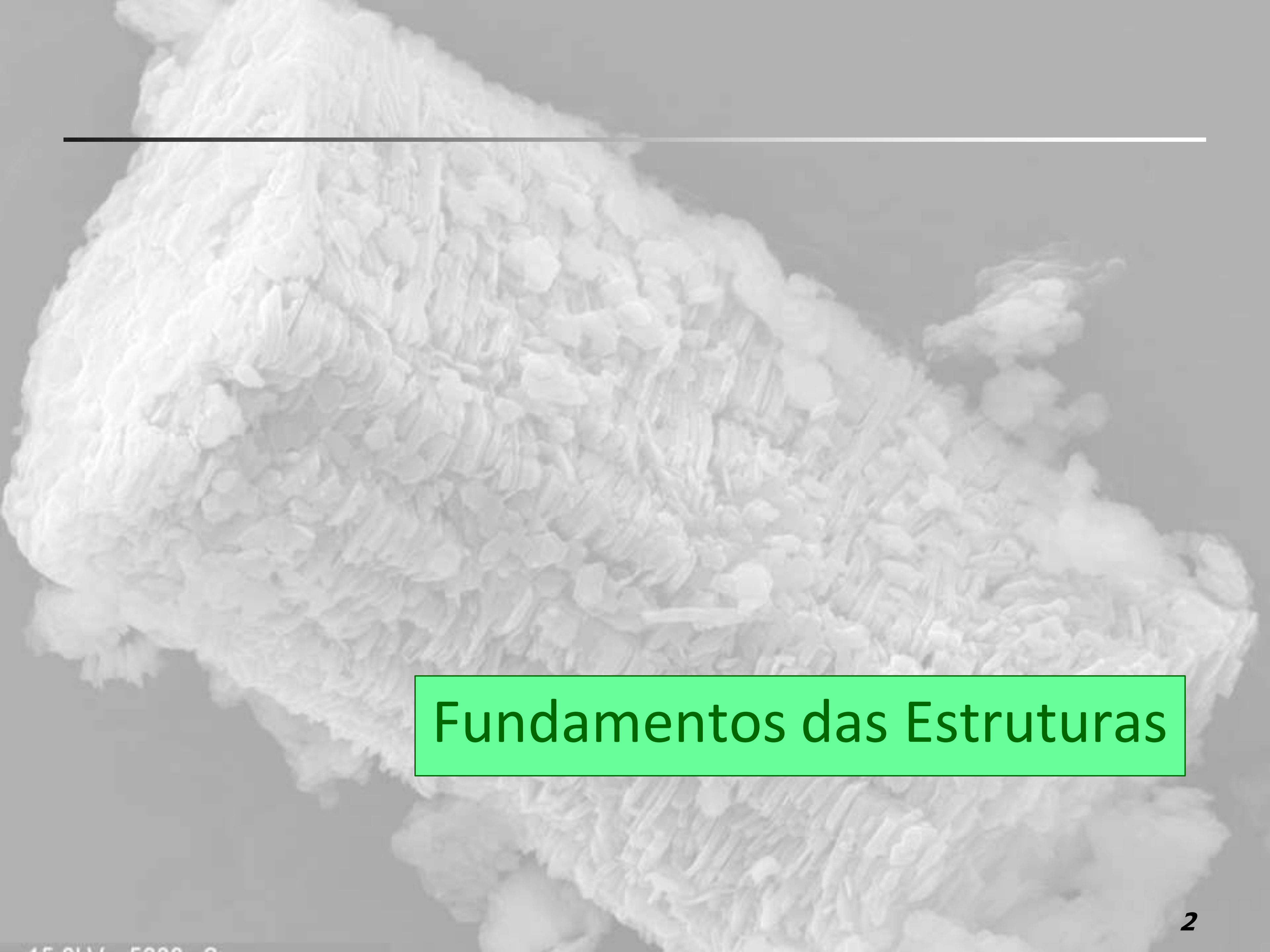
Aula 2

Estrutura Cristalina dos Argilominerais

PMT 5846 – Ciência e Tecnologia de Argilas

Prof. Antonio Carlos Vieira Coelho

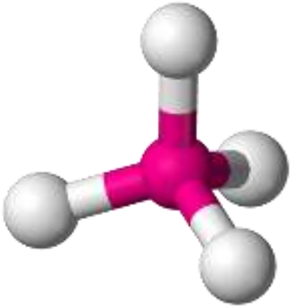
Departamento de Engenharia Metalúrgica e de Materiais
EPUSP - 2020

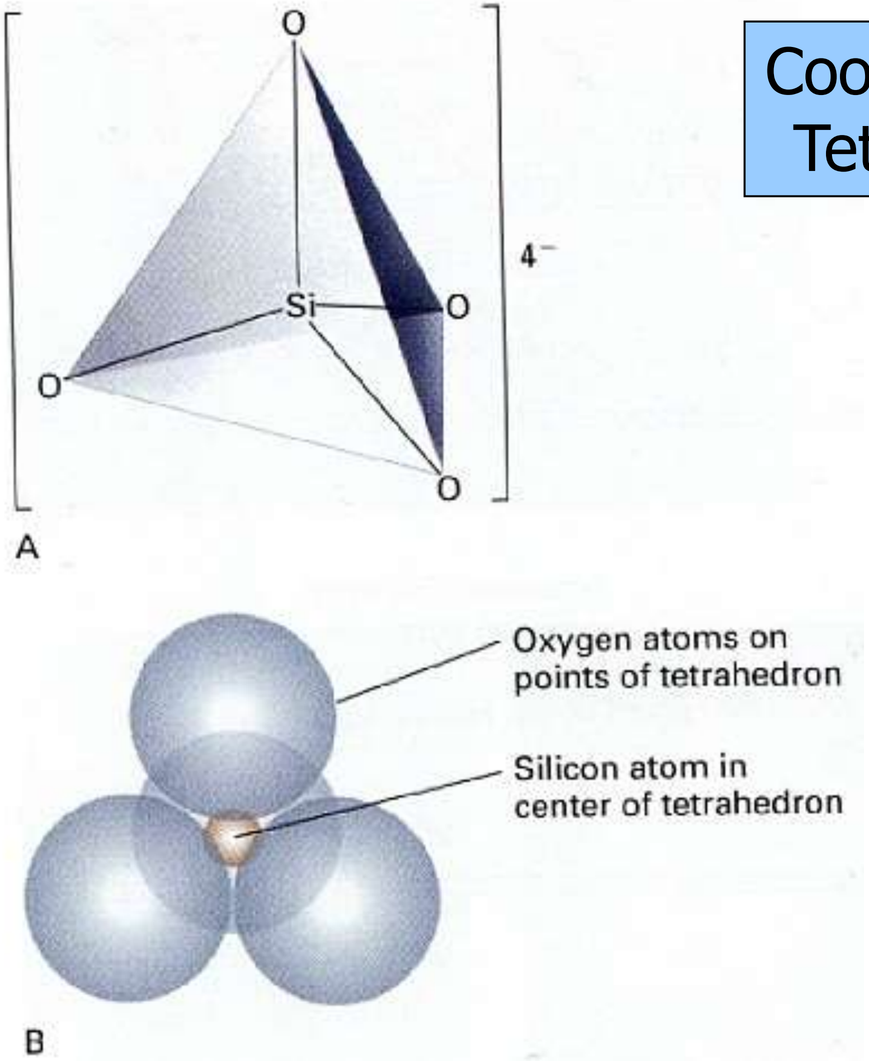


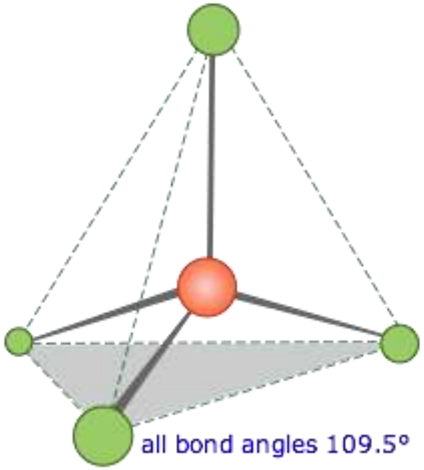
Fundamentos das Estruturas

Fundamentos da Estrutura dos Filossilicatos

Coordenação
Tetraédrica

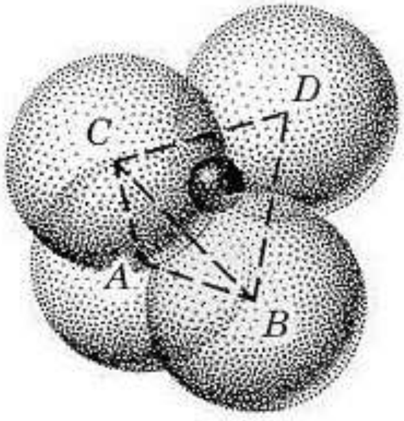


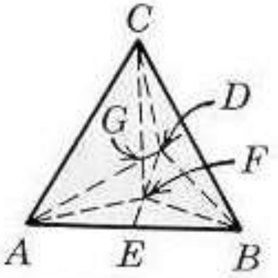




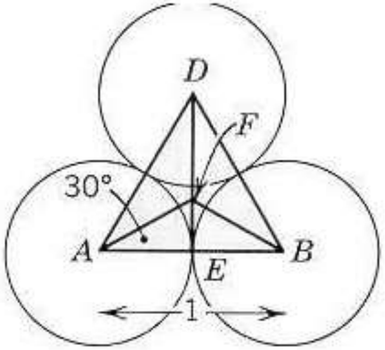
Folha Tetraédrica

Coordenação Tetraédrica (NC=4)





G is location of center of small ion, in center of tetrahedron



In base triangle

$$\cos 30° = \frac{AE}{AF}$$

$$\therefore AF = \frac{AE}{\cos 30°} = \frac{\frac{1}{2}}{\cos 30°}$$

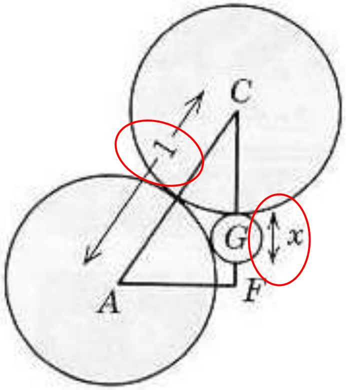
$$= \frac{1}{2} \cdot \frac{2}{\sqrt{3}} = \frac{1}{\sqrt{3}}$$

In vertical triangle CAF

$$CF = \sqrt{AC^2 - AF^2} =$$

$$\sqrt{(1)^2 - \left(\frac{1}{\sqrt{3}}\right)^2} = \sqrt{1 - \frac{1}{3}}$$

$$\sqrt{\frac{2}{3}} = .81649$$



Also $CG = \frac{3}{4}\, CF$, because center of tetrahedron G is $\frac{1}{4}$ up from the base.

Furthermore $CG = \frac{1}{2} + \frac{1}{2}x$

$$\therefore \frac{1}{2} + \frac{1}{2}x = \frac{3}{4} \cdot .81649 = .6124$$

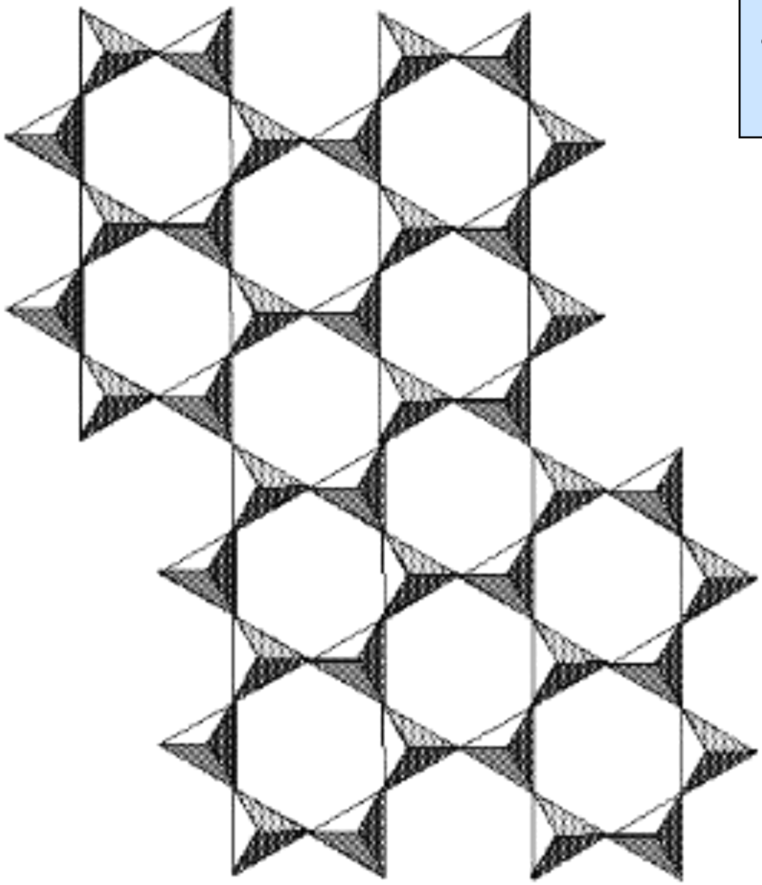
$$\therefore \frac{1}{2}x = .612 - .5 - .1124$$

$$x = 0.225$$

Folha Tetraédrica

Arranjo na folha tetraédrica:

- ***três vértices*** compartilhados (**basais**) ;
- o ***quarto vértice*** fica perpendicular ao plano (**apical**)



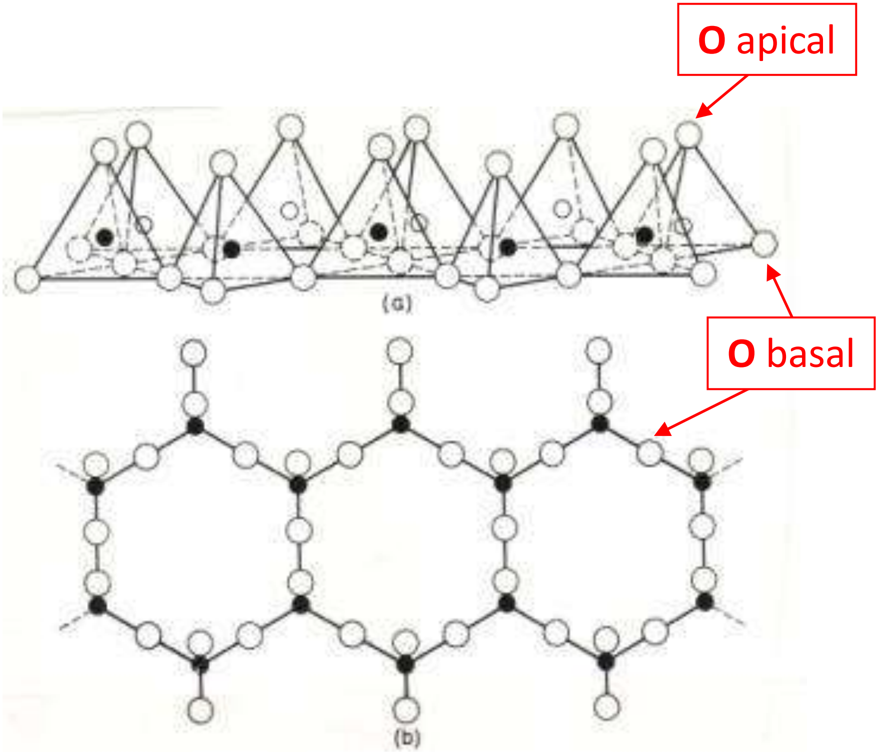
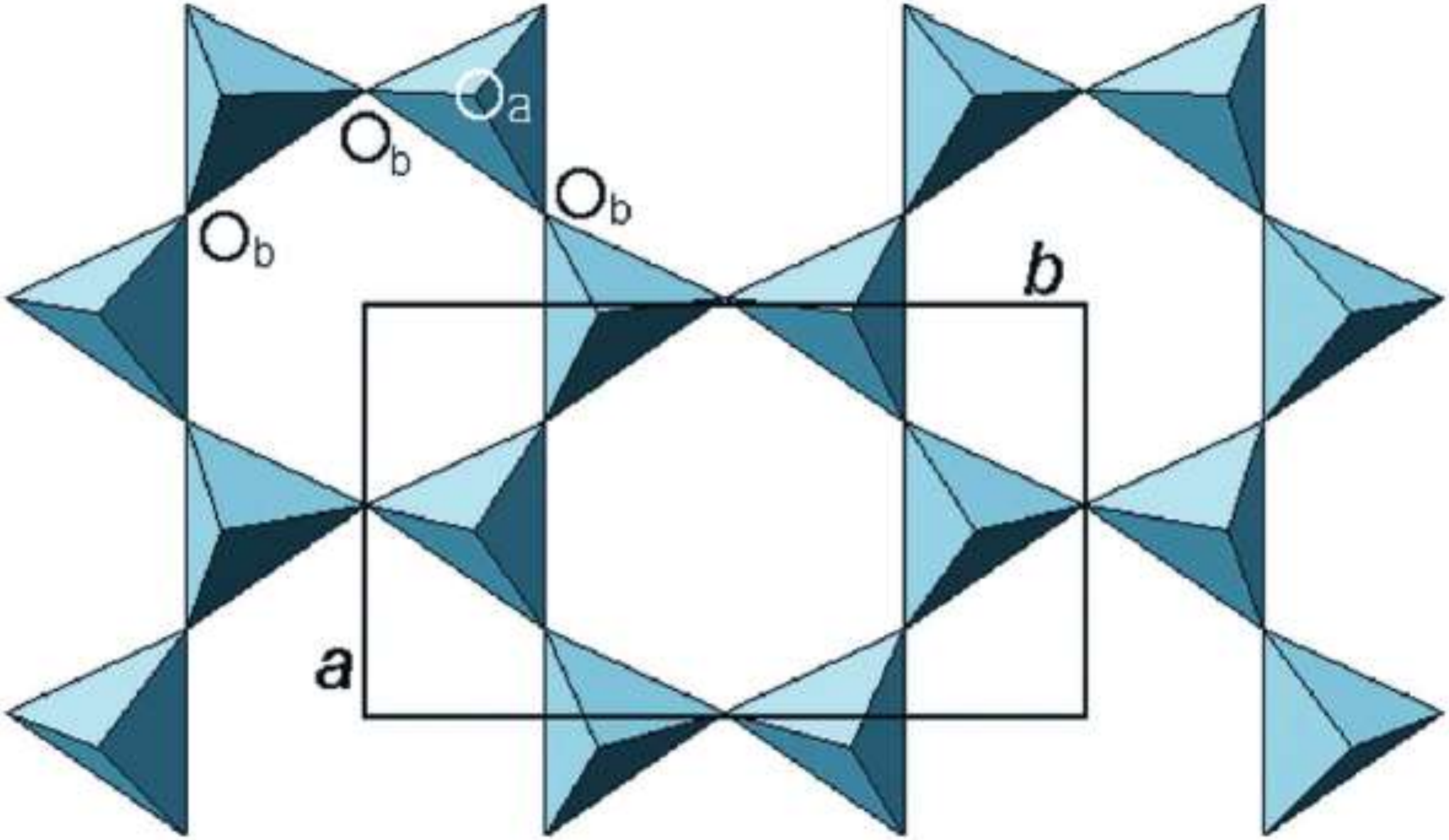


Figure 2: Diagrammatic sketch of sheets of silicon tetrahedra: (a) in perspective; (b) looking down on the tetrahedra, i.e., projected on the plane of the base of the tetrahedra; after Grim, 1968.

