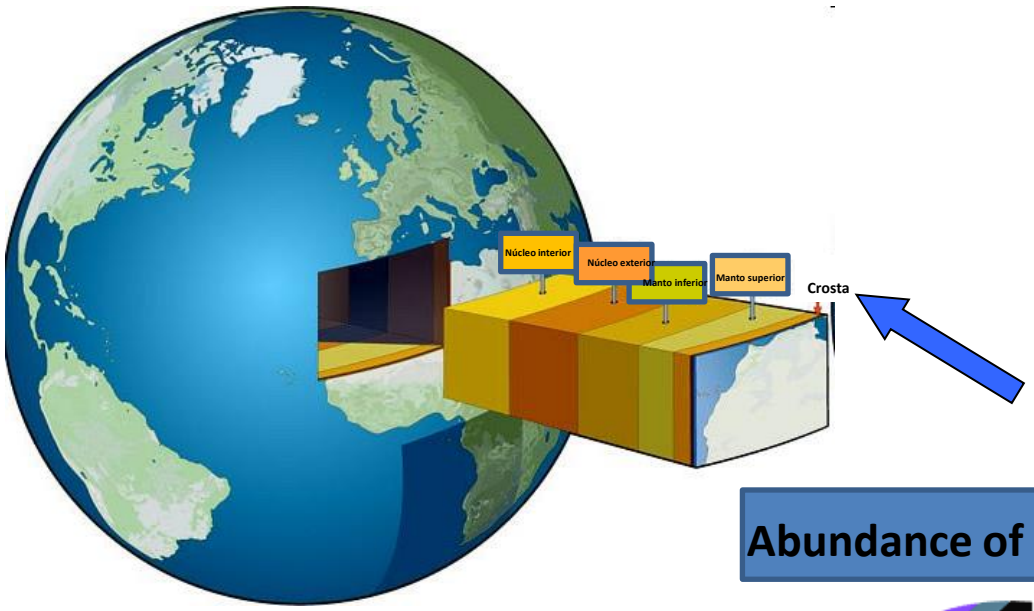
# MATERIAIS CERÂMICOS E VIDROS

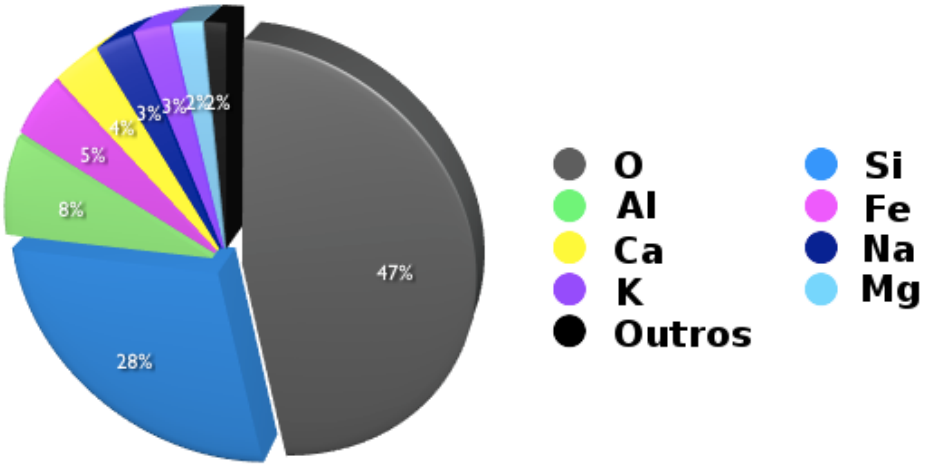
## SILICA AND SILICATES

# Silica in earth crust



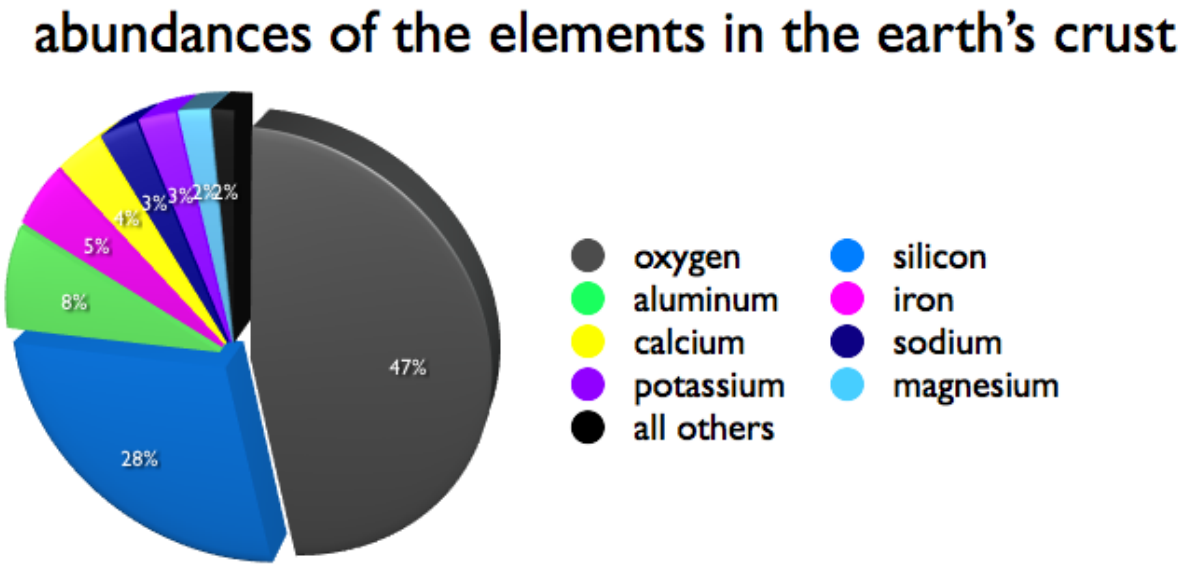

**O, Si, Al, Fe, Ca, Na, K, Mg**

**Abundance of chemical elements on earth's crust**




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

# Silica Abundance




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

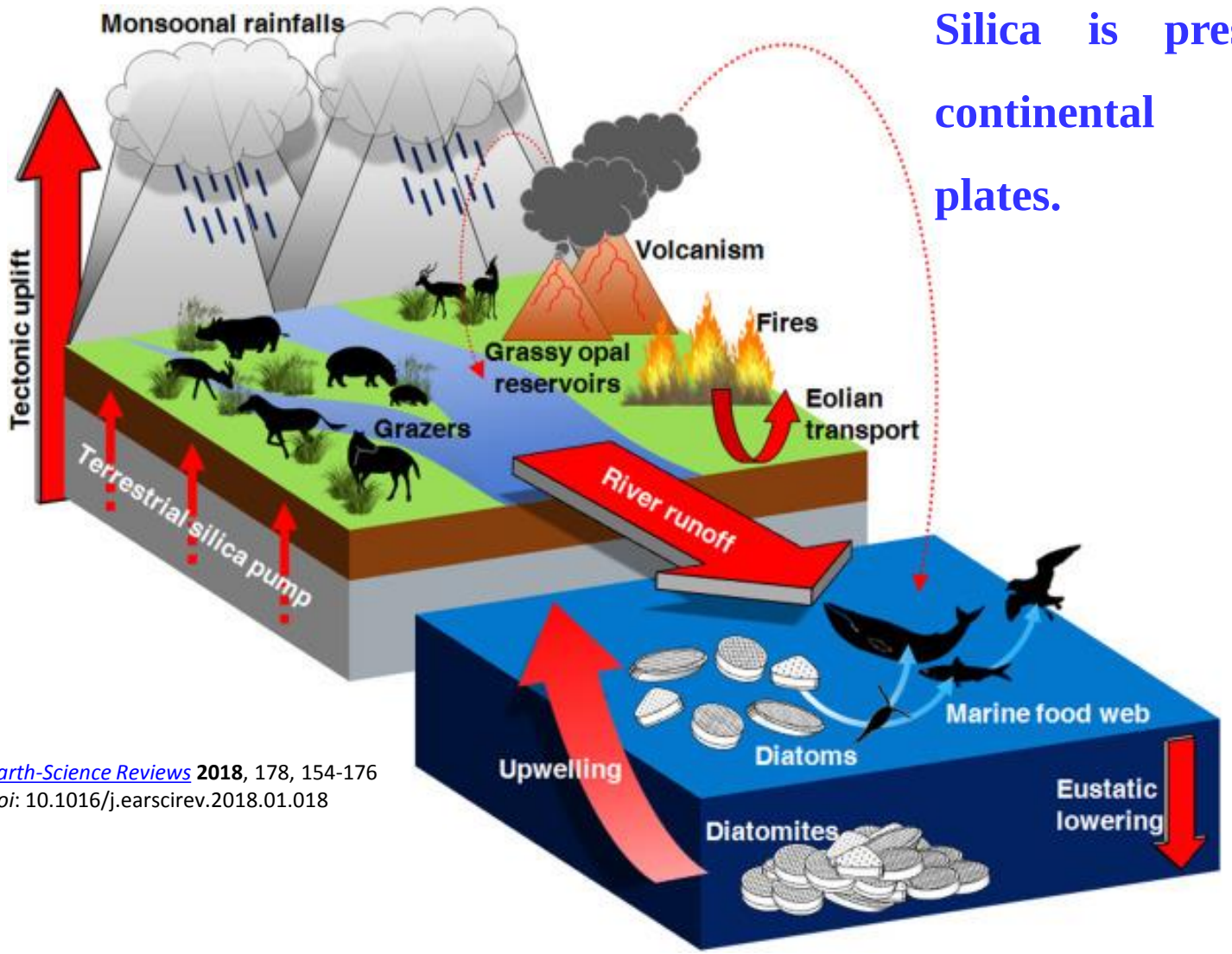
https://fundamateria.wordpress.com/category/seed/

→ Silicon is one of **the most abundant elements in the earth's crust**, but it occurs chiefly in combination with oxygen as silica, **$SiO_2$**, and with oxygen and other elements as **silicates**.

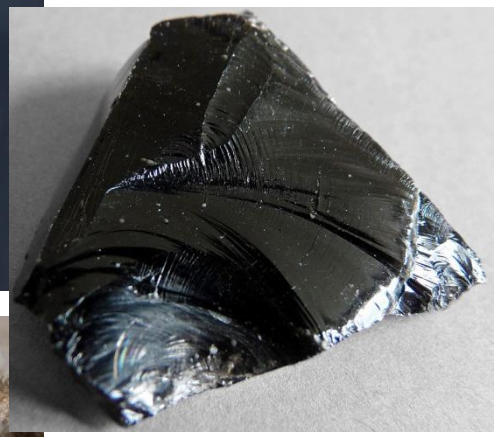
→ **Silica** is a **polymorphic substance**, capable of existing in several different forms, all having the same empirical formula but differing in the arranjement of the structural units – **quartz**, **tridimite** and **cristobalite** are the most abundant forms in earth's crust.

# Silica in earth crust

**Silica is present in both continental and oceanic plates.**




*Earth-Science Reviews* **2018**, 178, 154-176
*doi*: 10.1016/j.earscirev.2018.01.018



# Silica in earth crust

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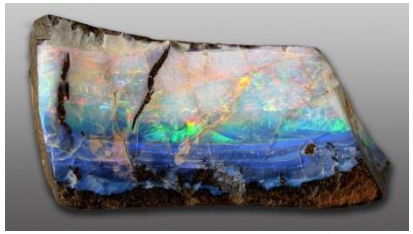
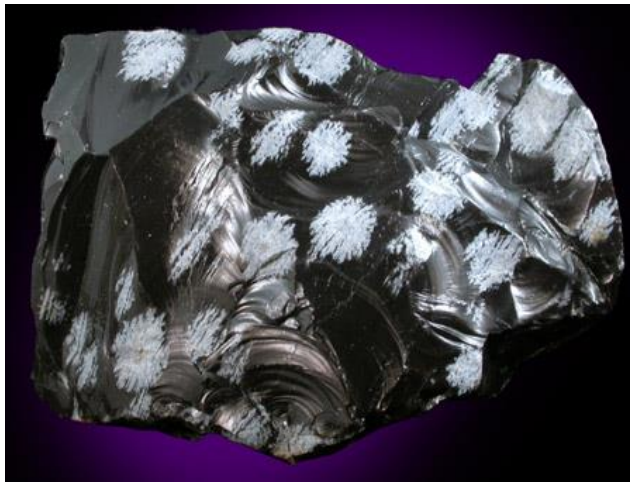
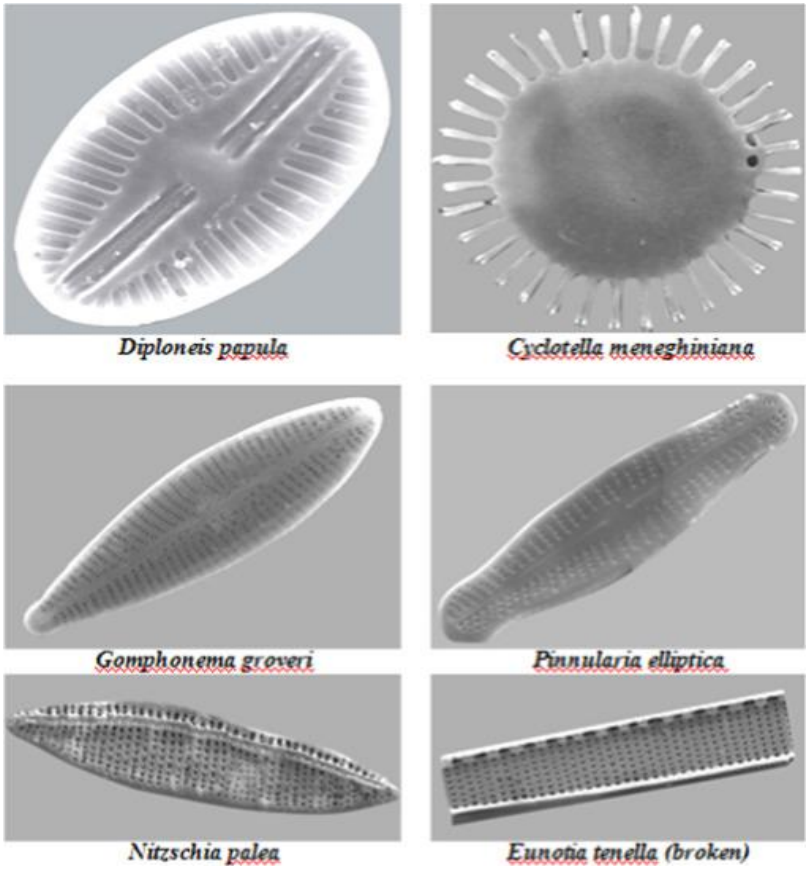


Silica is the most abundant mineral in the Earth's crust (~75 wt%). In the **continental plate**, silica's prevailing geologic crystalline polymorphs are quartz, tridymite and cristobalite, (present in minerals such as feldspars, micas, zeolites or talcs), while the most common amorphous phases are obsidian (present in volcanic rocks like pozzolans, and ashes, and in rocks that suffered meteoric impact) and opals accounts for Gtons per year, vastly outweighing that produced industrially.



# Silica in earth crust

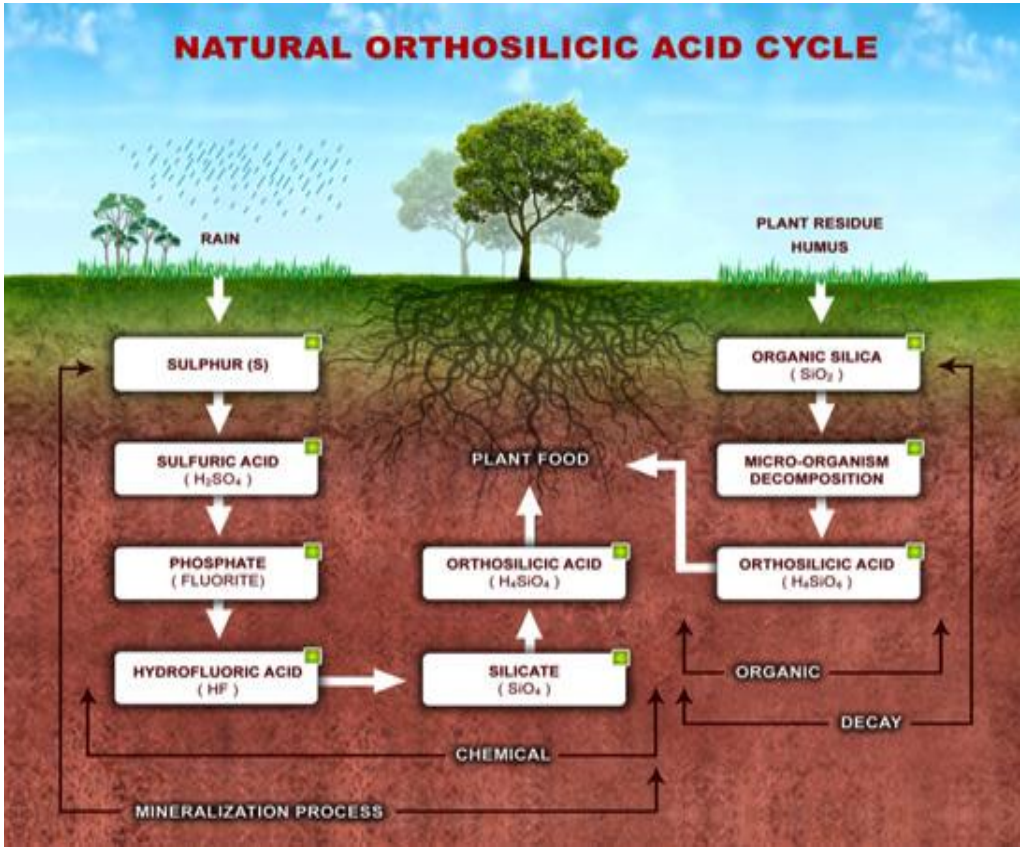



*Data Brief* **2017**, *10*, 63–68.

The skeleta of diatoms (*Diatomeae*, 5 µm up to 60 µm) are formed with silica.

**Silica is present in both continental and oceanic plates.**

In the **ocean plates**, diatomaceous earth constitutes a significant amorphous silica (a-$SiO_2$) source. This highly reactive biogenic silica deposit layer resulted from the silica-based skeletal remains of tiny aquatic organisms (diatomaceous and silicified phytoplankton) deposited over millions of years, and may include minor amounts of quartz, oxides of Ca, Mg, Fe and Al, and even some organic matter, depending on their location.




# Silica in earth crust

**Silica is present in the food chain.**

http://www.mybloomina.com/silicon-premium.html

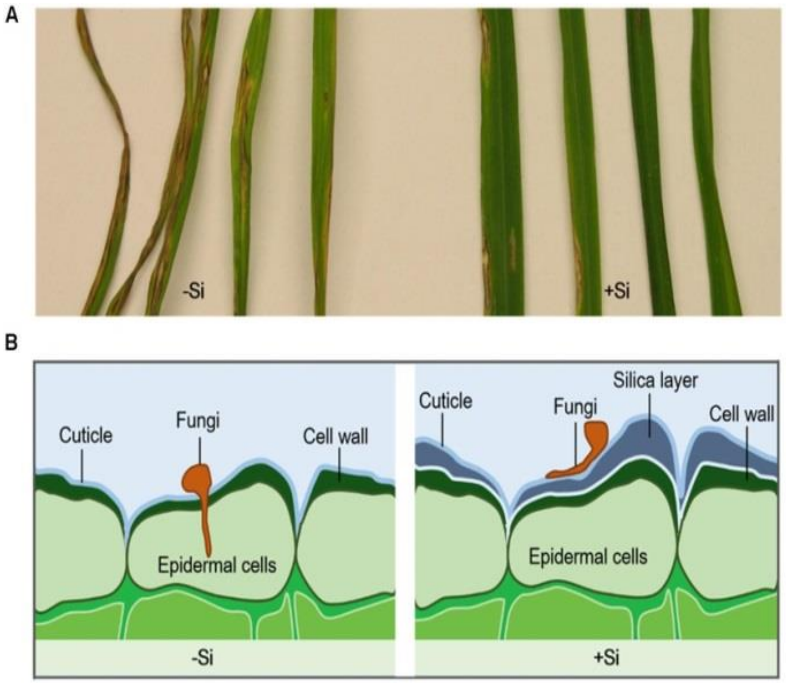
More importantly, silica performs an essential role in many forms of life.

The weathering and deterioration of rocks allows for high silica contend in soils in the form of soluble $[Si(OH)_4]$ or $Si(OH)_3O^-$ species (with concentrations ranging from 0.1 to 0.6 mM), allowing its uptake by plants, thus **entering the food chain**.

Biogenic silica occurs in many single-cell organisms, as natural amorphous structures with the composition $SiO_n(OH)_{4-2n}$.

