FACULTY OF SCIENCE,QENA
كلية العلوم بقنا

جامعة جنوب الوادى

اسم المقرر: مقرر خاص - رابعة شعبة جيولوجيا

كود المقرر : ٤١١ج

الفصل الدراسى الأول

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Special Course (Clay Mineralogy)

By:

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GEOLOGY OF CLAYS

- Clays occur under a limited range of conditions in geological space [time & temperature (correlated with depth)].
- They are mainly found at the surface of the earth.
- Their origin is mostly initiated in the weathering environment (at rock-atmosphere interface).
- Some clays form at the water-sediment interface (at deep sea or lake bottom).

GEOLOGY OF CLAYS

- A smaller number of clays form as a result of the interaction of aqueous solutions and rocks, either at some depth in the sedimentary sequence or in the late stages of magmatic cooling (hydrothermal alteration).
- Hydrothermal alteration often leads to the accumulation of useful heavy metals, such as gold, tungsten and uranium.
- The extensive alteration of rocks due to hydrothermal alteration can produce ***pure clay deposits*** which are of economic interest, e.g. clays for ceramics.

WHY CLAYS FORM

- Most clays are the result of the interaction of aqueous solutions with rocks.
- The dissolution and recrystallization which occur at this reaction is the process by which clay minerals are formed and transformed.
- The proportion of water, compared to that of the interacted solids (rocks), determines **the rate and type of chemical reaction** **and ultimately the type of the formed clay mineral.**

WHY CLAYS FORM

- Dissolution is the first step of most water-rock interactions.
- The greater the renewal of the water input (rain or fluid circulation) the more dissolution will occur.
- As the ratio of water to rock approaches ***ONE***, the reactions are more and more dominated by incongruent dissolution, in which **certain elements go into solution** and **others remain in the solid state in the skeleton of the altered rock.**

WHY CLAYS FORM

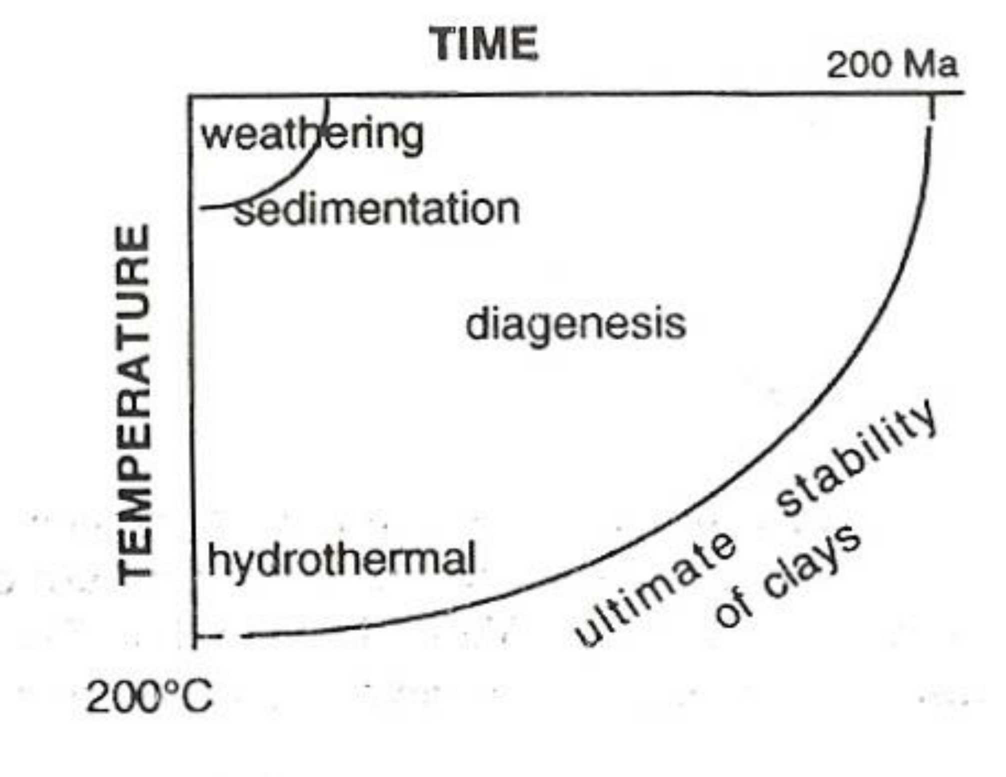
- The new solid are generally ***clay minerals.***
- They are hydrated, and they have a ***special physical structure*** which is very different from that of the pre-existing minerals which reacted with the aqueous solution.
- The newly formed minerals (clay minerals) have a **greater volume** due to their hydration than the original minerals.
- The formation of clays results in an aggregates of lower density than the initial rock minerals.

WHERE CLAYS FORM

- The clay environment is limited to a certain range of temperatures and limited in time.
- The stability of most clays is attained at the surface of the earth (i.e., the upper several hundreds of meters of the earth’s crust).
- When temperatures exceed 50 to 80°C the clays become unstable and they begin to change into other minerals, either other clay minerals or different mineral structures such as micas, feldspars, etc..

WHERE CLAYS FORM

- The range of origin and evolution of clay and its stability in time and temperature coordinates is given in the following figure.



WHERE CLAYS FORM

- The rate of change of clay is dependent upon temperature.
- The higher the temperature, the faster the change.
- In geological situations, the rapid heating occurs during magma intrusion within country rocks or when lava spills out onto the earth's surface.
- Tectonic events can produce fractures and thereby introduce hot hydrothermal fluids. These fluids heat the rocks locally at approximately the same rates as the intrusion of magma.

WHERE CLAYS FORM

- Such events are rapid, and ***they create unstable minerals assemblages*** due to the high rate of thermal and induced chemical change.
- Such assemblages are highly localized in the Earth's crust.
- **By contrast**, the normal sequence of sedimentation and burial, the formation of sedimentary rocks from clay rich sediments, take several millions or hundreds of millions of years.

WHERE CLAYS FORM

- After the creation of clays at very surface of the earth and beginning their migration shortly after their formation by river transport, eventually reaching large bodies of water such as littoral ocean environment.

CLAY FORMATION
(THE CHEMICAL NECESSITY)

- The origin of clays is found in the interaction of silicate mineral rocks & water.
- This indicates not only that clays are hydrous but also that clays are more hydrous than the minerals in most rocks.
- The overall reaction of **Rock + Water → Clay**

  is the reasonable starting point
- The mechanism by which water "hydrates" silicate minerals that of **hydrogen exchange.**

CLAY FORMATION

(THE CHEMICAL NECESSITY)

- Most clay minerals contain **(OH) molecules** which have a specific role in the mineral structure.
- The chemistry of the hydration mechanism is one of exchange of hydrogen ions instead of cations, such as:

Feldspars + hydrogen ions → Clay (kaolinite) + Cations + Solids (Silica) + water.

$$2KAlSi_3O_3 + 6H^+ \rightarrow Al_2Si_2O_5(OH)_4 + 2K + 4SiO_2 + H_2O$$

CLAY FORMATION

(THE CHEMICAL NECESSITY)

- The reaction produces *clays* and other minerals.
- Silica is a common by-product of hydration reactions, it can go into aqueous solution or it can form a solid phase such as **"quartz" or "amorphous silica".**
- The chemistry of the reverse (dehydration mechanism) can be written as:

Clay (Kaolinite) → Aluminosilicate + Qz + water

$$\mathbf{Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_5 + SiO_2 + H_2O}$$

CLAY FORMATION
(THE CHEMICAL NECESSITY)

- However, part of the material of the initial anhydrous mineral from which the clay forms is lost to the altering solution.
- The altering aqueous solution finds its way, most often, into the ocean where there is large amounts of dissolved ions derived from the alteration of silicate minerals into clay minerals.
- The ions of greatest in abundance are **Na, K and Ca**

CLAY FORMATION

(THE CHEMICAL NECESSITY)

- The chemical necessity of exchange of hydration for mobile mono-and di-valent ions **is the motor of clay formation at the Earth's surface.**
- Also, the process operates at different rates under different climatic conditions.
- This process is very often not fully achieved before erosion strips off the partially reacted material.
- The sediments are most often a mixture of different phases in different states of chemical equilibrium with each other.

CLAY FORMATION
(THE CHEMICAL NECESSITY)

- The amount of chemical change is governed by two determinant factors in the reaction rate:

time & temperature

- The higher the temperature, the faster the reaction proceeds and the lower the temperature, the slower the reaction.

- The range of temperatures in which clays form is from 4°C (ocean bottom) to approximately 400°C (under short thermal pulses during hydrothermal alteration).

CLAY FORMATION
(THE CHEMICAL NECESSITY)

- The time spans can range from hours **(laboratory experiments and intrusions)** to hundreds of millions of years **(burial diagenesis).**
- The process of hydration of solids and clay formation occurs at the earth’s surface, but it is slow

COMPOSITION & MINERALOGY OF CLAY MINERALS

COMPOSITION & MINERALOGY OF CLAY MINERALS

- Clay minerals were initially defined on the basis of their crystal size.

- They were determined as the minerals whose particle diameters were **less than 2 µm.**

- **Previously,** the clay minerals were could not be dealt with , but the advent of reliable X-ray diffractometers allow one to distinguish between the different mineral species found in the < 2 µm grain size fraction.

- Today we know much more about clay mineral XRD properties.

COMPOSITION & MINERALOGY OF CLAY MINERALS

- **Clays are physically & chemically active.**
- **They combine with water to make pastes, slurries & suspensions, by attracting water molecules to change their effective physical particle size.**
- **Clays take various chemical substances (ions or molecules) onto their surfaces or into the inner parts of their structures.**
- **So, becoming chemical agents of transfer or transformation.**

COMPOSITION & MINERALOGY OF CLAY MINERALS

- Clays can easily exchange these ions or molecules for others, or they can promote such reactions.
- The path to understanding clays is through a study of their different properties, **chemical or physical.**
- The methods of study (**X-ray diffraction, thermal stability, SEM & infrared spectroscopy** among others) are attempts to study.
- The different methods of investigation give us a composite understanding of the clay sample properties.

COMPOSITION & MINERALOGY OF CLAY MINERALS

- Studies of clay properties can be divided into ***three major groups:***

1. *The physical properties of particle shape* and consequent surface area.
2. *The crystallographic structure & the disposition of the constituent atoms in a clay crystal.*
3. *The mineral families* determined by chemical substitutions in the structures.

