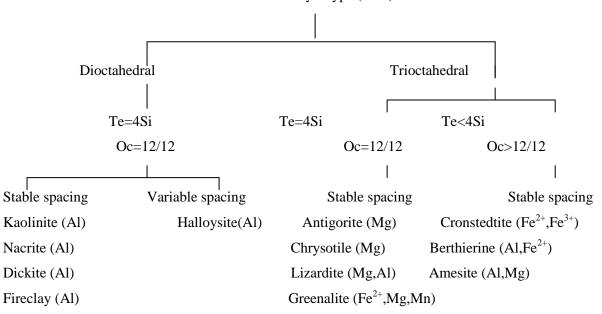
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2. PYROPHYLLITE – TALC GROUP:

This group comprising 2:1 (T>O>T>) layer minerals, devoid of cationic substitutions or charge deficit (x=0). The minerals therefore present a high structural stability. Pyrophyllite represents the dioctahedral type whereas talc represents the trioctahedral. Both minerals result from hydrothermal or diagenetic processes.

Table: Classification of major 1:1 clay minerals (After Caillère et al., 1982)



1:1 layer type (T.O.)

3. MICA GROUP:

The mica structure consists of 2:1 layer marked by noticeable substitutions, and by strong negative charges neutralized by large univalent interlayer cations. The layer charge $(x\sim1)$ results from:

- Substitution of trivalent cations (R^{3+}) for Si⁴⁺ in tetrahedral positions.
- Substitution of univalent (R^{1+}) or divalent (R^{2+}) for R^{2+} or R^{3+} .
- Vacancies in octahedral positions.

Most of interlayer cations are univalent and associated with no or only few molecules of water. This broad group is characterized by a stable spacing on X-ray diagrams and well-shaped but irregular edged on electron micrographs. It includes both dioctahedral and trioctahedral minerals. Most of the species are encountered in clayey, silty and sandy fractions of sedimentary rocks. The general formula of mica is:

X – Na, K, Ca (also Ba, Rb, Cs etc.) in 12-fold coordination.

 \mathbf{Y} – Al, Mg, Fe²⁺ (Mn, Cr, Ti, Li etc.) in 8-fold coordination.

 \mathbf{Z} – Si or Al (perhaps Fe³⁺, Ti) in 4-fold coordination.

Subdivision of micas into dioctahedral and trioctahedral depends on the number of Y-ions (i.e. whether four-dioctahedral or six- triocthedral coordination). Nevertheless mica group and brittle mica group are divided according to the X-ion, in the common micas X is largely K or Na, but the so-called brittle mica is largely Ca.

Common					
micas	Dioctahedral	MuscoviteK ₂ Paragonite Glauconite	Al ₄ Na ₂ (K,Na) _{1.2-2.0}	Si ₆ Al ₂ Al ₄ (Fe,Mg,Al) ₄	$\begin{array}{c} 2\\ Si_{6} Al_{2}\\ Si_{7\text{-}7.6} Al_{1\text{-}0.4} \end{array}$
Brittle micas	Dioctanedrai	Margarite Ca ₂	Al ₄	Si ₄ Al ₄	
Common micas	Trioctahedral	Phlogopite Biotite Zinwaldite Lepidolite	$\begin{matrix} K_2\\K_2\\K_2\\K_2\\K_2\end{matrix}$	$(Mg,Fe)_6$ $(Mg,Fe,Al)_6$ $(Fe,Li,Al)_6$ $(Li,Al)_{5-6}$	Si ₆ Al ₂ Si ₆₋₅ Al ₂₋₃ Si ₆₋₅ Al ₂₋₃ Si ₆₋₅ Al ₂₋₃
Brittle micas		Clintonite	Ca ₂	(Mg,Al) ₆	Si _{2.5} Al _{5.5}

General formula for the dioctahedral micas is:

$$(K,Na,H_2O)$$
 $(Al,Fe^{3+})_{2-x}(Mg,Fe^{2+})$ $(Si^{2+}_xAl_{1-x})O_{10}$ $(OH)_2$

Examples:

Muscovite (stable polytype)