# Silica in earth crust

**Silica is present in the food chain.**




*Eur. J. Plant Pathol.* **2010**, 128, 39–49
doi: 10.1007/s10658-010-9625-x

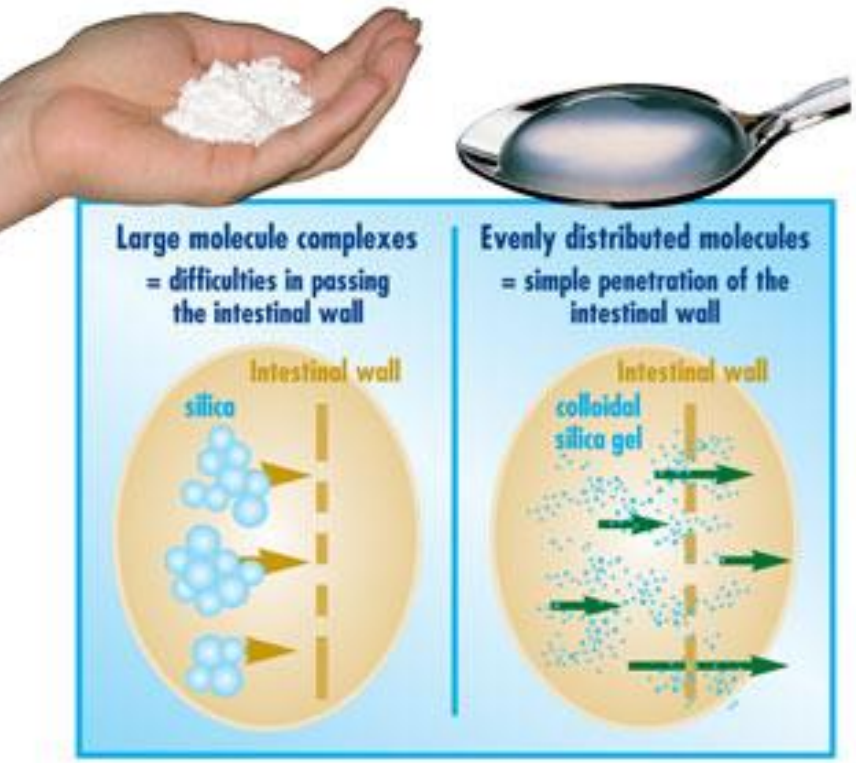
Silica is known to favor the healthy growth, development and reproduction of plants, increase their resistance to fungi, enhance their mechanical resistance, apart from not being detrimental when excessively collected.

# Silica in human body

In the human body, silica's effects in health, aging and disease are still being explored, notwithstanding its average content of ca. 260 ppm, very close to the magnesium level (accounting for 18 g in a person with 70 kg).

- Silica is pivotal in calcium phosphate nucleation, determinant in bone mineralization, growth and self-healing during dislocations and fractures.
- Aluminum absorption and (eventual) intoxication in human body (particularly important in Alzheimer's disease) may be prevented by silica ingestion, through the bonding to Al in the gastrointestinal tract.
- Maintenance of health in the immune system and reduction of the risk of atherosclerosis are other of silica attributes.
- Silica also accounts for the maintenance of tissue integrity by stabilizing the glycoproteins associated with collagen, thus playing a central role in the structural integrity of nails, hair, and skin.

# Silica in human body



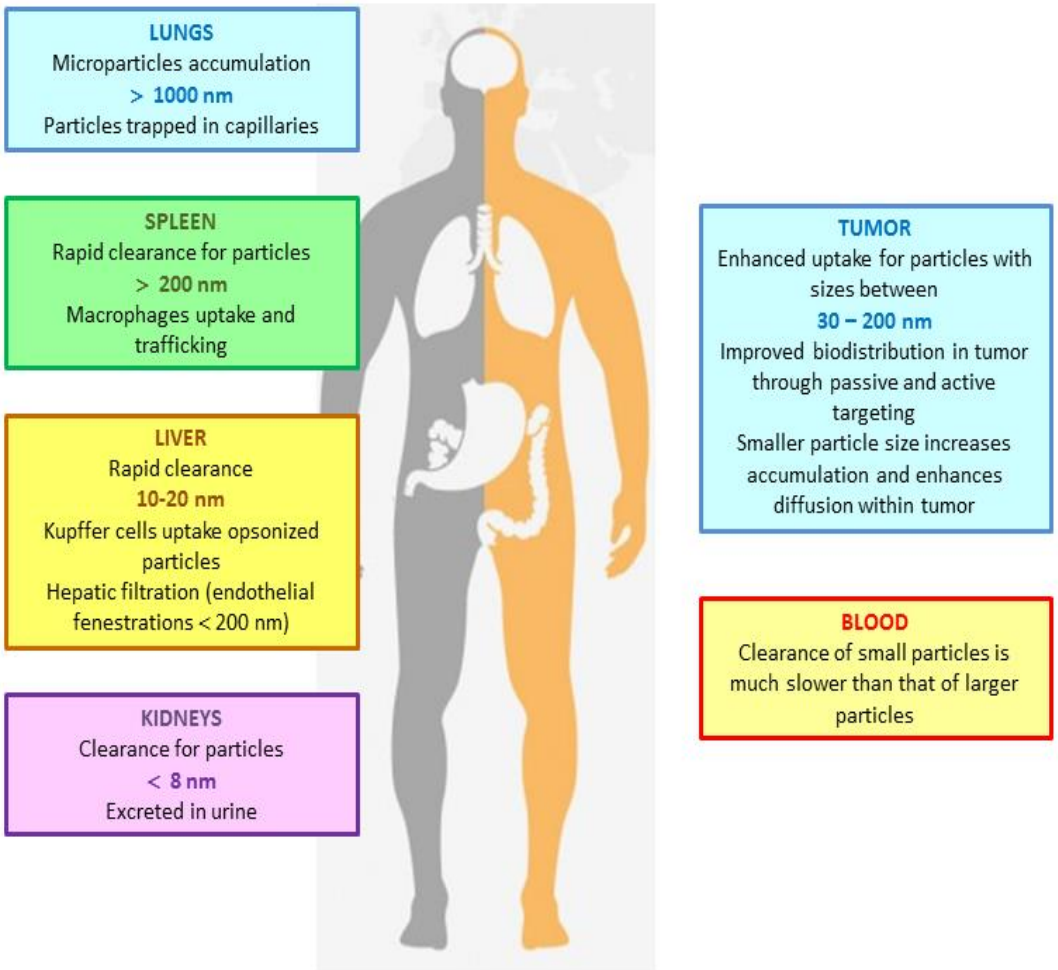

http://www.lholmesassociates.com/newsletters/naka/archive/naka_1105.html

Amorphous silica could enter in the human body via the gastro-intestinal tract (in colloidal form) and has been part of human dietary either as medical clay, or as food additive (labelled E551).

Contrary to crystalline silica (nano and micro particles), associated with lungs cancer and silicosis, a-$SiO_2$ (nano and micro particles) seem essentially nontoxic.

# Silica in human body

As to toxicity, **amorphous silica solubility (~120–170 ppm**, at the temperature and pH of the body fluids, **36–37 °C** and **7.35–7.45**, respectively), allowed an easier silica elimination (as silicic or poly(silicic) acid) which are non-toxic and diffuse through the blood stream or the lymphatic system to be eventually cleared in the urine, preventing its accumulation in kidneys, liver or spleen (contrary to the crystalline polymorphs counterparts).




Molecules. 2018 Aug 13;23(8). pii: E2021. doi: 10.3390/molecules23082021.

# Silica in human body

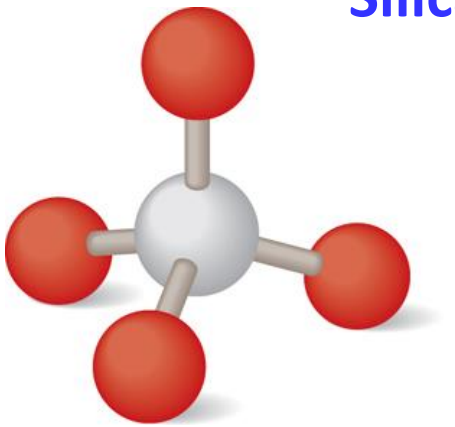
## The effect of cristallinity on silica solubility

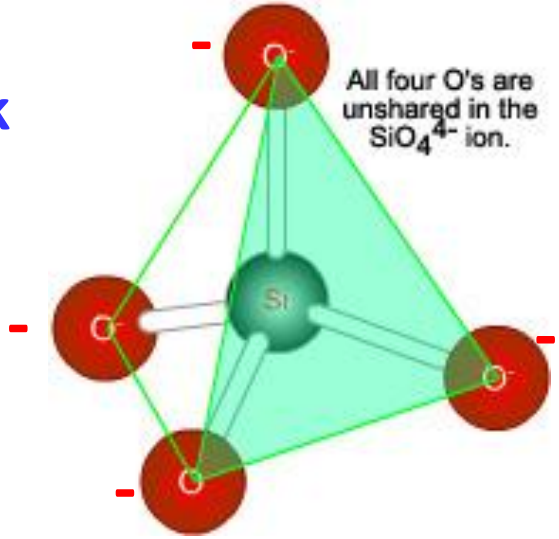
Amorphous silica phases lacked the regular long-range order purposed by the classical crystal growth and dissolution models which difficult the understanding of its dissolution mechanism. Yet, a-$SiO_2$ phases shared with the silica crystalline polymorphs the fundamental unit, the $(SiO_4)^{4-}$ tetrahedron, and short range structural order (at length scales up to 20 Å), despite variations in Si-O-Si bond lengths and angles. The a-$SiO_2$ atomic scale disorder enabled the loss of surface $(SiO_4)^{4-}$ $Q^3$ units into solution (creating vacancy islands) and keeping unchanged the a-$SiO_2$ surface Gibbs energy. As a consequence, dissolution rates of amorphous silica phases, which involves an equilibrium between the solid phase and dissolve monomer $Si(OH)_4$, scaled linearly with increasing driving force (undersaturation).

At pH values above 8, the presence of $[H_3SiO_4]$ ion in addition to $Si(OH)_4$ is responsible for the high silica solubility at this pH values (as the concentration of $Si(OH)_4$ in equilibrium with the solid silica phase is not pH dependent).

# Silica in
# CLAYS and Quartz

# Silica Tetrahedron – the building block



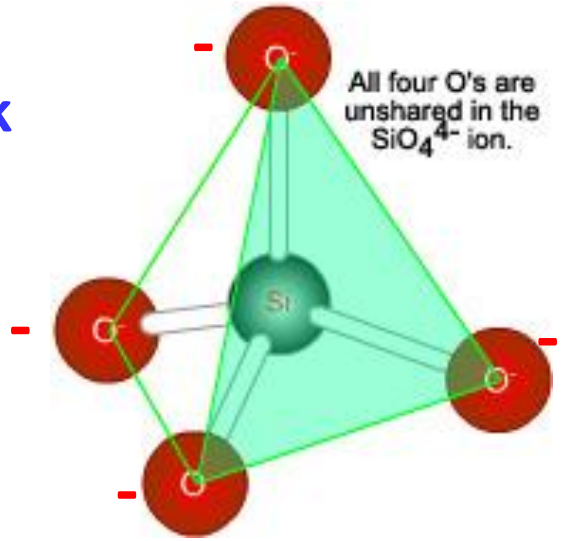


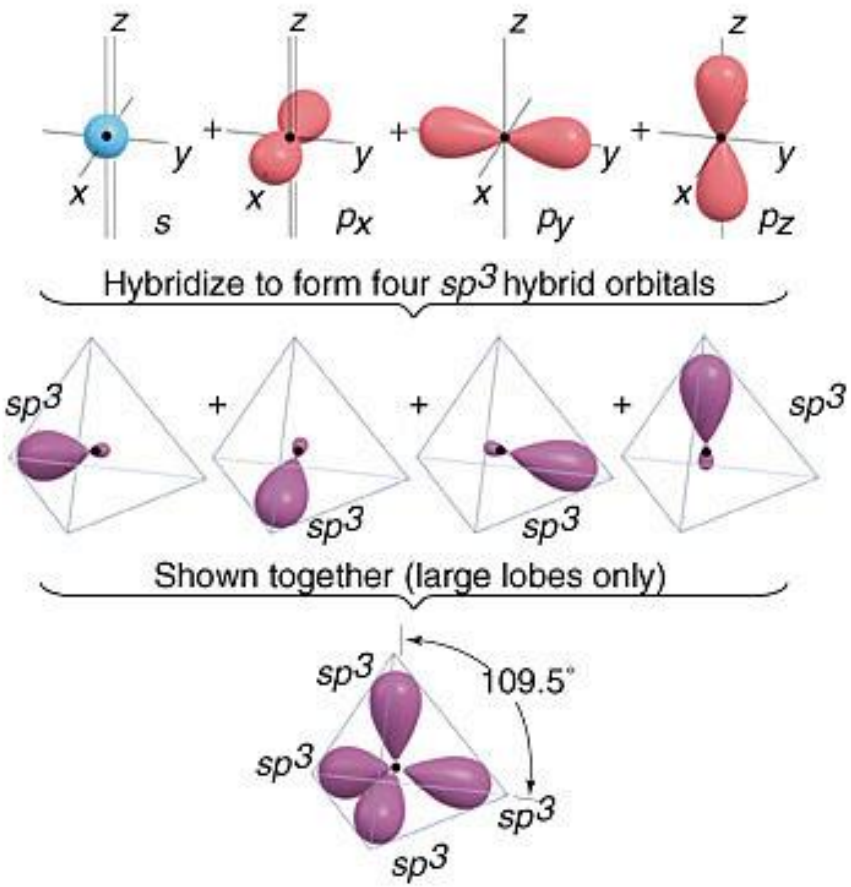

→ The Si-O bond has sufficient **ionic character** to enable us to regard all forms of $SiO_2$ as being composed of **$Si^{4+}$** and **$O^{2-}$** ions.

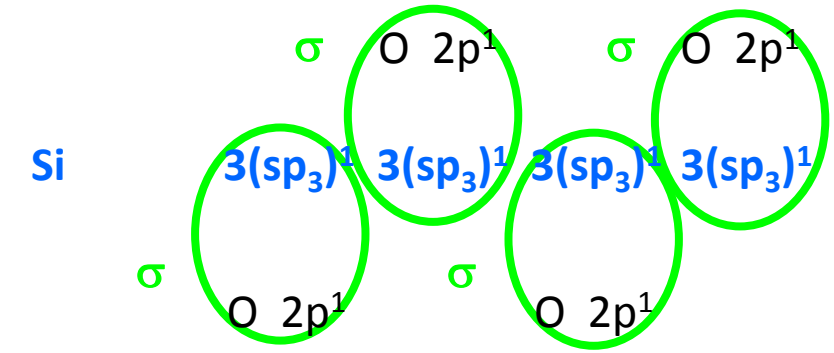
→ The **radius ratio of silicon to oxygen is 0.28** corresponding to a predicted **coordination number of 4**, which agrees with the observed value for the majority of crystalline and amorphous forms of silica.

→ Each **$Si^{4+}$ ion** in silica is sorrounded by **four oxygen ions**, forming a **tetrahedron**, having a triangular base and three triangular sides meeting at na appex.

# Silica Tetrahedron – the building block



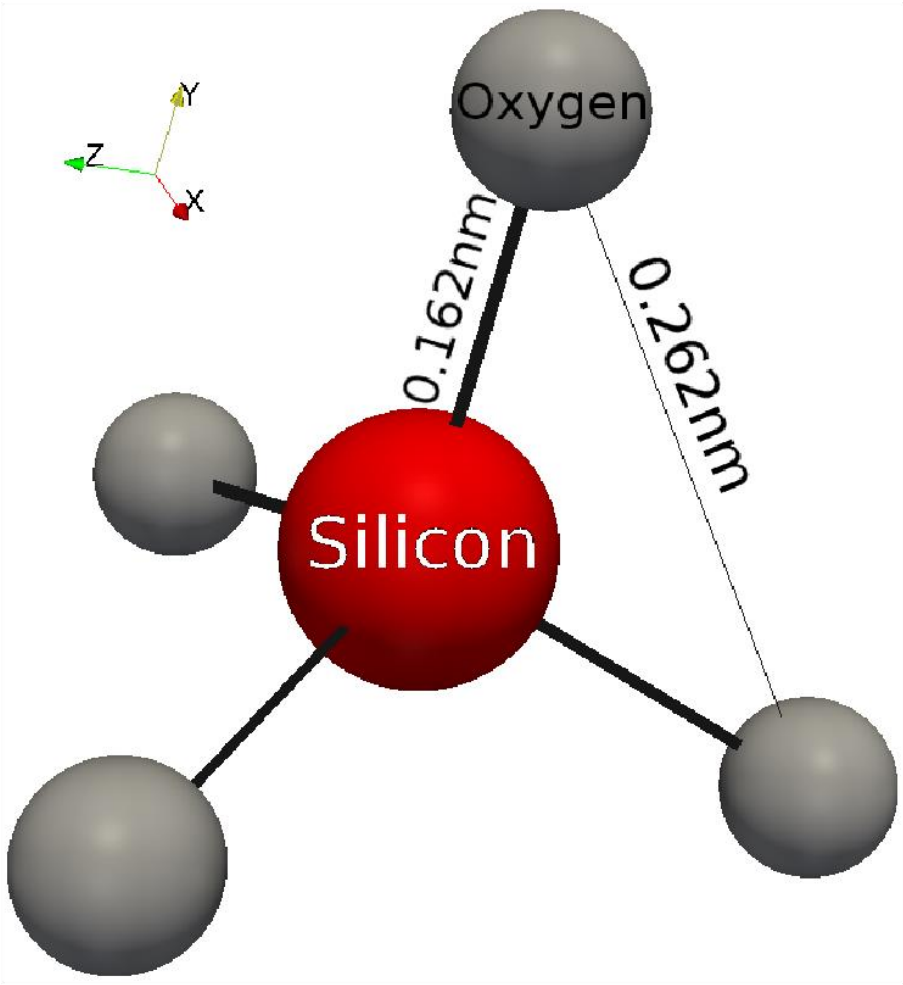

[Si] = [Ne] $3s^2$ $3p_x^1$ $3p_y^1$ $3p_z^0$

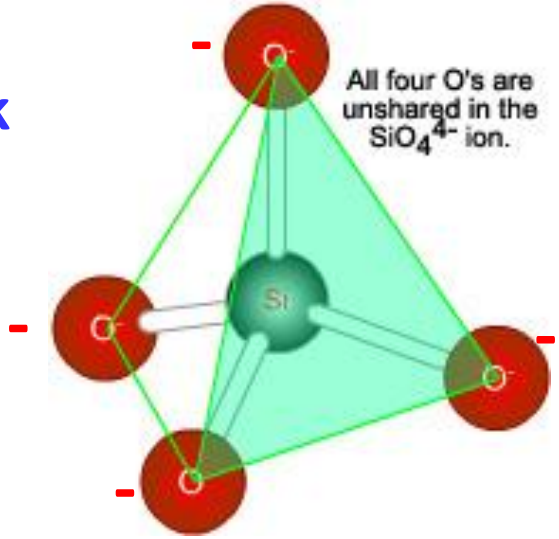
[Si] = [Ne] $3(sp_3)^1$ $3(sp_3)^1$ $3(sp_3)^1$ $3(sp_3)^1$

[$O^-$] = [He] $2s^2$ $2p_x^2$ $2p_y^2$ $2p_z^1$

[O] = [He] $2s^2$ $2p_x^2$ $2p_y^1$ $2p_z^1$

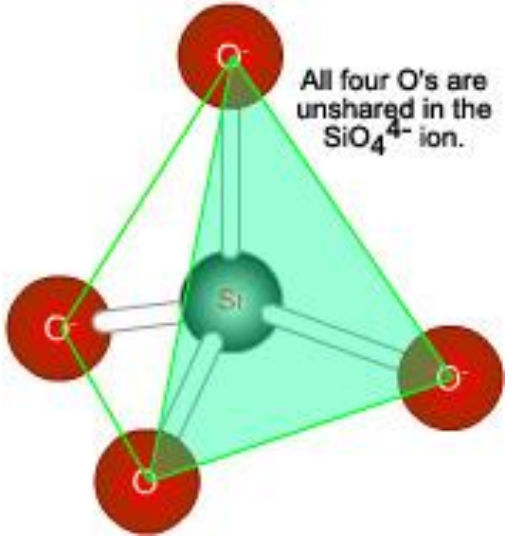
# Silica Tetrahedron – the building block



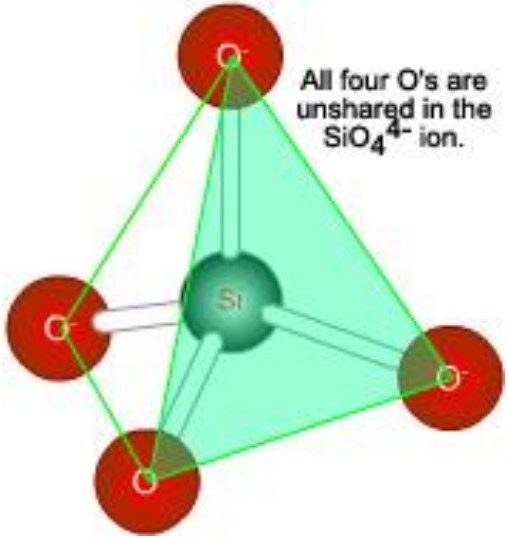

**The basic building block of all silicates is the $SiO_4^{4-}$ tetrahedron!**

# Silica Tetrahedron – the building block




→ The **[SiO4]$^{4-}$ group** is of course **incapable of independent existence** and **requires four positively charged units to balance the negative charges**; these groups may be other **$SiO_2$ 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**.