PHYSICAL PROPERTIES OF CLAY MINERALS

(Particles & Shapes)

- Although clays are fine grained minerals with particle diameters of < 2 µm, but not all mineral grains in nature below 2 µm are of the same mineral type.
- ***Non clay minerals, such as quartz, carbonates & metal oxides*** can often form 10-20% or more of a naturally occurring clay-sized assemblage.

PHYSICAL PROPERTIES OF CLAY MINERALS

(Particles & Shapes)

- The small grain size of the clay crystals automatically gives them a ***special property;*** *they have a large surface area compared with the volume of the particle.*
- **The properties of clays are determined by their surfaces.**
- **If the clay particles are not chemically active, they will behave as other minerals of the same grain size and shape.**

PHYSICAL PROPERTIES OF CLAY MINERALS

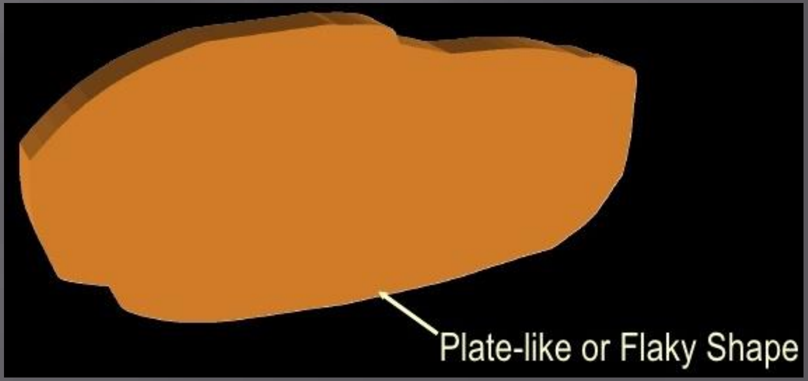
(Particles & Shapes)

- However, the clay minerals have the particularity of being ***sheet-shaped*** (hence the name ***phyllosilicate***).
- This means that they have more surface area than other minerals of the same size which tends to be cubes or spheres.
- The ratio of length to thickness of sheet-shaped clay particles is normally near "**20**".
- This makes the surface area of a clay particle nearly *three times* that of a cube of the same volume.

PHYSICAL PROPERTIES OF CLAY MINERALS
(Particles & Shapes)

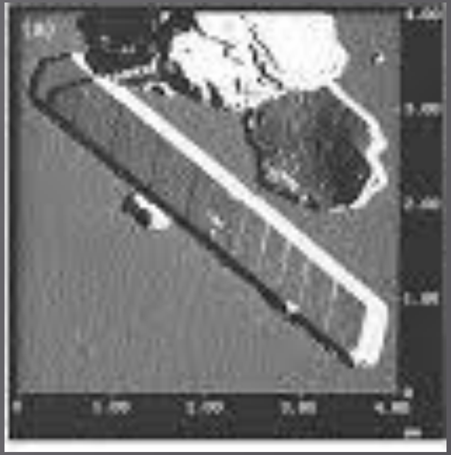
- Clay minerals can be divided into ***three groups*** on the basis of particle shape:

1. ***Flakes:*** sheets of equal dimension in two directions & a thickness of 1/20 in the other.

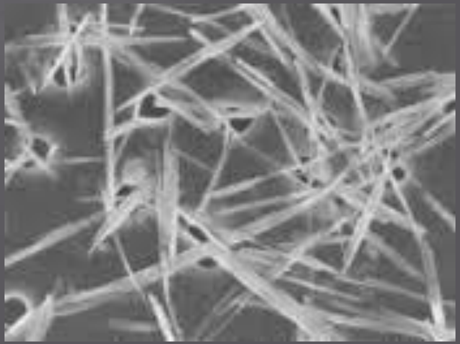


PHYSICAL PROPERTIES OF CLAY MINERALS
(Particles & Shapes)

2. *Laths:* sheets of a linear aspect where the width is great in one direction and much less in the other. The thickness is always much less than the other two directions.



3. *Needles:* Two directions are similar in dimension, whereas the last one is much greater.



CLAYS & WATER

- Clay mineral crystals have very special effect on water molecules.
- The clay mineral surface attracts the polar water molecules through weak charge forces, and the crystals are covered by several layers of water molecules.
- Some clay minerals have a special property which allows them to incorporate water molecules into their structure.

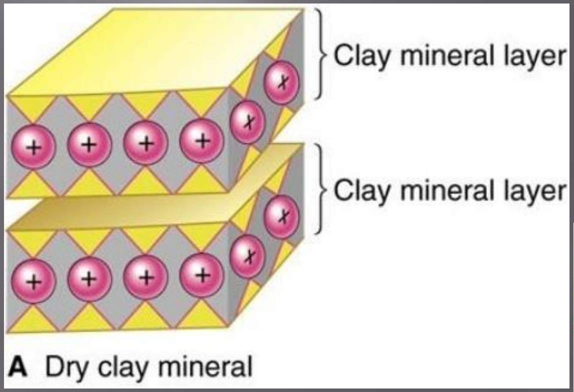
CLAYS & WATER

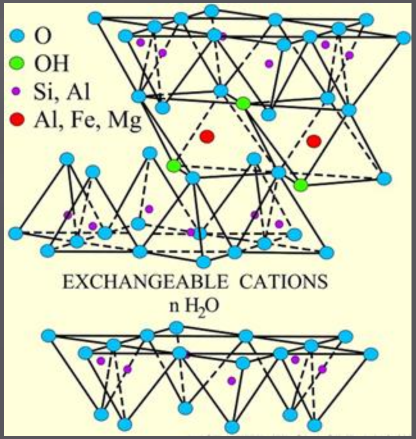
- This water changes the dimension of the clay particles as it goes into or out of the clay structure.
- **These are called expanding or swelling clays.**
- **The other clays are called non- expanding or non-swelling clays.**
- The incorporation of water molecules into the clay structure is reversible under atmospheric conditions, being directly related to the ***ambient water vapour pressure & temperature.***

CLAYS & WATER

- The more humid the air, the more water can be found in between the silicate layers of the clay structure.

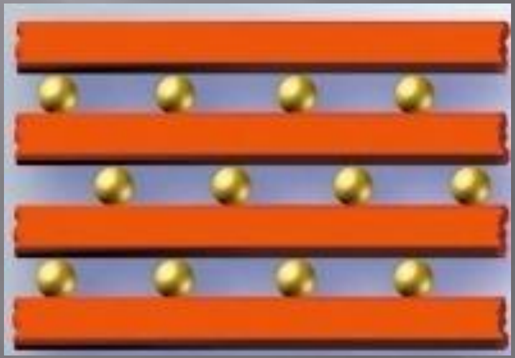
- Swelling clays have a basic silicate structural sheet layer of 10A°.

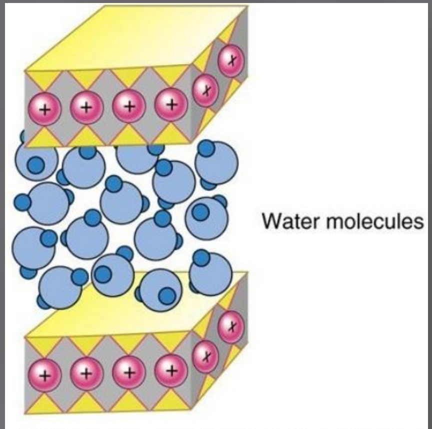




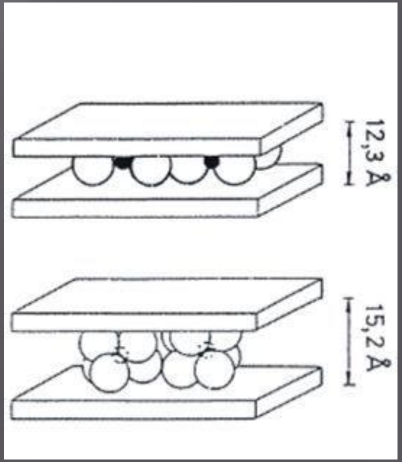
CLAYS & WATER

- The water introduced around a hydrated cation (usually one or two charge) forms either:
  - Two-layer structure of 5.2A° thickness
  - or layer of 2.5A° thickness under less humid conditions or higher temperatures.





B Expansion due to adsorption of water



CLAYS & WATER

- Extreme hydration can produce 17A° three layer structure.
- In aqueous solution, one can form 19.5A°.
- All in all, hydration can vary the volume of clay particles by **95%.**

MIXTURES OF WATER & CLAYS

a- Water-clay mixtures

- When clays are added to an aqueous solution, there is a gradual change in the structure of the water solution as the clay particles become more abundant.
- **A slurry (suspension of clays in water) is formed which become viscous in proportion to the amount of clay present.**
- **If other organic or inorganic molecules are associated on the clay surfaces, the clay acts as a carrier keeping the other molecules homogenously dispersed in the suspension.**

MIXTURES OF WATER & CLAYS

a- Water-clay mixtures

- **In modern industry, for example,** clays are used to produce paint matrices, in which the pigment is dispersed and hold in suspension by clay particles.

MIXTURES OF WATER & CLAYS

b- Clay-Water mixtures

- When one add water to clay powder, the clay picks up the water and distributes it around the particles.
- When relatively little water is present, and the clay are just covered with water layers, ***the result is cohesive but plastic mass.***
- The weak forces of these aggregates allow the particles to slide over one another, given a certain plasticity and ***the mixture is called Mud.***

MIXTURES OF WATER & CLAYS

b- Clay-Water mixtures

- The plasticity of clay-water mixtures formed the basis of ceramics and pottery industries.
- The easy absorption of the water allows one to model the resulting plastic material.
- Progressive drying leaves a coherent, solid material of any shape which when heated can be transformed into useful rigid solid product such as plate or mug.

- The two extremes of clay-water mixture proportions are useful to us in different manufacturing processes, from making bricks to applying paints to colour the surfaces.