K Al2 (Si3 Al) O10 (OH)2

Phengite

K (Al_{1.5}R²⁺_{0.5}) (Si_{3.5}Al_{0.5}) O₁₀ (OH)₂

Glauconite

$$R^{1+}_{0.78}(Fe^{3+}_{1.01}Al_{0.45}Mg_{0.39}Fe^{2+}_{0.2})_{2.05}$$
 (Si_{3.65}Al_{0.35}) O₁₀ (OH)₂

Celadonite

 $R^{1+}_{0.83}(Fe^{3+}_{0.72}\,Al_{0.49}\,Mg_{0.63}\,Fe^{2+}_{0.21})_{2.05}\,(Si_{3.81}\,Al_{0.19})\,O_{10}\,(OH)_2$

Muscovite and phengite chiefly originate from metamorphic and silica-rich igneous rocks. Glauconite forms a large part of the green granules present on the upper part of the continental margins. Celadonite is an iron-rich mica-like glauconite, with less significant tetrahedral substitution; it constitutes an alteration product of volcanic rocks.

The general formula of the trioctahedral micas is:

 $\frac{K_{x-y+2z}}{\text{Interlayer}} \underbrace{[(Mg,Fe^{2+})_{3-y-z} R_y^{3+} \#_z] (Si_{4-x}R_x^{3+})O_{10} (OH,F)_2}{\text{Octahedra}} \underbrace{-\text{Tetrahedra}}_{\text{Tetrahedra}} An$

Interlayer Octahedra Tetrahedra Anionic group

- means vacancy of positive charge

x,y,z – means rate of substitution in tetrahedral or octahedral sheets.

Examples:

Phlogopite

 $(K_{0.93}Na_{0.04}Ca_{0.03})(Mg_{2.77}Fe^{2+}{}_{0.10}Ti_{0.11})(Si_{2.88}Al_{1.12})O_{10}(OH)_{1.49}F_{0.51}$

Biotite

 $(K_{0.78}Na_{0.16}Ba_{0.02})(Mg_{1.68}Fe^{2+}{}_{0.71}Fe^{3+}{}_{0.19}Ti_{0.34}Al_{0.19}Mn_{0.01})(Si_{2.86}Al_{1.14})O_{11.12}(OH)_{0.71}F_{0.17}O_{1.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}O_{11.12}$

Biotite, a very common mineral, and phlogopite, mainly issue from ferromagnesian crystalline rocks.

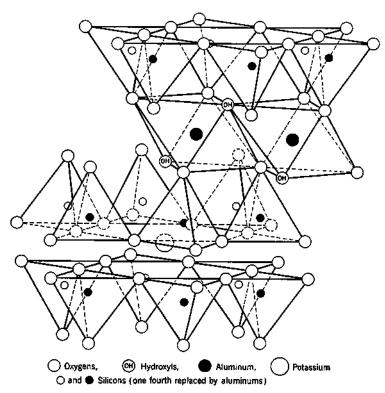


Fig. 2-8. Diagrammatic sketch of the structure of muscovite, after Jackson and West (1930).

Illite - Illite is the name geologists usually give to the micaceous mineral present in the clay-sized fraction of sedimentary rocks. Statistically illite is predominantly of dioctahedral

type close to muscovite, because muscovite is a very common mineral and one of the more stable micas. Nevertheless illite generally contains more <u>Si, Mg, H₂O and less K</u> than the ideal muscovite. In fact the term illite can disgnate all types of small micas, and sometimes corresponds to a mixture of micaceous minerals of different origins. The dominant type of sedimentary illites can often be determined by using roentgengraphic, electron microscope and microchemical techniques.

4. BRITTLE MICAS:

Brittle micas differ from true micas by a higher layer charge (-2 per formula unit instead -1), and by divalent compensation cations in interlayers instead of univalent ones. They result from the erosion and alteration of crystalline schists. They are rarely incorporated in the clay-sized fraction of sedimentary rocks, because of their resistance to fragmentation and low abundance at the surface of the Earth. Brittle micas comprise both dioctahedral and trioctahedral types.

