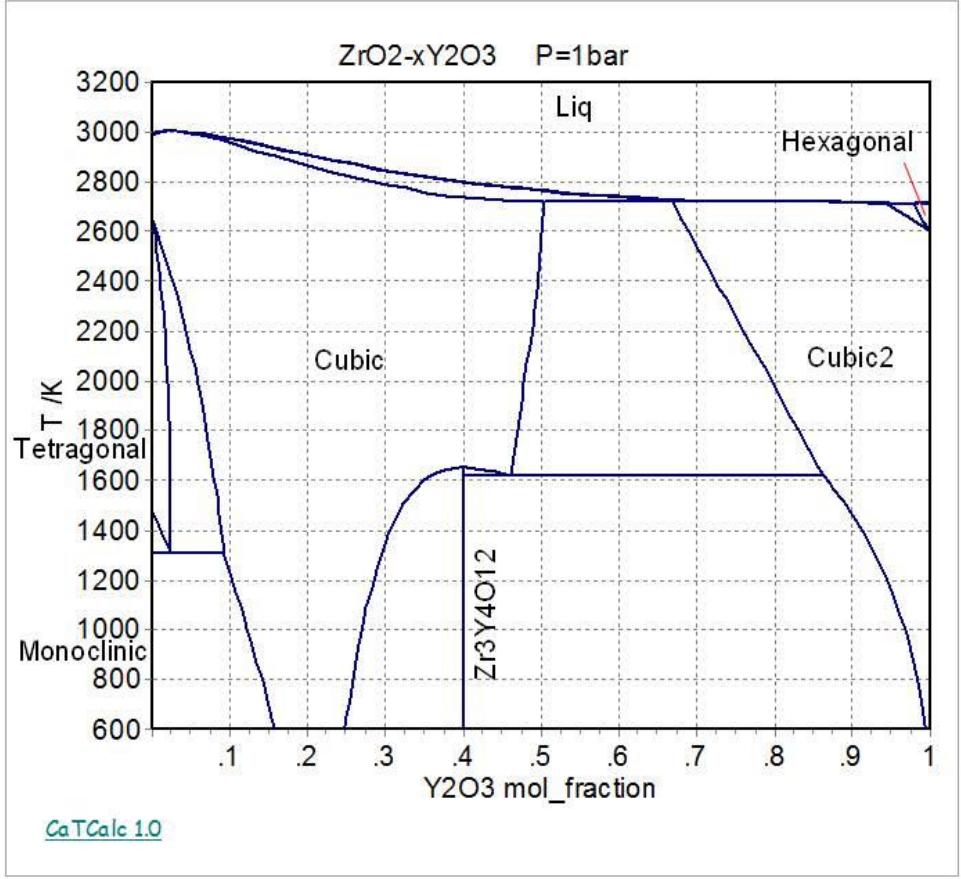
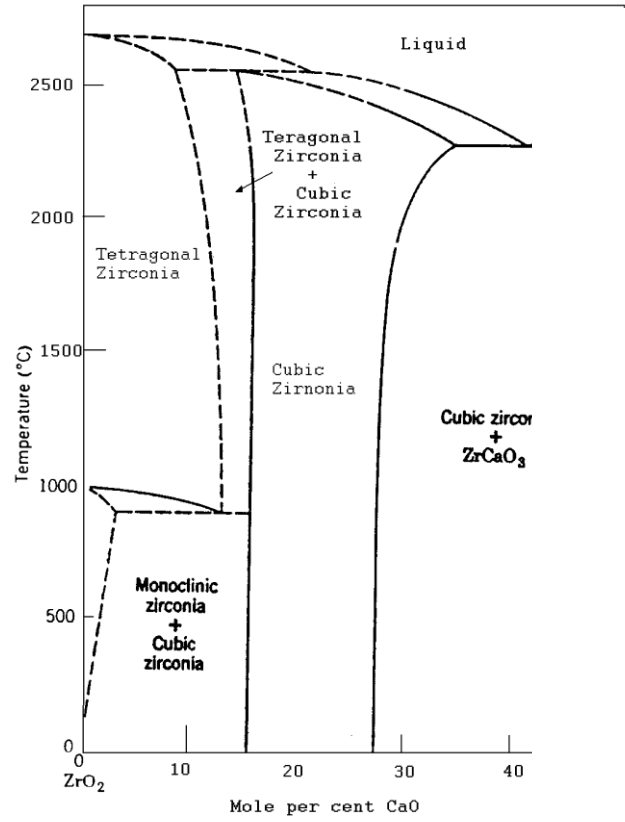
**Zirconia** is another interesting oxide.  $ZrO_2$  shows particularly problematic properties. Depending on T, it suffers allotropic transformations, partly causing big volume changes. At slightly above 1000°C the low T form changes to high T phase. **This may occur during sintering!** Normally this occurs at slightly lower temperatures, and a hysteresis loop is shown.