EXCHANGE OF IONIC SPECIES (CEC)

EXCHANGE OF IONIC SPECIES (CEC)

- *A very important property of clay surfaces is* **their chemical activity & their interaction with ions in aqueous solutions.**
- These solutions often include ***dissolved species.***
- These species are normally composed of charged ions or molecular species which can be **attracted by a charged surface & adsorbed onto the surfaces.**
- **Clays have this charged surface.**

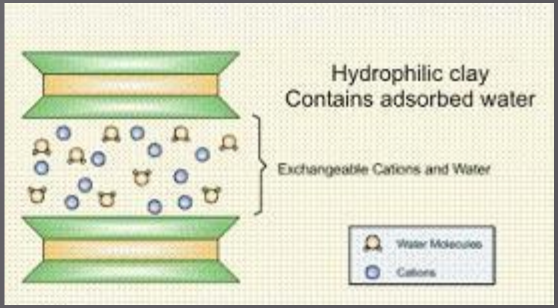
EXCHANGE OF IONIC SPECIES (CEC)

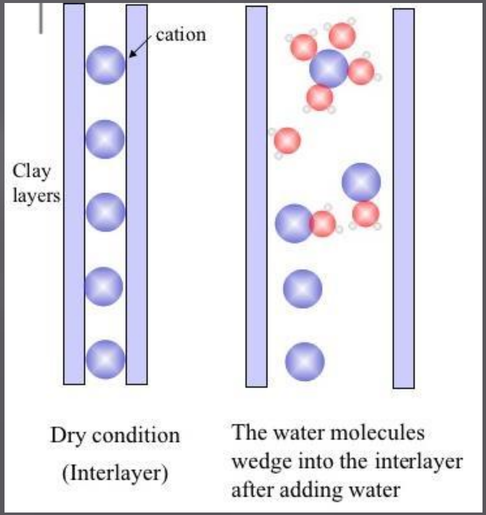
- The ions are ***absorbed*** by the clays ***into internal crystallographic sites.***
- The absorbed ions are normally accompanied by water molecules, ***expanding the clays, when in aqueous solution.***
- **In this way,** the chemical action of the surface area is increased greatly ***about 25 times*** **or more.**

EXCHANGE OF IONIC SPECIES (CEC)

❖ The property of adsorbing & absorbing ionic species in solution is called ***"Cation Exchange Capacity (CEC)"***.

❖ This capacity is measured in terms of the ***total number of charged ions which can be fixed onto the surface of clays.***





EXCHANGE OF IONIC SPECIES (CEC)

- **The measurement of “CEC”** ***is that of the number of moles of ionic charge fixed on 100 gm of dry clay.***
- **Often “CEC” is expressed in meq (milli-equivalent).**
- **However, the attraction of the ions onto clay surface (internal or external) is not the same for all species.**

EXCHANGE OF IONIC SPECIES (CEC)

- There is also a selection between different species of ions available in solution. *Some are strongly attracted to the clay surfaces than others.*
- This selection effect depends upon *the type of clay & its chemical composition*, as well as *the affinity of the ions to remain in a free hydrated state in the aqueous solution.*
- The composition of the aqueous solution can also affect the attraction of ions for clay sites.

EXCHANGE OF IONIC SPECIES (CEC)

- When an ion is held on clay surface ***(either adsorbed or absorbed)*** ***and displaced by another*** due to the change in its aqueous concentration , ***the ion is called "desorbed".***
- *If the desorbed ion is replaced by another ionic species introduced into the aqueous solution,* ***it is termed "exchanged".***
- ***The process is known as "ion exchange" or "cation exchange" .***

EXCHANGE OF IONIC SPECIES (CEC)

- **The selectivity or preference of the clay for one dissolved species over another** is of great importance to the fate of material as it passes in contact with clay.
- Hence, the clays can be used to capture a specific ion in solution relative to other ions present.
- **This effect is called "cation selectivity".**
- **Organic molecules also often can be attracted as absorbed or adsorbed species.**
- **Therefore, clays can be vehicles or transport of organic molecules.**

CRYSTALLOGRAPHIC STRUCTURE OF CLAY MINERALS

CRYSTALLOGRAPHIC STRUCTURE OF CLAY MINERALS

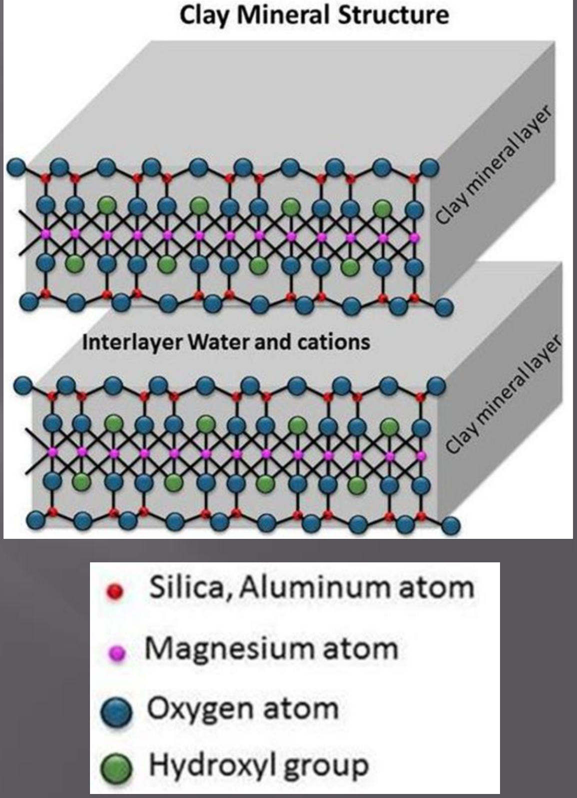
- Clays are called phyllosilicates, because their grains shape is that of sheet.
- This aspect has a fundamental cause concerning the inner structure, or the bonding direction of the constituent atoms.
- i.e., the strong forces are essentially in a two dimensional array.
- The stronger the bond the more tightly the hold atoms & conversely, the weaker the bond the more likely it will be broken.

CRYSTALLOGRAPHIC STRUCTURE OF CLAY MINERALS

- Thus, because the bonds are easily broken in only one direction, ***a sheet structure results.***
- Also, when the crystals are growing, they tend to grow faster in the strongly bonded direction.
- ***Hence, the extension of the crystal is essentially in two dimensions.***
- ***Therefore, the thickness of phyllosilicates is*** *1:20* ***compared to width and length.***

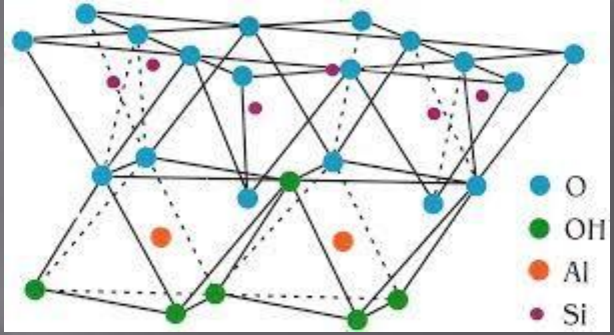
CRYSTALLOGRAPHIC STRUCTURE OF CLAY MINERALS

- The ionic bonding in clays is ***highly covalent.***
- *Roughly, **oxygen** represents half of the present ions and the cations **silicon** & **aluminum** are the major constituents.*
- *These ions form highly covalent units which inetrlinked into what is called “**network**”.*



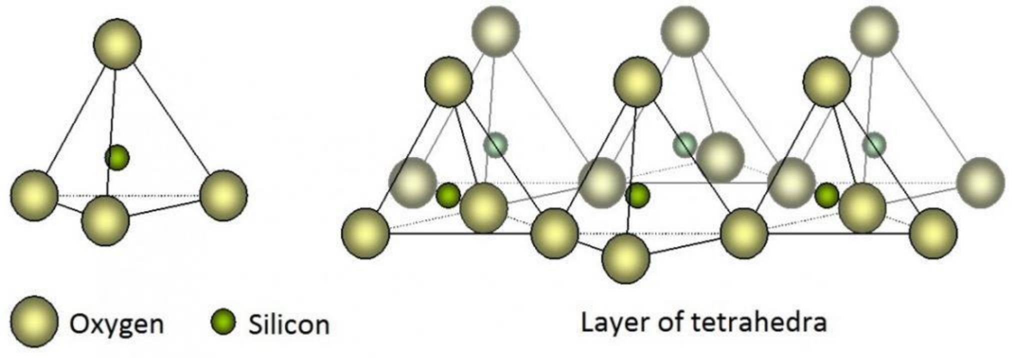
CRYSTALLOGRAPHIC STRUCTURE OF CLAY MINERALS

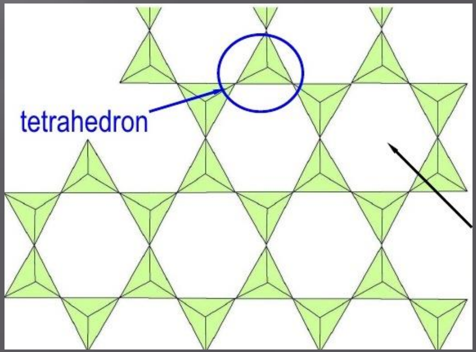
- The networks of clay structures are built of interlinked polyhedra composed of oxygen anions & silicon, or aluminum cations (tetrahedral & octahedral layers)
- The majority of cations are ***silicon*** and hence the name ***silicates*** is given to clays.



TETRAHEDRA

- The tetrahedron unit is composed of one silicon ion is surrounded by four oxygen ions.
- Polyhedra is the interlinking of tetrahedron units through oxygen sharing.



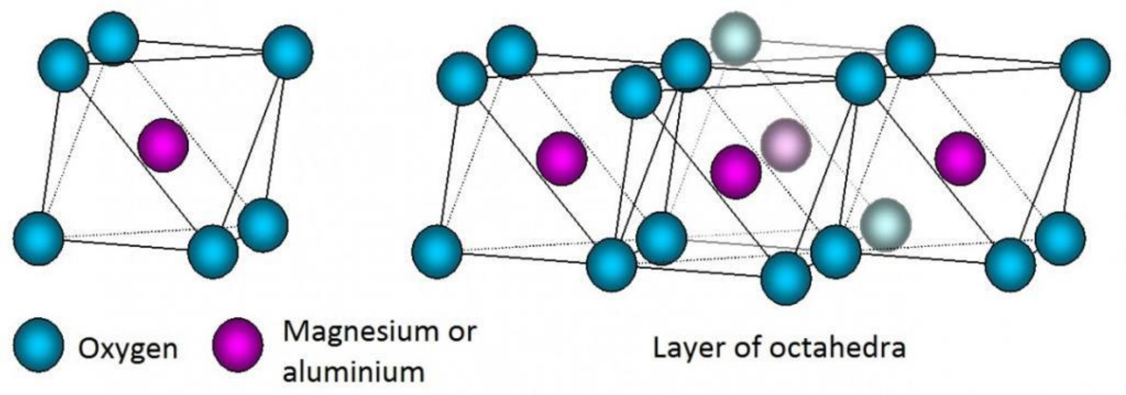


TETRAHEDRA

- The ***positive cationic charge*** for silicon is ***"four"***.
- This value is less than the total ***negative charge*** of the oxygen ions, which is "***eight***".
- ***This leads to each of oxygen ion is shared with another cation.***

OCTAHEDRA

- Aluminum, magnesium or ferrous ions form polyhedral with six oxygens or hydroxyls.
- The number of present cations **can vary between two & three.**
- **For example, $3Mg^{2+}$ ions present or $2Al^{3+}$ ions in the octahedral sites.**



OCTAHEDRA

- The basic requirement is that a **total positive charge of six (6^+)** be present .
- When three cations are present, it is called ***"trioctahedral"*.**
- When two cations are present, it is called ***"dioctahedral"*.**
- These *two types* are fundamental to the classification scheme of clay minerals.