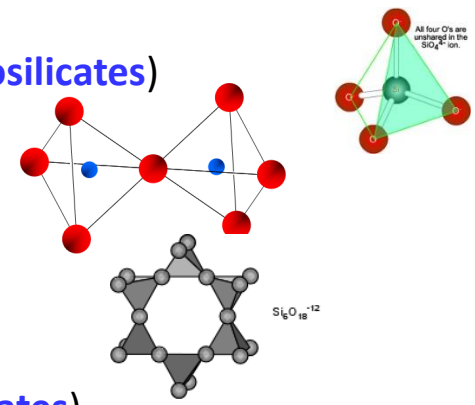

# AND NOW LET'S PLAY WITH THE SILICA TETRAHEDRON!

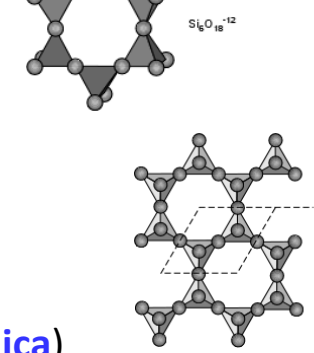
# Silica Tetrahedron – the building block

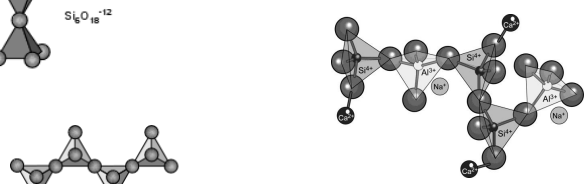
→ **Silicon** is located in the **center of the tetrahedron** and **surrounded by 4 oxygens at the corners**. This group is **electrically unbalanced ($(SiO_4)^{4-}$)**, so that **the oxygen atoms are combined with other cations to compensate their negative charges.** The number of vertices shared by each tetrahedron may be 0, 1, 2, 3 or 4.

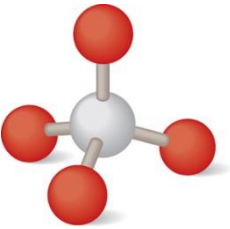
→ Tetrahedra may also join by their bases to form hexahedral molecules **($(Si_2O_4)_n^{2n-}$).** Depending on the number of oxygens that coordinate with other silicon cations, large groups of silicates may form in different shapes:

- **$Q^0$** no oxygens shared: isolated molecules (**orthosilicates**)
- **$Q^1$** one oxygen shared: pairs (**pyrosilicates**)
- **$Q^2$** two oxygens shared: rings (**metasilicates**)
- **$Q^2$-$Q^3$** two-three oxygens shared: chains (**bisilicates**)
- **$Q^3$** three oxygens shared: planes (**phyllosilicates**)
- **$Q^4$** four oxygens shared: tridimensional structures (**silica**)



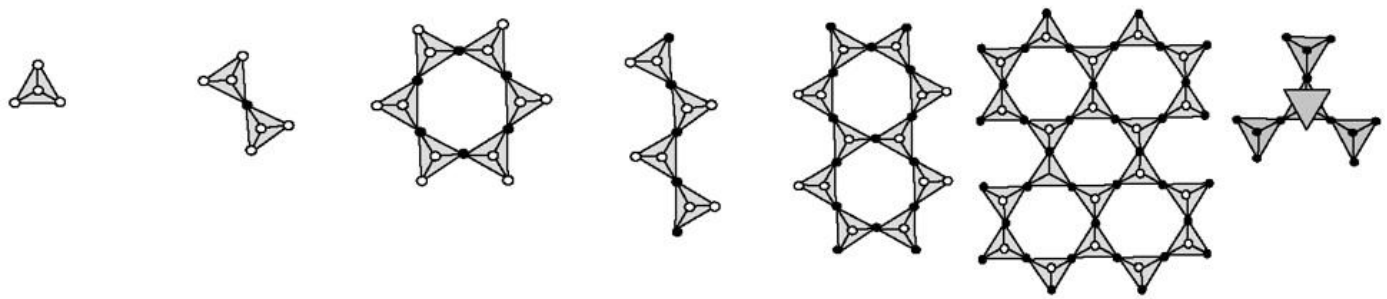





# Silica Tetrahedron – the building block

| | $Q^0$ | | $Q^2$ | $Q^2$ | $Q^3$ | $Q^3$ | $Q^4$ |
|---|---|---|---|---|---|---|---|
| Anionic unit | $SiO_4^{4-}$ | $Si_2O_7^{6-}$ | $Si_6O_{18}^{12-}$ | $Si_2O_6^{4-}$ | $Si_4O_{11}^{6-}$ | $Si_2O_5^{2-}$ | $SiO_2$ |
| 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 ($cm^{-1}$) | 790-850 | 890-950 | - | 930-1000 | - | 1020-1100 | 1150-1200<br>1060-1070 |

○ NBO
● BO
△ Silicon Tetrahedra



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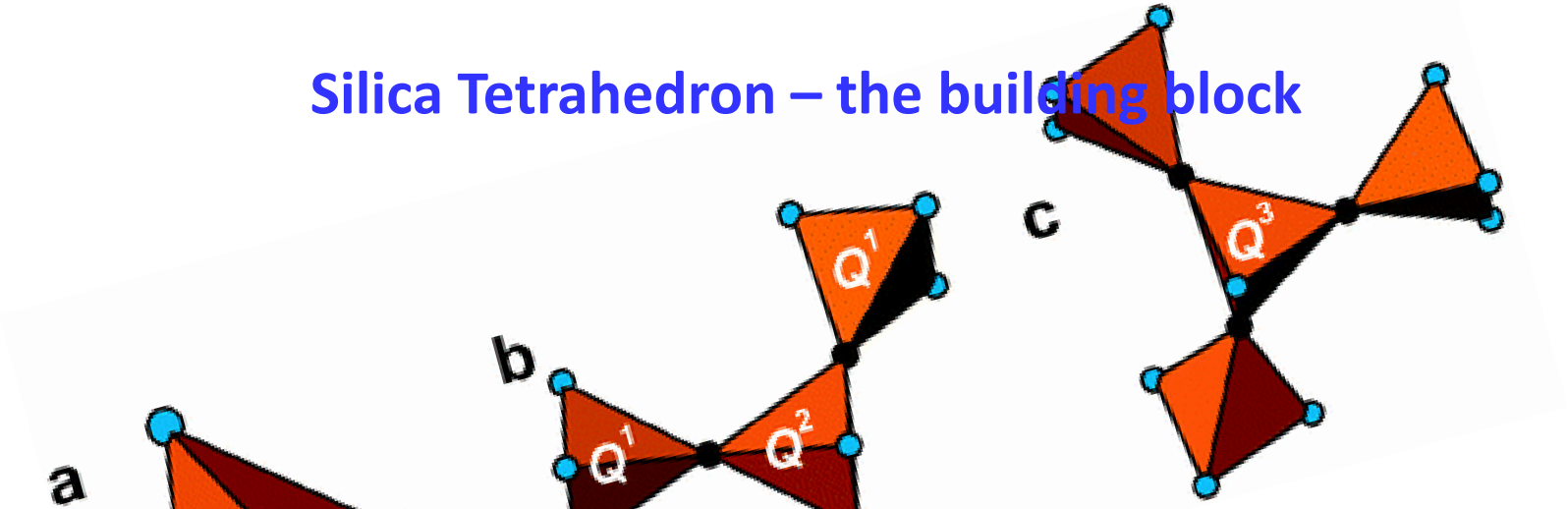
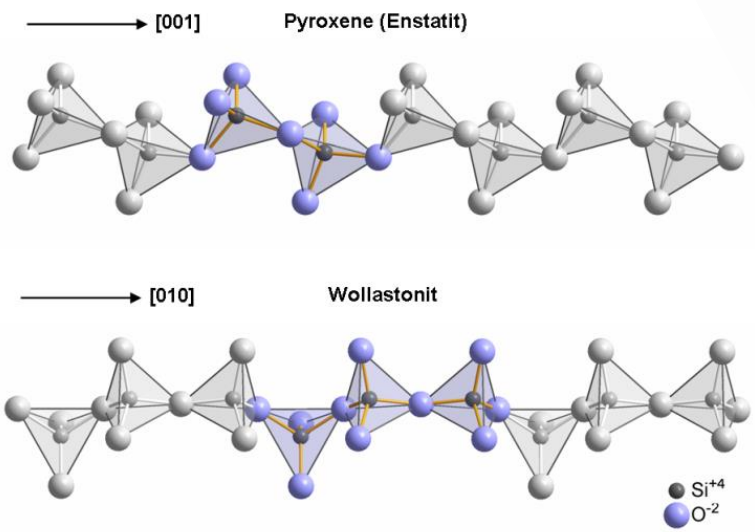
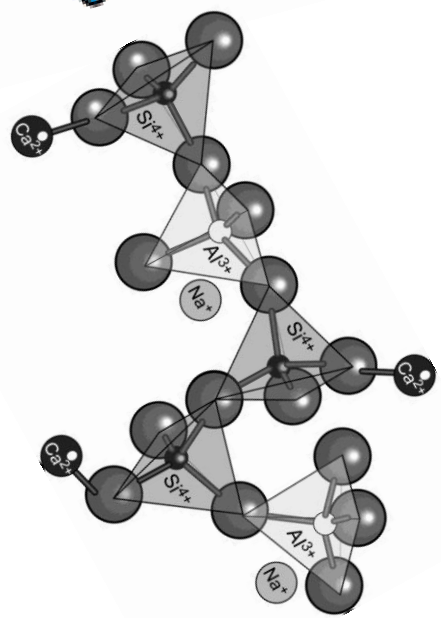
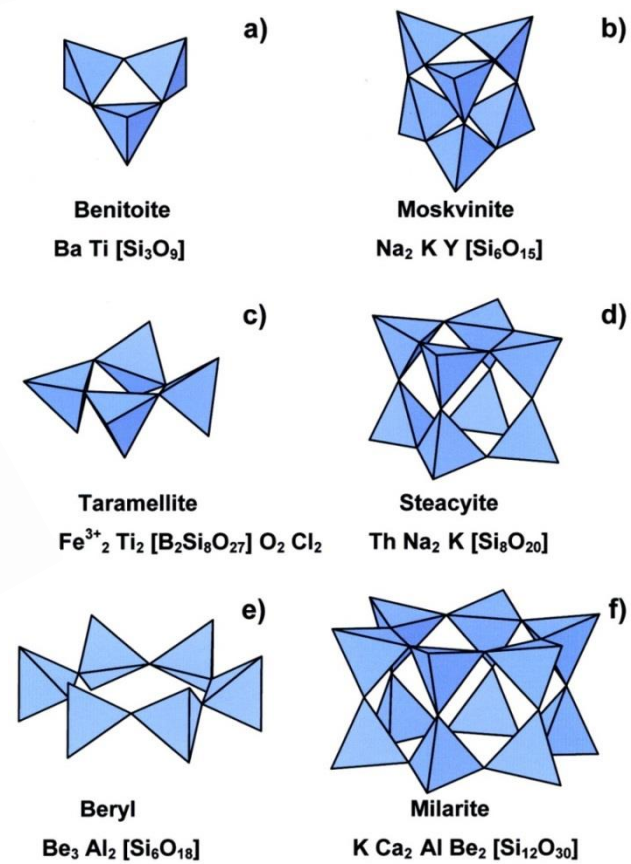
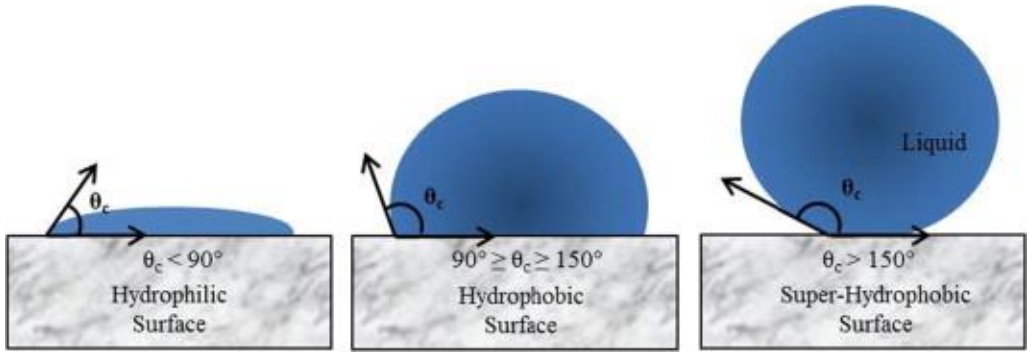


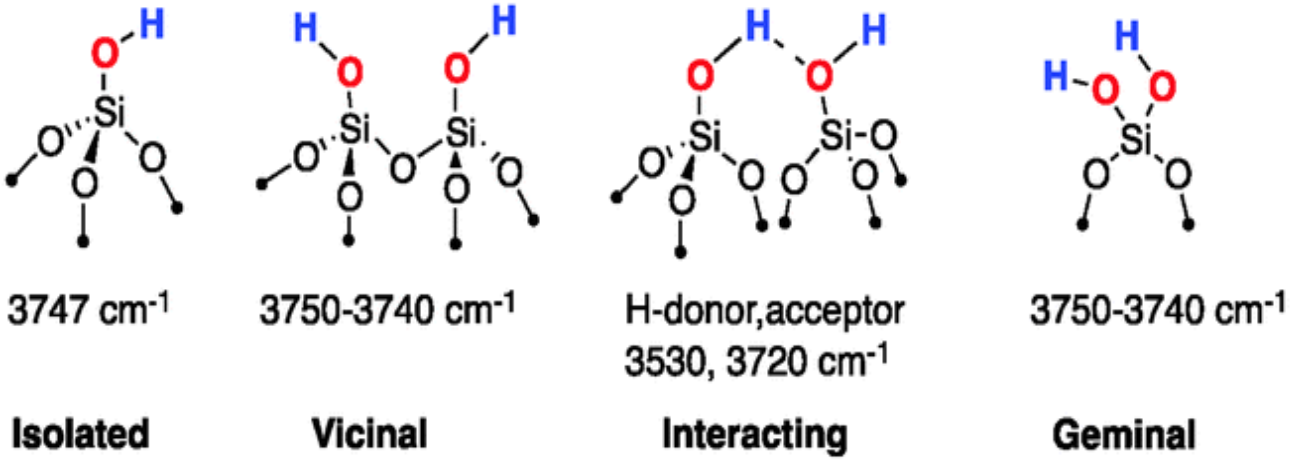



# The effect of $Q^n$ on silica wettability



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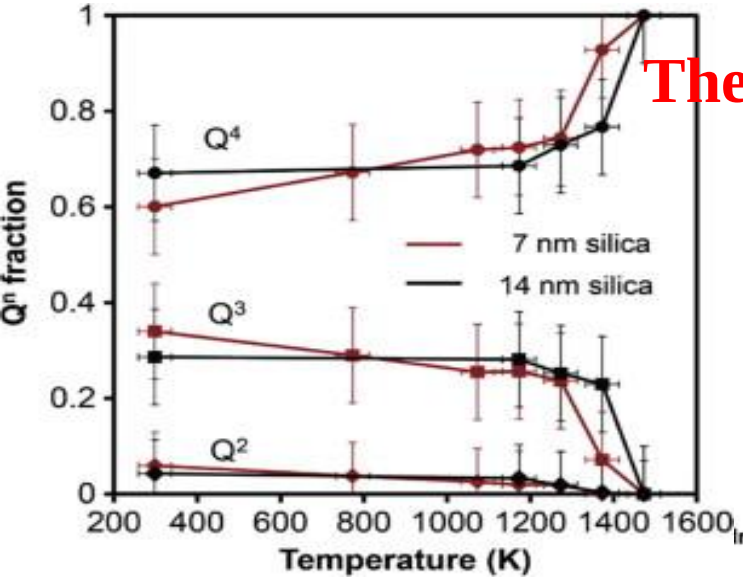
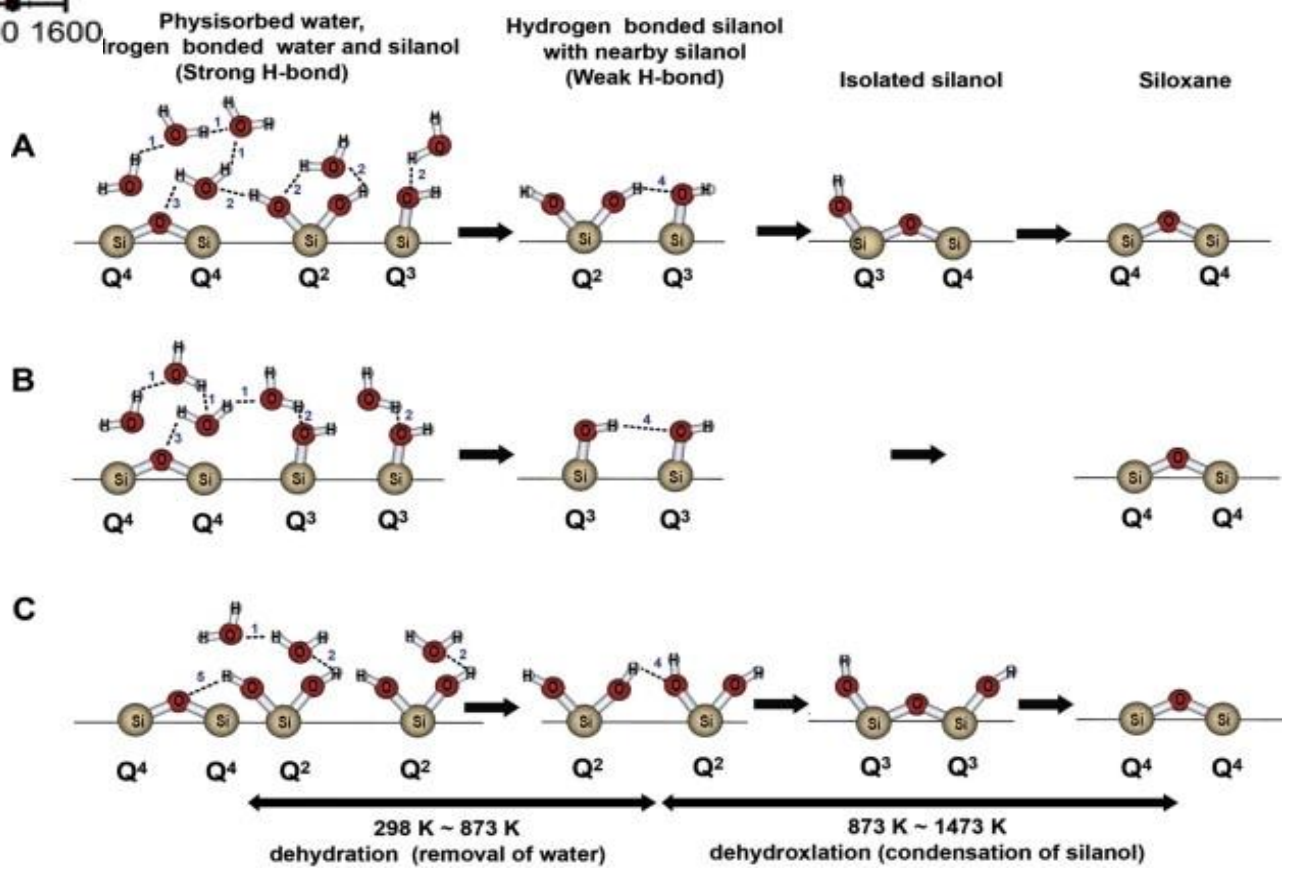


# AND NOW LET'S STUDY SOME SILICA NATURAL MINERALS!

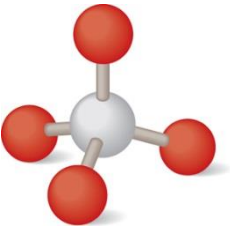
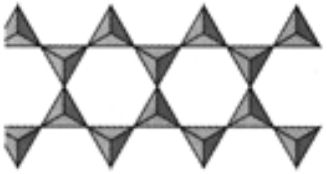
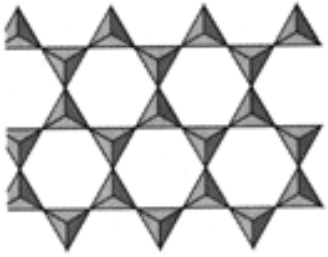
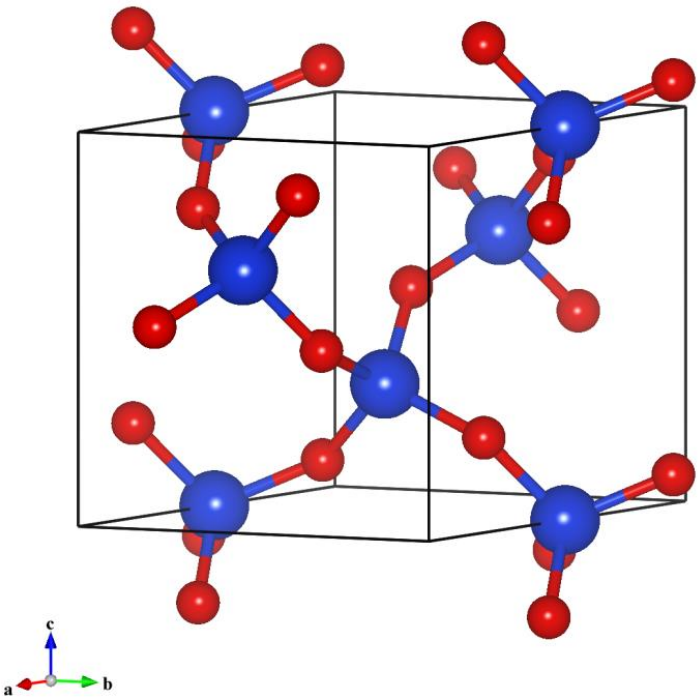