The enormous volume changes cause **stresses and cracks**, and this is the reason why **components cannot be made of pure  $ZrO_2$** .

This phase transformation can be prevented if almost **20 mol% calcium or yttria** is added, which causes a solid solution formation, avoiding the zirconia phase allotropic phase transformation.

# 1.5 Ceramic raw materials

## Zirconia



MDT 2011

ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> 縦断面図

## 1.5 Ceramic raw materials

# *Organics*

# 1.5 Ceramic raw materials

## Organics

More than 95% of the ceramic materials are processed as suspensions either during their preparation or during shaping. In many cases the required solvent is water, but organic solvents can also be used. Wetting agent, defoaming or conservation agents are normally added to the suspension.

Binders increase the body's green strength often necessary for the transport of the parts after shaping to the kilns.

Binders can be modified by adding plasticizers or softeners.

Releasing and anti-blocking agents reduce the friction in compression molds and increase the powder consolidation.

Binders and plasticizers are used to increase the interval of ignition and avoid crack formation during burn out.

So, normally ceramic masses consist of ceramic powders and a large number of organic additives.

This makes the whole system very complex and the understanding of the ignition products extremely difficult.

## 1.5 Ceramic raw materials

### Organics

Components	Function
Ceramic powder	Matrix
Sintering additives	Consolidation agent
Solvent	Dispersion
Deflocculant	Control of surface charge, pH value
Dispersant/surfactant	De-agglomeration
Wetting agent	Reduction of surface tension
Anti-foaming	Reduction/elimination of foaming
Conserving agents	Prevention from bacteria or <i>algae</i> development
Binder	Mechanical strength of the green body
Plasticizer	Flexibility
Softener	Flexibility
Lubricant	Reduction of attrition with matrix/molds



# 1.5 Ceramic raw materials

## Organics

There are a large variety of organic additives depending on the shaping process. Prior to the sinter, the additives must be burn out or must be regained by condensation.

There are different binders, plasticizers, condensers and wetting agents depending on the nature of the solvent -organic solvents and water based solvents.

# 1.5 Ceramic raw materials

## Organics

Dry Pressing	Dispersants	Polyacrylates, huminates
	Binder	Polyvinyl alcohols, tyloses, waxes
	Flow agent	Polyethylene glycols
Slip casting	Dispersants	Polyacrylates, fish oil
	Binder	Polyvinyl alcohols
		Polysaccharides, polyvinyl butyrals
		Water, trichloroethylene, ethanol
Tape casting	Dispersants	Oleates, polyacrylates, fish oil
		Phosphoric acid ester
	Binder	Polyvinyl butyrals, polyvinyl alcohols
		Acrylic resin, plastic dispersions
	Softener	Phthalates, polyethylene glycols
		Phosphoric acid ester
	Dispersion agents	Toluol, trichloroethylene, methanol
		Ethanol, methyl isobutyl ketone, water

# 1.5 Ceramic raw materials

## Organics

Injection moulding	Dispersants	Oleates, polyacrylates
	Binder	Polyethylene, polystyrene, waxes
	Flow agent	Polyethylene glycols
	Porosity inducing agents	Caster oil
Extrusion	Dispersants	Polyacrylates
	Binder	Polyvinyl alcohols, tyloses
	Flow agents	Polyethylene glycols, glycerine

# 1.5 Ceramic raw materials

## Organics

To understand the coupling behavior of organic additives on surface of oxide ceramic particles, we may observe the surface of alumina particle.

Ceramic powders normally have a **high specific surface area** with a **negative surface charges**, due to **unsaturated valences at their surfaces because of incomplete coordination atoms**.

When this charged surface gets in contact with **water** the surface becomes **hydrated**. When in contact to **air humidity** their surfaces also hydrate.

**The number of the developing –OH groups** at the surface depends on the number of the oxygen atoms at the surface, and this in turn depends on the crystal structure.

With regard to alumina the oxygen ions are saturated with H at a **pH ~9**, this means that at this pH value the particles are electrically neutral (**isoelectric point**).

## Further reading

- **Clays and Ceramic Raw Materials**, W. E. Worrall, Applied Science Publishers (1975)
- **Ceramics and Glasses. V4 Engineered Materials Handbook**. ASM International. The Materials Information Society (1991)
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- **Engineering Ceramics**, M. Bengisu (Ed.) Springer (2001)
- **Structure and Properties of Ceramics**. V80, A. Koller (Ed.), Elsevier Science (1994)
- **Argilas. O que são e para que servem**. C. F. Gomes, Fundação Calouste Gulbenkian

## 1.5 Ceramic raw materials

**And now let's see how industry prepare  
ceramic raw materials!**