LAYER STRUCTURES THROUGH LINKAGE

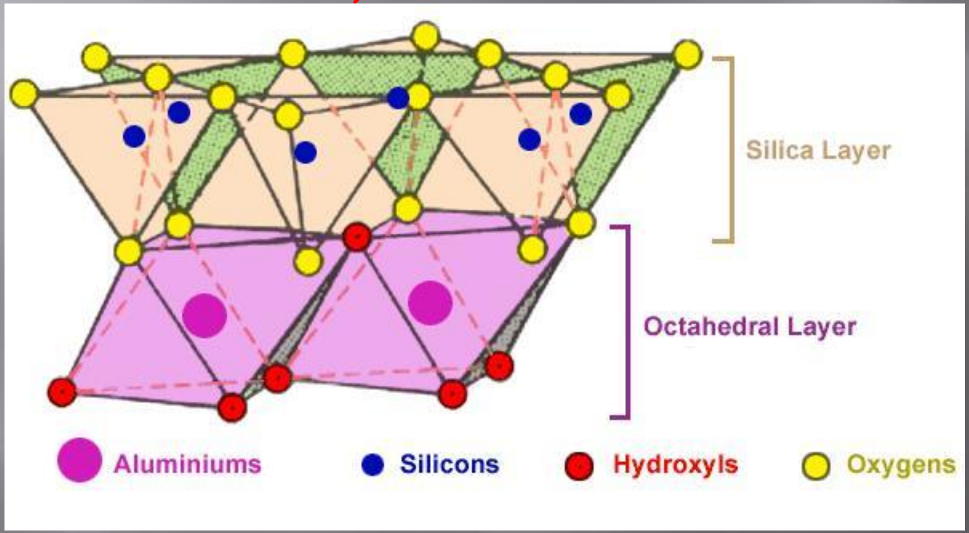
- In most clay structures the tetrahedral layers and octahedral layers are linked together in sheet structure.
- The linkage is done through the apical oxygen.
- This oxygen sharing occurs in the Z direction of the structure.

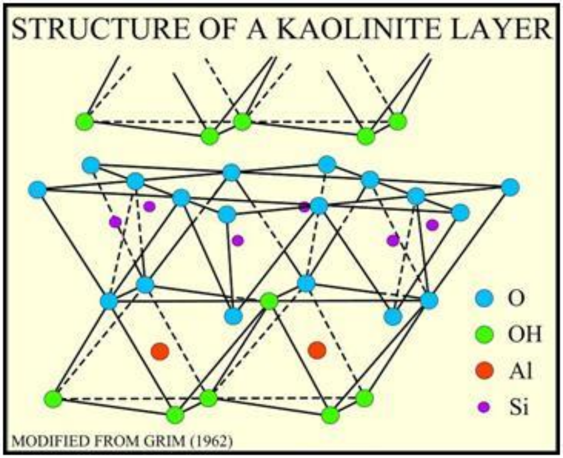
REPEAT DISTANCES

- The tetrahedral & octahedral units, when interlinked to form a sheet, give a constant thickness.
- The thickness of the tetrahedral layers is considered to be **3.4A°** & the octahedral layers is thinner.
- The combinations seen in natural minerals as follows:

REPEAT DISTANCES

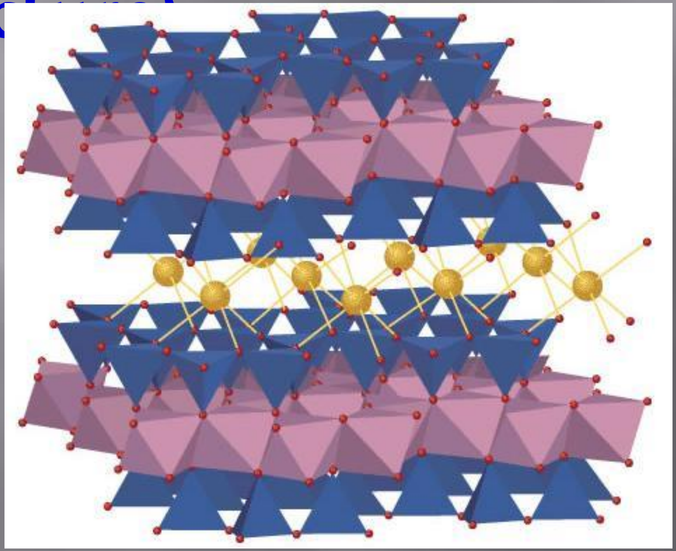
- One tetrahedral + one octahedral layer = 7A° unit layer. (1 : 1 structure)

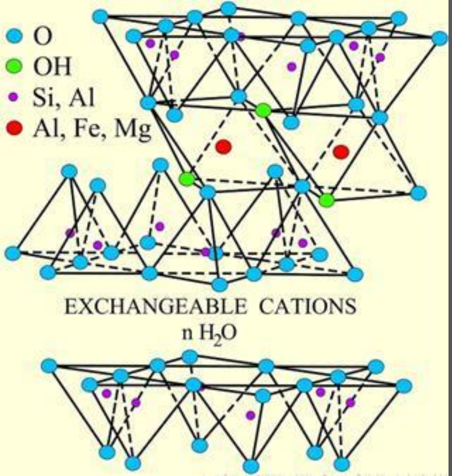




REPEAT DISTANCES

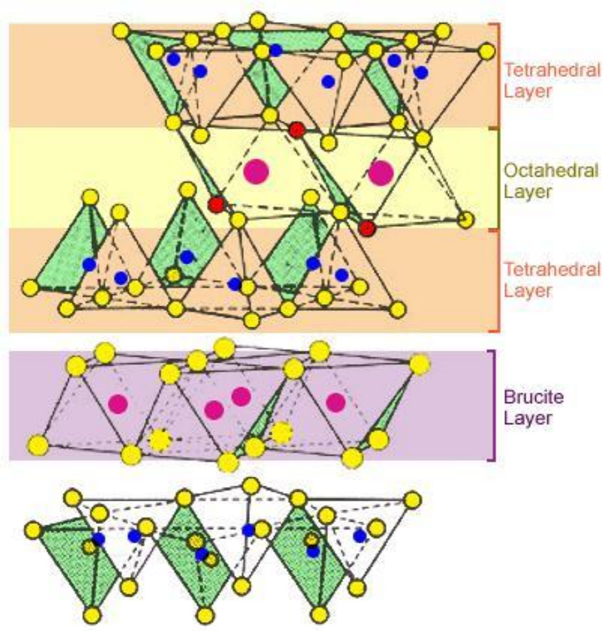
- **Two tetrahedral + one octahedral layer = 10A° unit layer. (2 : 1 struc**

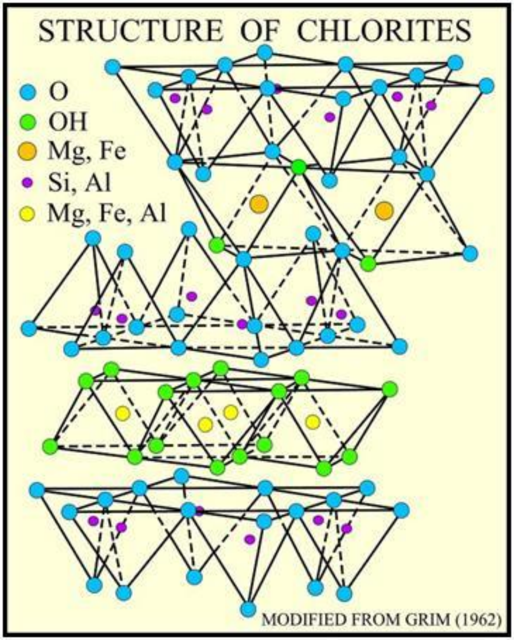




REPEAT DISTANCES

- **Two tetrahedral + Two octahedral layer = 14A° unit layer. (2 : 1: 1 structure)**





MINERAL FAMILIES

MINERAL FAMILIES

- There are two different properties of clays are used to describe & classify clay minerals:

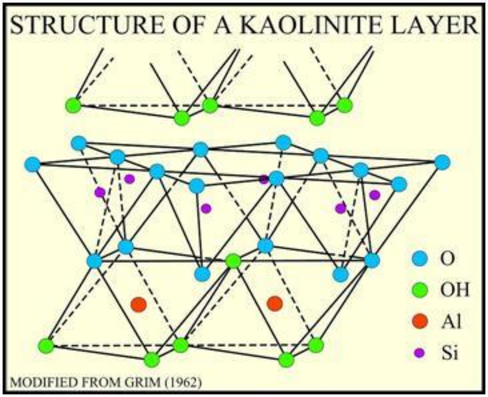
1) Their swelling properties (expanding minerals & non-expanding minerals *for only* ***10 A°*** *minerals).*

2) Basic crystallographic repeat unit of the layer structures.