**TABLE 2.2**

## Major Silicate Structures

| GEOMETRY OF LINKAGE OF $SiO_4$ TETRAHEDRA | | EXAMPLE MINERAL | CHEMICAL COMPOSITION |
|---|---|---|---|
| *Isolated tetrahedra:* No sharing of oxygens between tetrahedra; individual tetrahedra linked to each other by bonding to cation between them |  | Olivine | Magnesium-iron silicate |
| *Rings of tetrahedra:* Joined by shared oxygens in three-, four-, or six-membered rings |  | Cordierite | Magnesium-iron-aluminum silicate |
| *Single chains:* Each tetrahedron linked to two others by shared oxygens; chains bonded by cations |  | Pyroxene | Magnesium-iron silicate |
| *Double chains:* 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 |
| *Sheets:* Each tetrahedron linked to three others by shared oxygens; sheets bonded by cations |  | Kaolinite<br>Mica (muscovite) | Aluminum silicate<br>Potassium-aluminum silicate |
| *Frameworks:* Each tetrahedron shares all its oxygens with other $SiO_4$ tetrahedra (in quartz) or $AlO_4$ tetrahedra |  | Feldspar (orthoclase)<br>Quartz | Potassium-aluminum silicate<br>Silicon dioxide |

# $Q^4$: Quartz

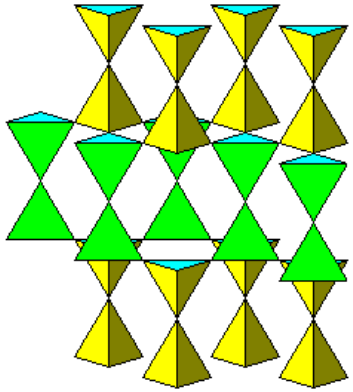


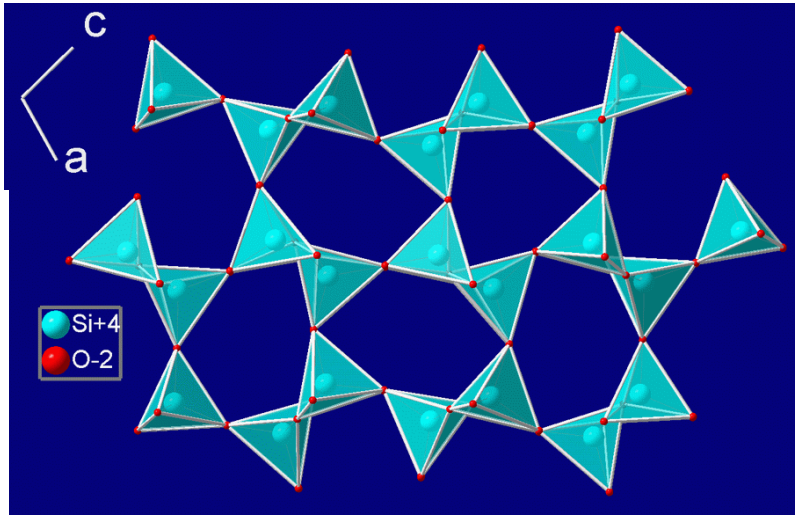

→ In **quartz**, the best-known crystalline form of silica, the Si-O-Si bonds joining neighbouring tetrahedra do not form a straight line but are bent round to give spiral chains.

→ Starting with any $Si^{4+}$ ion, passing through silicon and oxygen alternately, spiral chains (**$Si_3O_3$**) 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.

# $Q^4$: Tridymite



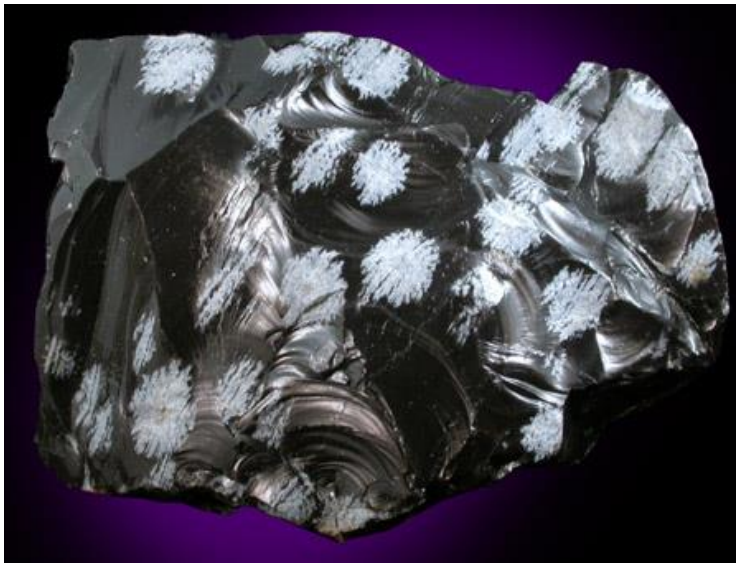



→ In **tridymite** the silica tetrahedra are linked to form rings, each containing six oxygen and six silicon ions.

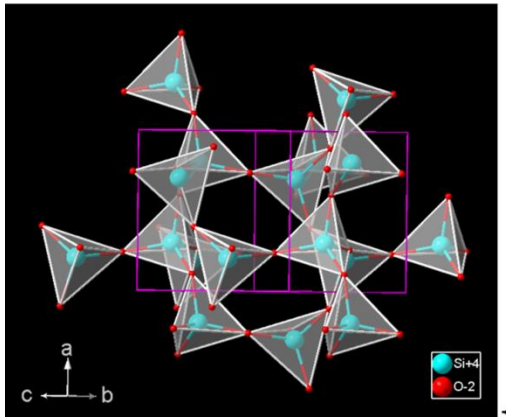
→ These $Si_6O_6$ rings are joined to form planes throughout the structures, each plane being linked to a neighbouring one by bridging oxygen ions.

→ 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.

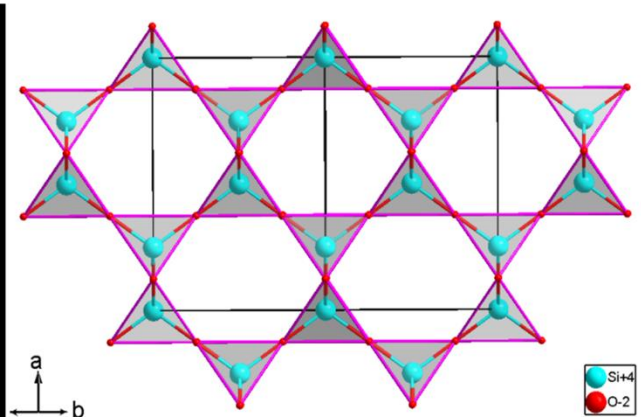
# $Q^4$: Cristobalite



α-cristobalite




β-cristobalite

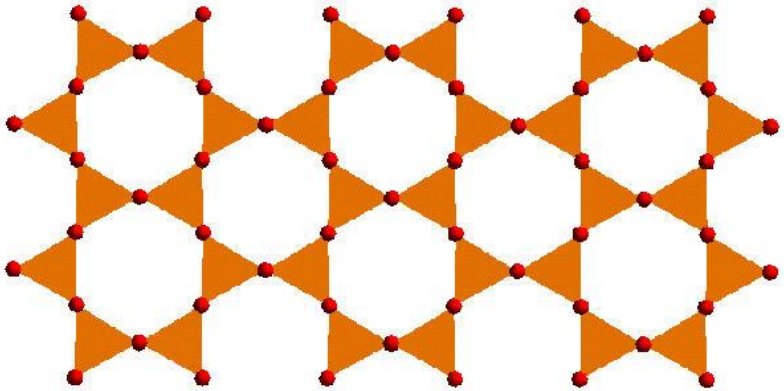


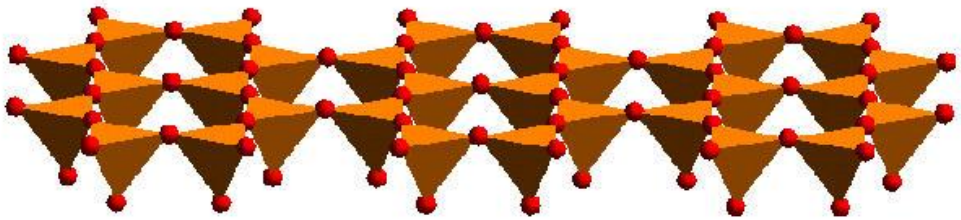

→ In **cristobalite** the silica tetrahedra are linked to form rings, each containing six oxygen and six silicon ions.

→ These **$Si_6O_6$** 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.

# $Q^3$: Sheet Structures (phyllosilicates)



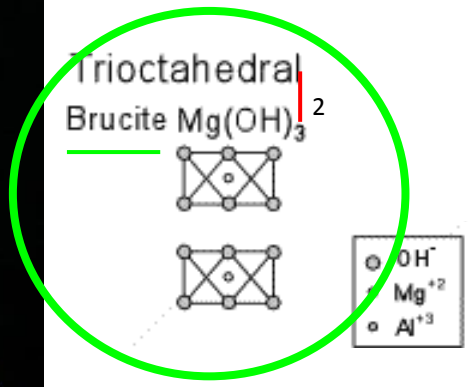


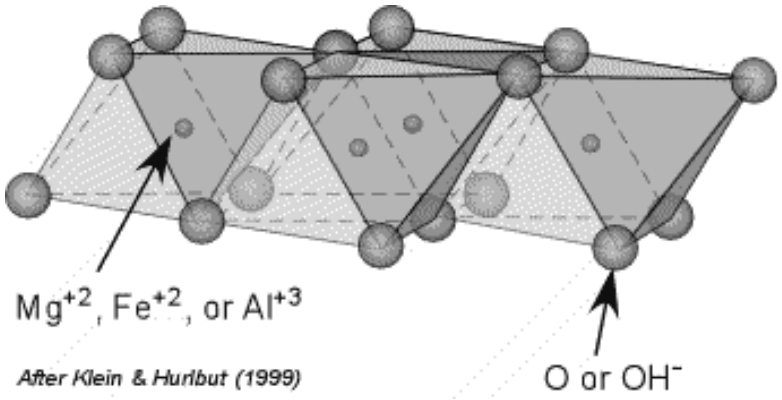
→ Carrying the notion of linking silica tetrahedra a stage further, a **complete sheet of silicon-oxygen six-membered rings** is formed just by condensing a number of pyroxene or amphibole units.

→ Such sheets, with a repeat formula **$Si_2O_5^{2-}$** are capable of **indefinite extension in two dimensions**; this is because the oxygen valancies within the plane are itself are 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**.

# Other Sheet Structures: Brucite



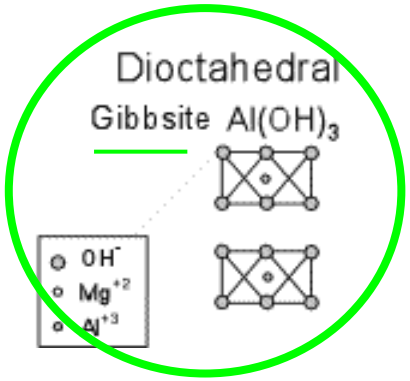



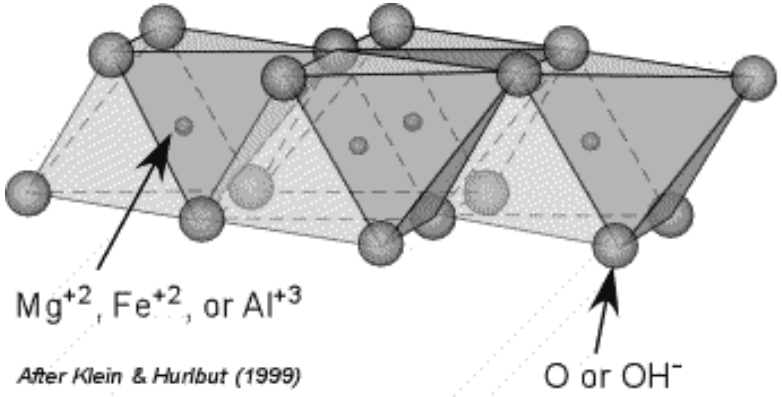

→ **Brucite** is the mineral form of **magnesium hydroxide**, with the chemical formula **$Mg(OH)_2$**.

→ 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**.

# Other Sheet Structures: Gibbsite



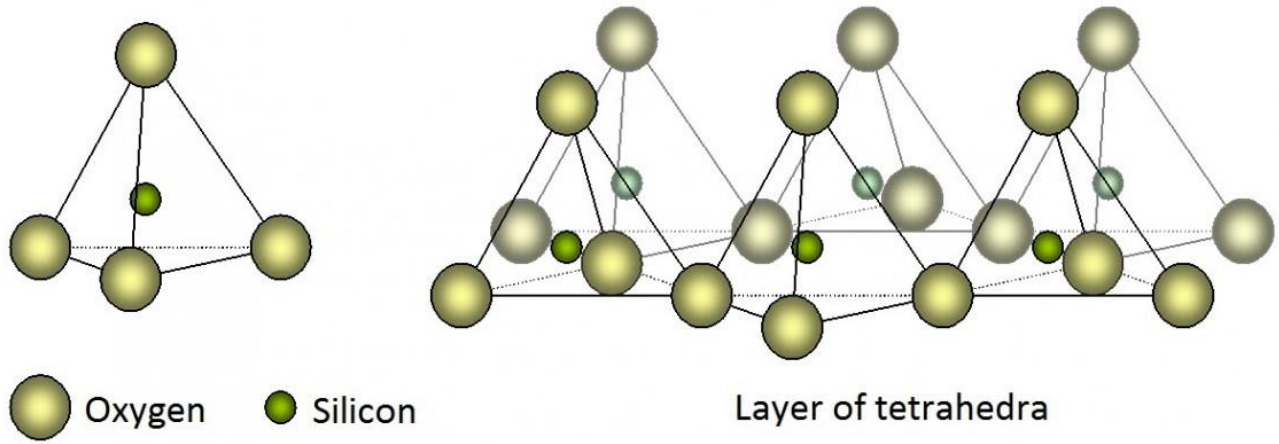




→ Brucite is closely related to **gibbsite**, **$Al(OH)_3$**. However the extra charge in gibbsite's aluminum (+3) as opposed to brucite's magnesium (+2) requires that **one third of the octahedrons to be vacant of a central ion in order to maintain a neutral sheet**.

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

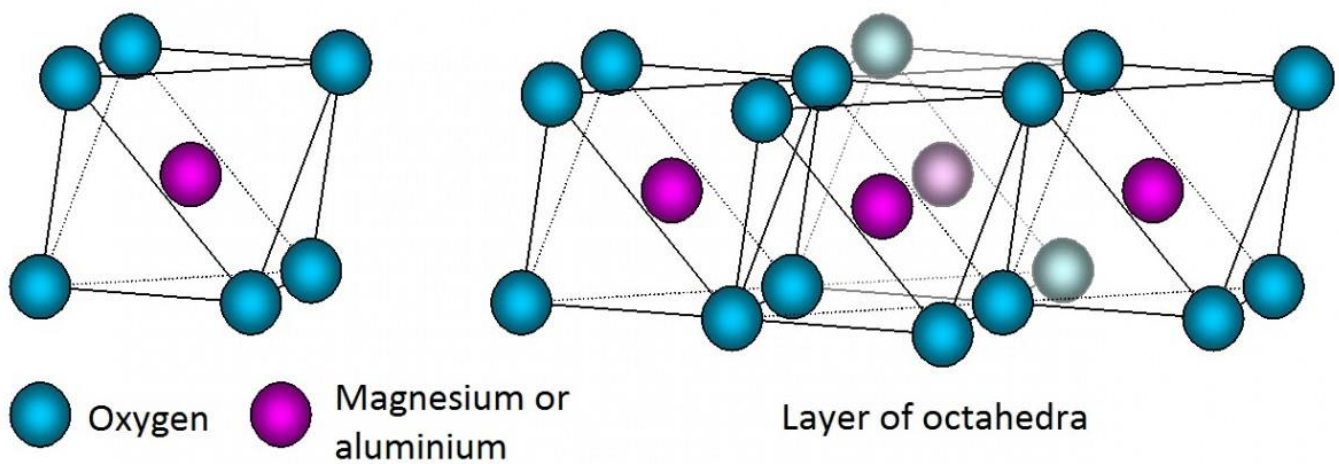
# $Q^3$: Clay Minerals (phyllosilicates)

→ In the synthesis of natural clay minerals, the first step is the production of sheet minerals like $Si_2O_5^{2-}$ (silica-like) plus $Mg(OH)_2$ (brucite) or $Al(OH)_3$ (gibsite).




$Si_2O_5^{2-}$

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




$Mg(OH)_2$ or $Al(OH)_3$

# $Q^3$: Clay Minerals (phyllosilicates)

→ **Clays** are one of the **major mineral components of the soil**, with a wide diversity of chemical and 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 **aluminossilicates**. 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**.

# $Q^3$: Clay Minerals (phyllosilicates)

→ **Phyllosilicates** are the most important group of soil. Phyllosilicates form by **silica tetrahedron (T) sharing three vertices**; **the fourth vertices 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**.

# $Q^3$: Clay Minerals (phyllosilicates)

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

**Gibbsite layer** + **silica layer** — **brucite layer**+**silica layer**

**Kaoline group** — **Serpentine group**

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

**Silica + Gibbsite** + **silica** — silica+**brucite** +**silica**

**Pyrophyllite group** — **Talc group**

**Montmorillonite** — **Montmorillonite**

**Mica group** — **Chlorite group**

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

# $Q^3$: 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 $[Al_2(OH_4]^{2+}$ (i.e. **having removed two OH groups**) and the **silica sheet** as $(Si_2O_5)^{2-}$, we arrive at the composite formula $Si_2O_5.Al_2Si_2O_5(OH)_4$, or $Al_2Si_2O_5(OH)_4$, 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.