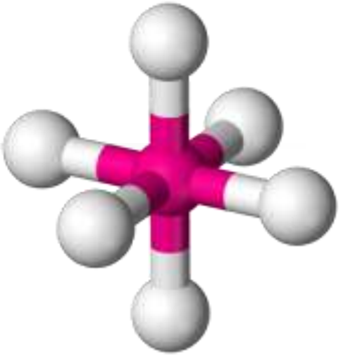
Folha Tetraédrica



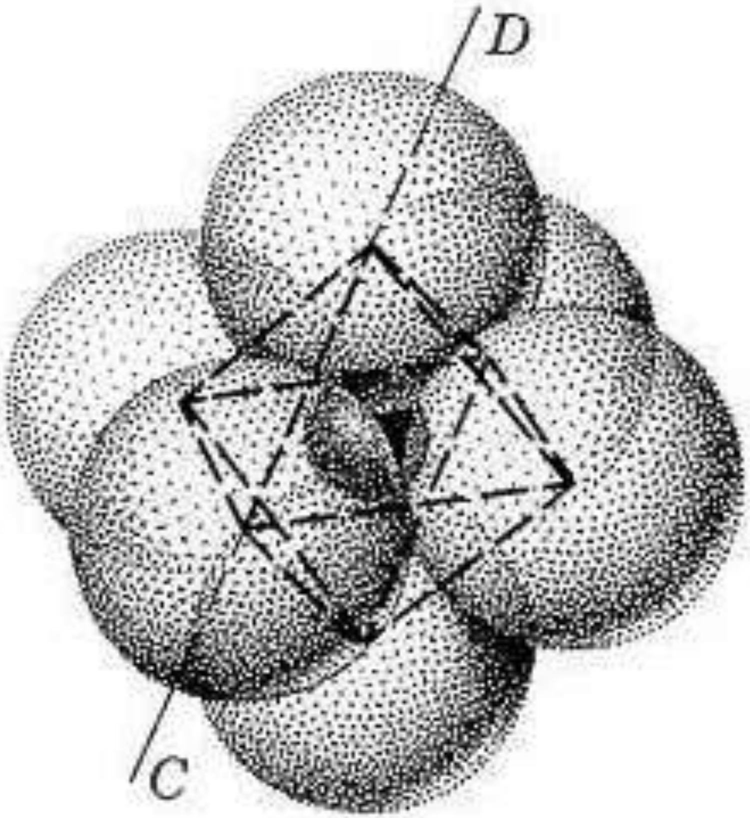
Tetrahedral sheet. O_a and O_b refer to apical and basal oxygen atoms, respectively. *a* and *b* are the unit-cell parameters

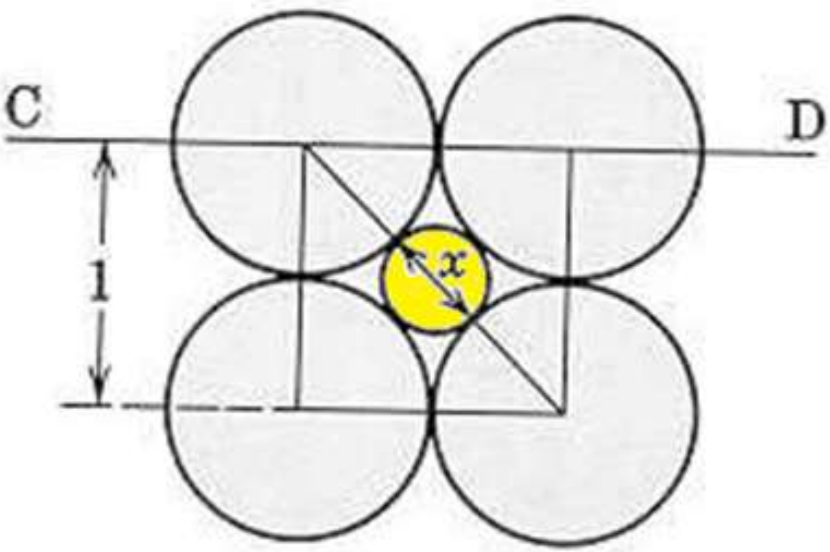
Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

Folha Octaédrica



Coordenação
Octaédrica





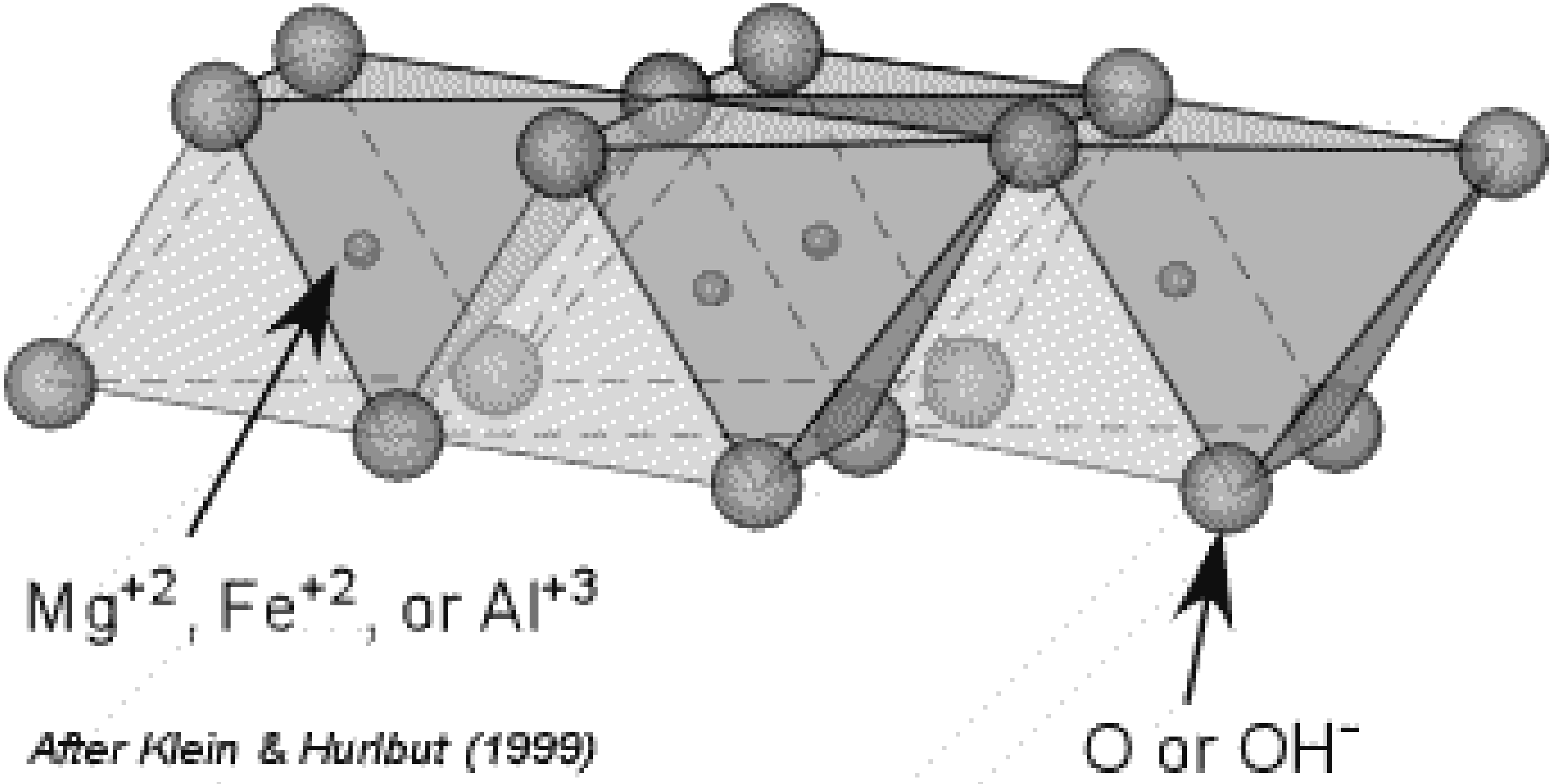
$$(1 + x)^2 = (1)^2 + (1)^2$$

$$1 + x = \sqrt{2} = 1.414$$

$$x = 0.414$$

Folha Octaédrica

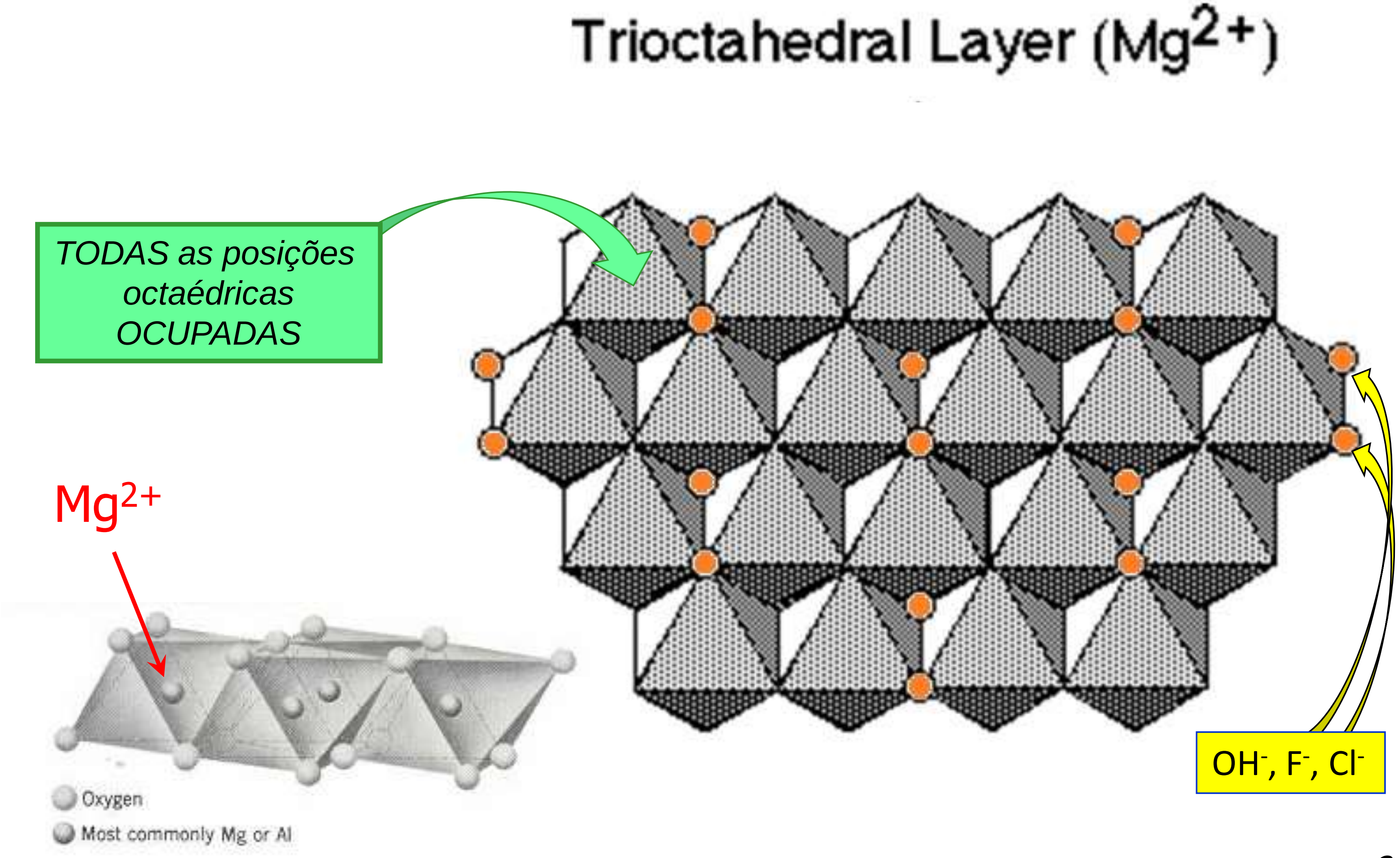
Infinitely extending sheet of XO6 octahedra. All octahedra lie on triangular faces



After Klein & Hurlbut (1999)

Folha Trioctaédrica

3 em cada **3** posições octaédricas **ocupadas** por cátions **divalentes**


Trioctahedral Layer (Mg^{2+})

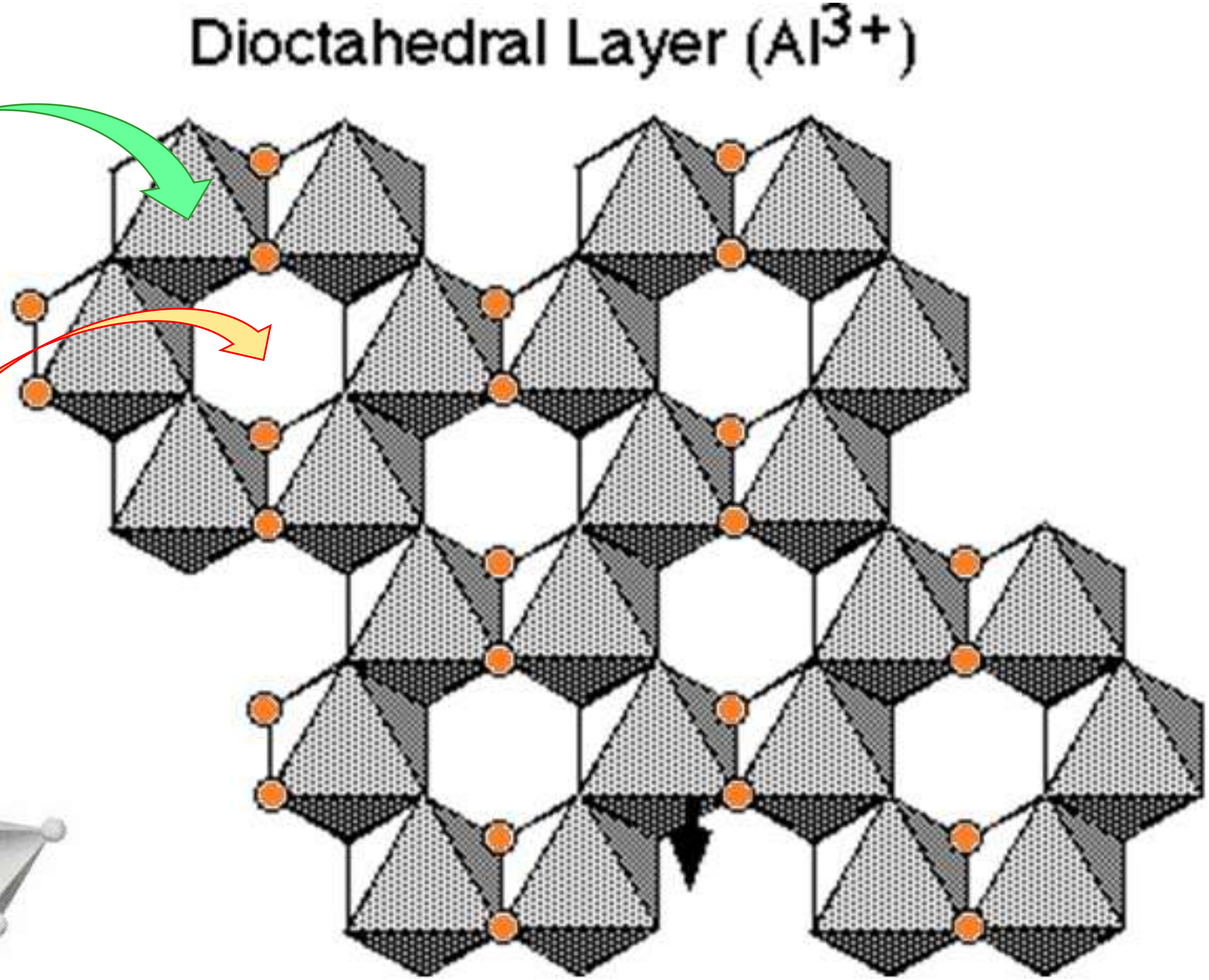
TODAS as posições octaédricas OCUPADAS

Mg^{2+}

OH$^-$, F$^-$, Cl$^-$

Folha Dioctaédrica

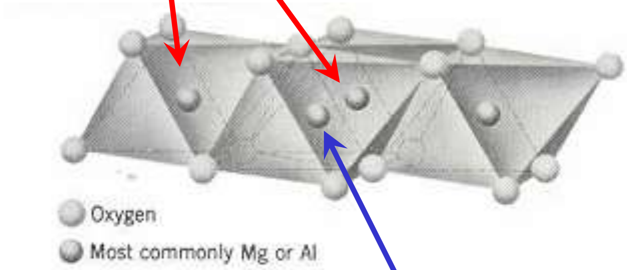
2 em cada **3** posições octaédricas **ocupadas** por cátions **trivalentes**



posição octaédrica OCUPADA

posição octaédrica VAZIA

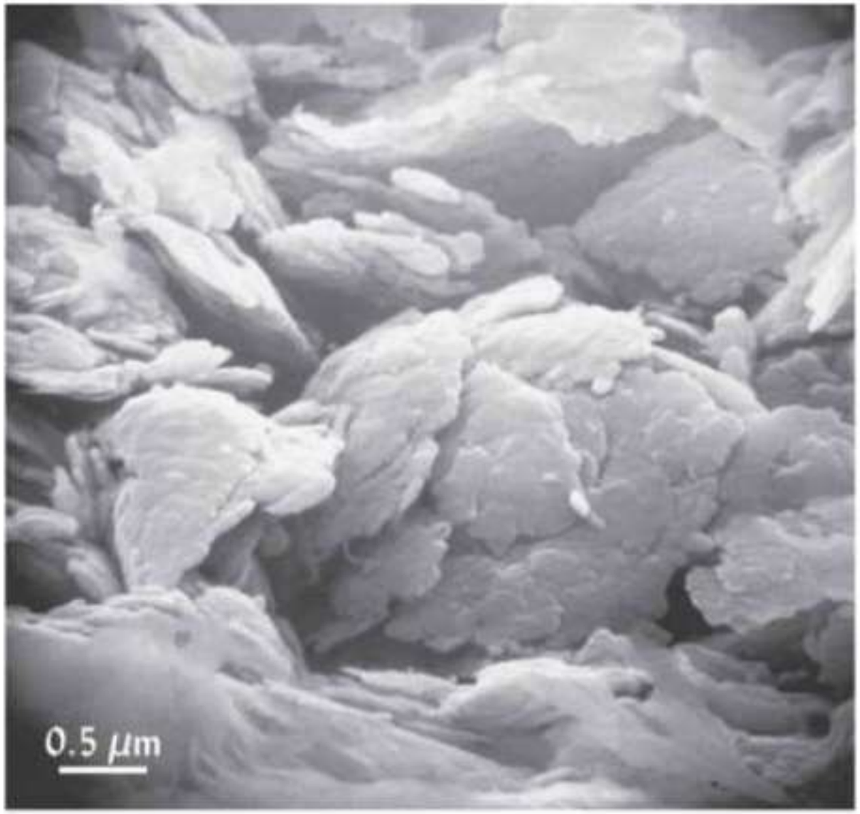
Al^{3+}



posição não ocupada

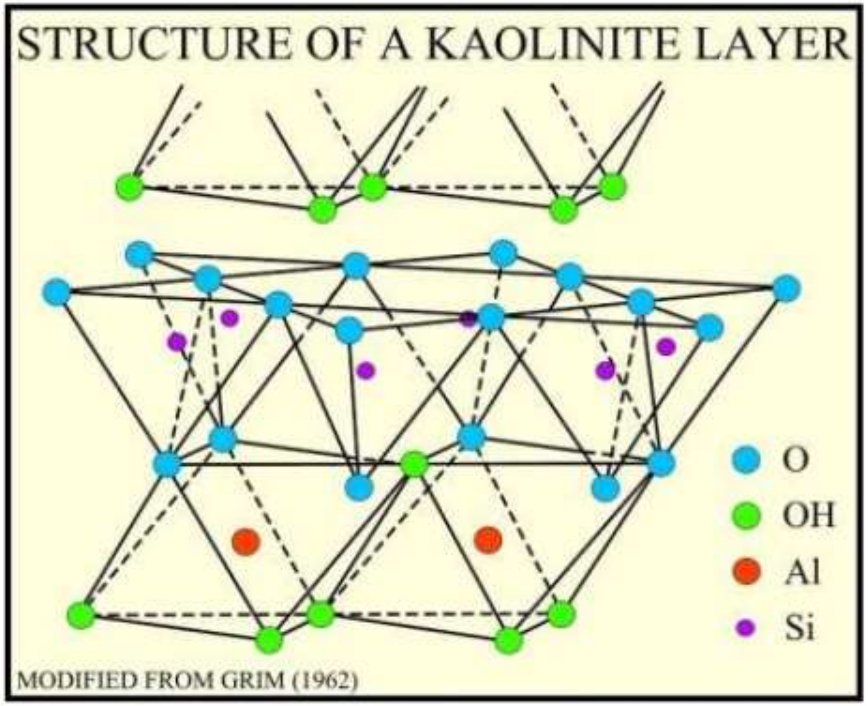
The Common Structure of Phyllosilicates

- All *phyllosilcates* can be considered to be formed by *superposed atomic planes parallel to the (001) face*.
- Thus, a way to describe their crystal structure is to consider how each of these planes is occupied by cations and anions on the one hand and how they are linked together on the other hand.
- The *first level of spatial organization of the atomic planes* will be assigned here as ***"sheet"*** (a cation plane sandwiched between two anion planes)



From atomic Sheets to Layers

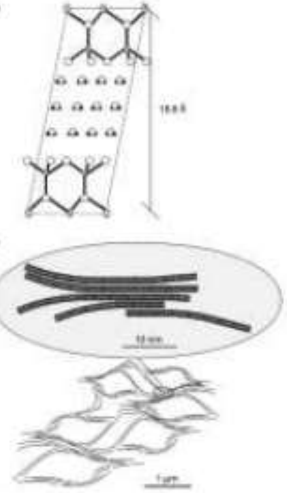
- *Clay minerals, phyllosilicates, are composed of a combination of two types of layer structures* which are coordinations of ***oxygen anions*** with ***various cations***.
- ***Two types of sheets*** are known following the number of anions coordinated with the cations, one of six-fold coordinations (***tetrahedra***) and the other of eight-fold coordination (***octahedral*** coordination).