Margarite: Ca Al₂ (Si₂Al₂) o_{10} (OH)₂ Clintonite: Ca (Mg₂Al) (SiAl₃) O_{10} (OH)

5. VERMICULITE GROUP:

Vermiculites are T.O.T. minerals with water associated with cations in the interlayer, determining a basal spacing close to 14 Å. The water molecules are strongly linked to the layer structure (layer charge>0.6), which considerably limits the possibilities of expandability. Most macroscopic vermiculites are of a trioctahedral type and result from alteration of mica or chlorite. Example: Mg_3 (Si₃Al) O₁₀ (OH)₂ Mg_{0.5} (H₂O)₄

Clay-sized vermiculites can be either trioctahedral, and result from pedogenesis or diagenesis.

6. SMECTITE GROUP:

Smectite constitute large group of T.O.T. minerals, marked by a low layer charge (x<0.6). This characteristic determines a weakness of the linkage between the different layers of a given particle, and allows considerable swelling phenomena as well as possibilities of rotation. The interlayers are occupied by cations (mainly Na, K, or Ca) and by one to several layers of water (basal spacing from 10 to 18 Å). The shape of smectites varies according to the conditions of genesis: flakes, curls, laths of different sizes, etc. Smectite minerals may form in different chemical environments, most of them being surficial soils or sediments. This is the reason why they are present in various chemical compositions, in both dioctahedral and trioctahedral subgroups. Octahedral substitutions are very frequent, tetrahedral substitutions occur commonly. Examples:

Dioctahedral smectites (Al, Al-Fe or Fe smectites)

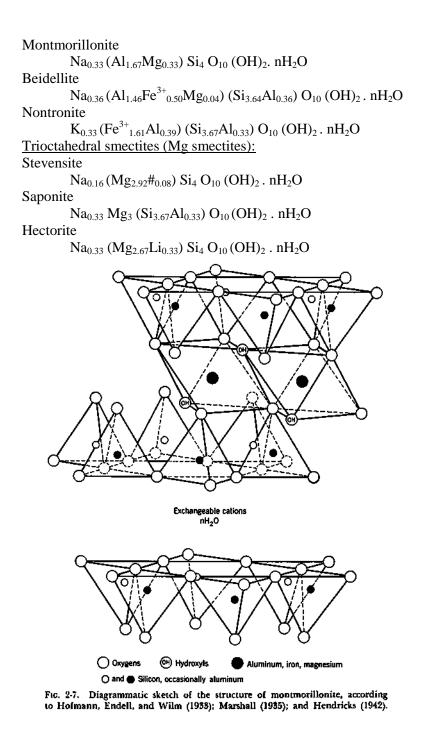
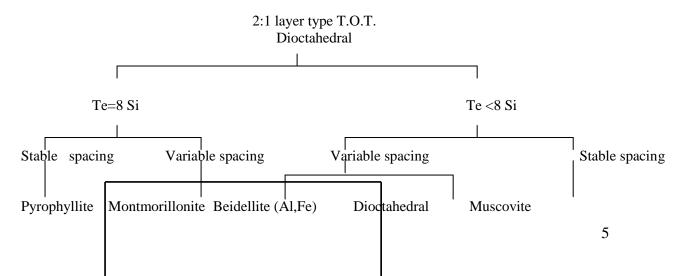


 Table
 : Classification of major 2:1 dioctahedral clay minerals (after Caillère et al., 1982).



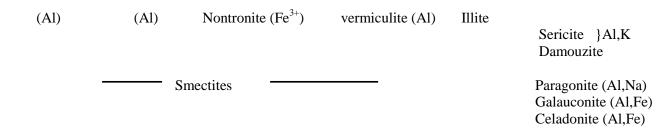
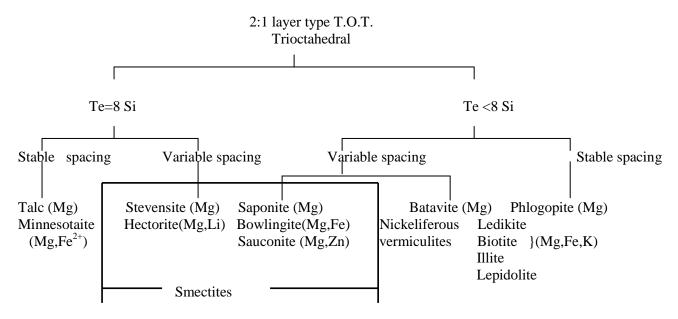


Table :Classification of major 2:1 trioctahedral clay minerals (after Caillère et al., 1982).