The layer structure distance method gives the following categories as a result of octahedral-tetrahedral linkage, namely: 7 A°, 10 A° & 14 A°

7 A° MINERALS
(one octahedral + one tetrahedral layer)

- These mineral types can be divided into two groups ***based upon the octahedral ion species present.***

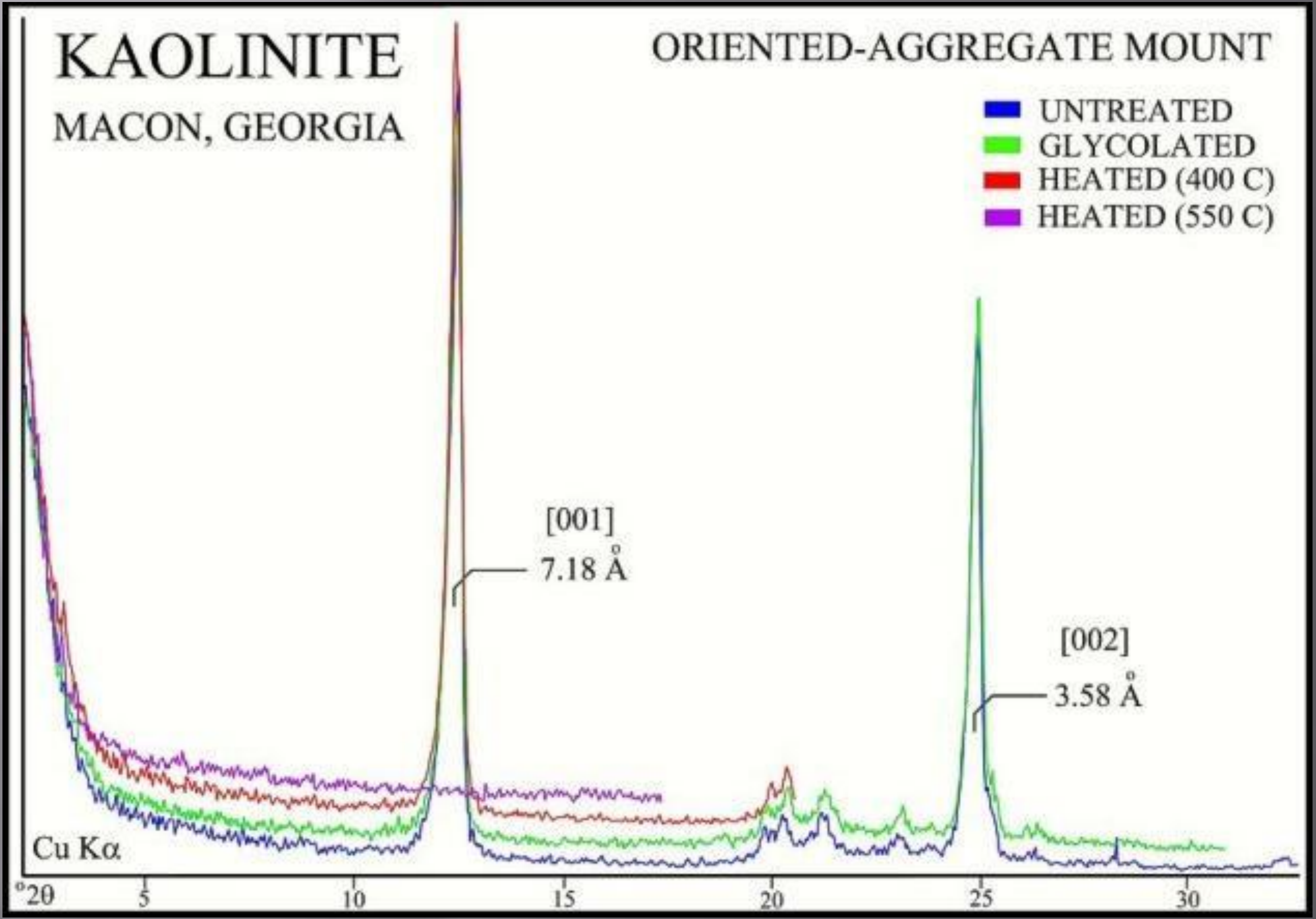


Kaolinite ***[$Al_2Si_2O_5(OH)_4$]:***

It has two Al^{3+} and very minor Fe^{3+} ions; *it is therefore dioctahedral mineral.*

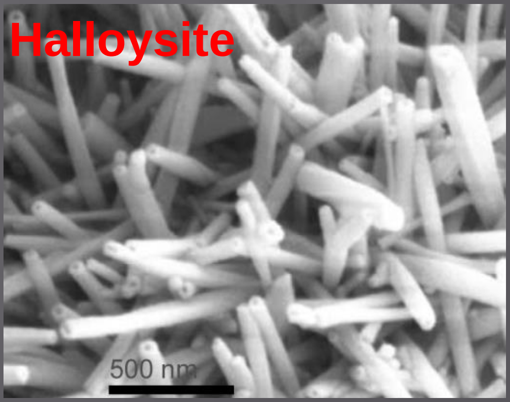
Dickite: is a high temperature polytype of kaolinite with minor structural variation.

Kaolinite
(XRD PATTERN)



7 A° MINERALS
(Halloysite)

- ***Halloysite:*** has the composition & structure as Kaolinite, except for an additional water layer between the layers which distorts the sheet structure into *tubul*



7 A° MINERALS (Berthierine-Serpentines)

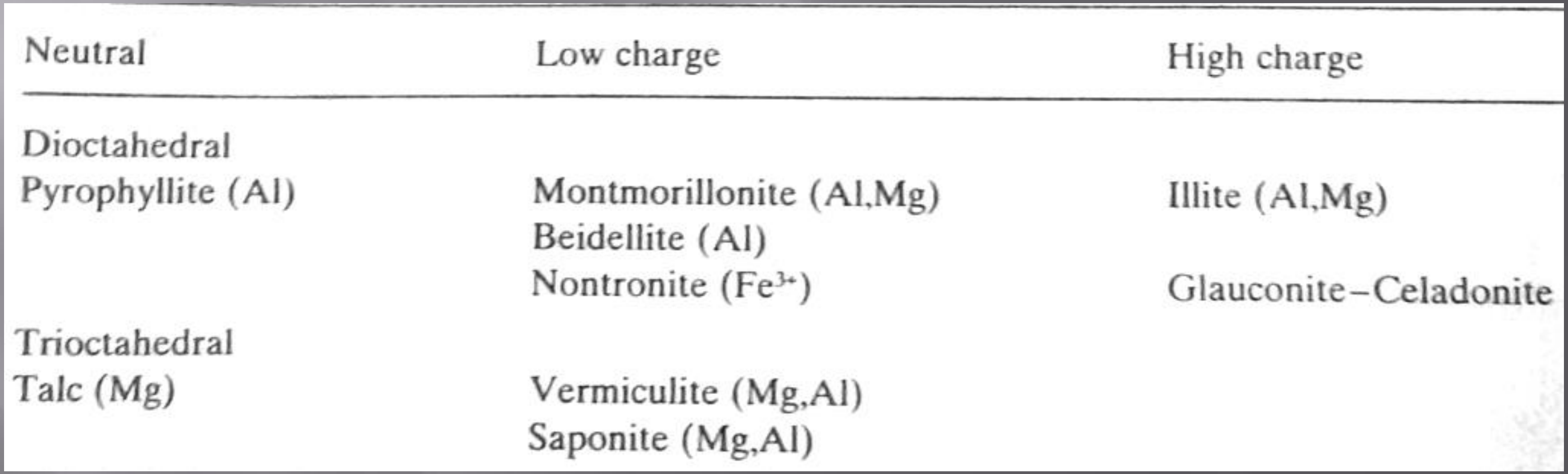
- *Berthierine-Serpentines* have between 3 & 2.5 ions present. The majority of these ions are divalent.
- *Hence, they are trioctahedral minerals.*
- *The substitution of from 3 to 2.5 ions is called the octahedral substitution.*
- The composition is as follows:

  $[(R^{2+}R^{3+})_{3\text{-}2.5}\textit{octahedral}\ (Si, Al)_2\ \textit{tetrahedral}\ O_5\ (OH)_4]$
- *Electrostatic balance is maintained by the next substitution:* $(3R^{2+}) = 1.5\ R^{2+} + R^{3+}$

10 A° MINERALS

(two tetrahedral + one octahedral layer)

The various 10 A° mineral types are listed below



Neutral	Low charge	High charge
Dioctahedral		
Pyrophyllite (Al)	Montmorillonite (Al,Mg)	Illite (Al,Mg)
	Beidellite (Al)	
	Nontronite (Fe^{3+})	Glauconite–Celadonite
Trioctahedral		
Talc (Mg)	Vermiculite (Mg,Al)	
	Saponite (Mg,Al)	

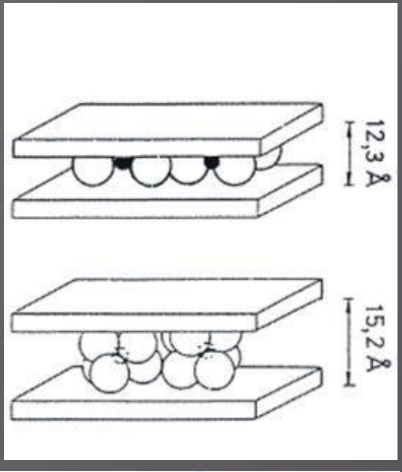
10 A° MINERALS

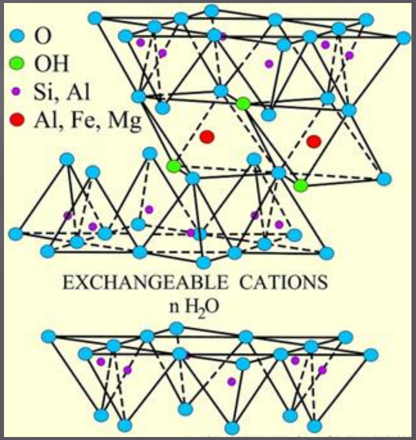
Low charge (Expanding) Minerals

- These minerals are given the group name of **"Smectites".**
- Low charge on 10A° structure allows hydrated ions or polar ions to be inserted between the layers (absorbed).
- The average interlayer distance changes & the mineral is called swelling or expanding.
- The usual interlayer distance for swelling minerals is greater than 10A° due to the presence of hydrated ions.
- This property gives these minerals a very special character.