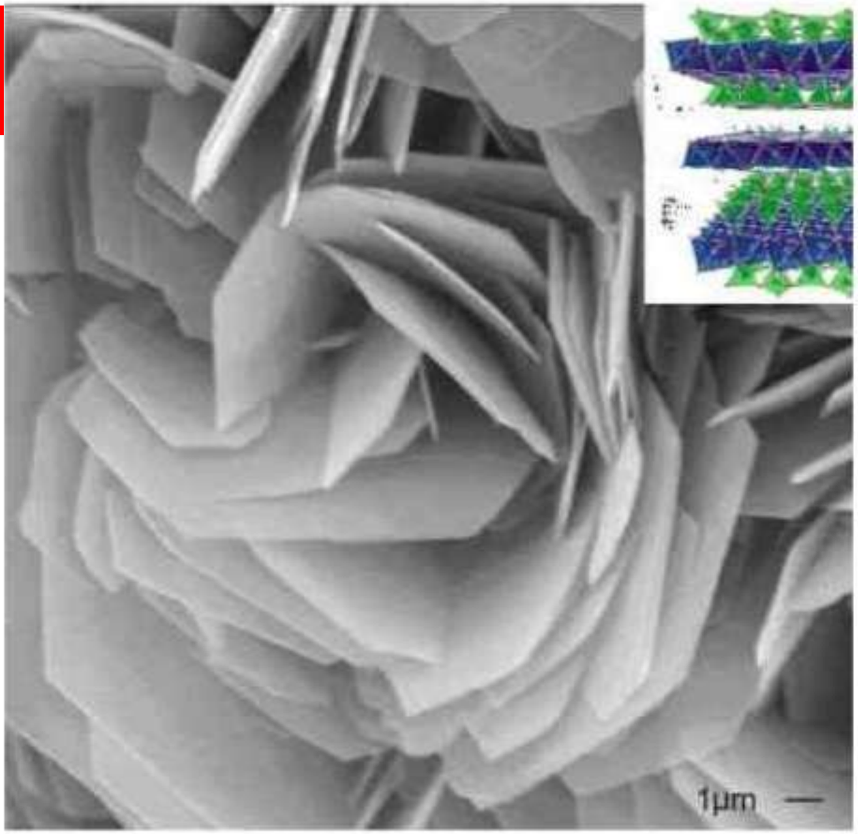


MODIFIED FROM GRIM (1962)

The Common Structure of Phyllosilicates

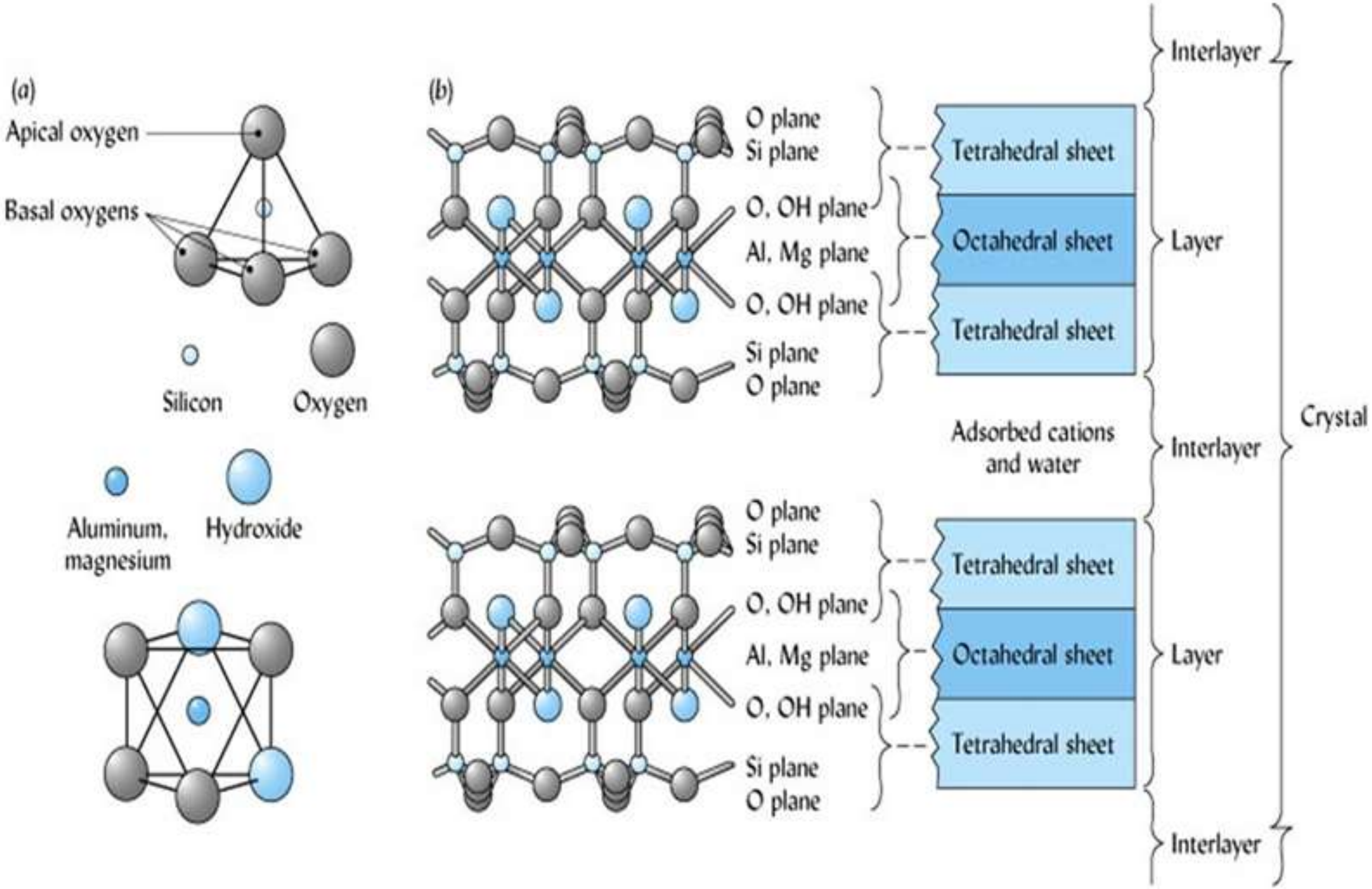
- The *second level of organization* being an association of sheets called ***"layer"***.
- *The third level of organization* to be presented is the way that layer stack and how thay are bonded together to form ***"crystallites"***.





Filossilicatos

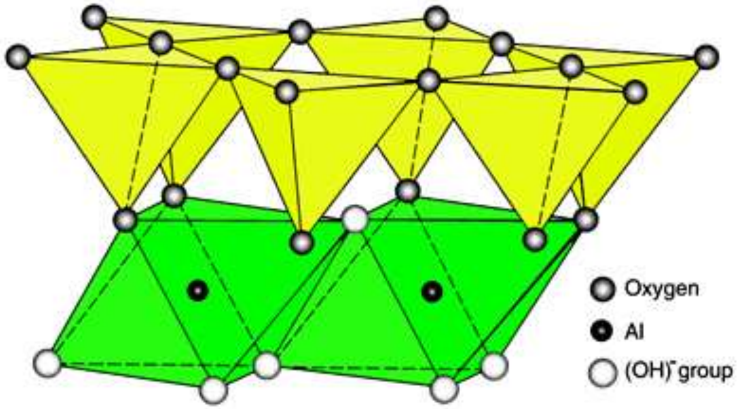
folha *(tetraédrica, octaédrica)* → **camada** *(1:1, 2:1)* → **cristal** *(empilhamento camada + Interlamelar)*



Exemplos de Filossilicatos

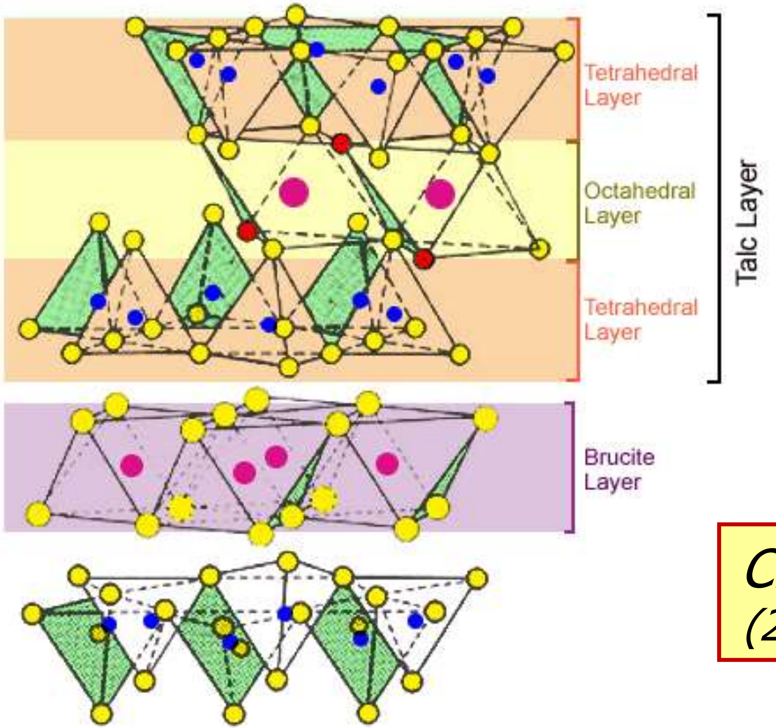
Caulinita

(1:1)



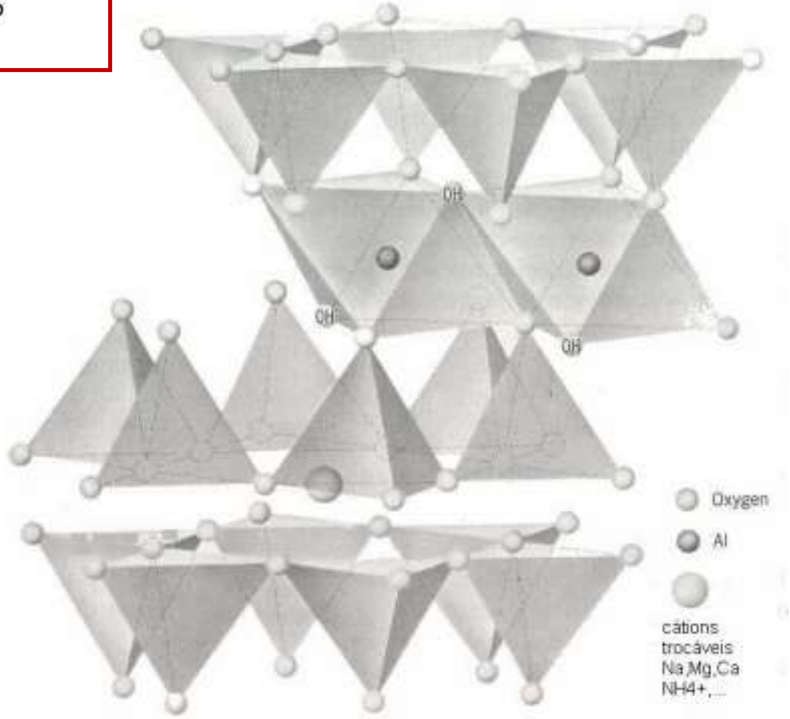
Clorita

(2:1:1)



Esmectita

(2:1)



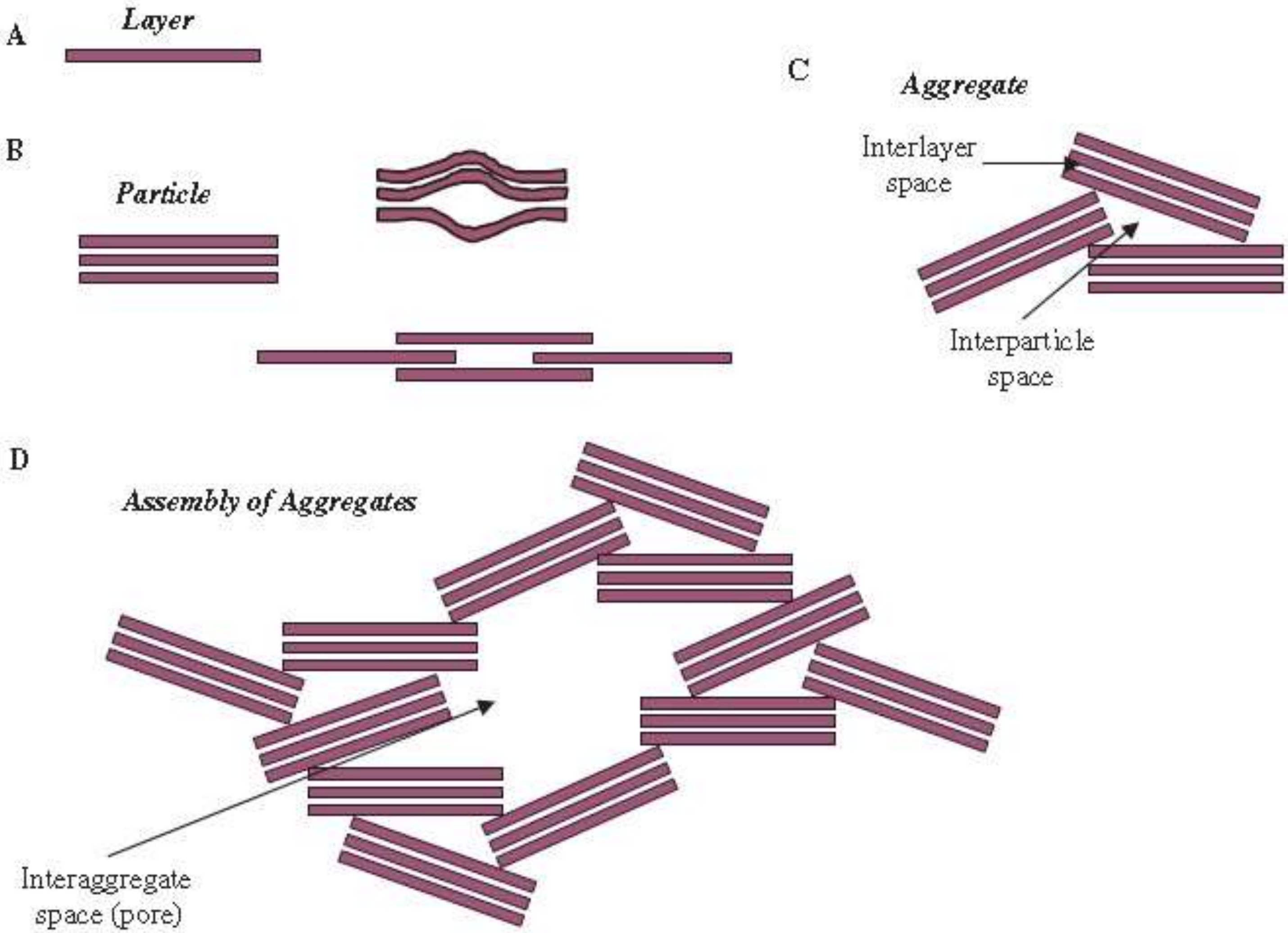
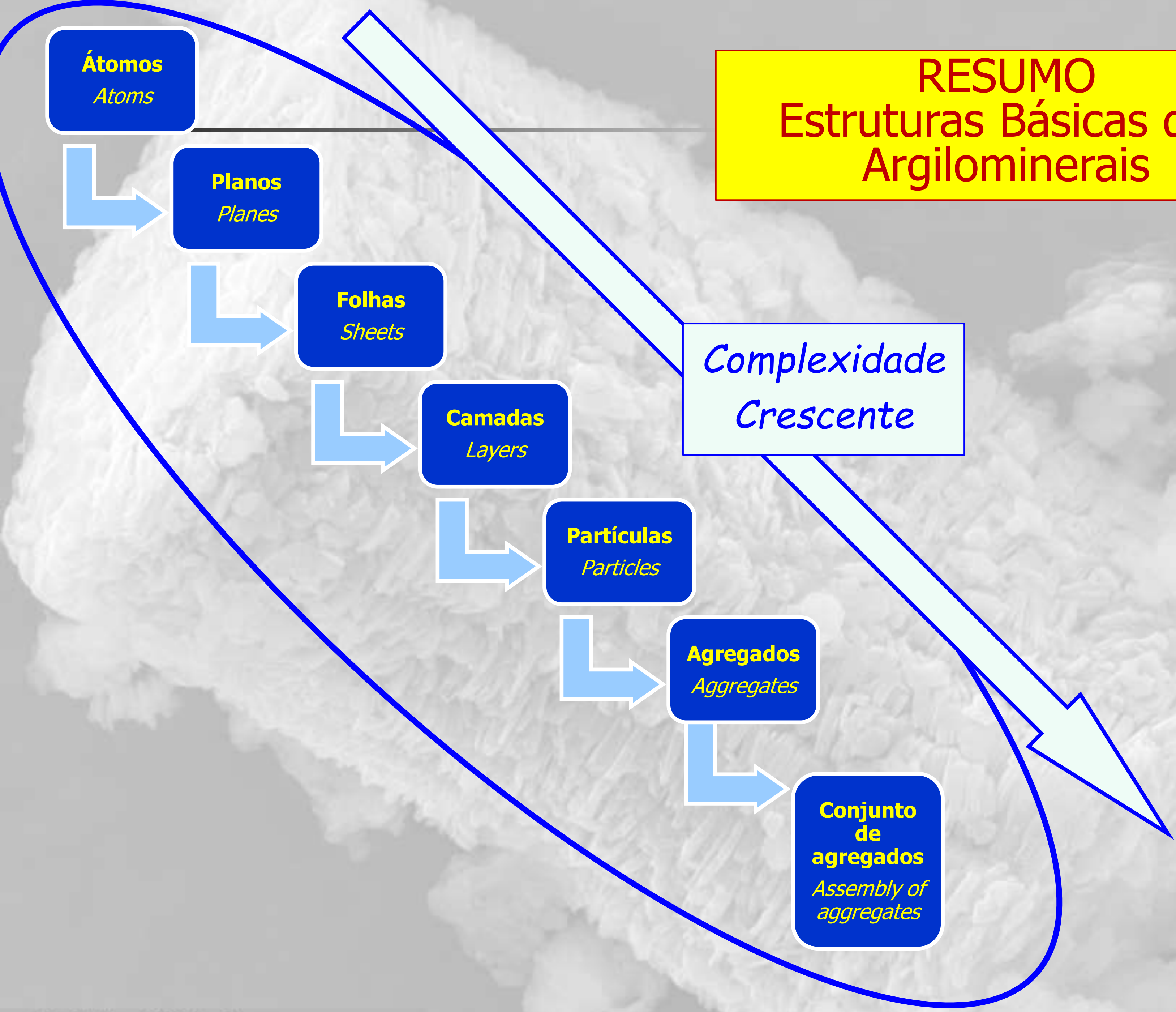


Fig. 1.1. Diagram showing (A) a clay mineral layer; (B) a particle, made up of stacked layers; layer translation and deformation can give rise to a lenticular pore; (C) an aggregate, showing an interlayer space and an interparticle space; and (D) an assembly of aggregates, enclosing an interaggregate space (pore).