7. CHLORITE GROUP:

Chlorites are considered either as a 2:1 layer group with a hydroxide interlayer, or as a 2:1:1 layer group. Their typical structure shows a regular alternation of negatively charged trioctahedral micaceous layers and of positively charged octahedral sheet. The basal spacing of the structure unit is close to 14 Å; it is invariable for true chlorites, because T.O.T. layers and O interlayers are strongly bound. The tetrahedral substitution of Al for Si induces a variable charge deficit, which is partly compensated by an excess of charge in the interlayer octahedral sheet ("brucite sheet") and perhaps in the layer octahedra. A few chlorites, however, are typically dioctahedral (aluminous, i.e., dombassite), and some species present a combination of dioctahedral layers and trioctahedral hydroxide interlayers (cookeite,sudoite). Chlorites generally display flat particles of various sizes (from <1 μ m to >1mm), with well-defined outlines and sometimes polygonal edges. They chiefly originate from crystalline igneous or metamorphic rocks, or from the alternation of some volcanic rocks.

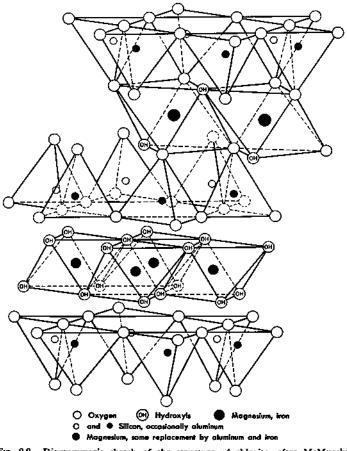


Fig. 2-9. Diagrammatic sketch of the structure of chlorite, after McMurchy (1934).

Examples of simplified formulas:

Name I	nterla	yer	Layer	Tetrahe	dra Anion	
	0	ctahedra	octahe	dra		group
Chlorite s.s	. (M	$g_{3-y}Al_1Fe^{3+}_{y})$	Mg_3	(Si _{4-x} Al _x) O_{10} (OH)8
Dombassite	e	Al _{2+1/3}	Al_2	(Si ₃ Al)	O ₁₀ (OH)8
Sudoite	(M	g _{2.3} Al _{0.7})	Al_2	(Si _{3.3} Al	O_{10} O ₁₀ (OH) ₈	

Iron-rich chlorites, or chamosites, occur commonly in iron-ore deposits. Their x-ray diffraction patterns differ from those of ferriferous kaolinite (berthierine) by the presence of a small (001) reflection (14Å) and from those of true chlorite by the increasing height of this reflection after heating.

Swelling chlorites or pseudo-chlorites expand like smectites when immersed in water or ethylene glycol, but resist heating like chlorites. They appear to represent an alternation of smectitic layers and octahedral brucitic sheets.

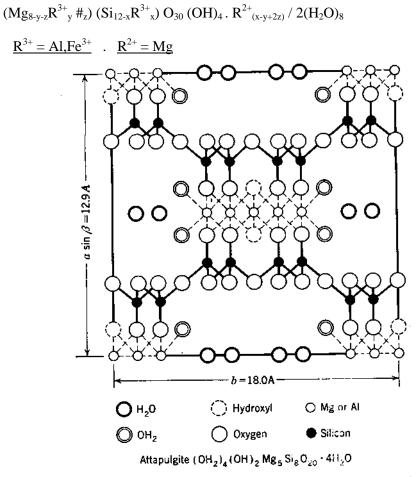
8. PALYGORSKITE – SEPIOLITE GROUP:

Often called fibrous clays or pseudo-layered clays. Palygorskite and sepiolite consist of bundles of well-defined and elongated fibers or laths. Their structure comprises continuous tetrahedral sheets forming a hexagonal-mesh arrangement (Si,O), alternating with discontinuous octahedral sheets (Mg, O, OH) extending in a single direction and forming ribbons. The ribbon structure is responsible for the fibrous shape of the clay particles. The ribbons are alternately arranged above and below the continuous hexagonal sheet of tetrahedra, the transverse section resembling a hollow brick structure. The empty spaces are filled with zeolitic water. Palygorskite and speiolite are both magnesium-rich clay minerals, differing from each other by width of inverted ribbons (broader for sepiolite) and by specific chemical characters. Palygorskite is less magnesian and presents more structural diversity than sepiolite. The substitution lead to incorporating Al in tetrahedra, and Al for Fe in octahedra. Xylotile is a sepiolite in which Mg is partly replaced by Fe³⁺. All fibrous clays form under surficial conditions in soils or sediments.

Palygorskite

$$(Mg_{5\text{-}y\text{-}z}R^{3\text{+}} \ \#_z) \ (Si_{8\text{-}x}R^{3\text{+}}) \ O_{20} \ (OH)_4 \ . \ R^{2\text{+}}_{(x\text{-}y\text{+}2z)} / \ 2(H_2O)_4$$

Sepiolite



Schematic presentation of the structure of attapulgite, after Bradley (1940).

9. MIXED-LAYERS:

Mixed-layered or interstratified clays refer to remarkable phyllosilicate structures, characterized by a vertical stacking sequence of two or more types of single layers. The layers involved can be of 2:1, 2:1:1 and even 1:1 types. The possibility of mixed layering results from the rather weak chemical and structural linkage existing between the successive layers in a given clay particle. As the basal surfaces of all different types of clay layers present similar sheets of oxygen and hydroxyl arranged in a hexagonal mesh, layers with different internal arrangements can stack together and still keep mobile interfaces. Such structural features are almost unique in the mineralogical range and are responsible for the common occurrence of mixed-layered clay minerals. Most mixed-layers can be considered as clay species intermediate between two single clay minerals. They mainly form through weathering or middle-late diagenesis, but also characterize some hydrothermal and sedimentary environments. Three main types of interstratification are recognized:

1) A periodic alternation of layers of two types A and B refers to regular or ordered mixedlayers:

ABABABAB..... or AABAABAABAAB.....

These minerals show well-defined reflections on x-ray diagrams and tend to be given specific names: **hydrobiotite** for illite-vermiculite, **corrensite** for chlorite-smectite, etc. Sometimes they are called by linking the name of both their components (e.g. regular illite-smectite, regular kaolinite-smectite).

2) A random alternation of each type of layer corresponds to irregular and randomly mixedlayered clays:

AABABBBAAABAABA

This group often corresponds to poorly defined x-ray diffraction patterns, with dome-, plateau- or wedge-like shapes, and locations at intermediate positions between those of the single minerals involved. The random mixed-layers are very common and develop particularly in soil profiles. They include both two- and three-component systems, identified by using reference charts and curves. They are labeled by the types of layers responsible for the interstratification.

Examples are:

Irregular illite-vermiculite

Irregular smectite-vermiculite

3) Partially ordered structures appear to exist, especially in some soils. Intermediate between both former types, they are little known and not specifically labeled.

Table : Examples of mixed-layer clay minerals.

Layer types	Specific name				
1) Regular or subregular alternation of two layer types:					
Muscovite-montmorillonite	Rectorite (allevardite)				
Illite-smectite	Bravaisite				
Glauconite-smectite					
Chlorite-smectite	Corrensite				
Dioctahedral chlorite-smectite	Tosudite				
Mica-vermiculite	Hydrobiotite				
Talc-saponite	Aliettite				
Kaolinite-smectite					
2) Irregular alternation of two layer types:					
Illite-smectite					
Glauconite-smectite					
Mica-vermiculite					
Mica-chlorite					
Mica-dioctahedral chlorite					
Smectite-chlorite					
Chlorite-vermiculite					
Kaolinite-smectite					
3) Three-component systems:					
Illite-chlorite-smectite					
Illite-smectite-vermiculite					