# $Q^3$: 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**.

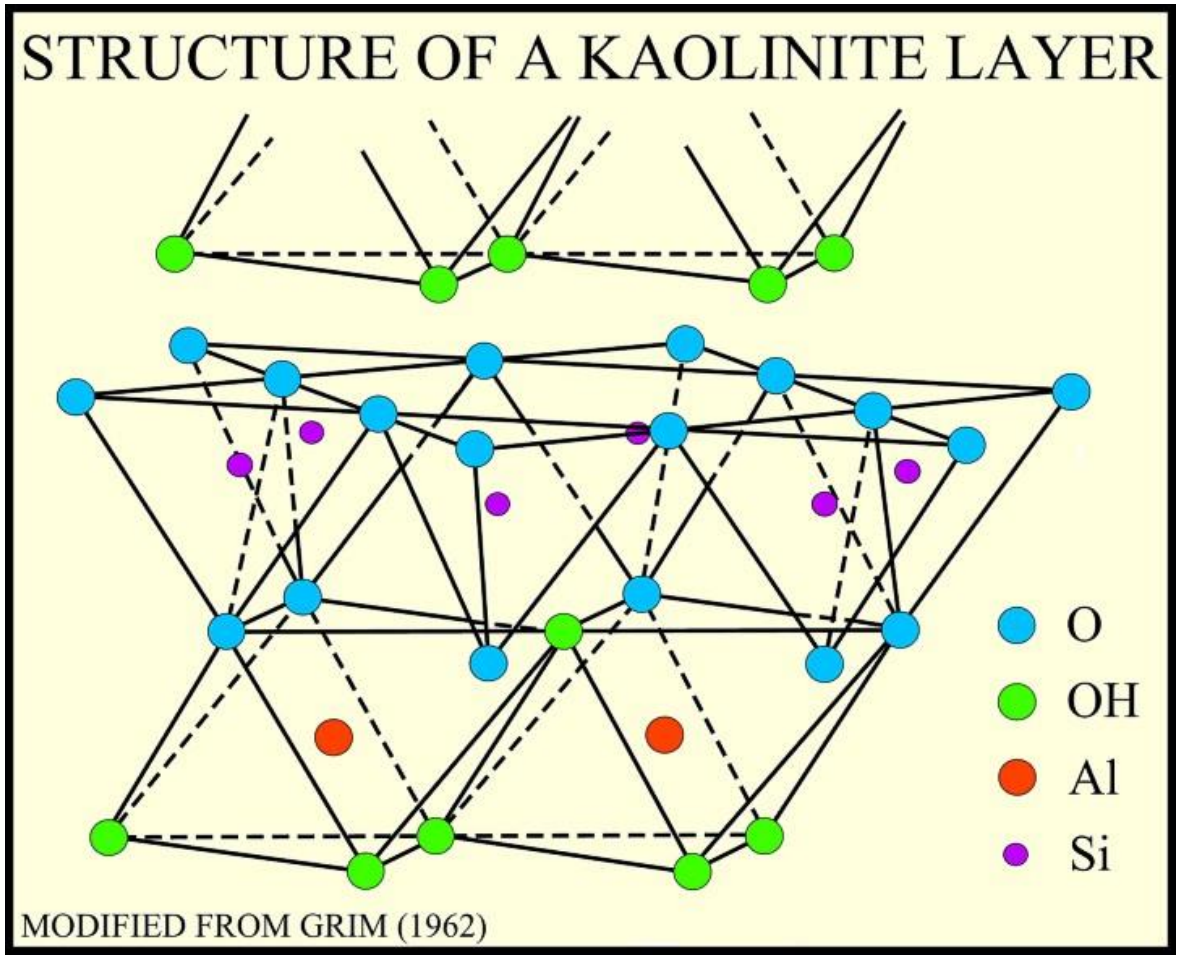
→ There are **three possible ways of filling three sites by two ions**, thus giving rise to **one source of variation in the unit layers.**

→ 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.**

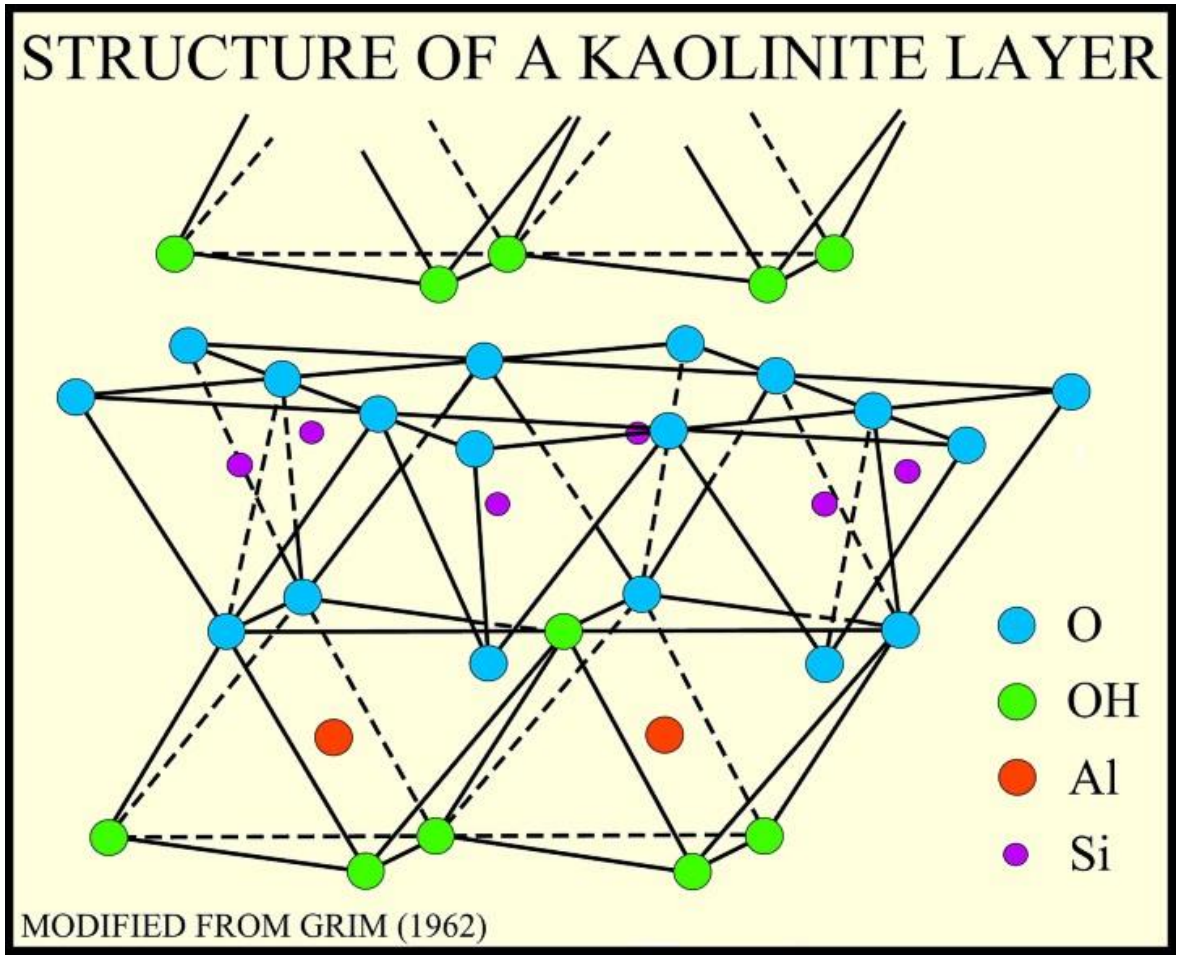
# $Q^3$: Clay Minerals (phyllosilicates)

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



# $Q^3$: Clay Minerals (phyllosilicates)

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




**Kaolinite**
**layer charge balance**

6 $O^{2-}$.....-12
4 $Si^{4+}$.....+16

4 $O^{2-}$, 2 $OH^-$ .....-10
4 $Al^{3+}$.....+12
6$OH^-$.....-6

Charge Net.....0

# $Q^3$: Clay Minerals (phyllosilicates)

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

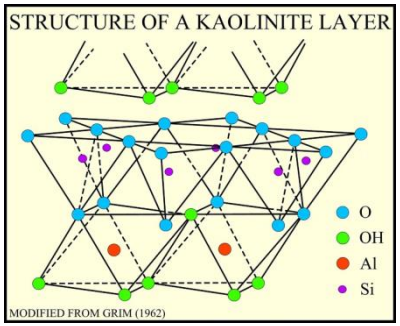
http://www.guptagrinding.com/kaolin-powder.htm

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

→ The unit cell is **triclinic**, with **a=5.15Å**, **b=8.95Å** and **c=7.39Å**.

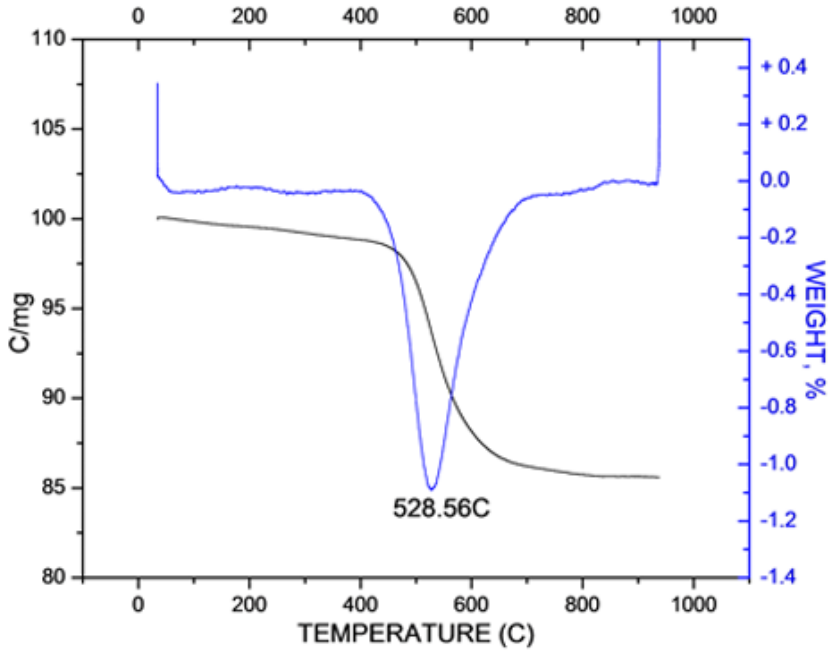
# $Q^3$: Clay Minerals (phyllosilicates)

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




**Kaolinite**

**DSC, TGA**




http://www.opticon1826.com/articles

→ A **small endothermic peak** occurs at about **100ºC**, caused by the evolution of **adsorbed water**.

→ At about **500ºC** 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 **1000ºC**, and is associated with a **recrystallization** process.

# $Q^3$: 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 α- and β-angles, though the γ-angle is still 90 ° 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 **$Al_2Si_2O_5(OH)4_2H_2O$**.

→ The **extra $2H_2O$** in hydrated **halloysite increases the c-dimension** by about **2.9Å**.

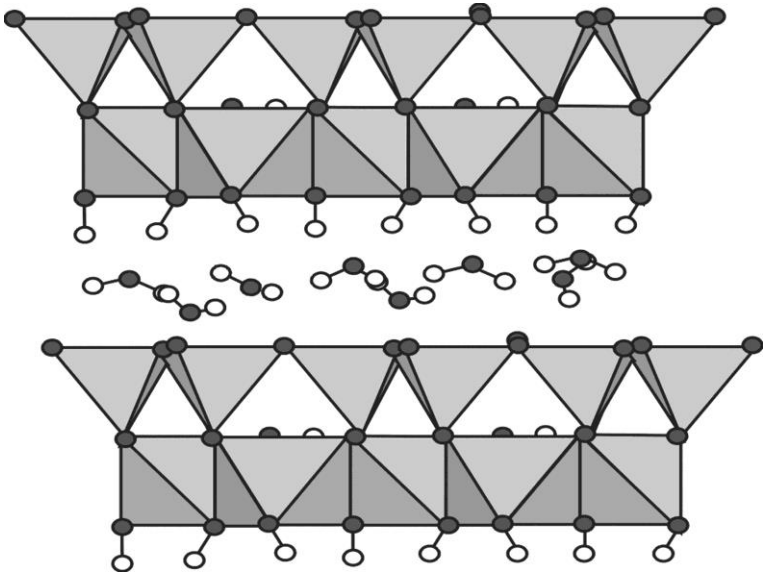
→ **Halloysite** is an **expanding type sheet silicates;** as the water is incorporated into the structure the mineral increases its volume.

# $Q^3$: Clay Minerals (phyllosilicates)

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

### Halloysite

Expanding type sheet silicate



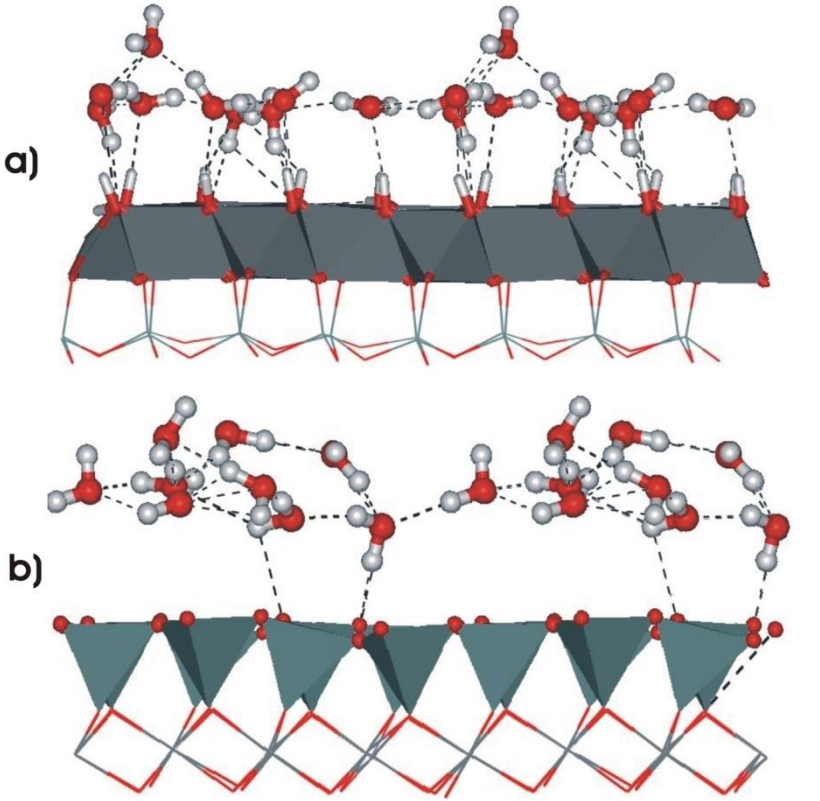



**Figure1.** Distribution of the monomolecular water layer on the a) octahedral and b) tetrahedral surfaces of the kaolinite layer.

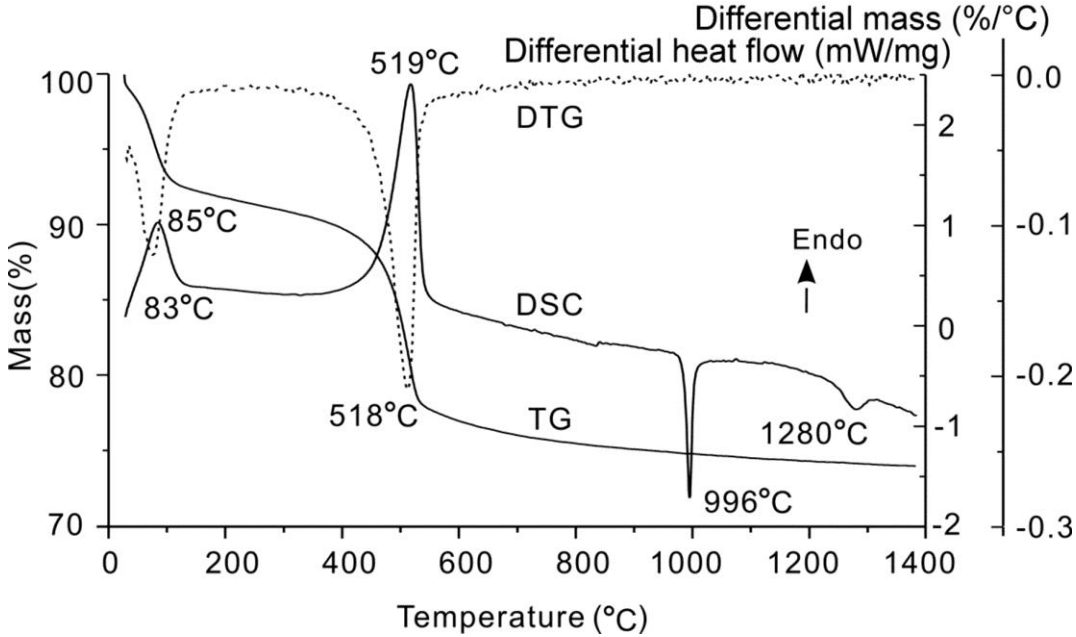
http://www.univie.ac.at/qccd/hpsc/2003/Tunega/report2003.html

Expanding type sheet silicate

# $Q^3$: Clay Minerals (phyllosilicates)

**Halloysite**

**DSC, TGA**




→ The **halloysite** starts **loosing water at temperatures above 60 °C** and eventually is converted to the meta form.

→ Compared to kaolinite, there is **an additional endothermic peak at 150ºC**, due to the **huge loss of water**.

→ The **main endothermic peak** for halloysite occurs, as for kaolinite, at around **600ºC**.

→ There is also the **exothermic peak**, as for kaolinite, at **1000ºC**.

# $Q^3$: 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**, $Al_2Si_4O_{10}(OH)_2$, and **talc**, $Mg_3Si_4O_{10}(OH)_2$. **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.

# $Q^3$: Clay Minerals (phyllosilicates)

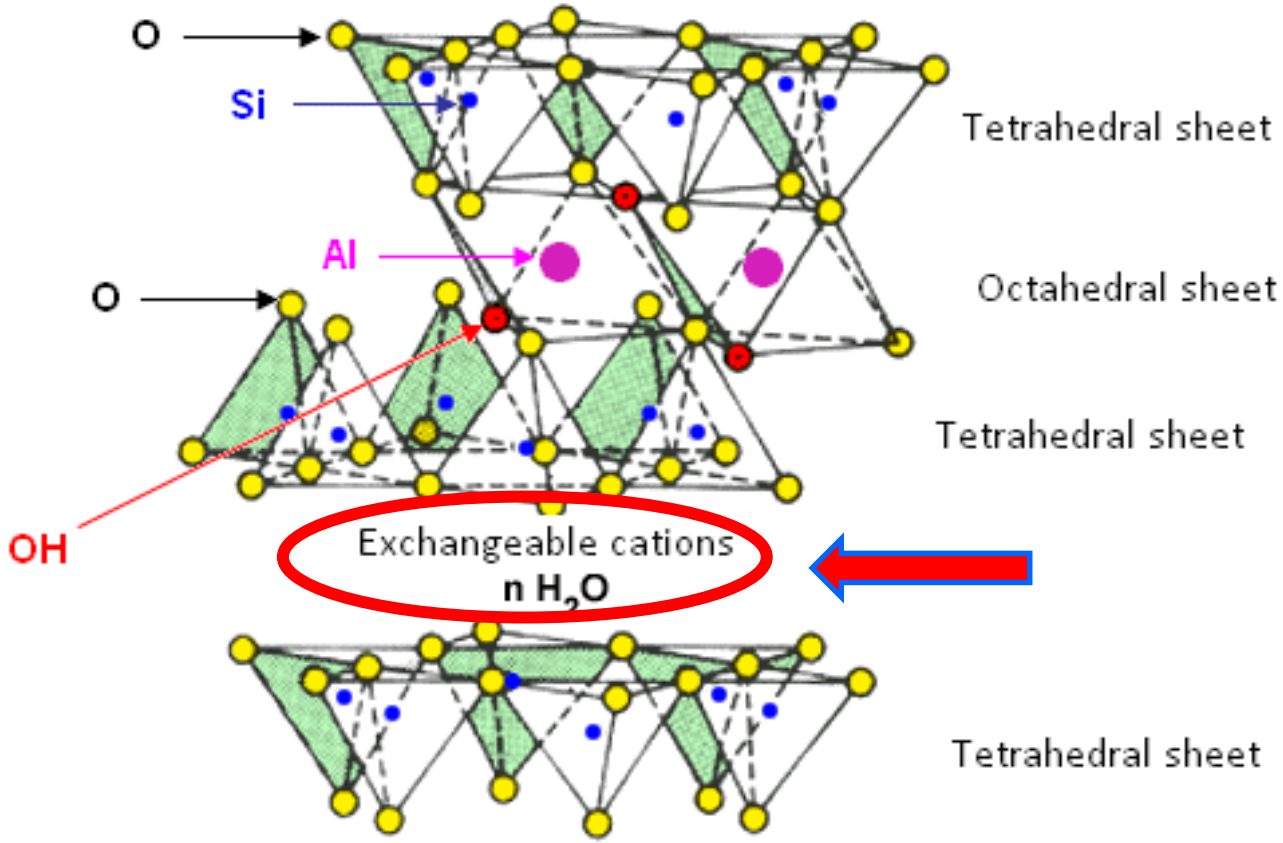
## The montmorillonite-type group (2:1)

→ 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 litium**; 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.