RESUMO
Estruturas Básicas dos Argilominerais



Átomos
Atoms

Planos
Planes

Folhas
Sheets

Camadas
Layers

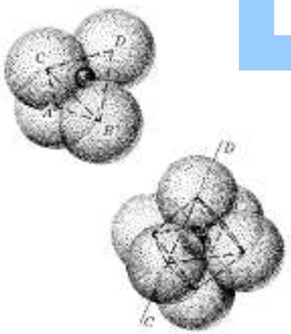
Partículas
Particles

Agregados
Aggregates

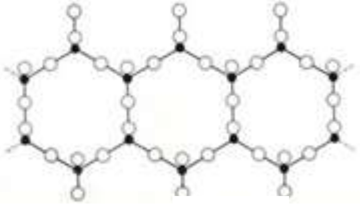
Conjunto de agregados
Assembly of aggregates

Complexidade Crescente

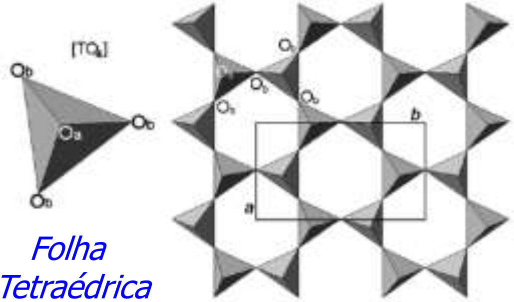
Átomos
Atoms



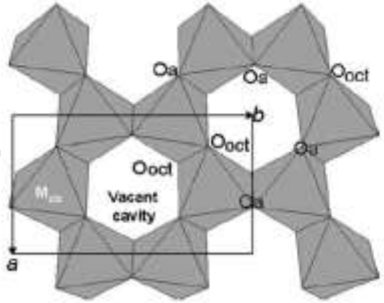
Planos
Planes



(hkl)

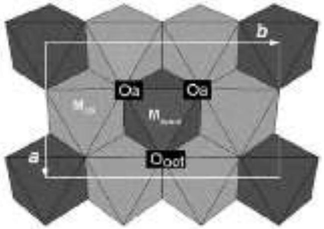


Folha Tetraédrica



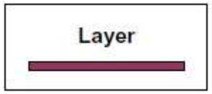
Folha Dioctaédrica

Folhas
Sheets

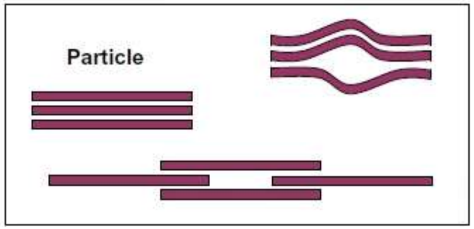


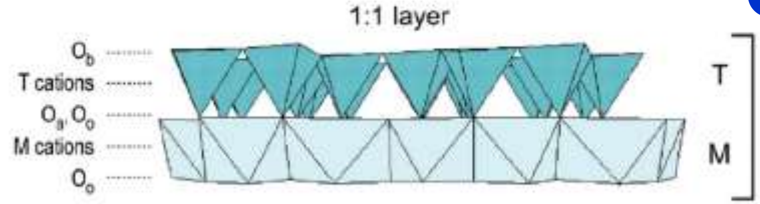
Folha Trioctaédrica

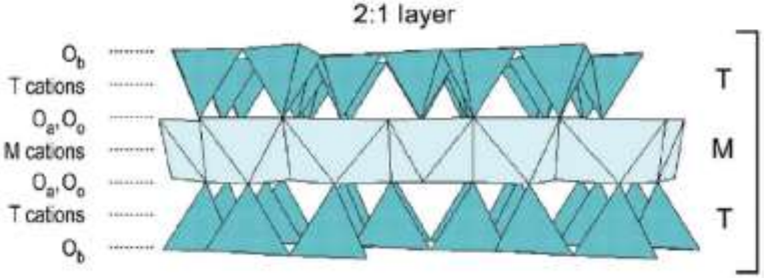
Camadas
Layers



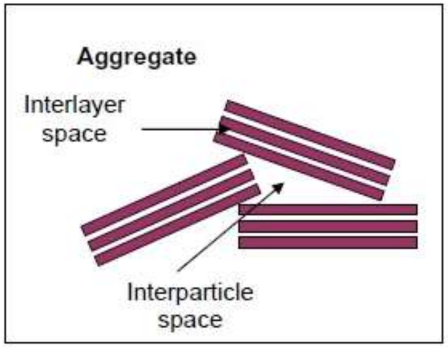
Partículas
Particles



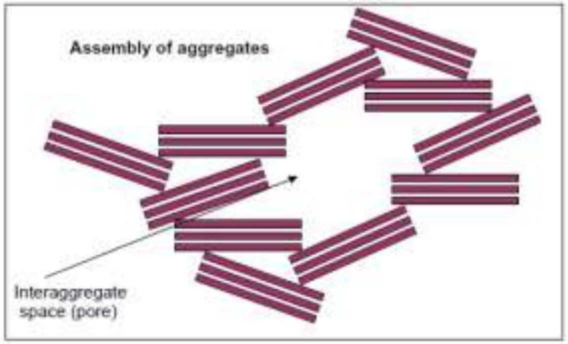




Agregados
Aggregates

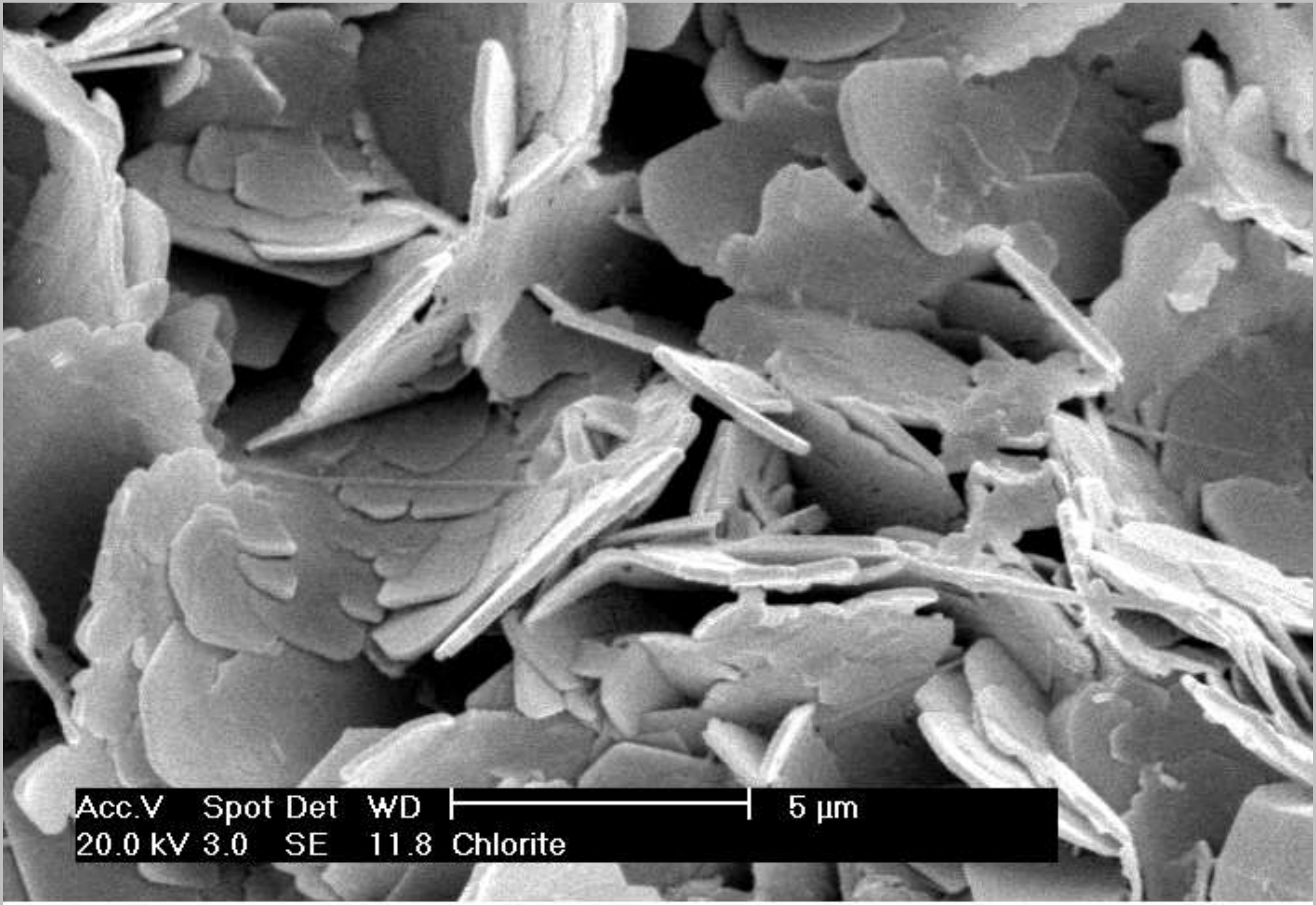


Conjunto de agregados
Assembly of aggregates



Exemplos de Morfologias de Argilominerais

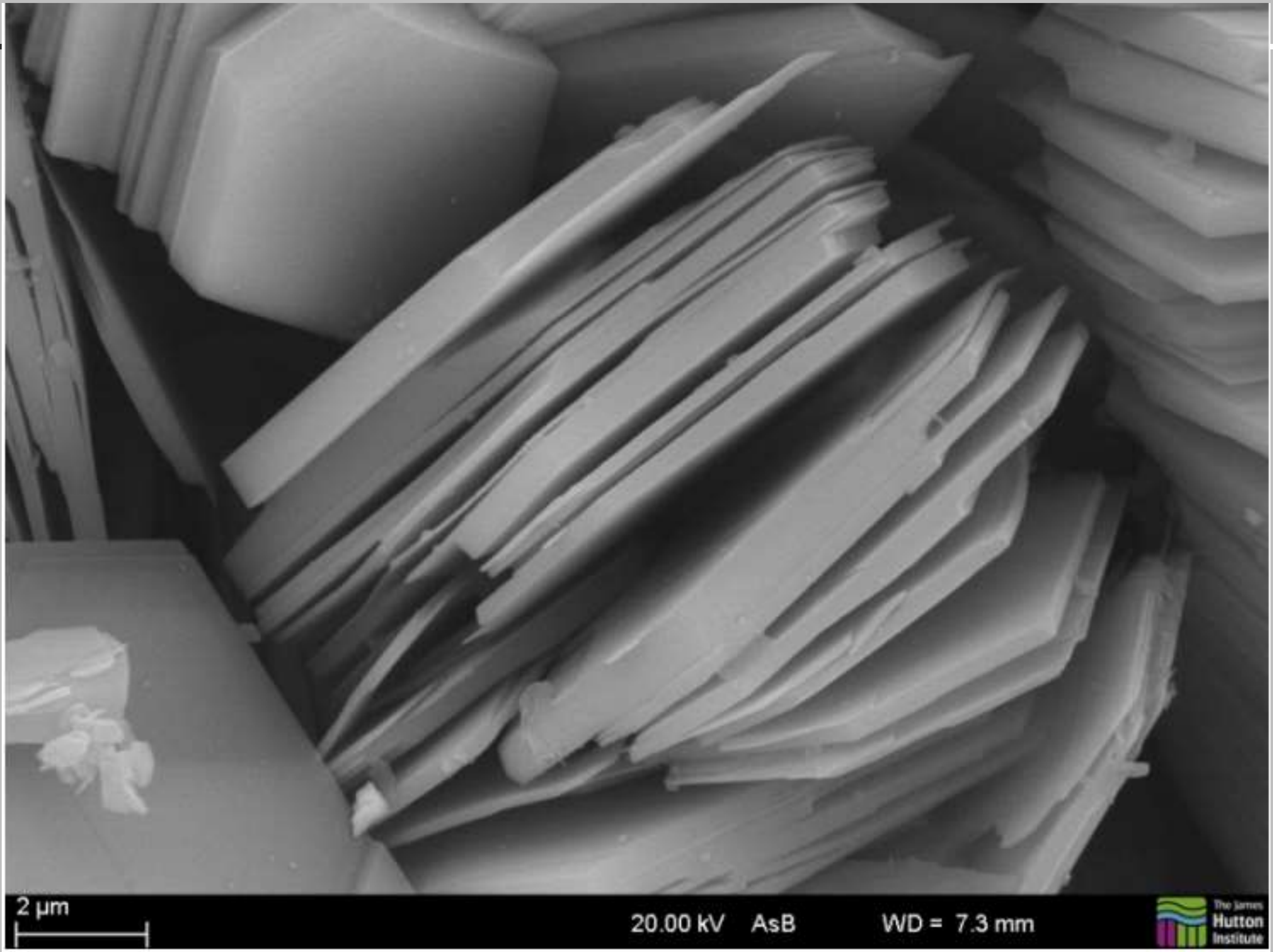
Imagens de Filossilicatos : Clorita



Mg-rich chlorite, Rotliegend, Northern Germany. Field of view ≈ 23 µm wide. Photo courtesy of M. Roe, Macaulay Institute.

Fonte das imagens: Images of Clays : https://www.minersoc.org/images-of-clay.html

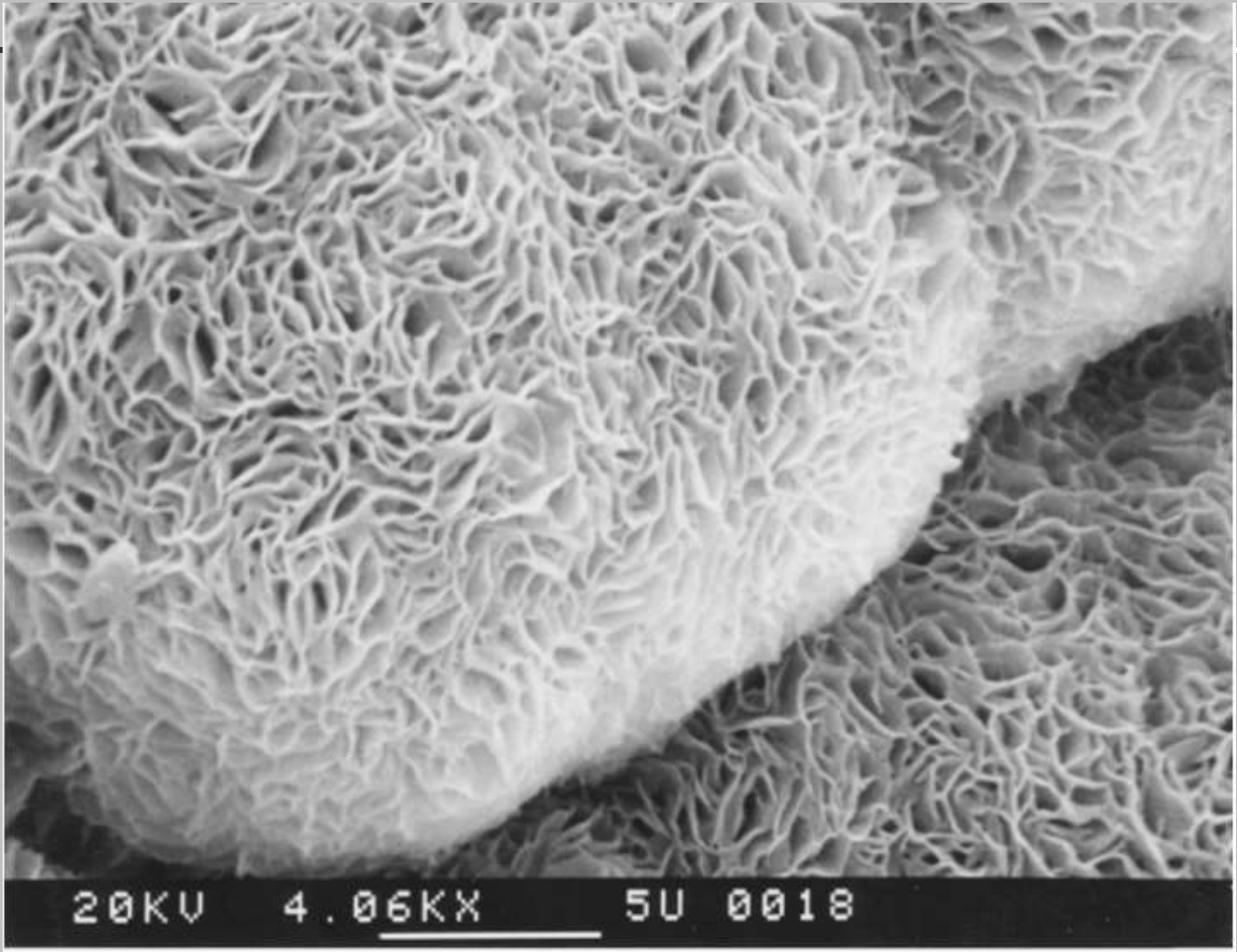
Imagens de Filossilicatos : Caulinita



Close up of kaolinite in Jurassic sandstone, UK North Sea, (polytype confirmed by XRD). Field of view ≈ 20 µm. Evelyne Delbos, The James Hutton Institute.