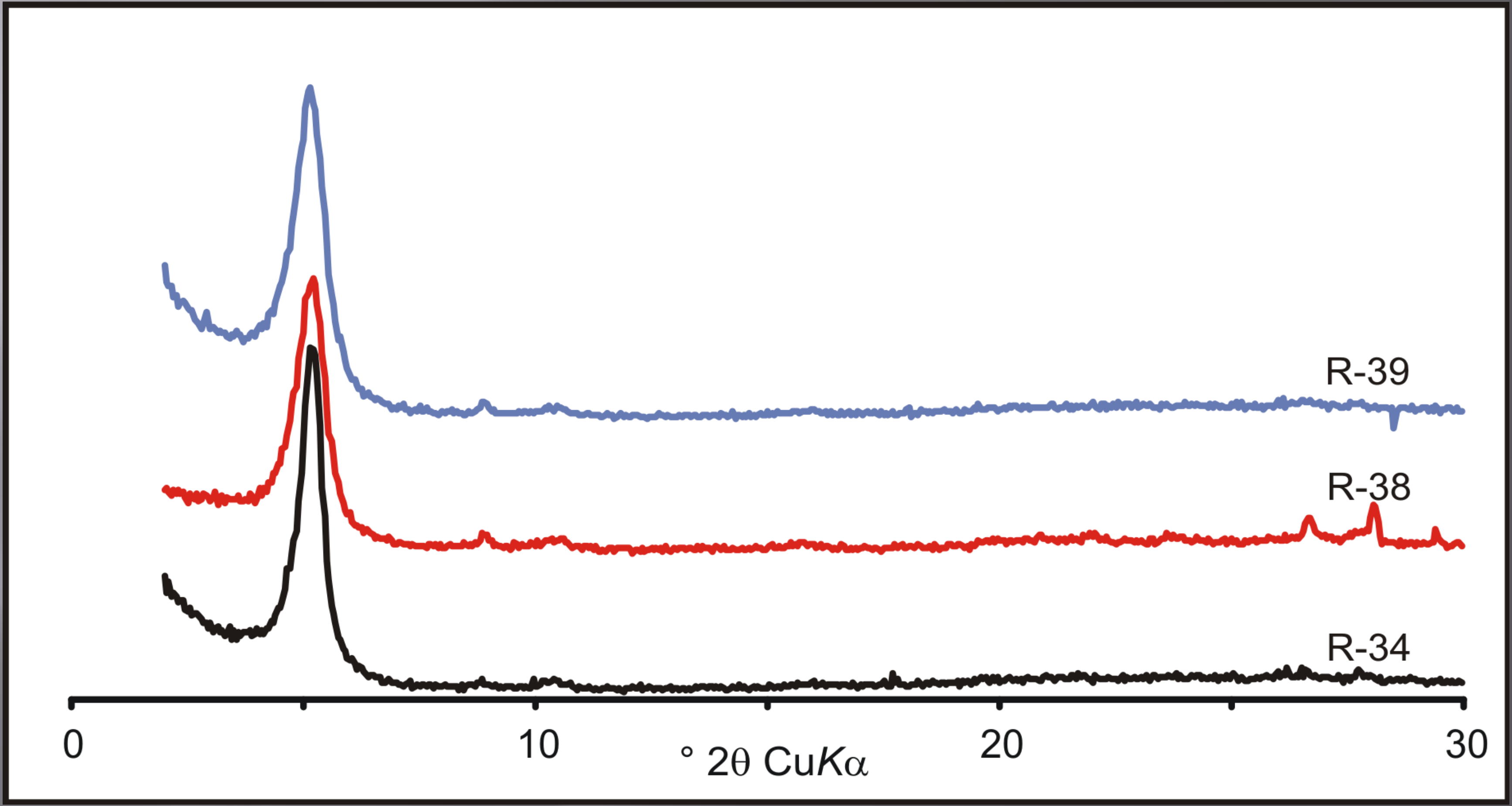
Low charge (Expanding) Minerals (SMECTITES)

- The normal basal spacings are 12.5A° for one water layer & 15.2A° for two water layers.
- Ethylene Glycol is used to stabilize a swelling state to a basal spacing of 17A°.
- Ethylene Glycol is used in laboratory to determine the swelling clays.





XRD PATTERN OF SMECTITE



DIOCTAHEDRAL EXPANDING MINERALS

- ***Beidellite*** $[M^{0.n}(Al,Mg)_2(Si,Al)_4O_{10}(OH)_2xH_2O]$

  where $n < 0.5$
- This is an aluminous mineral.
- The two tetrahedral layers dominated by Si ions, with some substitution of Al.
- The octahedral layer is mainly aluminous.

DIOCTAHEDRAL EXPANDING MINERALS

- ***Montmorillonite***

  $[M^{0.n}(Al,Mg, Fe^{2+})_2Si_4O_{10}(OH)_2xH_2O]$

- It is an aluminous mineral.
- The two tetrahedral layers are almost occupied by Si ions .
- The charge imbalance comes from divalent ion substitutions **(Mg or Fe)** for the trivalent **Al** ions in the octahedral site.

DIOCTAHEDRAL EXPANDING MINERALS

- *Nontronite,*

  $[M^{0.n}(Al,Fe^{3+},Fe^{2+})_2(Si,Fe^{3+})_4O_{10}(OH)_2xH_2O]$

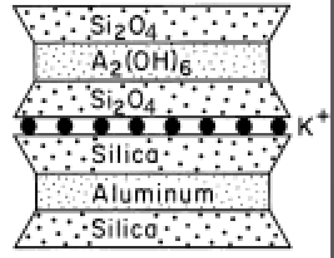
- It is a ferric mineral with minor substitution of **Al** and occasionally **Mg** ions in the octahedral layer.
- These substitutions as well as some substitution of **ferric ions** in the tetrahedral layer for **Si** give rise to the interlayer charge.
- **There is an intermediate compositions between the three types of dioctahedral expanding minerals.**

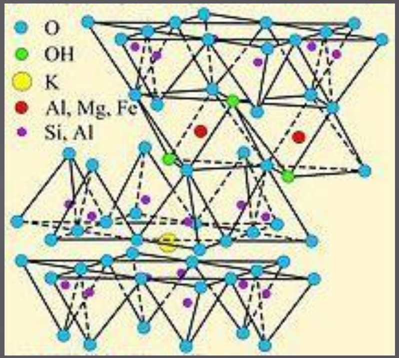
TRIOCTAHEDRAL EXPANDING MINERALS

- ***Saponite*** $[M^{0.n}(Al,Mg)_{3-2.5}\ (Si,Al)_4O_{10}(OH)_2nH_2O]$
- ***Stevensite*** $[M^{0.n}(Mg)_{<3}\ Si_4O_{10}(OH)_2nH_2O]$
- ***Vermiculite*** $[M^{0.n}(Mg,Fe,Al)_{<3}\ (Si,Al)_4O_{10}(OH)_2nH_2O]$
- Vermiculites can be described a high charge smectites.
- Vermiculite do not expand nor contract fully under conditions of hydration & heating.

High charge Minerals
(Mica-like minerals)

- In these minerals the charge imbalance is between 0.8 & 1.
- There is an inerlayer ion between the layer units.
- The interlayer ion is almost **K.**





High charge 10 A° Minerals (Mica-like minerals)

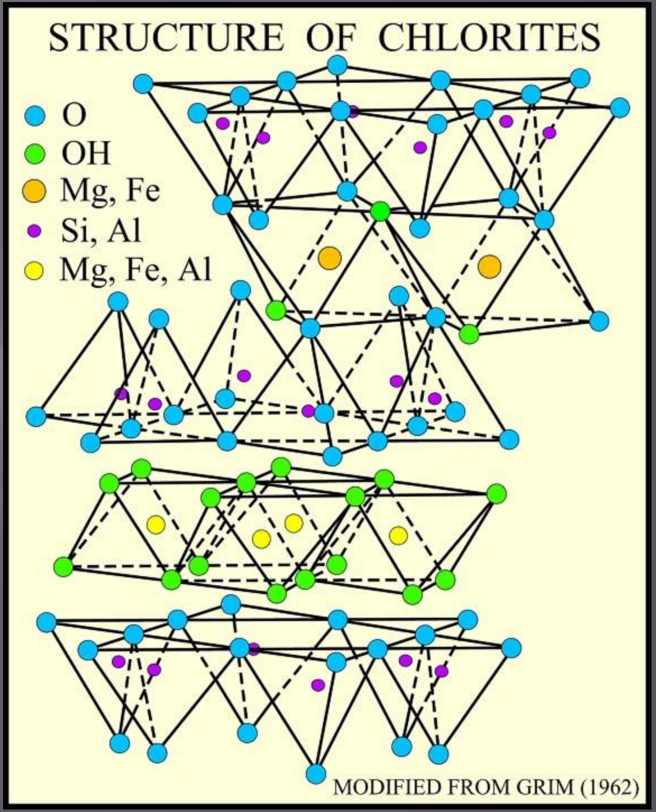
- *Illite,* $K_{0.8-0.9}(Al,Fe,Mg)_2(Si,Al)_4O_{10}(OH)_2$
- Illite is an aluminous 10A° mineral with some substitution of Fe^{3+},Fe^{2+} & Mg in the octahedral layer.
- Some **Al** substitution in the tetrahedral layer.
- **Si** content is usually than 3.5 ions.
- The interlayer **K** ion holding the layers firmly together.

High charge Minerals
(Mica-like minerals)

- *Glauconite-Celadonite,* $K_{0.8}$ $(Fe,Mg,Al)_2(Si,Al)_4O_{10}(OH)_2$
- These minerals are iron-bearing micaceous minerals.
- Divalent or trivalent iron greatly exceeding aluminum.
- Si content greater than 3.2 ions.
- The high iron content gives these minerals a green colour.

14 A° Chlorites (Two tetrahedral + Two octahedral layer, 2:1+1)

- In low temperature environments chlorite minerals are trioctahedral.
- The composition of chlorite is generally shown as: $(Si,Al)_8(Mg,Fe)_6O_{20}(OH)_4$



14 A° Chlorites

- Dioctahedral substitutions of trivalent ions (Al^{3+} and Fe^{3+}) occur in the octahedral sites.
- Some substitution of trivalent ions (Al^{3+}) occur in the tetrahedral site to compensates the substitutions in the octahedral site.
- Thus, the chlorite compositions are the result of complex, simultaneous substitutions.

14 A° Chlorites

- Complete homo-ionic substitution are known to occur between Fe^{2+} and Mg^{2+} in chlorites.
- Some Fe^{3+} is found in 14A° chlorites, in minor quantities of less than 15% of the octahedral sites.
- Al^{3+} is common to the chlorite structure in the octahedral sites with percentage ranges from 10% to 33%.
- Dioctahedral-trioctahedral substitutions can occur up to around 50%.
- In general the chlorites that derived from hydrothermal environment are more magnesian than those from surface environment.

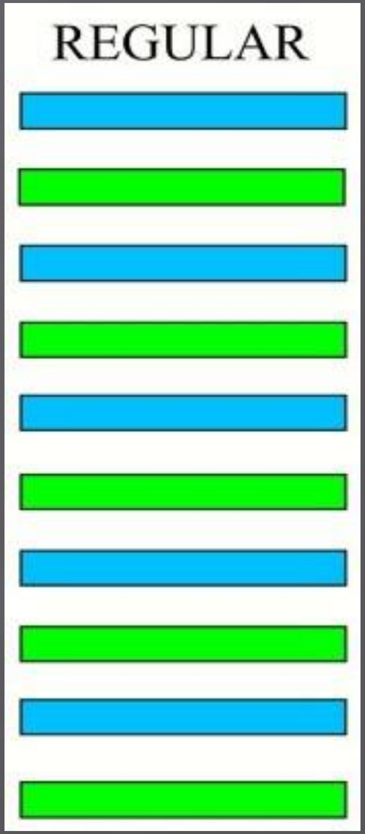
Mixed Layered Minerals

- Mixed layer minerals seem to be an expression of change in mineral stability, ***one phase is unstable and another is stable.***
- The change in phase is effected by ***the production of a series of intermediate composition crystallites which are actively changing their composition during the time.***
- ***Thus*** the mixed layer minerals are in fact a ***transition state*** present in the nature.