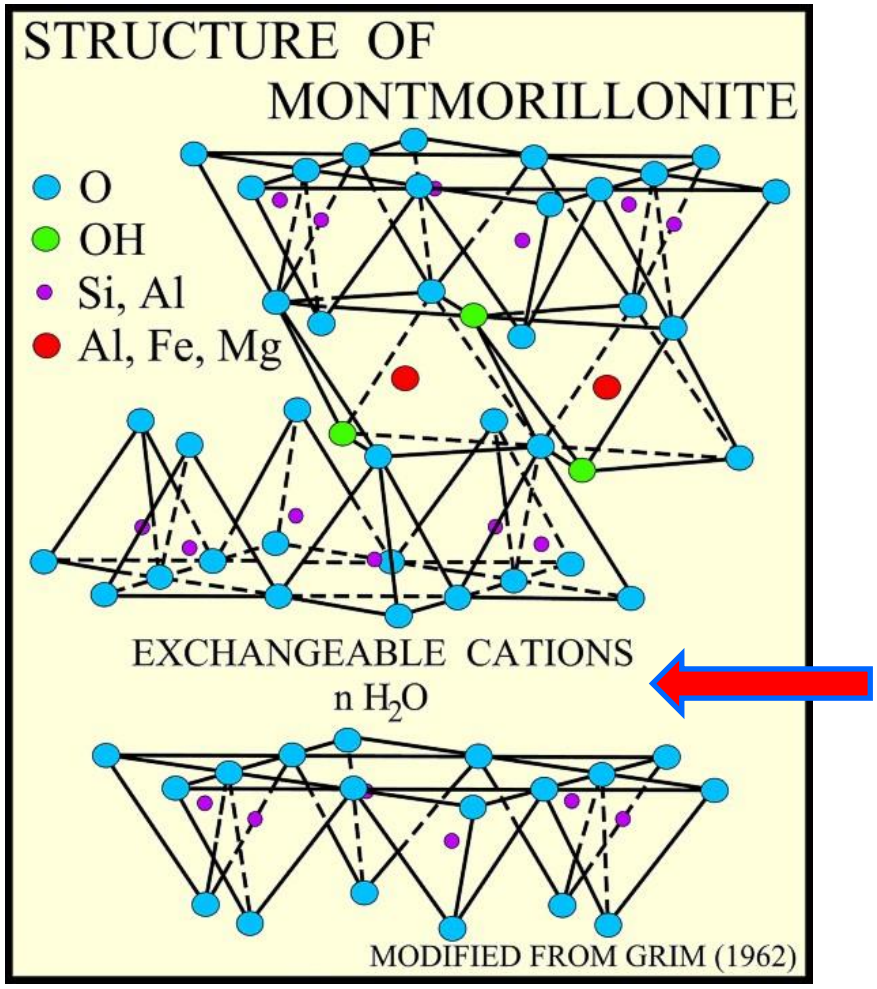
# $Q^3$: Clay Minerals (phyllosilicates)

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



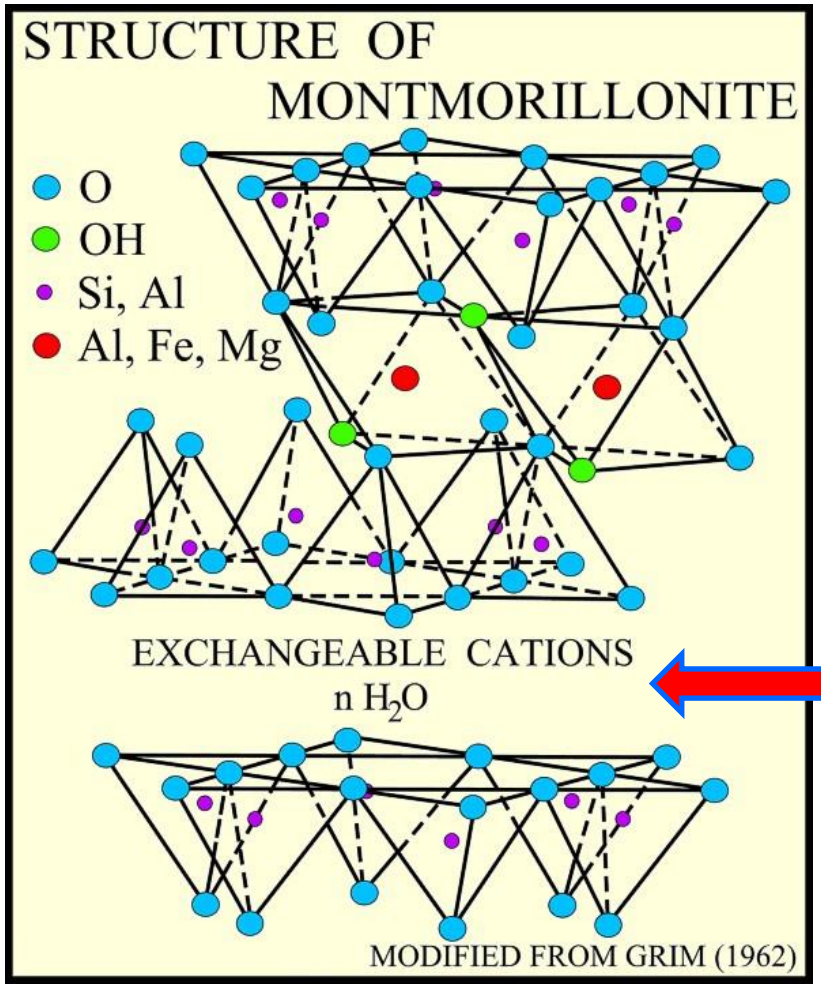
# $Q^3$: Clay Minerals (phyllosilicates)

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



# $Q^3$: Clay Minerals (phyllosilicates)

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




Montmorillonite
layer charge balance

6 $O^{2-}$.....-12
~~4~~ $Si^{4+}$, $Al^{3+}$.....~~+~~16

4 $O^{2-}$, 2 $OH^-$ .....-10
$Al^{3+}$, $Mg^{2+}$, $Fe^{2+}$, $Li^+$...~~vary~~
4 $O^{2-}$, 2 $OH^-$.....-10

6 $O^{2-}$.....-12
~~4~~ $Si^{4+}$, $Al^{3+}$.....~~+~~16

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

# $Q^3$: 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**.

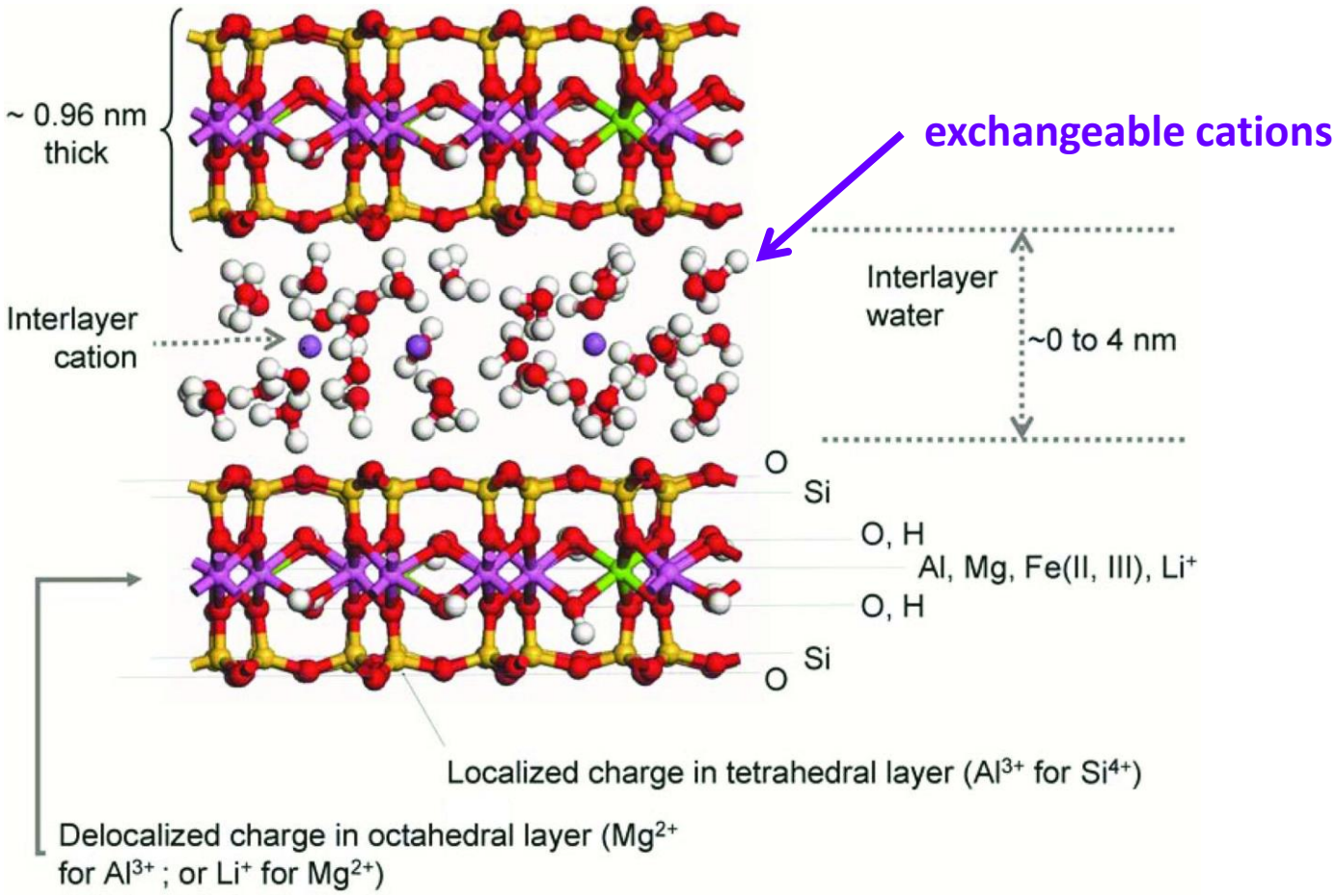
→ The unit layers can be forced apart by water and other polar liquids, causing the **basal spacing** (the perpendicular distance between equivalent planes) **to vary from about 10 to 15 Å for water**.

→ The structural formula is $Al_2Si_4O_{10}(OH)_2$.

# $Q^3$: Clay Minerals (phyllosilicates)

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

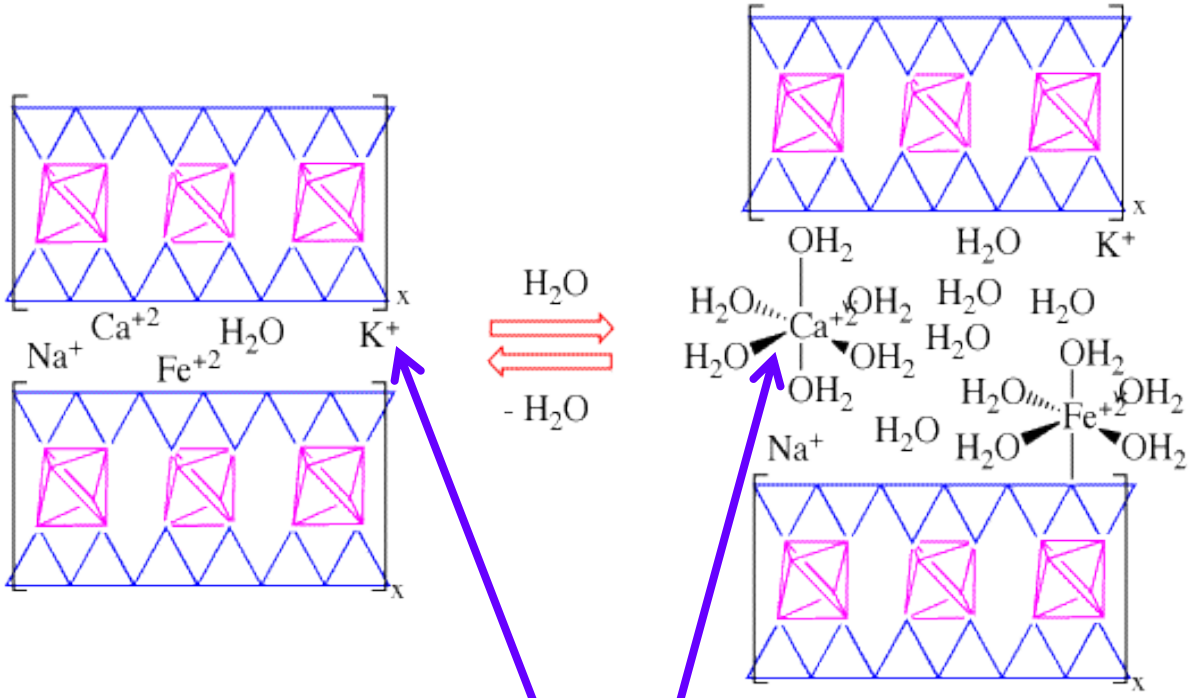
Expanding type sheet silicate



# $Q^3$: Clay Minerals (phyllosilicates)

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

Expanding type sheet silicate



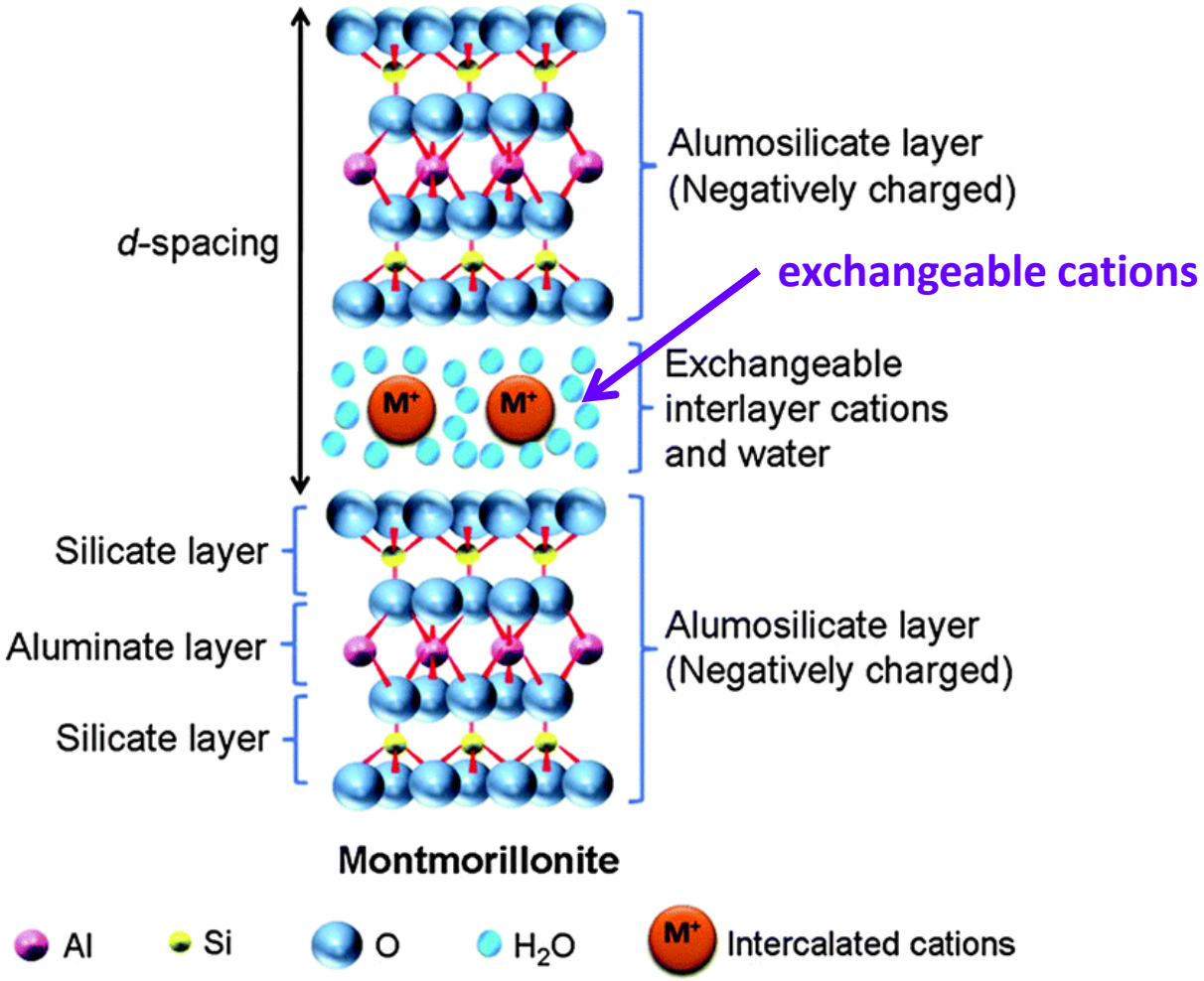

exchangeable cations

Expanding type sheet silicate

# $Q^3$: Clay Minerals (phyllosilicates)

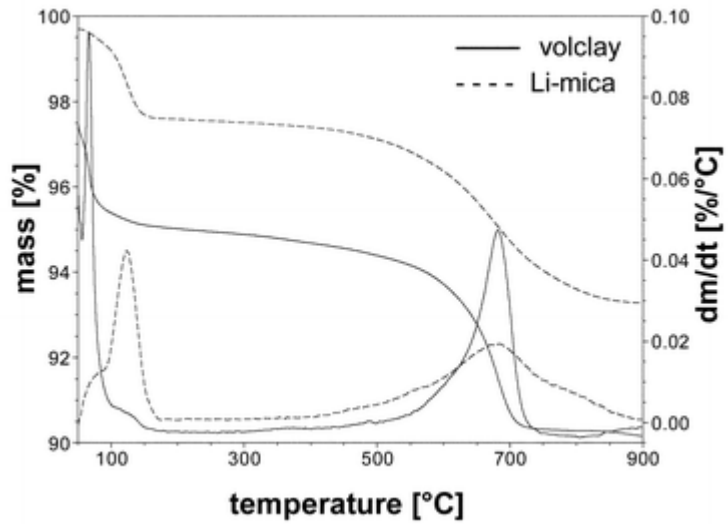
## The montmorillonite-type group (2:1)

Expanding type sheet silicate



# $Q^3$: Clay Minerals (phyllosilicates)

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




**DOI:** 10.1039/B302331A

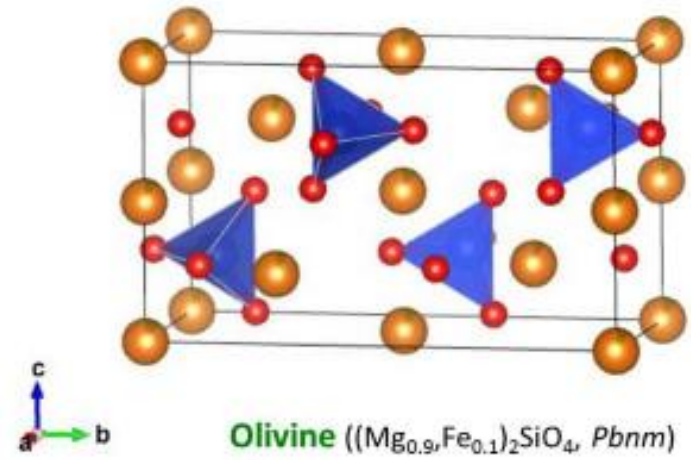
→ The **montmorillonite** all have in common a **large endotherm** at about **150ºC**, corresponding to the evolution of inter-layer water and water associated with exchangeable cations. The peaks varies in size and shape according to the nature of the cations and the lattice substitutions.

→ The **main endotherm**, corresponding to the **thermal decomposition of the mineral**, occurs at about **700ºC** and there is a **final exotherm** at about **1000ºC** as for kaolinite.

→ **Multiple low-temperature peaks** have also been reported around **150 to 200ºC**, for montmorillonites saturated with various cations, corresponding to partly hydration of the surface and partly to hydration of the cations.

# ADITIONAL INFORMATION

# $Q^0$: Island Structures (orthosilicates)



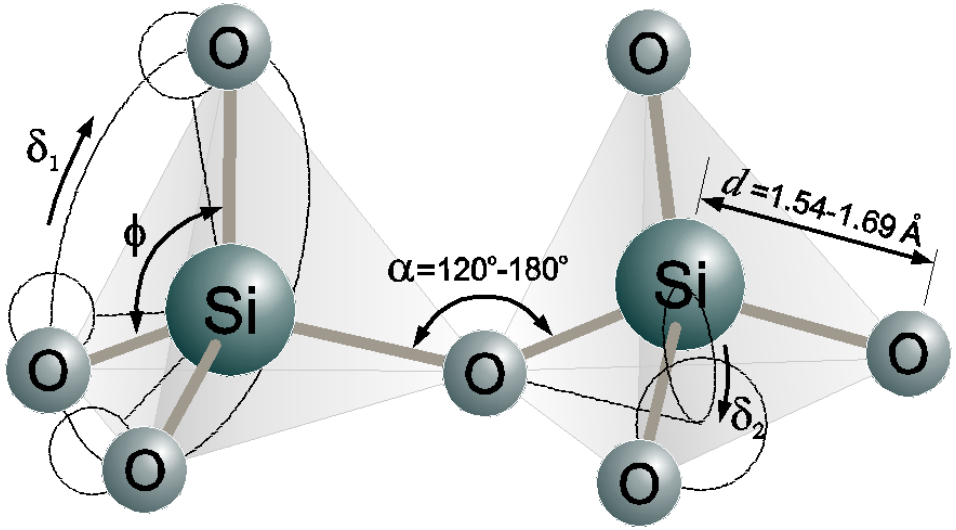

Olivine ($(Mg_{0.9},Fe_{0.1})_2SiO_4$, *Pbnm*)

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

→ In **olivine**, **neutrality** is achived by **metallic cations** (principally **Fe** and **Mg**) being attached to the four oxygen ions of the $[SiO_4]^{4-}$.

→ A complete crystal of olivine contains a very large number of $SiO_4$ units with their appropriate cations; it forms a **continuous network** because each atom is shared by two or more other atoms.

# $Q^1$: Group Structures (sorosilicates)

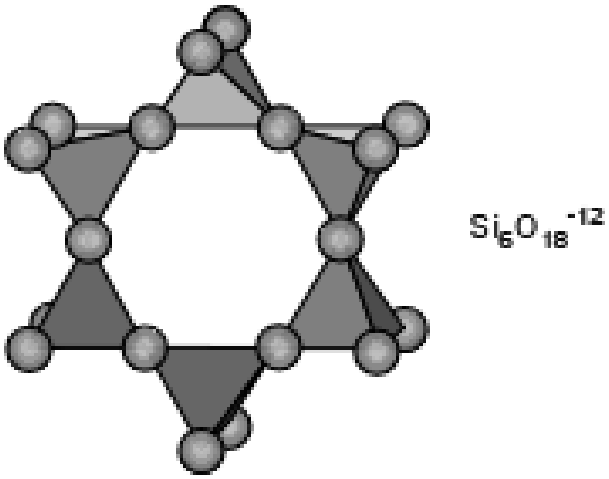




## Beryl or emerald

→ Instead of all the free oxygen valancies 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 **$Si_2O_7$**. Minerals of this type are rare (ex. **beryl** or **emerald**, with the formula **$(Be_3Al_2)Si_6O_{18}$)**.

# $Q^2$: Group Structures (cyclosilicates)



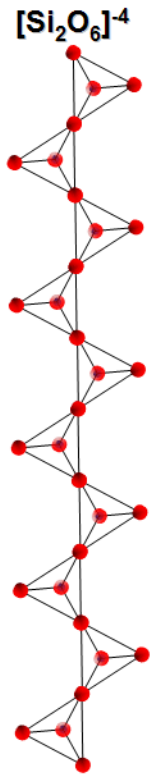

## Cordierite

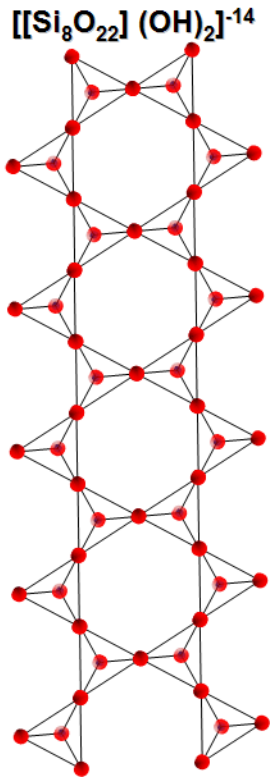
→ Instead of all the free oxygen valancies being satisfied by metallic cations, **two or more silica tetrahedra** may be **joined**, **corner to corner**, to form a group structure.