Fonte da imagem: Images of Clays : https://www.minersoc.org/images-of-clay.html

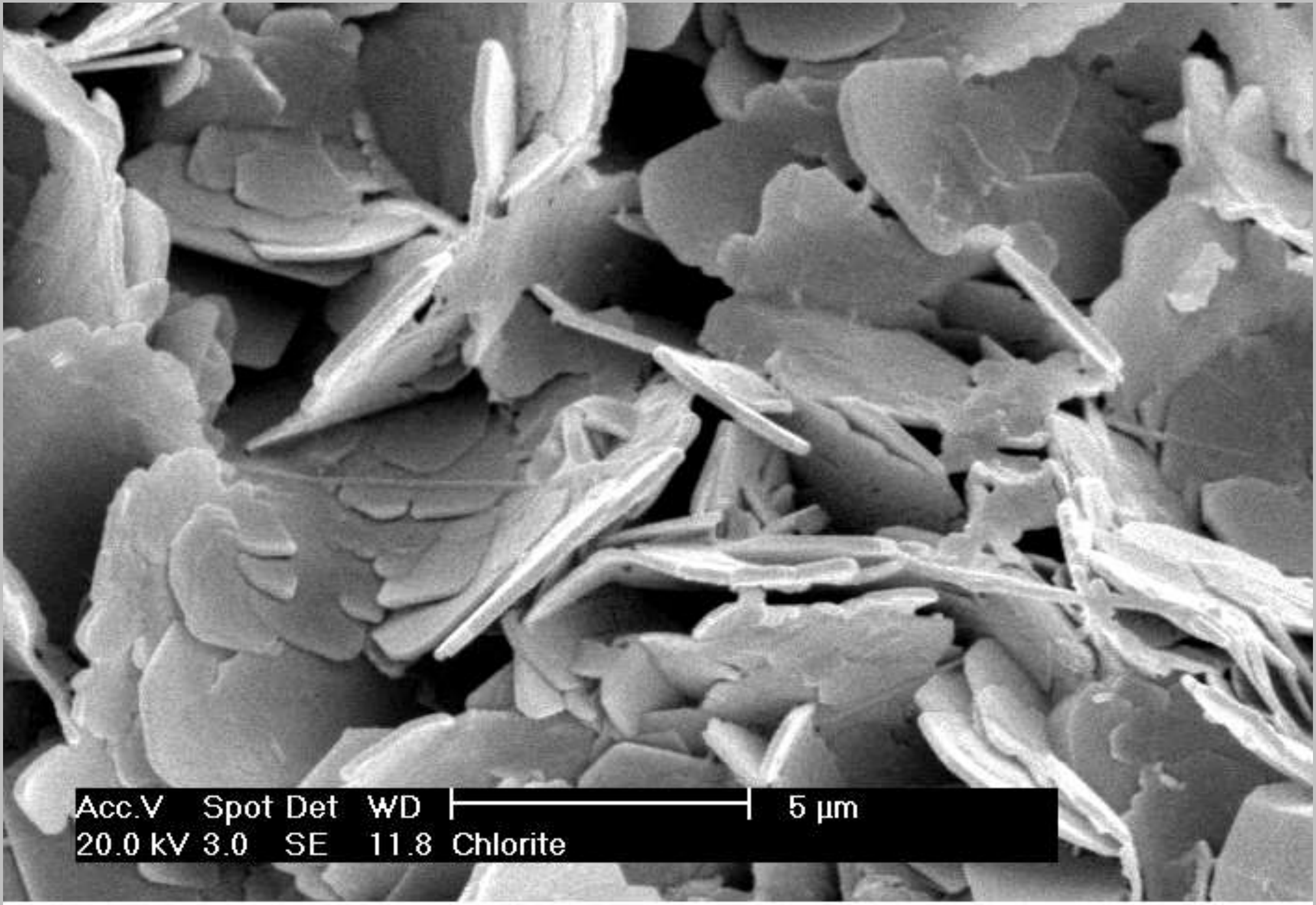
Imagens de Filossilicatos : Esmectita



Dioctahedral smectite from Yucca Mountain, Nevada, drill hole UE25a#1 and a depth of 1296.2 feet. Field of view ≈ 28 µm wide. Photo courtesy of Steve Chipera, Los Alamos National Laboratory.

Fonte da imagen: Images of Clays : https://www.minersoc.org/images-of-clay.html

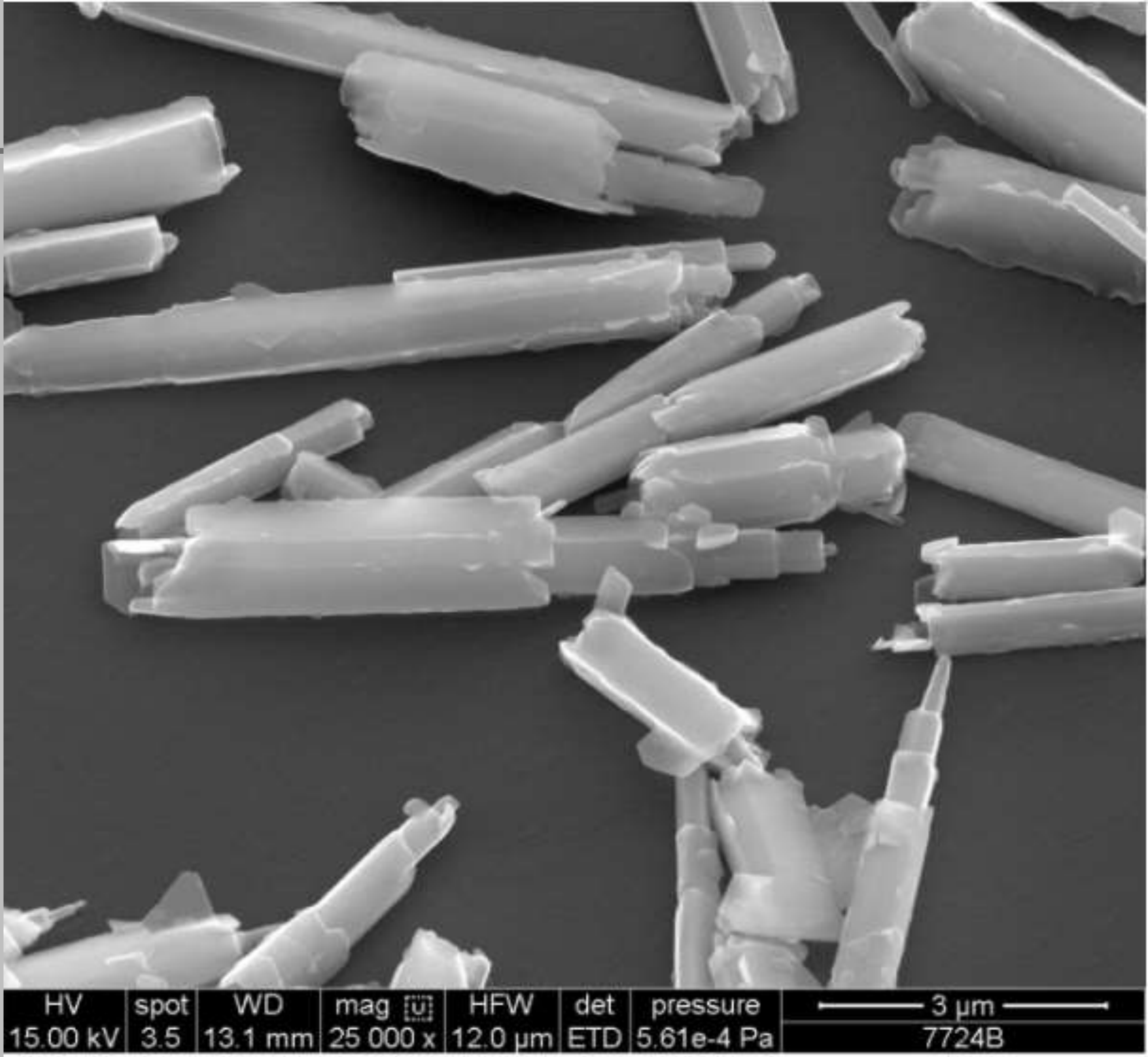
Imagens de Filossilicatos : Clorita



Mg-rich chlorite, Rotliegend, Northern Germany. Field of view ≈ 23 µm wide. Photo courtesy of M. Roe, Macaulay Institute.

Fonte da imagen: Images of Clays : https://www.minersoc.org/images-of-clay.html

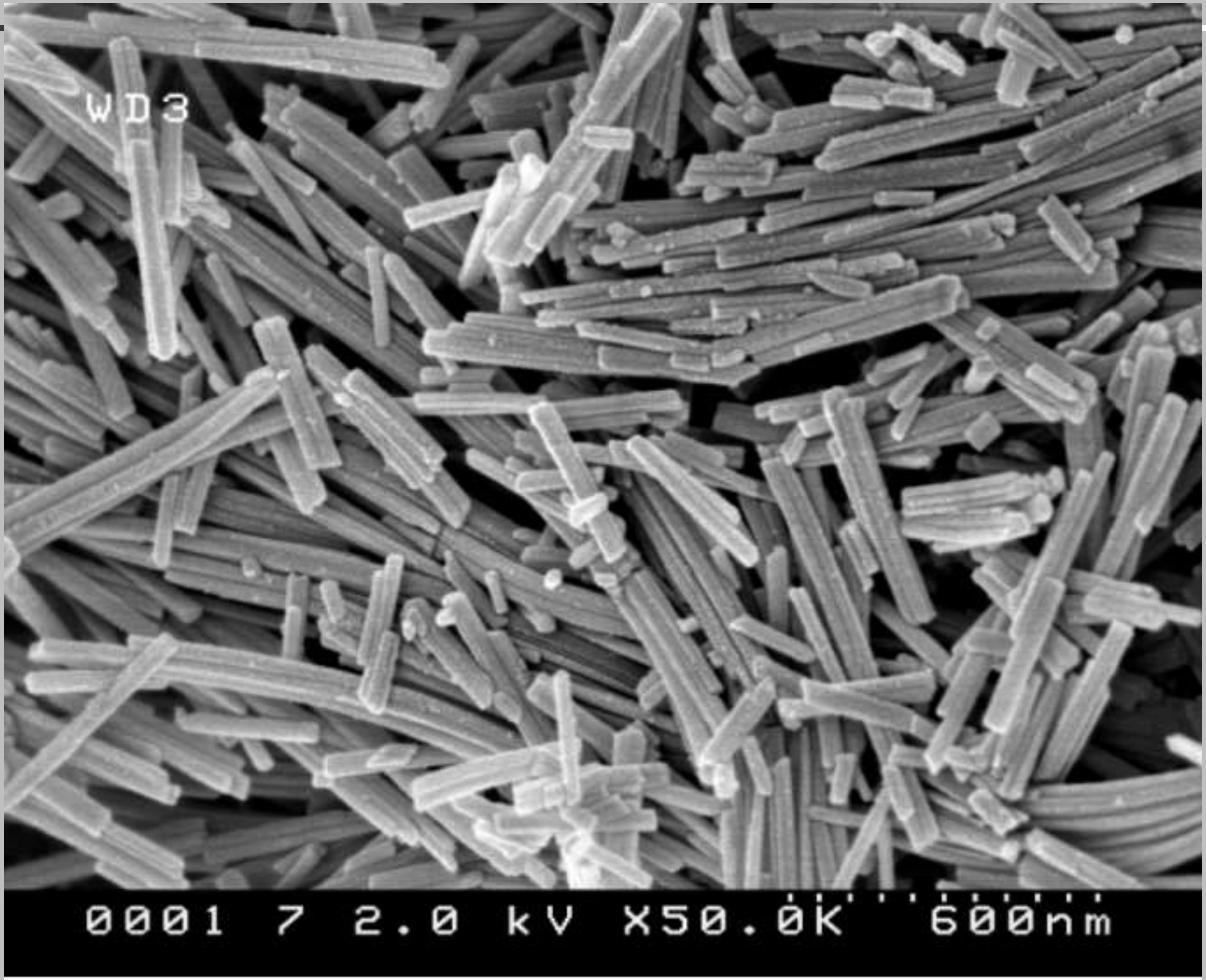
Imagens de Filossilicatos : Haloisita



Halloysite from quartz vein in brecciated Mesoproterozoic Burkett Granite, Lake Gilles, South Australia. Field of view ≈ 12 µm wide.Photo courtesy of Stuart McClure and John Keeling

Fonte da imagen: Images of Clays : https://www.minersoc.org/images-of-clay.html

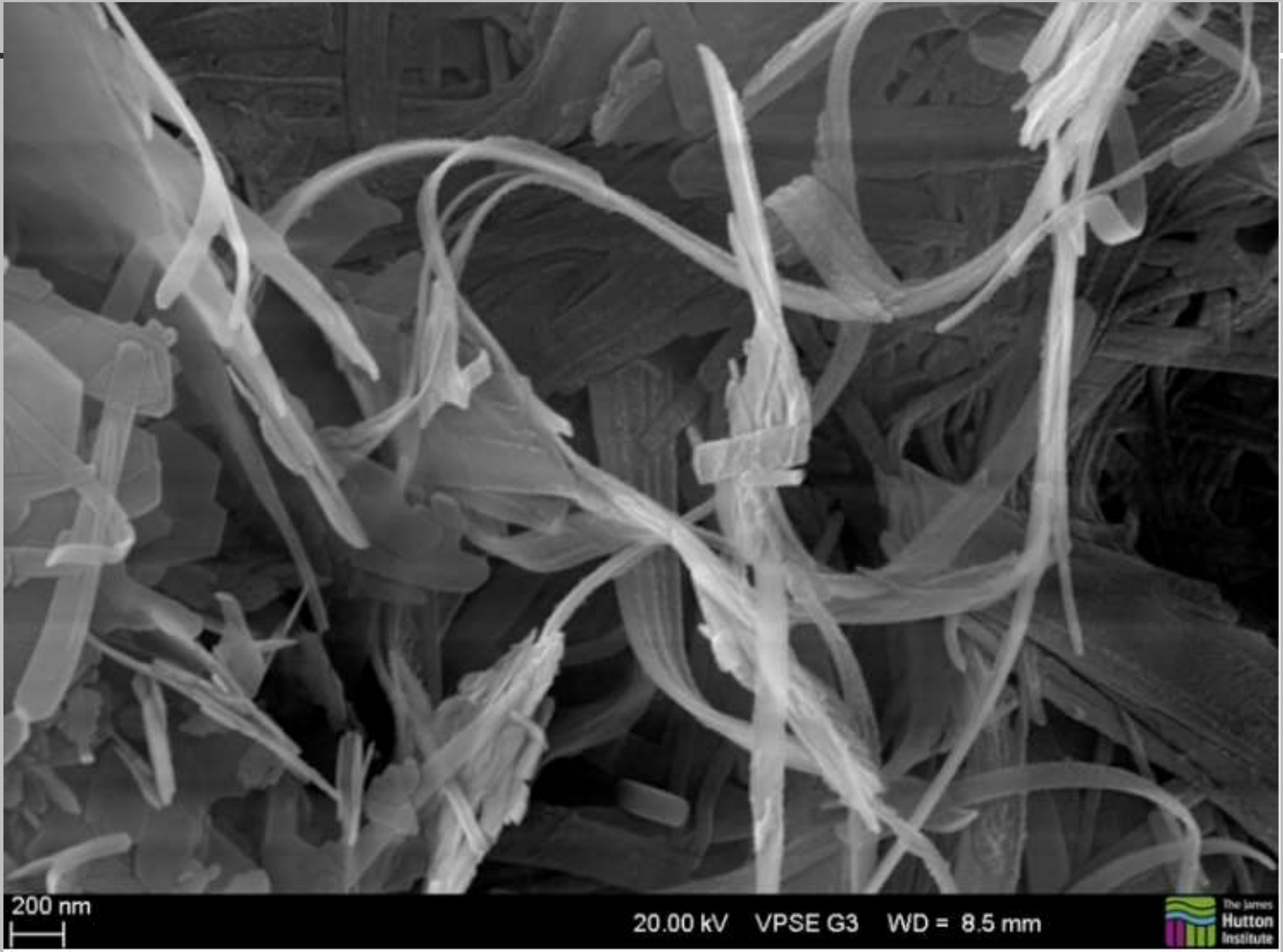
Imagens de Filossilicatos : Paligorsquita



Palygorskite from Jizda, Kazakhstan. Field of view ≈2.4 µm wide. Photo courtesy of Toshihiro Kogure.

Fonte da imagen: Images of Clays : https://www.minersoc.org/images-of-clay.html

Imagens de Filossilicatos : Ilita *(fibrosa)*



Mainly fibrous illite, Bone Spring Formation, Permian Basin, USA. Field of view ≈ 4.6 µm wide. Photo courtesy of Laura-Jane Strachan, James Hutton Institute.

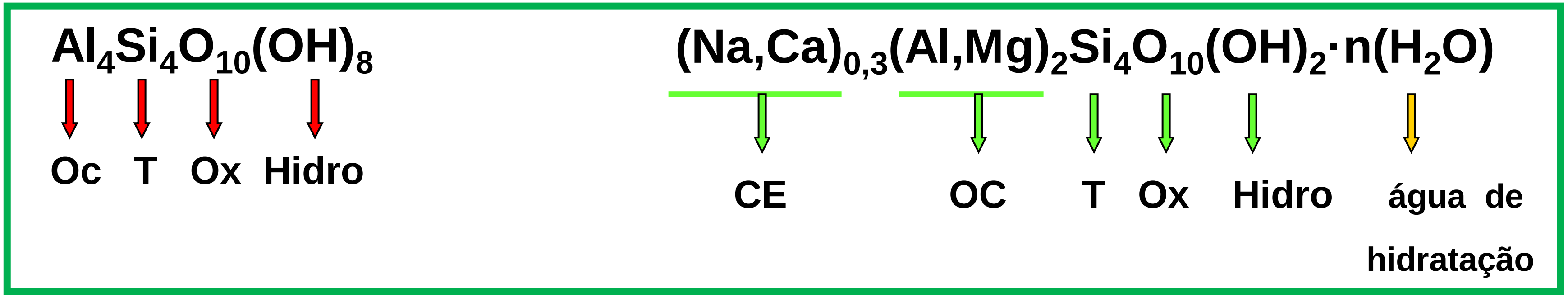
Fonte da imagen: Images of Clays : https://www.minersoc.org/images-of-clay.html

Famílias de Argilominerais

Fórmula Química dos Filossilicatos

Convenção da AIPEA para apresentação de fórmula química dos argilominerais *(filossilicatos)*

- Cátions compensadores de carga (**CE**) *(caso existam...)*
- Cátions da folha octaédrica (**OC**)
- Cátions da folha tetraédrica (**T**)
- Oxigênios (**Ox**)
- Hidroxilas (**Hidro**)
- Moléculas de água de hidratação *(geralmente, associadas aos cátions compensadores de carga)*



$$\underbrace{Al_4}_{\text{Oc}}\underbrace{Si_4}_{\text{T}}\underbrace{O_{10}}_{\text{Ox}}\underbrace{(OH)_8}_{\text{Hidro}}$$