Regular Mixed Layering Mineral Types

- The elements are repeated with regularity.
- The types of regular mixed-layer minerals are:

1. ***Mica/Smectite***
   - i. ***Dioctahedral : illite/smectite***
     - *(a) Rectorite (sodic mica)*
     - *(b) Allevardite (potassic mica)*
   - ii. ***Trioctahedral: biotite/smectite*** *(Hydrobiotite)*

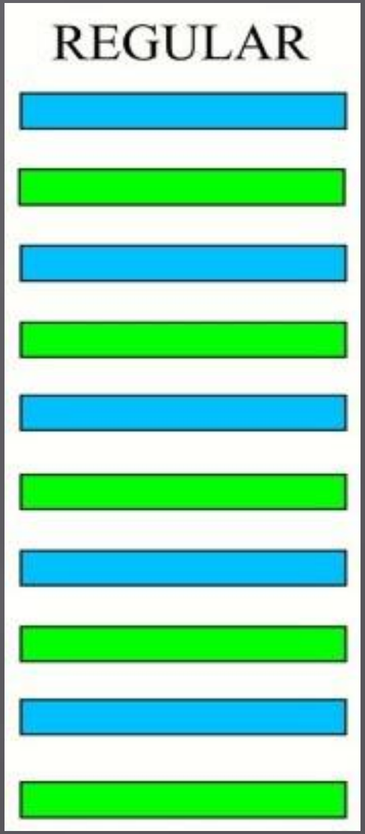


Regular Mixed-Layer Minerals

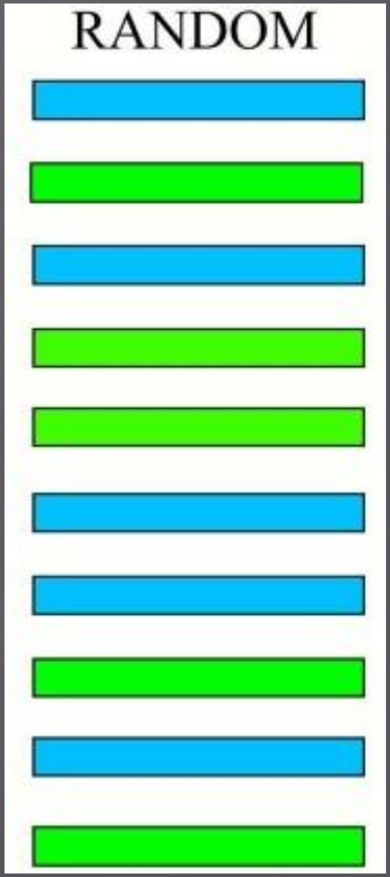
2. ***Chlorite /Smectite:***
   1. ***Dioctahedral : Sudoite***
   2. ***Trioctahedral : Corrensite***
   3. ***Dioctahedral - Trioctahedral :***

      Tosudite

- These minerals are found in high temperature situations such as hydrothermal alteration or upper limit of diagenesis.



Random Mixed-Layer Minerals



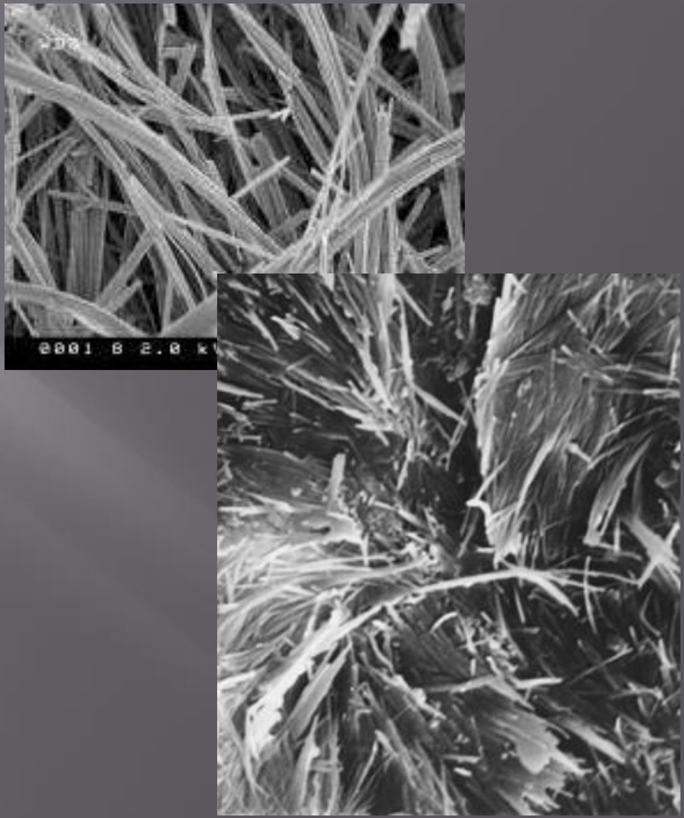
- These minerals seem to be related to the transition between two different minerals.
- The types of random mixed-layer minerals are:

1. Mica/Smectite:

  - ***i. Illite/Smectite***
  - ***ii. Biotite/Smectite***
  - ***iii. Celadonite/Smectite***
  - ***iv. Glauconite/Smectite***

SEPIOLITE AND PALYGORSKITE

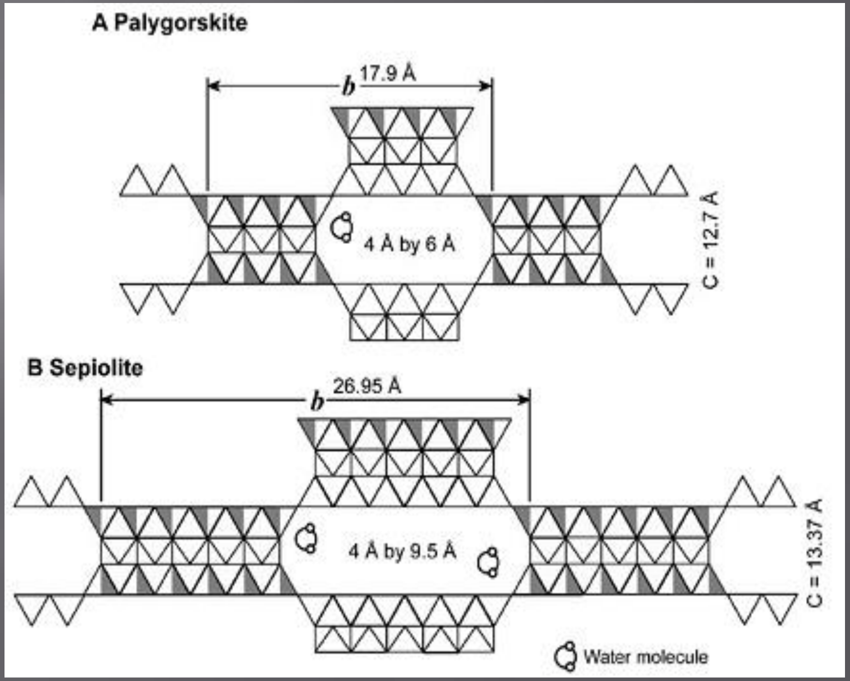
- Sepiolite and palygorskite are considered to be clay minerals ***because they are always small sized crystals (most often less than 2 µm long)*** ***& because they form in soils or sediments in surface conditions.***
- Their crystal shape is typically that of fibers or needles.



Scanning electron micrographs of palygorskite.

SEPIOLITE AND PALYGORSKITE

- They are hydrous with crystalline water.
- They have an absorbed water in their structure.
- Water molecules & exchange ions are found in the inner sites inside the linked chains of tetrahedra-octahedra.
- They can absorb organic molecules like smectites.



Diagrammatic sketch of the structures of palygorskite (A) and sepiolite (B).

SEPIOLITE AND PALYGORSKITE

- **The difference between palygorskite & sepiolite is in the composition of the unit cell & the length of fibers.**
- Palygorskite has a larger unit cell of 12 A° repeat distance than sepiolite, which has 10.5 A° repeat distance.
- Also, palygorskite contain much aluminum, whereas sepiolite is nearly aluminum-free, being composed almost exclusively of magnesium & silicon.
- Sepiolite fibers are longer than palygorskite fibers (10-15 A° for sepiolite and >5 A° for palygorskite).

BENTONITE APPLICATIONS

BENTONITE

- Made up mainly of **montmorillinite,** $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$
- Sodium montmorillonite has an exchange capacity which

generally is between 80 and 110 milliequivalents per 100 grams

BENTONITE

- Bentonites are comprised predominantly of the smectite group of minerals.
- The property of ion exchange and the exchange reaction are very important

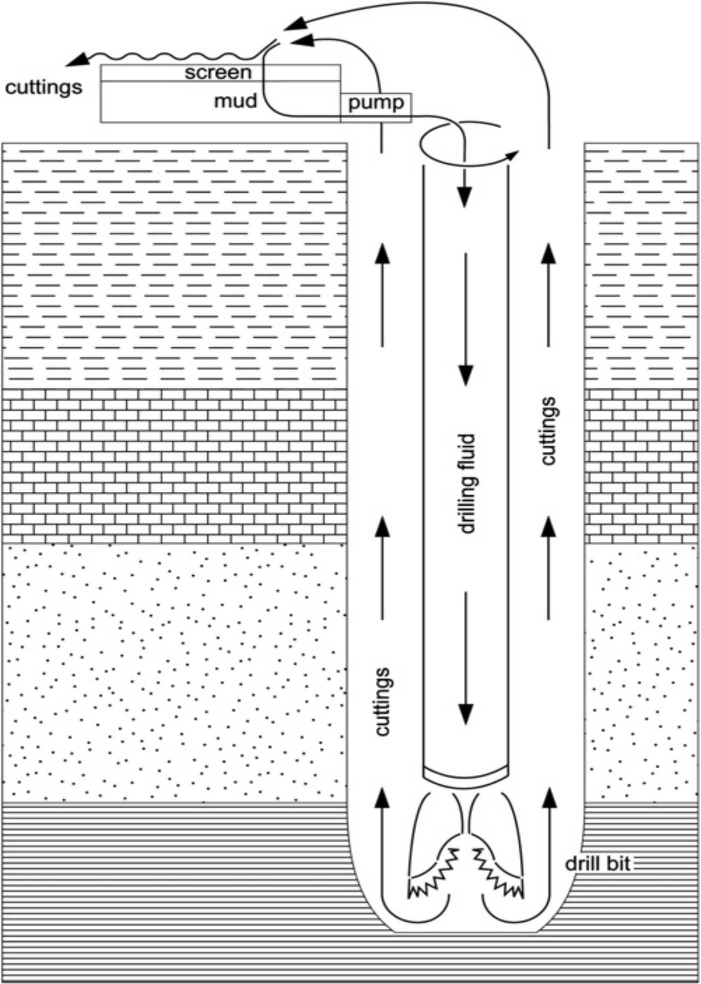
In many of the applications in which the smectite minerals are used.