→ Six units can be linked to form a ring structure, where the basic structure is $Si_6O_{18}^{12-}$. An example is mineral **cordierite**, $Al_3Mg_2(Si_5Al)O_{18}$, where one of the six silicons in the ring has been isomorphous substituted by an aluminium ion. The substitutiton of $Al^{3+}$ for $Si^{4+}$ upsets the charge balance, being the neutrality maintained by increasing the ratio of trivalent to divalent cations.

# $Q^2$-$Q^3$ : Chain Structures (inosilicates)

**Pyroxenes** $Q^2$



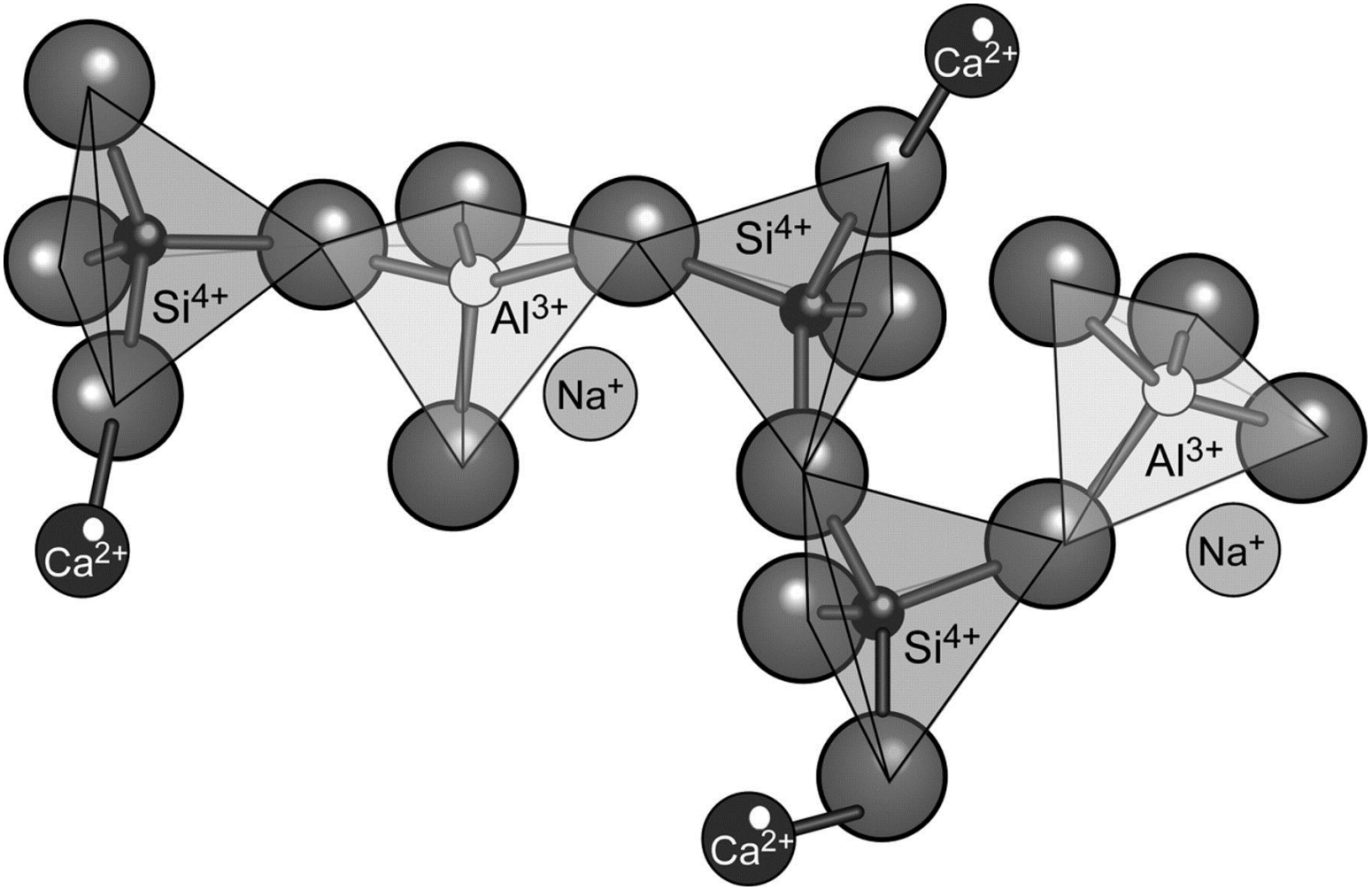

$Q^2$-$Q^3$ **Amphiboles**

→ By joining na 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 $SiO_3^{2-}$ as the repeated group while **amphiboles** have the $SiO_4O_{11}^{6-}$ group.

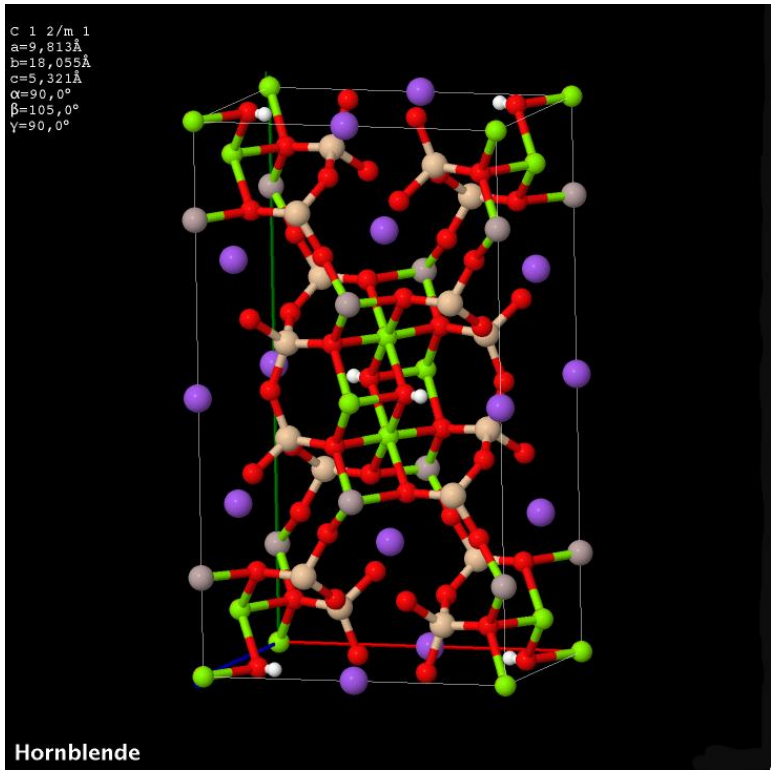
→ Owing to their chain structure, the piroxenes and amphiboles are fibrous, **asbestos like minerals**.

# $Q^2$-$Q^3$: Chain Structures (inosilicates)



# $Q^2$-$Q^3$: Chain Structures (inosilicates)

**Hornblende**




→ **Hornblende**, a naturally occuring amphibole found in igneous rocks, has the generaL formula **$(Ca, Na, K)_{2\text{-}3}(Mg, Fe, Al)_5(Si,Al)_2Si_6O_{22}(OH)_2$**. As the formula implies, many varieties and degrees of substituion occur in this mineral.

# $Q^3$: Clay Minerals (phyllosilicates)

https://commons.wikimedia.org/wiki/File:Nacrite_-_Mineralogisches_Museum_Bonn2.jpg

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

→ 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°**.

→ 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**.

# $Q^3$: Clay Minerals (phyllosilicates)


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

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

→ 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° but is equal to **96.8 °**.

→ In the unit cell, **$\alpha=\gamma=90$ °** and **a=5.15 Å**, **b=8.95 Å** and **c=14.4 Å**.

→ There are thus two kaolin units in each unit cell, the latter being **monoclinic**.

# $Q^3$: Clay Minerals (phyllosilicates)

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

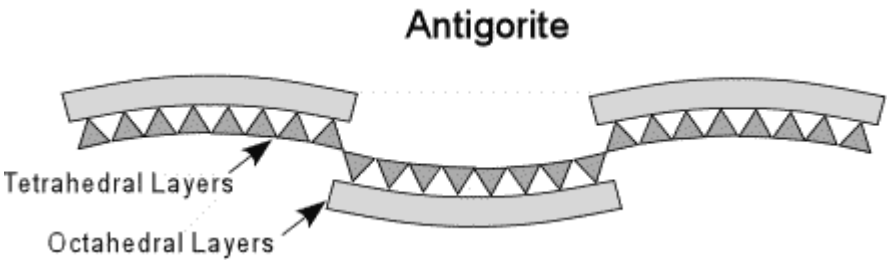
→ The **serpentine group** of minerals have a structure consisting of a **silica sheet** condensed with a **brucite sheet**, with the unit formula $Mg_3Si_2O_5(OH)_4$. This group is clearly **trioctahedral**, this being possible because three atoms of divalent magnesium carry only the same charge as 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.

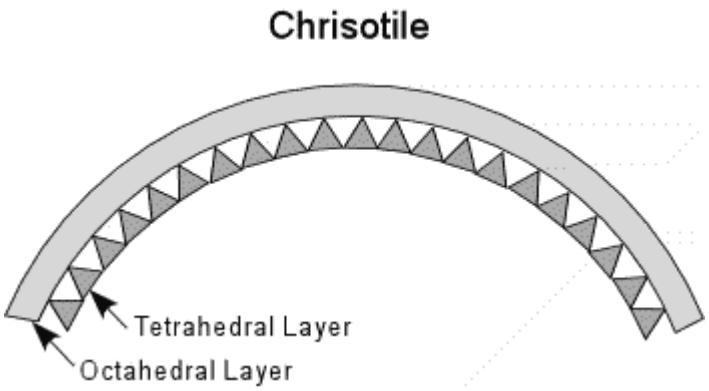
# $Q^3$: Clay Minerals (phyllosilicates)

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

→ The **serpentine group** of minerals has the formula - $Mg_3Si_2O_5(OH)_4$. 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



# $Q^3$: Clay Minerals (phyllosilicates)

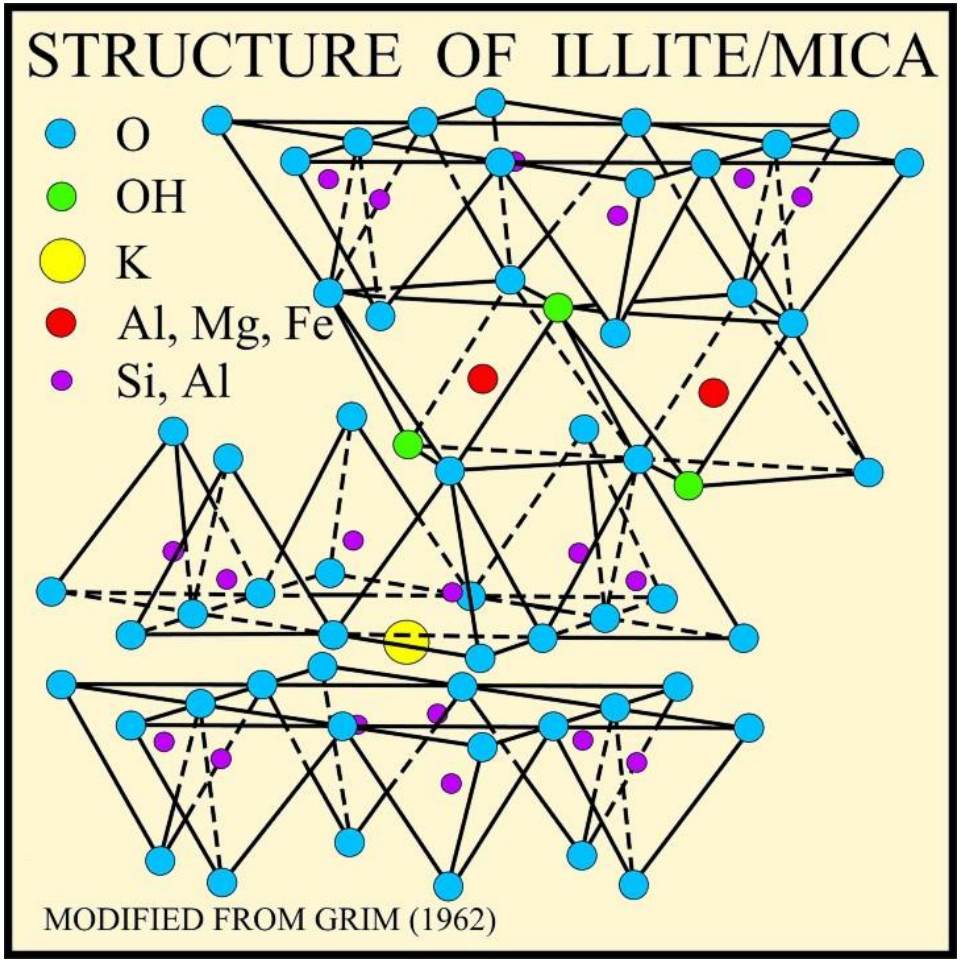

## The mica-type group (2:1)

→ 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** $Al_2Si_4O_{10}(OH)_2$, we substitute one whole atom of Al for a Si atom in the tetrahedral layer, to form the negatively charged unit $Al_2(Si_3Al)O_{10}(OH)_9^{22-}$. Let the charge deficiency now be balanced by one atom of potassium, and we arrive at potash mica or muscovite, $K.Al_2(Si_3Al)O_{10}(OH)_2$, or as it frequently written $KAl_3Si_3O_{10}(OH)_2$.

→ 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.

# $Q^3$: Clay Minerals (phyllosilicates)

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




Layer charge balance

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Charge Net

# $Q^3$: Clay Minerals (phyllosilicates)


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

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 depicted as consisting of a brucite-like layer (with some Al) sandwiched between tetrahedral layers that are similar to phlogopite.

# $Q^3$: Clay Minerals (phyllosilicates)

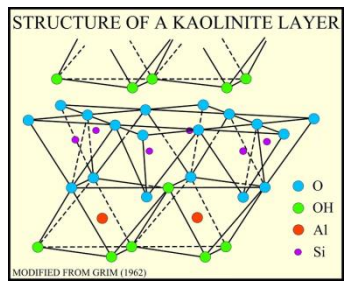
→ If we start with the **gibbsite** and **brucite** structures, and **replace 2 of the OH ions with O**, where the Oxygens are now the apical Oxygens of the SiO2 tetrahedral sheets, then we get:

**dioctahedral layer,** $Al^{+3}$

(**trioctahedral layer**, $Mg^{+2}$)

→ **Kaolinite**

**1:1**

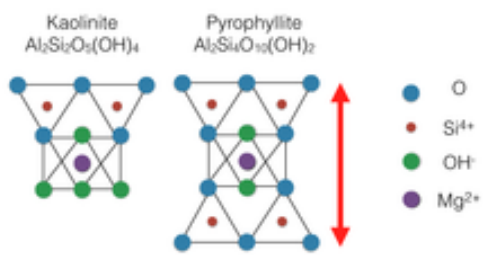



→ **Lizardite**

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

→ **Pyrophyllite**

**2:1**




→ **Talc**

# $Q^3$: Clay Minerals (phyllosilicates)

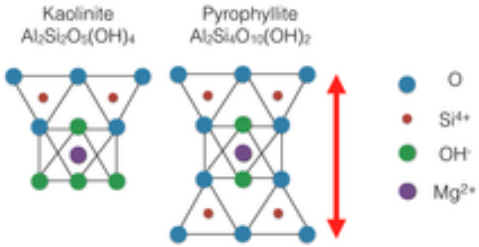
**dioctahedral layer,** $Al^{+3}$

(**trioctahedral layer**, $Mg^{+2}$)

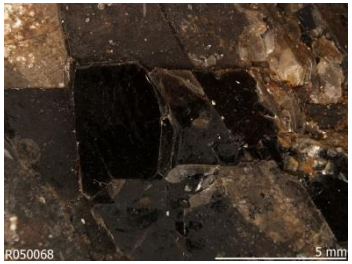
→ If in the pyrophyllite or talc minerals, an $Al^{+3}$ is substituted for every 4th $Si^{+4}$ in the tetrahedral layer, this causes an excess -1 charge in each T-O-T layer. To satisfy the charge, $K^{+1}$ or $Na^{+1}$ can be bonded between 2 T-O-T sheets in 12-fold coordination.

**2:1**

→ **Muscovite**


→ **Phlogopite**




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

→ **Margarite**


**2:1**

→ **Clintonite**

# $Q^3$: Clay Minerals (phyllosilicates)

## Expanding type sheet silicate

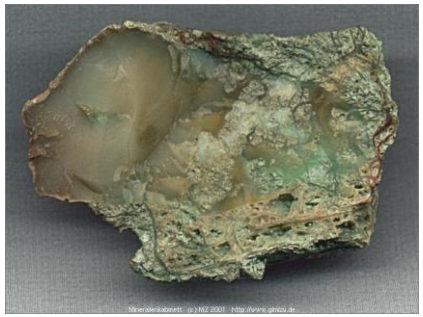
→ **Halloysite** is an **expanding type sheet silicates;** as the water is incorporated into the structure the mineral increases its volume.