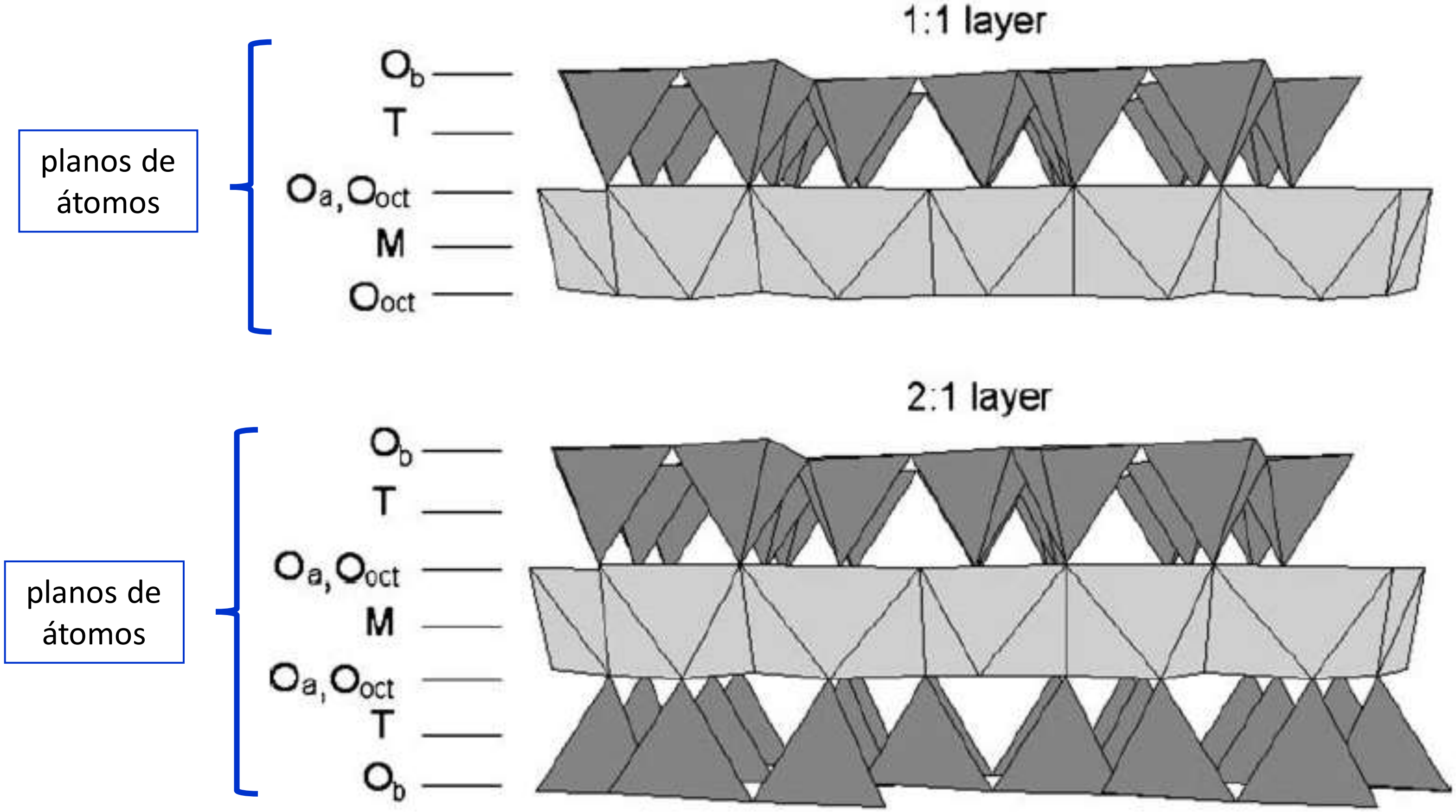
$$\underbrace{(Na,Ca)_{0,3}}_{\text{CE}}\underbrace{(Al,Mg)_2}_{\text{OC}}\underbrace{Si_4}_{\text{T}}\underbrace{O_{10}}_{\text{Ox}}\underbrace{(OH)_2}_{\text{Hidro}}\cdot\underbrace{n(H_2O)}_{\text{água de hidratação}}$$

Famílias de Argilominerais

- Os argilominerais são geralmente constituídos por **camadas** formadas por **folhas** contínuas de tetraedros SiO_4 condensados com folhas octaédricas – no plano cristalográfico ab – empilhadas de forma mais ou menos regular ao longo do eixo c.

- Os argilominerais se dividem em famílias, de acordo com o número de folhas tetraédricas que estão ligadas às folhas octaédricas:
  - argilominerais em camadas **1:1** (uma folha tetraédrica – uma folha octaédrica)
  - argilominerais em camadas **2:1** (duas folhas tetraédricas – uma folha octaédrica)

Argilominerais 1:1 e 2:1



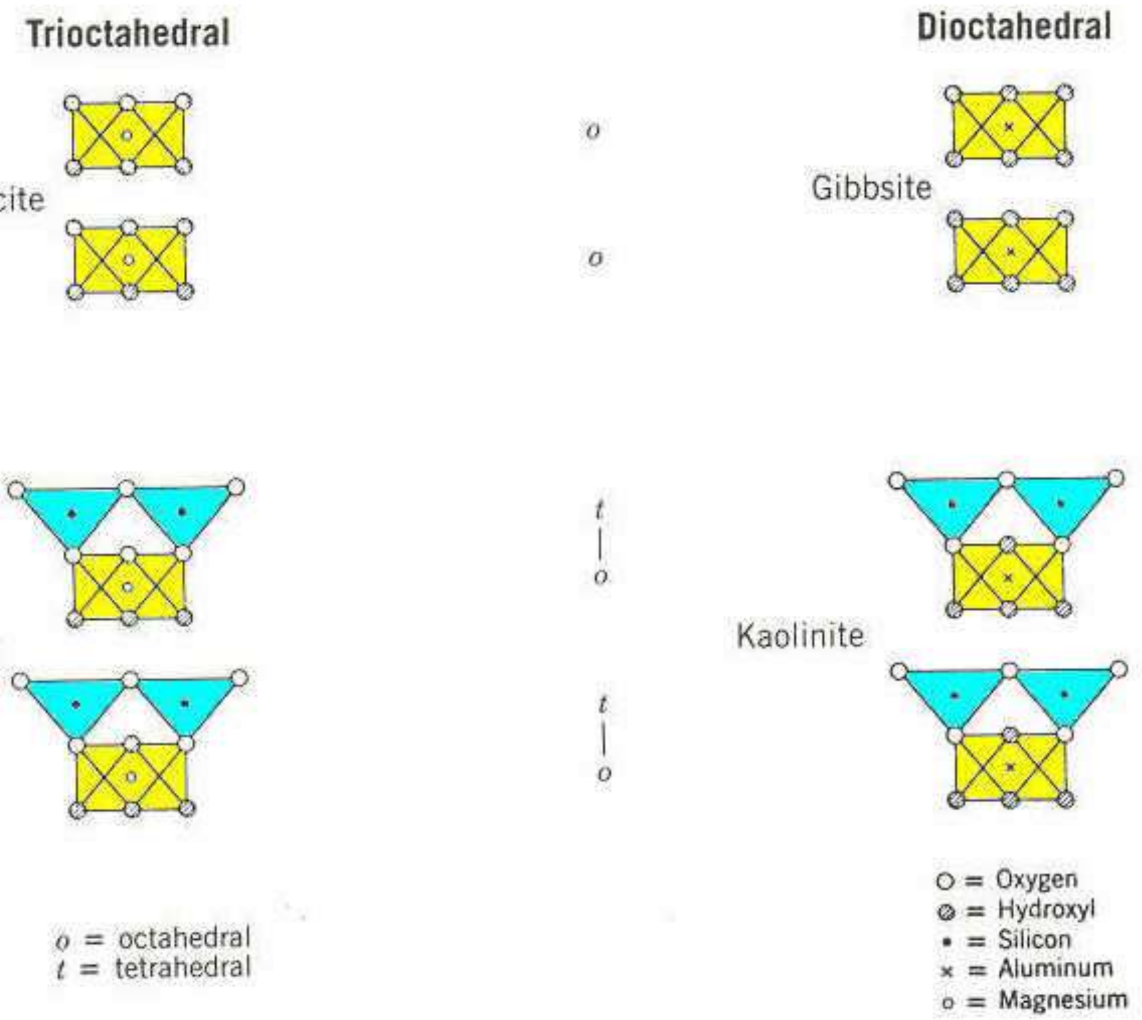
planos de átomos

planos de átomos

Models of a 1:1 and 2:1 layer structure. O_a, O_b, and O_{oct} refer to tetrahedral basal, tetrahedral apical, and octahedral anionic position, respectively. M and T indicate the octahedral and tetrahedral cation, respectively.

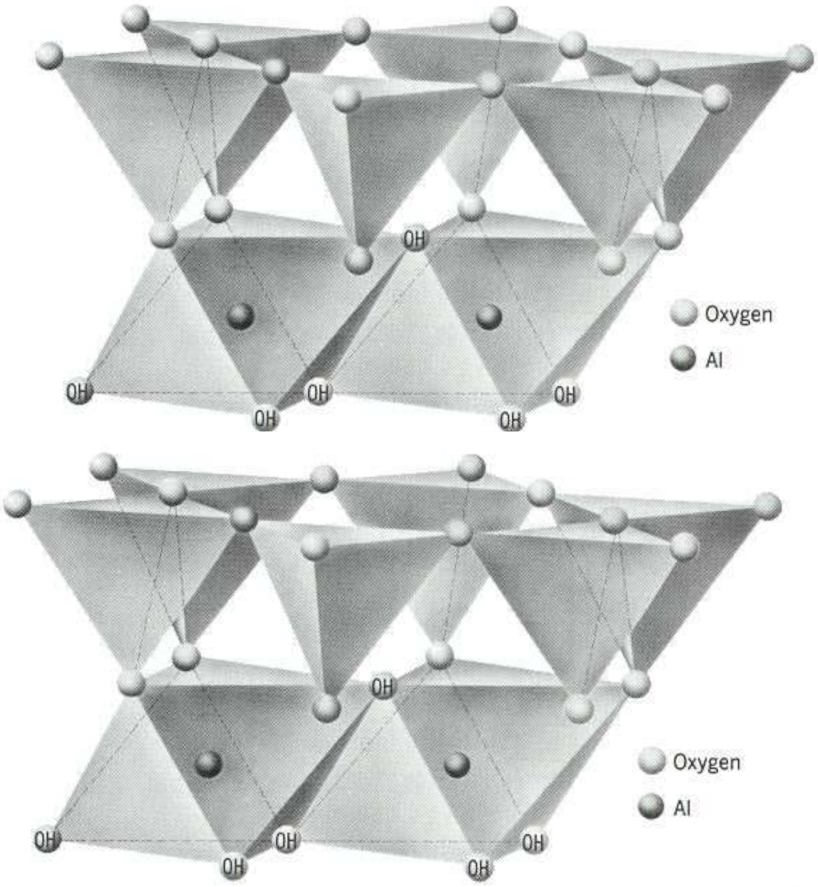
Argilominerais 1:1

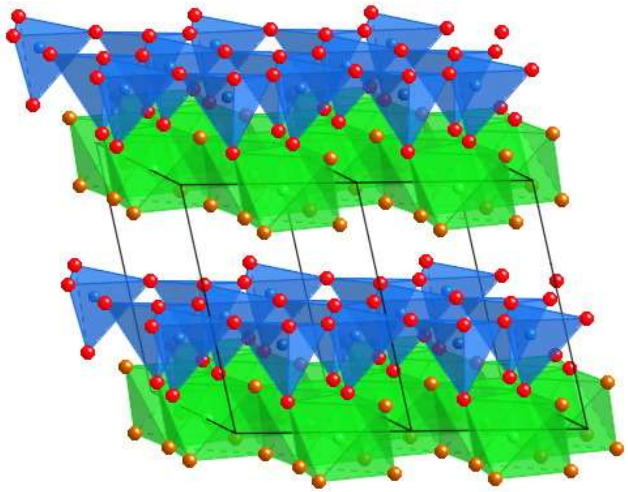
Estruturas de Argilominerais 1:1

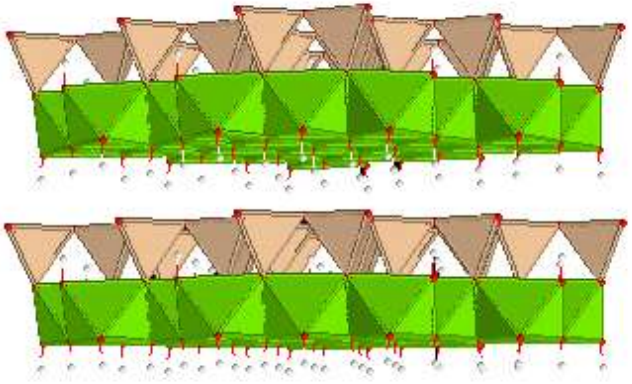


Estrutura dos Argilominerais 1:1

Estrutura da Caulinita



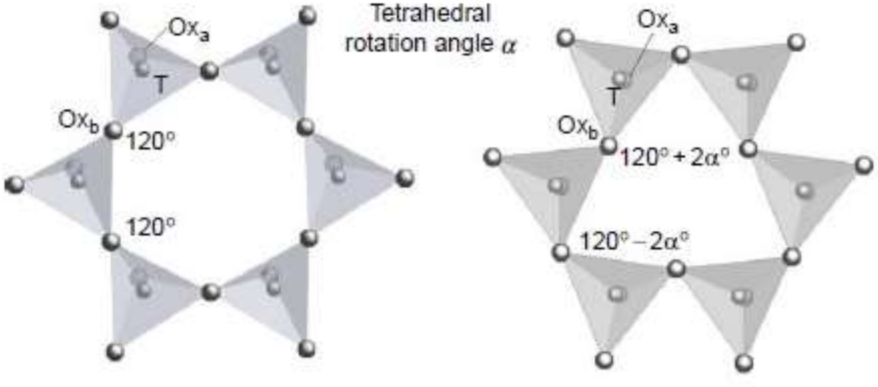


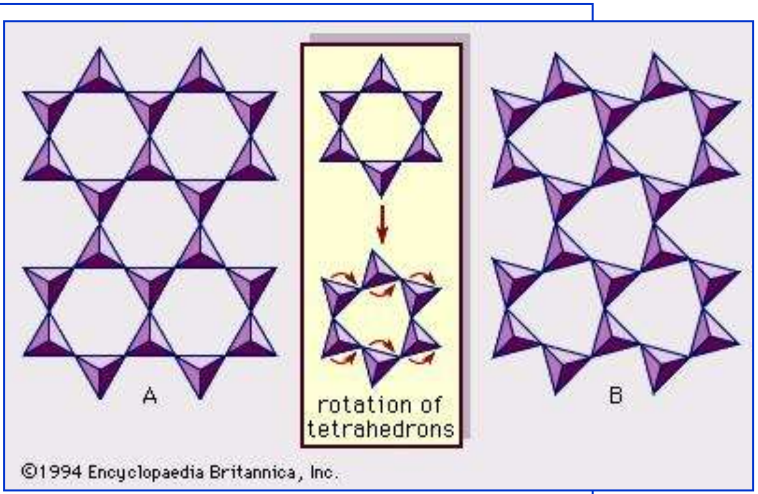


Caulinita : $Al_2Si_2O_5(OH)_4$
Dioctaédrica

Lizardita: $Mg_3Si_2O_5(OH)_4$
Trioctaédrica

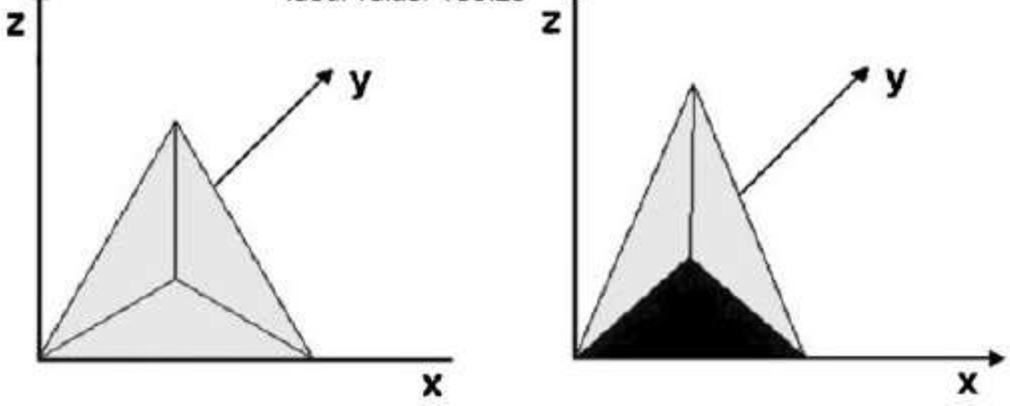
(a) α





©1994 Encyclopaedia Britannica, Inc.

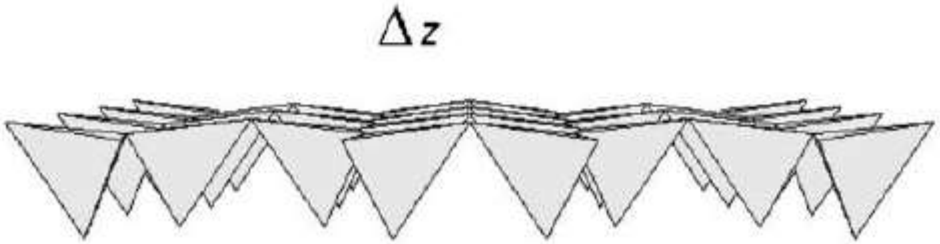
(b) τ



“Ajustes” na folha tetraédrica ...

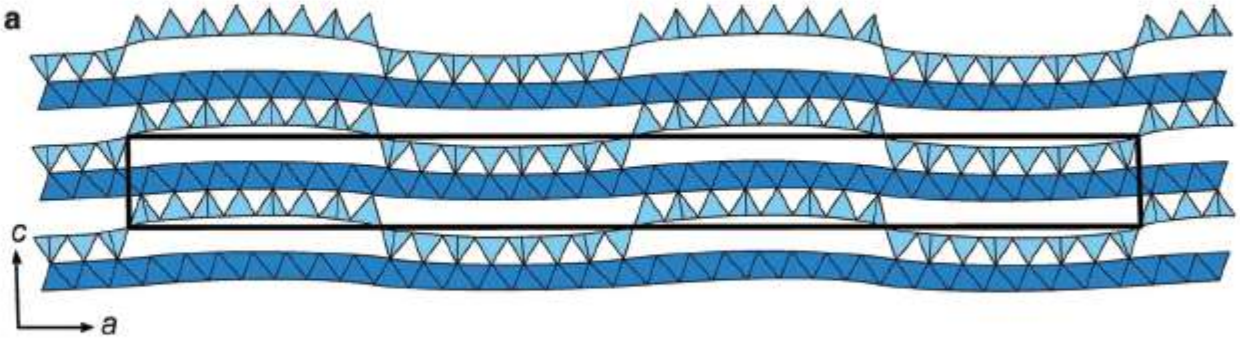
(...para “encaixar” na folha octaédrica...)

(c) Δz



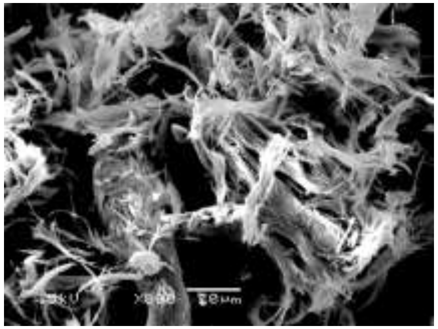
Individual tetrahedra and tetrahedral sheet adjustments in order to accommodate the tetrahedral sheet to the octahedral sheet. (a) tetrahedral ring rotation, α parameter; (b) tetrahedral flattening, τ parameter; (c) tetrahedral tilting, Δz parameter.