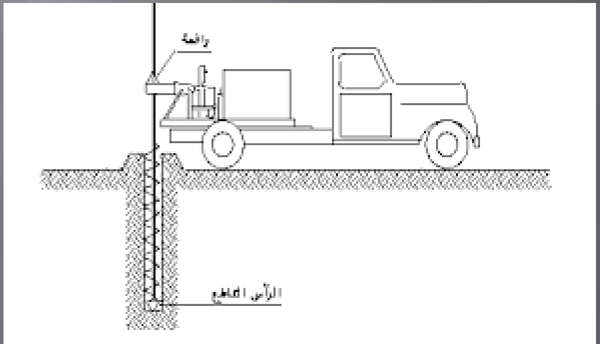
BENTONITE APPLICATIONS

1. DRILLING FLUIDS
2. FOUNDRY BONDS
3. ABSORBENTS
4. AEROSOLS
5. BARRIER CLAYS
6. MEDICINE
7. PENCIL LEADS

1. DRILLING FLUIDS

- Sodium montmorillonite (Na-bentonite) is the major constituent of freshwater drilling muds.





1. DRILLING FLUIDS

- **The function of the drilling mud is to :**

1. remove cuttings from the drill hole to keep formation fluids from penetrating into the drilling mud
2. lubricate and cool the bit
3. build an impervious filter cake on the wall of the drill hole to prevent the penetration of water from the drilling fluid into the formations and formation fluids from the drilling mud.

2. FOUNDRY BONDS

- Molding sands composed of silica sand and bentonite are used extensively

  in shaping metal in the casting process.
- Bentonite is used to provide

  the bonding strength and plasticity to the sand–clay mixture.
- Tempering water is added to the mixture to make it plastic and cohesive so that it can be molded around a pattern.
- The tempering water is a small percentage of the mix usually about 5%.

2. FOUNDRY BONDS

- The important properties of the sand–clay mix are green compression strength, dry compression strength, hot strength, flowability, and permeability.
- Other properties that are important are bulk density, durability, ease of shake out of the sand–clay mold from the casting, and cleanness of the surface of the cast metal after shake out.

3. ABSORBENTS

- Calcium bentonites are very good absorbent clays.
- This is because of their surface charge and surface area.
- Many of the calcium bentonites will absorb up to 100% of their dry weight of water and up to about 80% of their weight of oil.

4. Aerosols

- In some aerosols, very fine particle size sodium montmorillonite is used as a carrier for the ingredient such as a mosquito repellent.

5. Barrier Clays

- Sodium bentonites are used extensively for water impedance because of their high swelling capacity.
- The high swelling sodium bentonite swells and fills the pores and voids in the material into which it is incorporated preventing water or other liquids from moving through the barrier.
- Sodium bentonite is also used in landfills and toxic waste dumps as liners to prevent water from entering and liquids from exiting (Keith and Murray, 1994).

6. Medicines

- montmorillonite clay is taken for absorbing poisons, controlling the acidity of the stomach, stomach ache, fermenting and putrifying conditions, and diarrhea Robertson(1986)
- Montmorillonite has been used for a long time in the preparation of pastes, ointments, and lotions
- Recently, a hydrothermal bentonite from Nevada has been used to promote joint mobility and flexibility, i.e. arthritis
- Bentonites is also used as a binder in making some pills.

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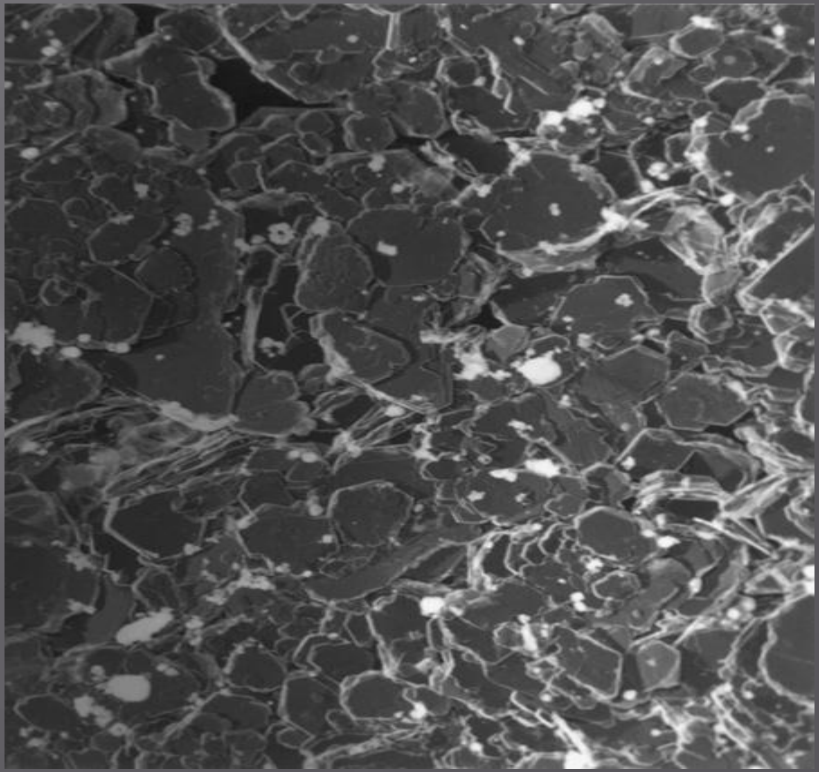
7. Pencil Leads

- Pencil leads are composed of graphite which is bonded with clay.
- The clay is a mixture of very fine particle size kaolinite and a small amount of bentonite, which improves the plasticity, green strength, and dry strength (Murray, 1961).
- The hardness of the lead is controlled by the percentage of the kaolin–bentonite mixture incorporated into the graphite.

APPLICATIONS OF KAOLIN

(1) Paper Industry

- One of the most important applications of kaolin is coating and filling paper .
- As a filler, kaolin is mixed with the cellulose fibers in wood pulp and as a coating, kaolin is mixed with water, adhesives, and various additives and coated onto the surface of the paper .



(2) Paint

- Paint is a significant market for kaolin, although it is considerably less than the market for paper coating and filling.
- About 600,000 tons annually are used worldwide as extender pigments in paint.
- The largest use is as a pigment extender in water-based interior latex paints.

(3) Ceramics

- Ceramics includes a wide range of products in which kaolins are utilized.
- These include dinnerware, sanitary ware, tile, electrical porcelain, pottery, and refractories .
- The term ceramic refers to the manufacture of products from earthen materials by the application of high temperatures .

(4) Rubber

- Kaolin is used in rubber because of its reinforcing and stiffening properties and it is relatively low cost in comparison with other pigments.
- In rubber goods which are black, the favored pigment is carbon black, but in non-black rubber goods, kaolin is used.
- There are two types of kaolins, hard clays which are fine in particle size and soft clays which are relatively coarse in particle size.

(4) Rubber

- Hard clays are used in non-black rubber goods where wear resistance is important. Examples are shoe heels and soles, tires, conveyor belt covers, and bicycle tires.
- Hard clays give stiffness to uncured rubber compounds which is important in the manufacture of rubber hose, tubing, jar rings, and extruded stocks to prevent sagging or collapsing during manufacture. Hard clay is also used to eliminate mechanical molding troubles in hard rubber goods, household goods, toys, and novelties.
- Other applications for hard clay in rubber are gloves, adhesives, butyl inner tubes, reclaimed rubber, and neoprene compounds.

(5) Plastics

- Kaolin is used as a filler in plastics because it aids in producing a smooth surface finish, reduces cracking and shrinkage during curing, obscures the fiber pattern when fiberglass is used as reinforcement, improves resistance to chemical action and weathering, and helps control the flow thermal stability, contributes to a high impact strength, improves properties .

(6) Catalysts

- The most important mineral used in the manufacture of carriers for catalysts is kaolin.
- The largest use of kaolin is in catalyst substrates in the catalytic cracking of petroleum.

(7) Portland cement

- Cement is made by mixing materials containing lime, silica, alumina, and iron oxide. This mixture is sintered and then pulverized at which time a retardant, gypsum is added.
- Kaolin is an ideal source of alumina and silica and also makes the cement whiter.

APPLICATIONS OF PALYGORSKITE AND SEPIOLITE

1. Laundry Washing Powders

Because of their high absorbency, palygorskite and sepiolite are used as additives in laundry washing powders to absorb salts and dirt particles and to keep the soap ingredients uniformly dispersed.

2. Medicines

- Palygorskite and sepiolite are used in certain liquid medications to keep the compounds in suspension and uniformly distributed.
- Also, because of their high active surface, drugs such as hydrocortisone can be retained and subsequently released at an appropriate rate (Forteza et al., 1988).

3. Cosmetics

- Many cosmetic formulations are blends of many diverse chemical compounds and the elongate palygorskite and sepiolite keep these chemicals in suspension and equally dispersed.
- These clays, because of their high absorbency for water and oil, make excellent face packs to cleanse the skin.
- They are used to give the skin opaqueness, eliminate shine, and cover up imperfections.

4. Asphalt

- Palygorskite is used as an emulsifier in asphalt.
- A positive property is that it acts as an emulsion stabilizer serving as a protective colloid.
- The asphalt when emulsified is much easier to apply and mix with aggregates.

5. Animal Feed Binders

- Both palygorskite and sepiolite are used as binders in making animal feed pellets.
- In addition to binding the feed pellet, these clays are excellent absorbents for aflatoxin.
- Some preliminary studies also indicated that dioxin is absorbed and is not release in the stomach or intestines of poultry or animals.

6. Agricultural Carriers

- The high sorptive capacity of palygorskite and sepiolite make these minerals very useful as carriers for pesticides, insecticides, and herbicides.
- Many of these chemicals are liquids or sticky pastes which would be difficult or impossible to use.

7. Tape Joint Compounds

- Finely pulverized palygorskite and sepiolite are used extensively to mix with adhesives used to fill joints and cracks in wall board.
- The filled joint or crack must be level and smooth and not shrink during drying.
- The elongate clay particles form a network which does not shrink as the adhesive dries.