→ 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.shtm

**Halloysite**

**smectite**



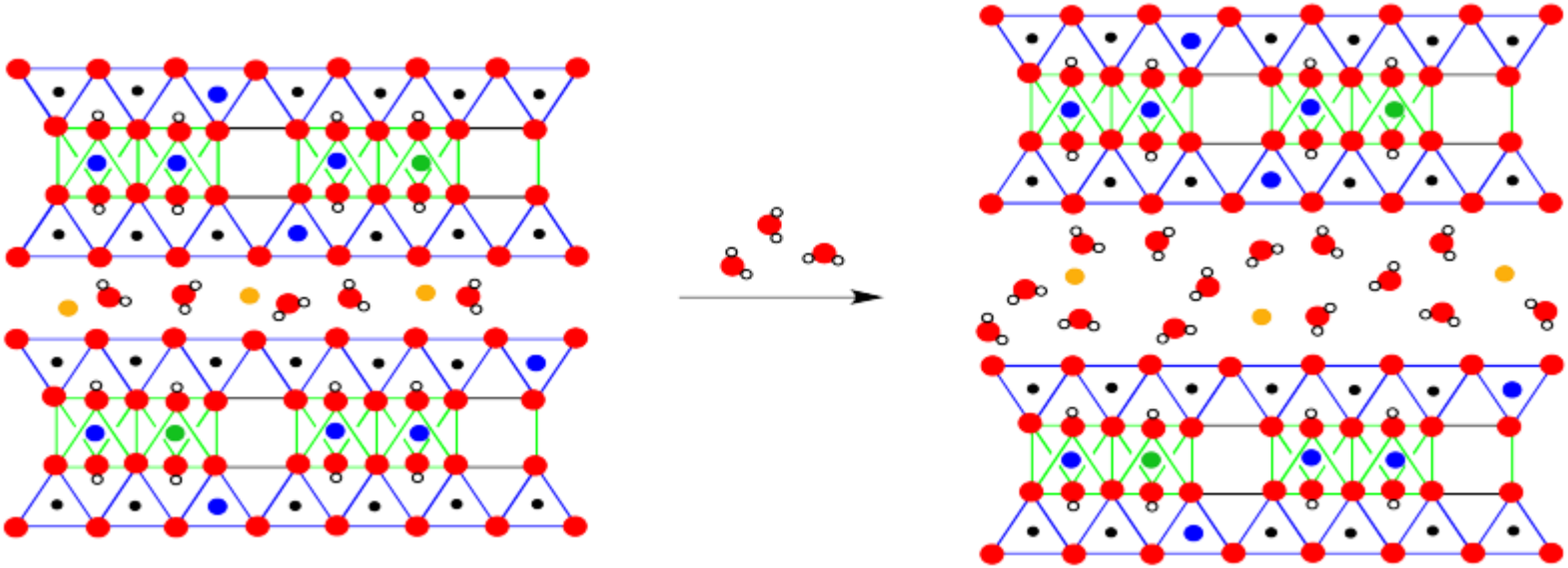
http://www.gimizu.de

**vermiculite**

# $Q^3$: Clay Minerals (phyllosilicates)

## Expanding type sheet silicate

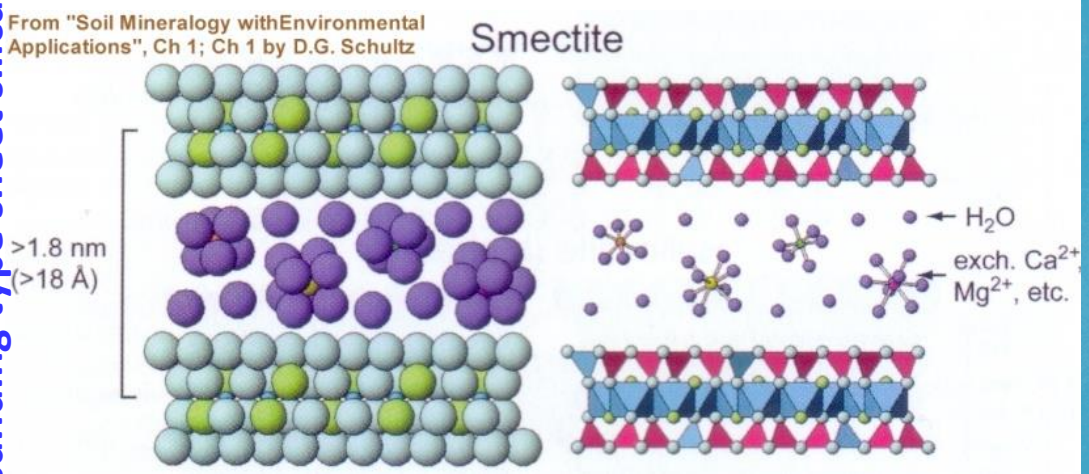
Expanding type sheet silicate

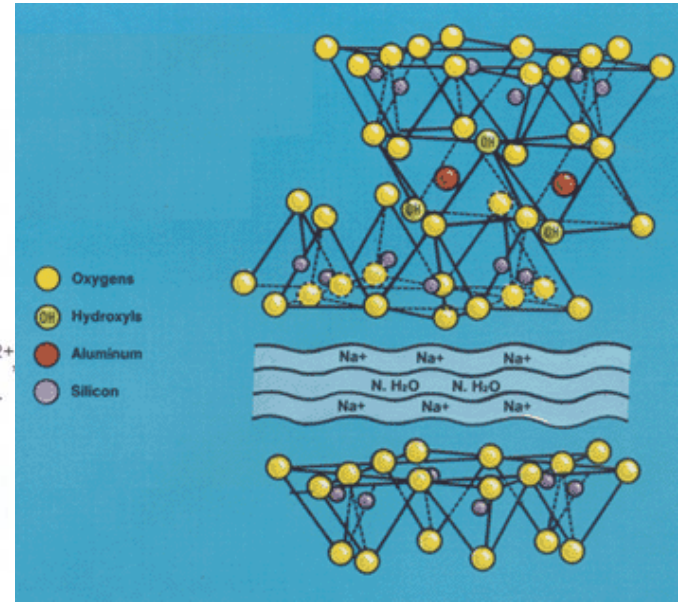


# $Q^3$: Clay Minerals (phyllosilicates)

## Expanding type sheet silicate

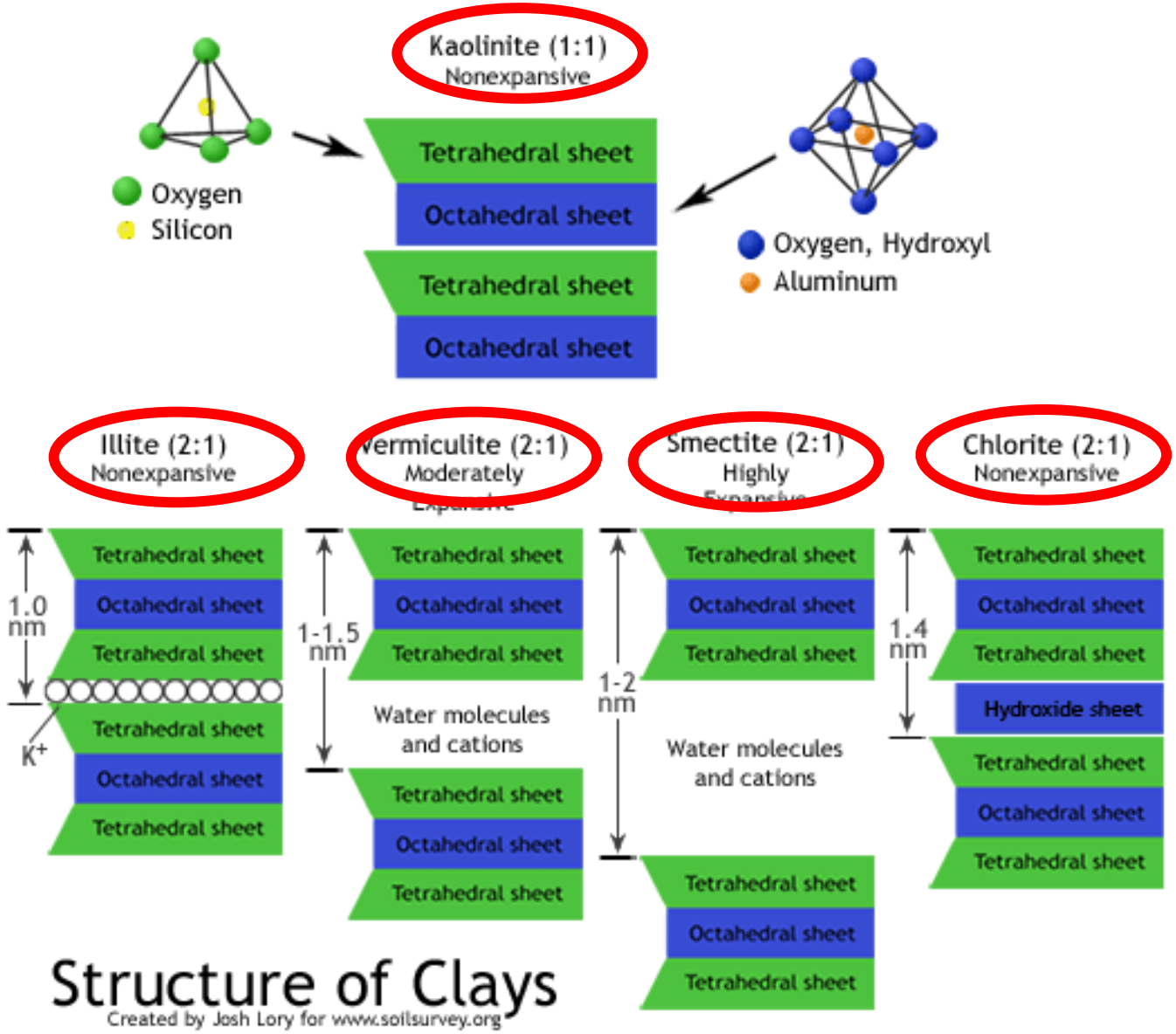
Expanding type sheet silicate



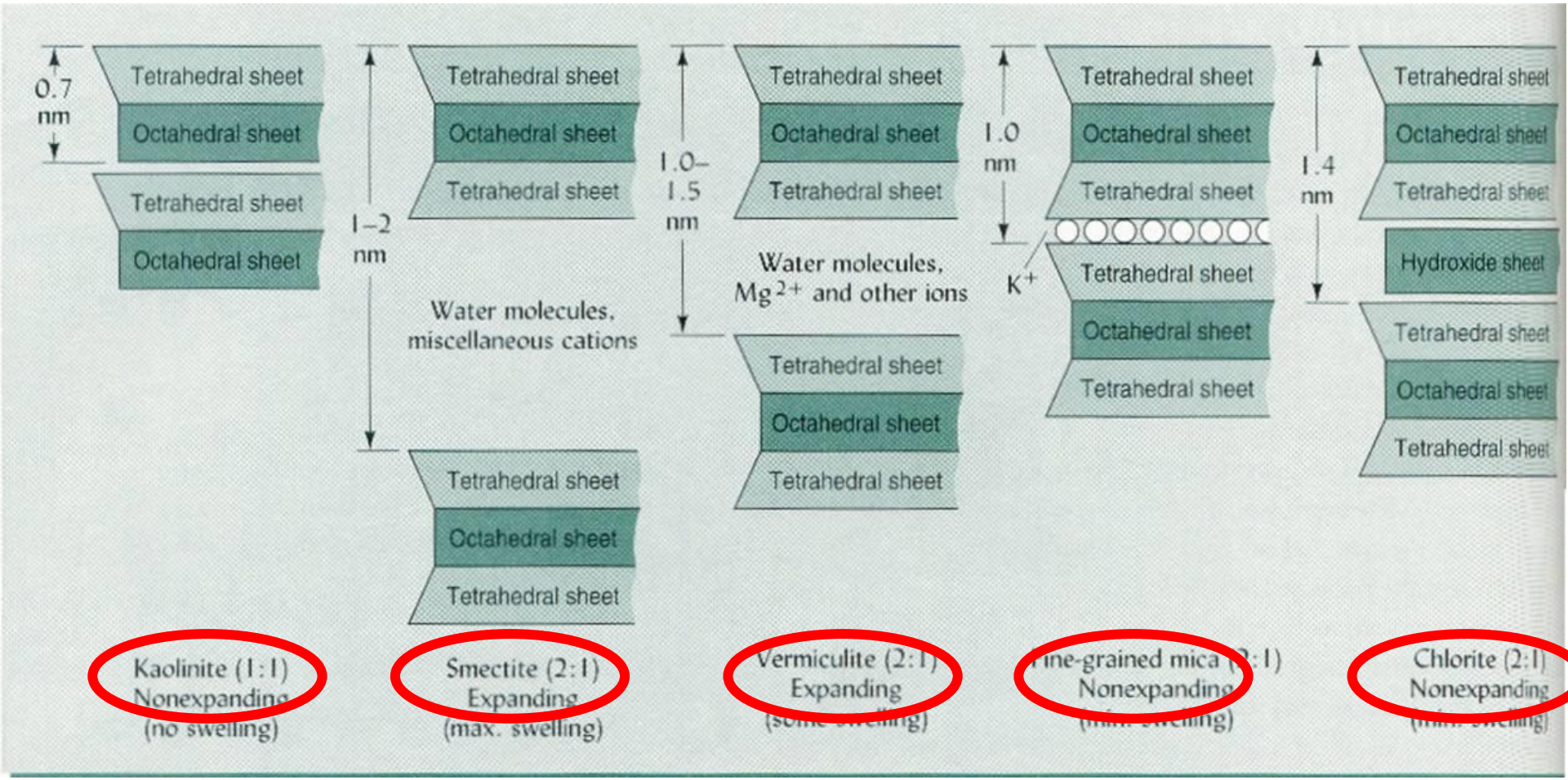




Expanding type sheet silicate

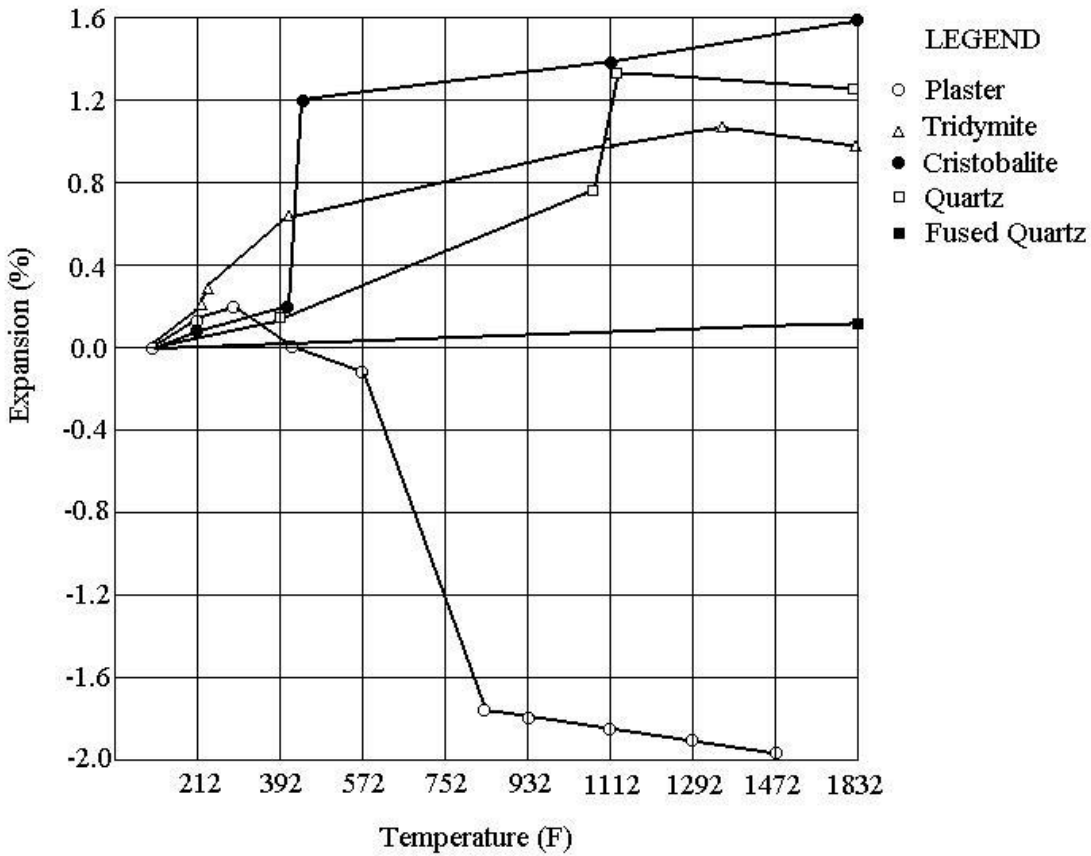
# $Q^3$: Clay Minerals (phyllosilicates)



# $Q^3$: Clay Minerals (phyllosilicates)



# $Q^4$: Quartzites and Sands (tectosilicates)

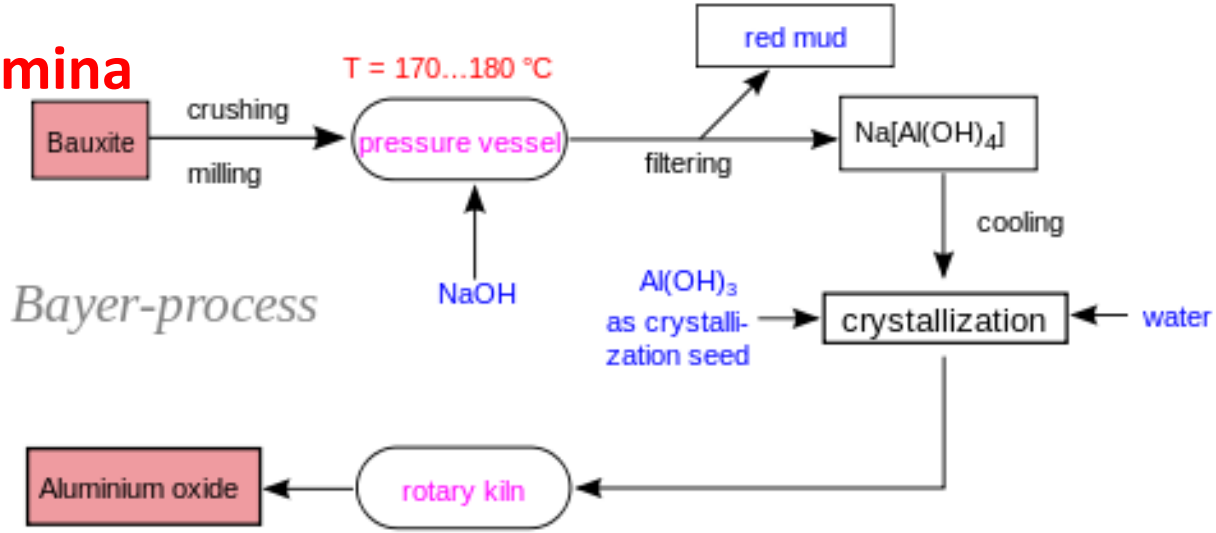


# *Other oxides*

# Other oxides

| Oxide | Density (g/cm3) | Melting Point (ºC) | Resistivity 225ºC | (Ω.cm) 1000ºC |
|---|---|---|---|---|
| BeO | 3.01 | 2570 | $10^{14}$ | $10^{8}$ |
| MgO | 3.57 | 2840 | $10^{14}$ | $10^{7}$ |
| CaO | 3.32 | 2580 | $10^{14}$ | $10^{6}$ |
| $Al_2O_3$ | 3.99 | 2050 | $10^{14}$ | $10^{8}$ |
| $Y_2O_3$ | 4.50 | 2450 | ------ | ----- |
| $ZrO_2$ | 5.56 Mon. 6.10 Tetr. | 2680 | $10^{11}$ | 10 |
| $HfO_2$ | 9.68 Mon. 10,0 Tetr. | 2900 | ----- | ----- |

# Alumina




**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 mm. Then they are processed with sodium hydroxide in an autoclave at a pressure of 40 bars and a temperature of about 250ºC. A sodium solution is formed dissolving the alumina hydrates as aluminates. Iron oxide, titanium oxide and $SiO_2$ 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 rotaty klin.

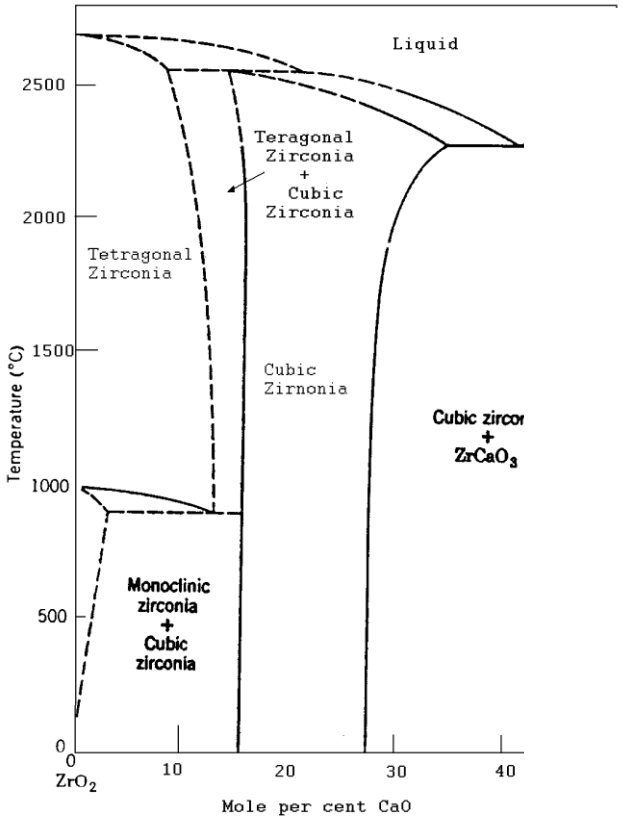
# Zirconia

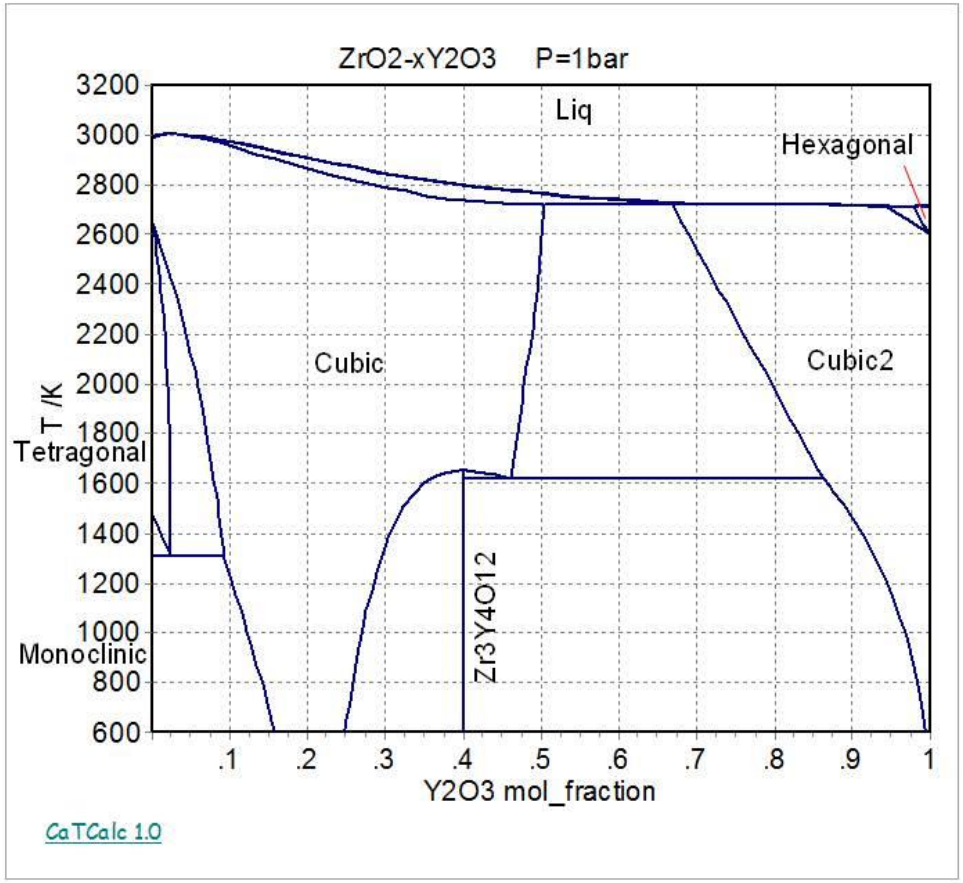
**Zirconia** is another interesting oxide. $ZrO_2$ shows particularly problematic properties. Depending on T, it suffers allotropic transformations, partly causing big volume changes. At slightly above 1000ºC the low T form changes to high T phase. This may occur during sintering! Normally this occurs 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 yttrea** is added, which causes a solid solution formation, avoiding the zirconia phase allotropic phase transformation.

# Zirconia




MDT 2011

ZrO2-Y2O3 縦断面図

# 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)
- **An Introduction to Ceramics and Refractories**, A. O. Surendranathan, CRC Press (2014)
- **Handbook of Advanced Ceramics**. S. Somiya, N. Claussen, K. Uchino, M. Kaneno, F. Aldinger, R. M. Spriggs, K. Koumoto. Academic Press (2003)
- **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