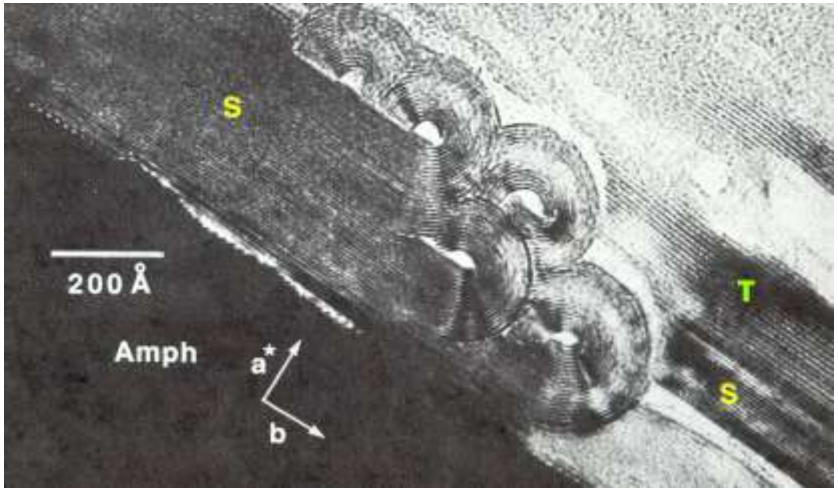
Argilominerais 1:1 Trioctaédricos

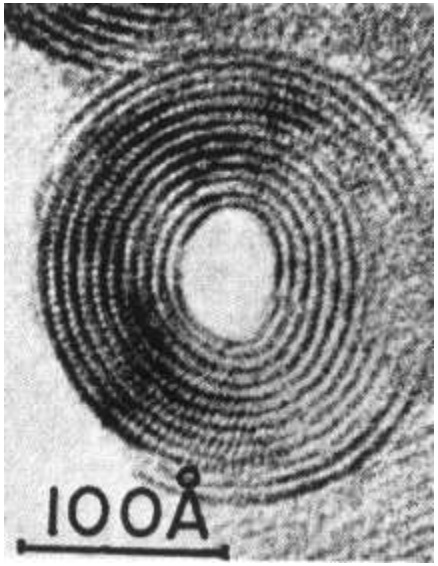


Estrutura da **Antigorita**
$(Mg,Fe^{2+})_3Si_2O_5(OH)_4$ - Trioctaédrica

Estrutura da **Crisotila** $Mg_3Si_2O_5(OH)_4$
Trioctaédrica



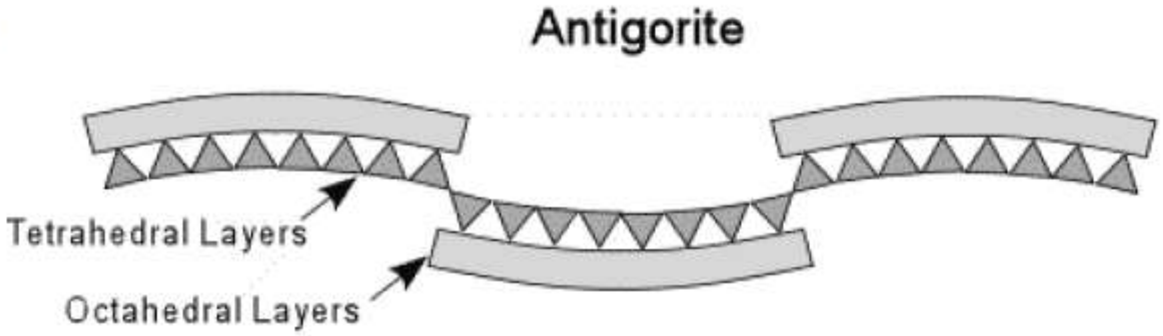




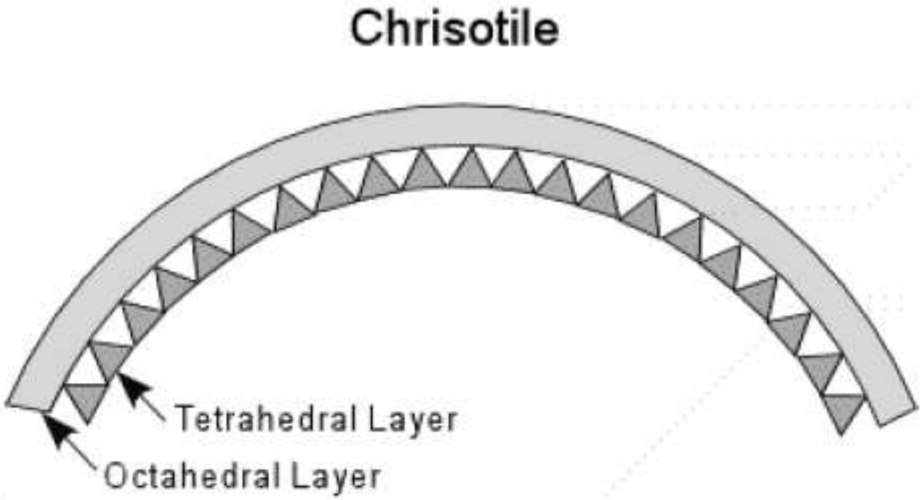
Argilominerais 1:1 Trioctaédricos

Antigorita e Crisotila

In Antigorite the bending of the sheets is not continuous, but occurs in sets, similar to corrugations, as shown here.



In Chrisotile, the bending of the sheets is more continuous, resulting in continuous tubes that give the mineral it's fibrous habit. The Chrisotile variety is commonly referred to as asbestos.



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

Argilomineral 1:1 Tubular : Crisotila *(trioctaédrica)*

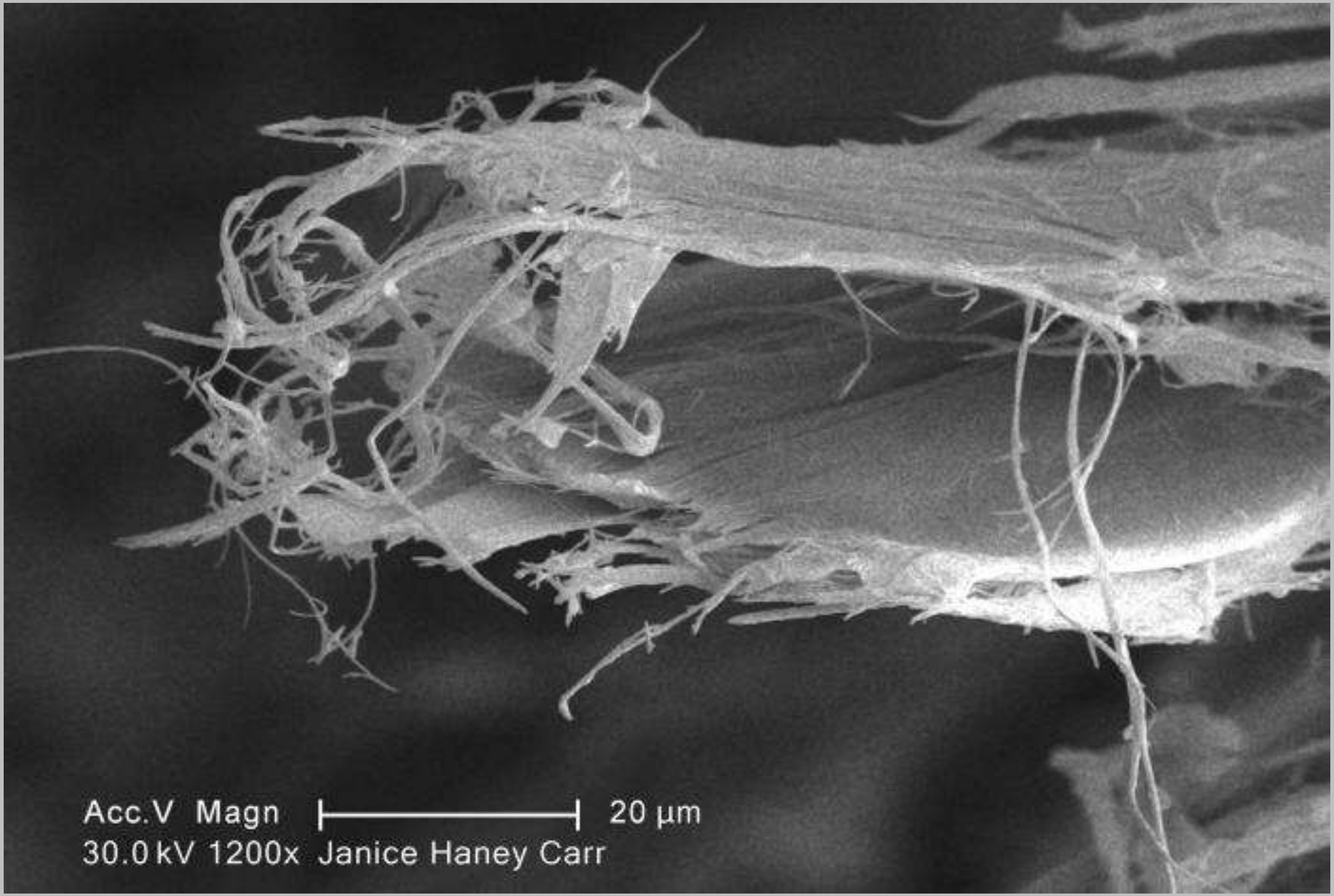
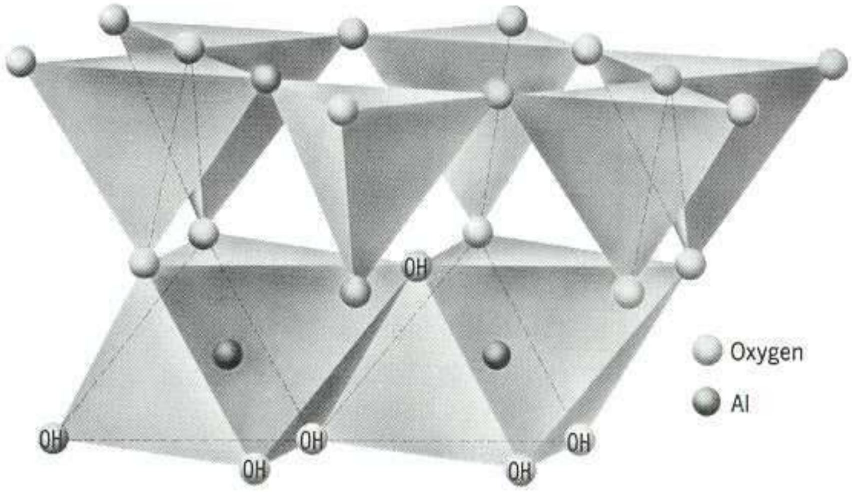
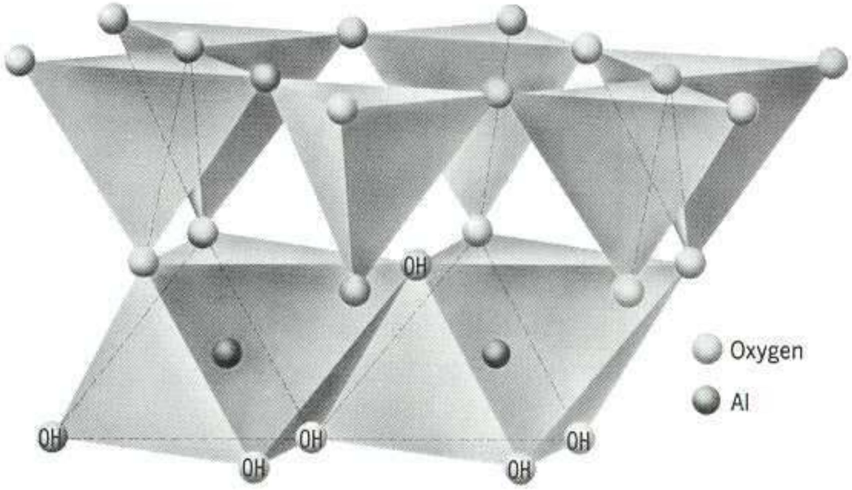


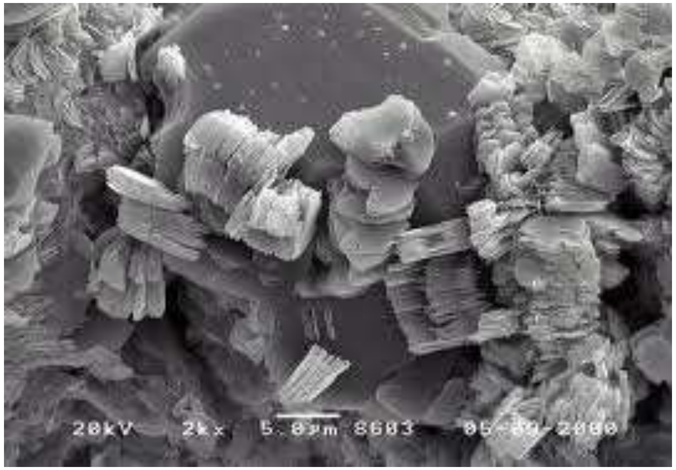
Imagem: Janice Haney Carr - CDC PHIL image library, PHIL #11065 (https://en.wikipedia.org/wiki/Chrysotile#/media/File:Chrysotile_SEM_photo.jpg)

Argilominerais 1:1 Dioctaédricos - **CAULINITA**

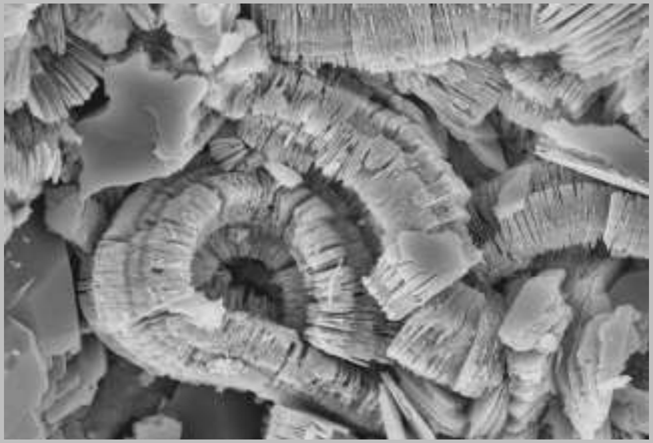




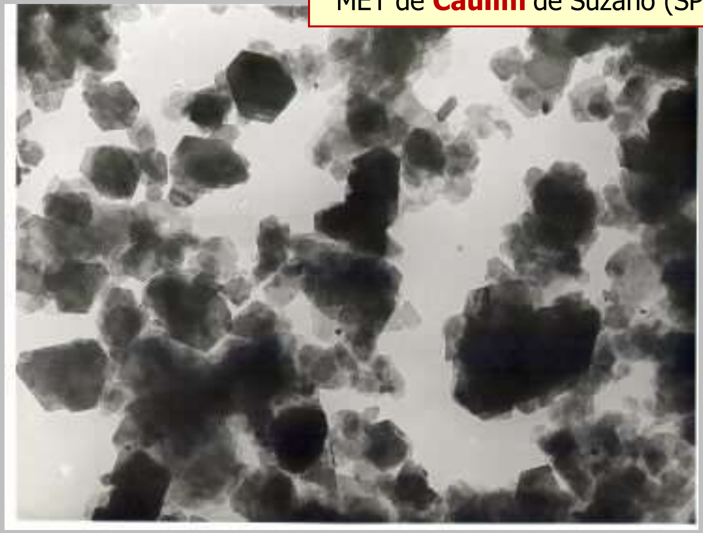
- Fórmula da cela unitária : $\mathbf{Al_4Si_4O_{10}(OH)_8}$
- Camadas 1:1 praticamente neutras.
- Espaços interlamelares normalmente sem cátions e sem água.
- **CTC** *(**C**apacidade de **T**roca de **C**átions; em inglês **CEC**)* **muito pequena**, devida a cátions na superfície externa e/ou nas bordas.
- Intercalação de espécies químicas no espaço interlamelar é possível em condições especiais.

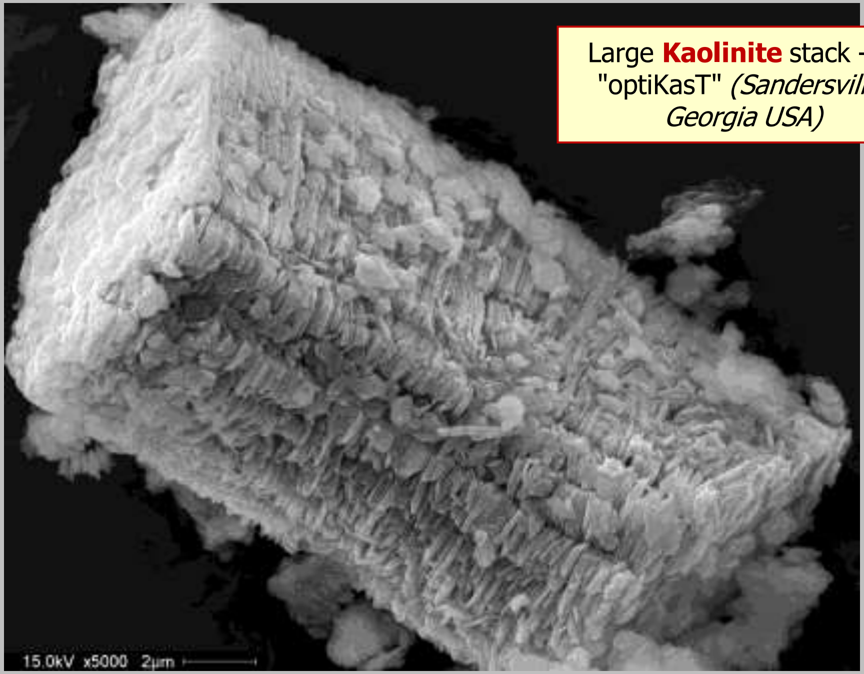


Imagens de MEV e MET de **CAULINITAS**

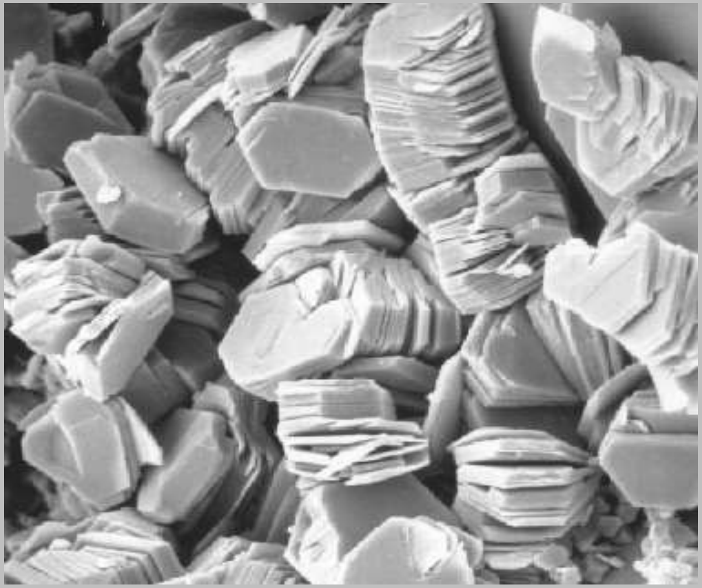


MET de **Caulim** de Suzano (SP)





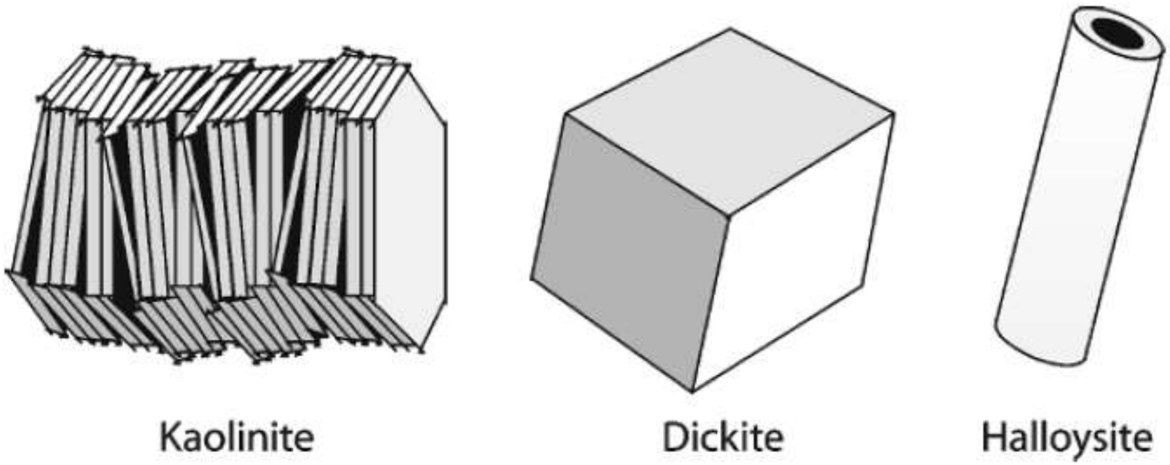
Large **Kaolinite** stack - in "optiKasT" *(Sandersville, Georgia USA)*



Politipos

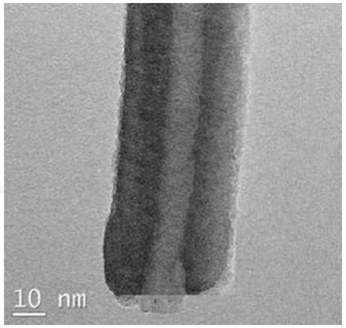
The sub-species are assigned as polytypes. They should always be designed by addition of a symbol of the stacking to the family name: 1M mica, 2M1 mica, Ib chlorite, IIb chlorite, etc. The kaolin family is an exception since polytypes are assigned different mineral names: kaolinite, dickite, nacrite, halloysite. This was probably due to the big difference of crystal morphology: hexagonal plates, rhombs or tubes (Fig. 1.9).

Fig. 1.9. Relation between polytype and crystal morphology for kaolin minerals

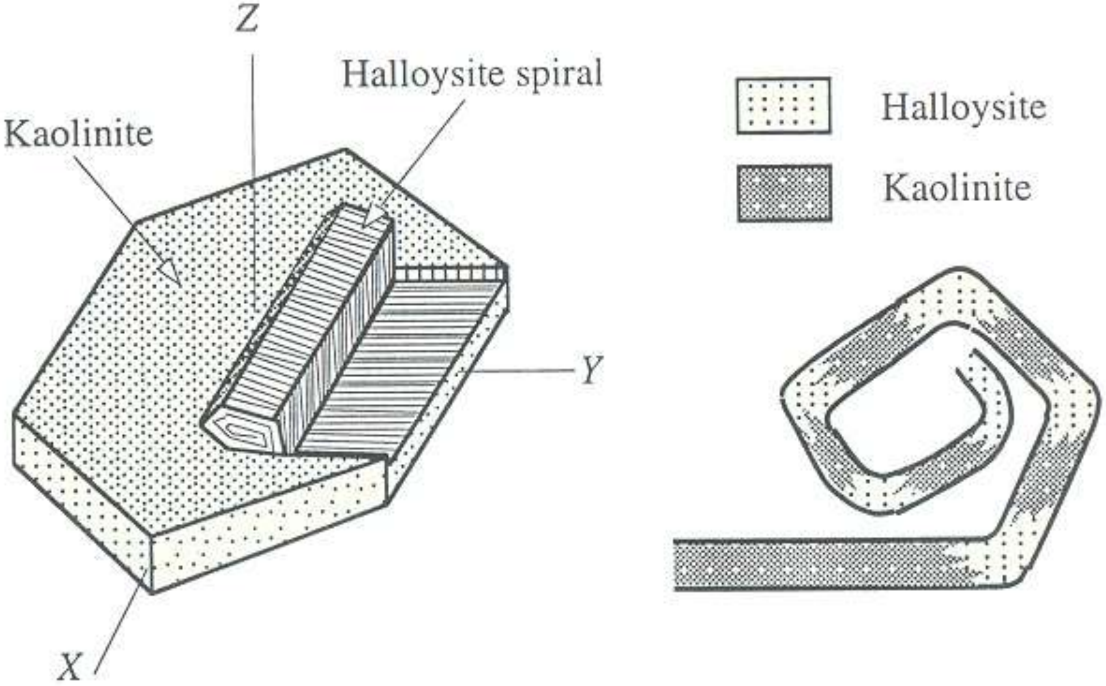


Velde, B.; Meunier, A. – The Origin of Clay Minerals in soils and Weathered Rocks. Springer. Berlin. 2008

Haloisita



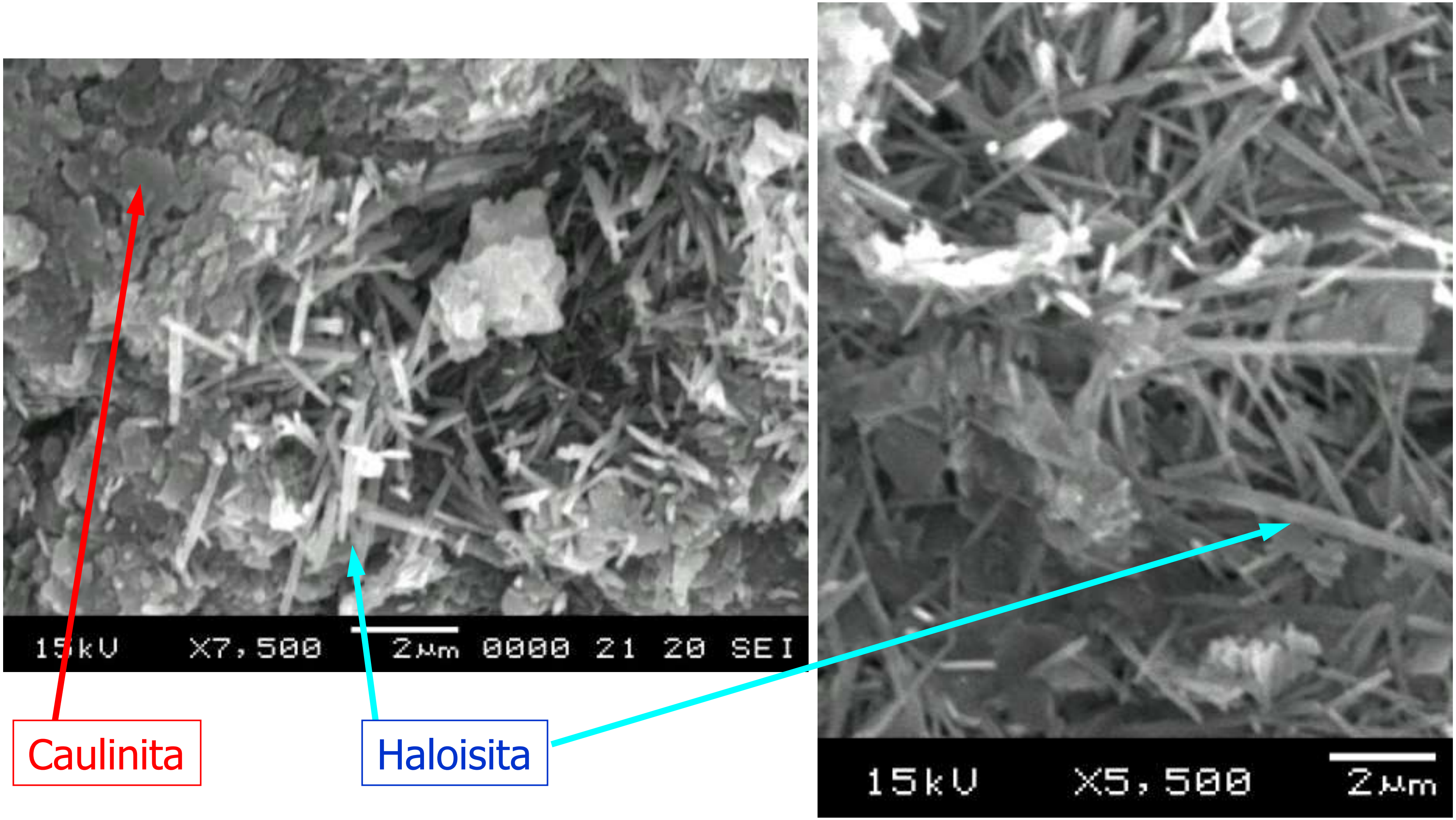
Argilominerais tubulares : Haloisita (Dioctaédrica)



Halloysite and kaolinite. Sketched from TEM photos, it seems difficult to argue for anything other than the halloysite forming from the kaolinite and inheriting a major part of the structure of the kaolinite. Robertson and Eggleton (1991) interpret the kaolinite as forming from muscovite by the loss of one tetrahedral sheet. Modified from Robertson and Eggleton (1991) with permission.

Caulim haloisítico de Juiz de Fora (MG)

Caulins contendo CAULINITA e HALOISITA *(Poços de Caldas – MG)*

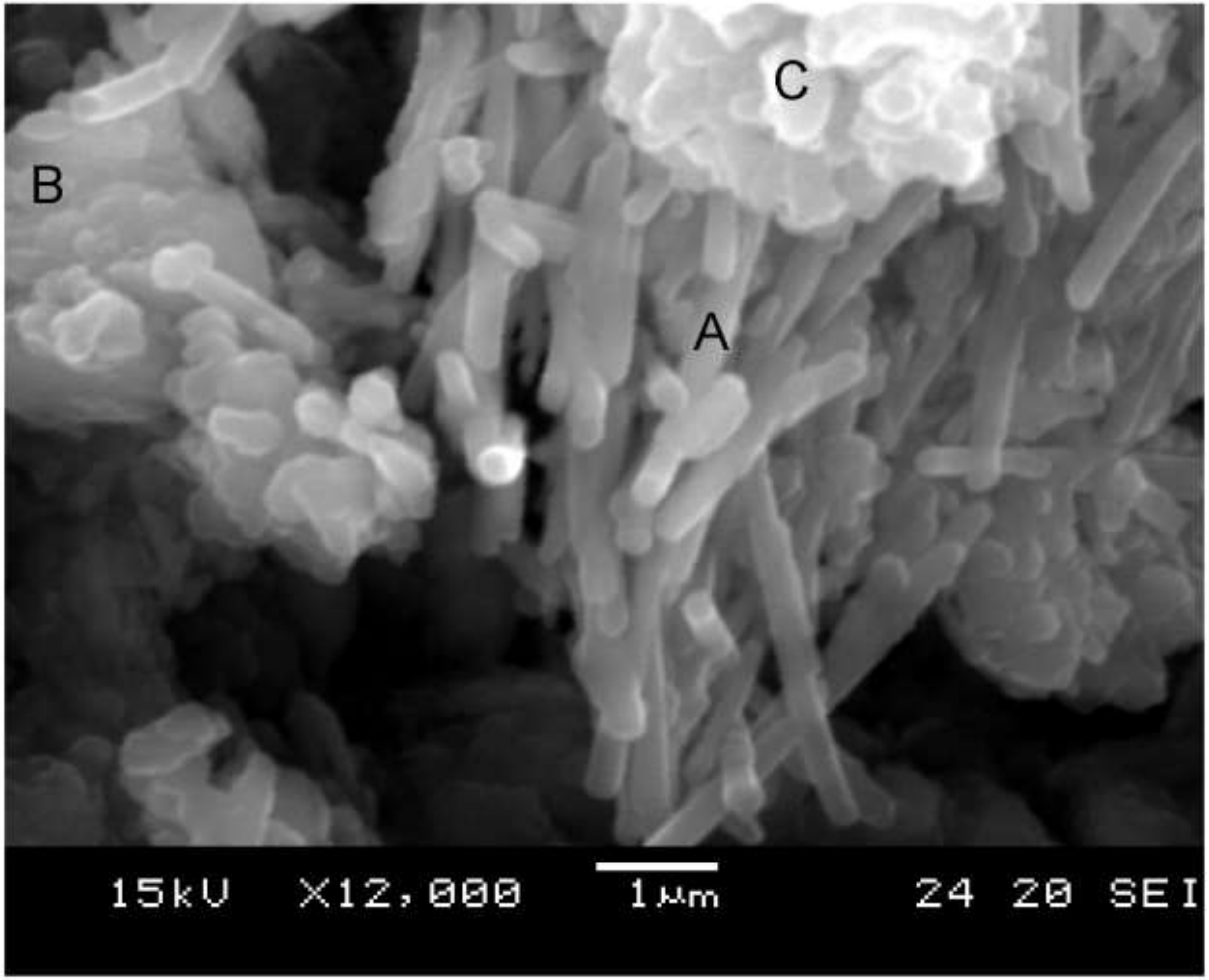


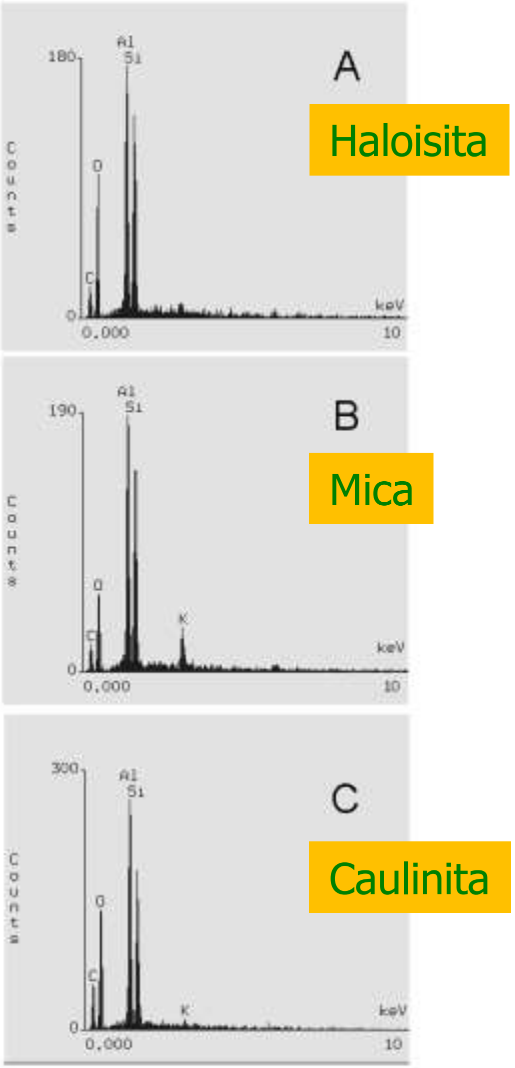
Caulinita

Haloisita

Caulim contendo CAULINITA, MICA e HALOISITA

(Poços de Caldas, MG)





Haloisita e Haloisita-$2H_2O$

Haloisita: $Al_2Si_2O_5(OH)_4$
Haloisita.$2H_2O$: $Al_2Si_2O_5(OH)_4 2H_2O$
...ambas Dioctaédricas

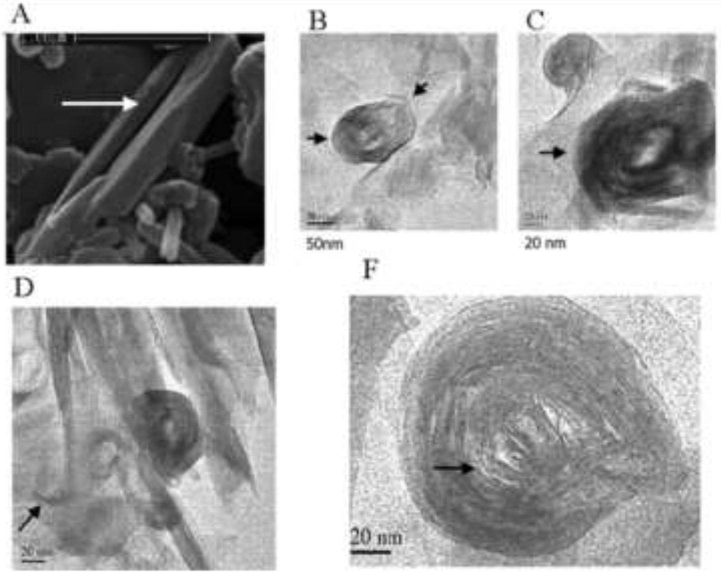
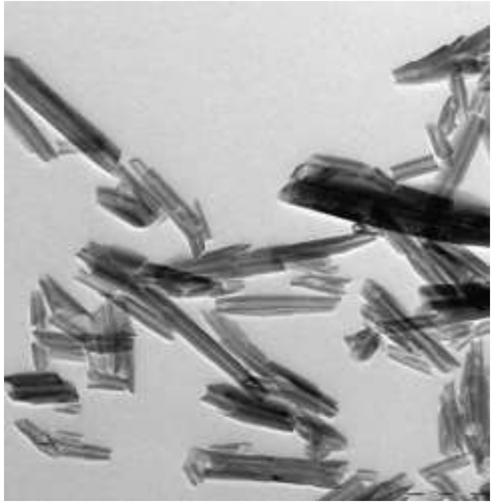
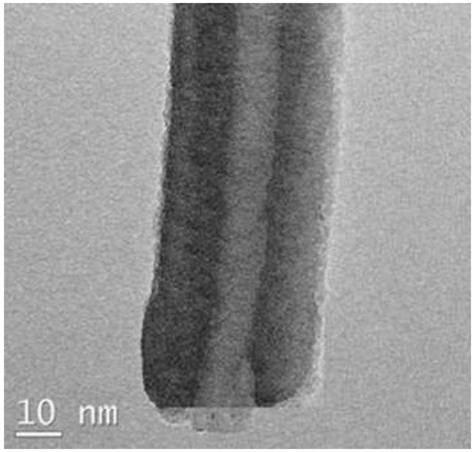
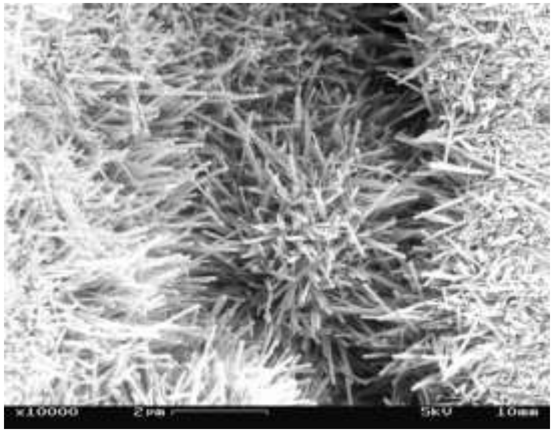
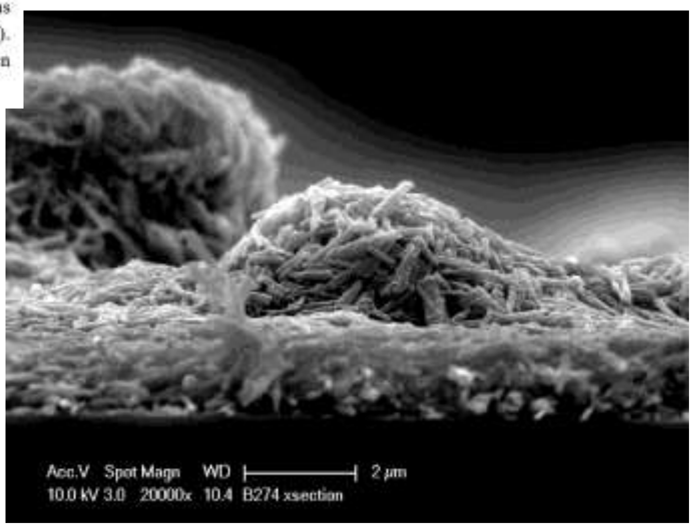


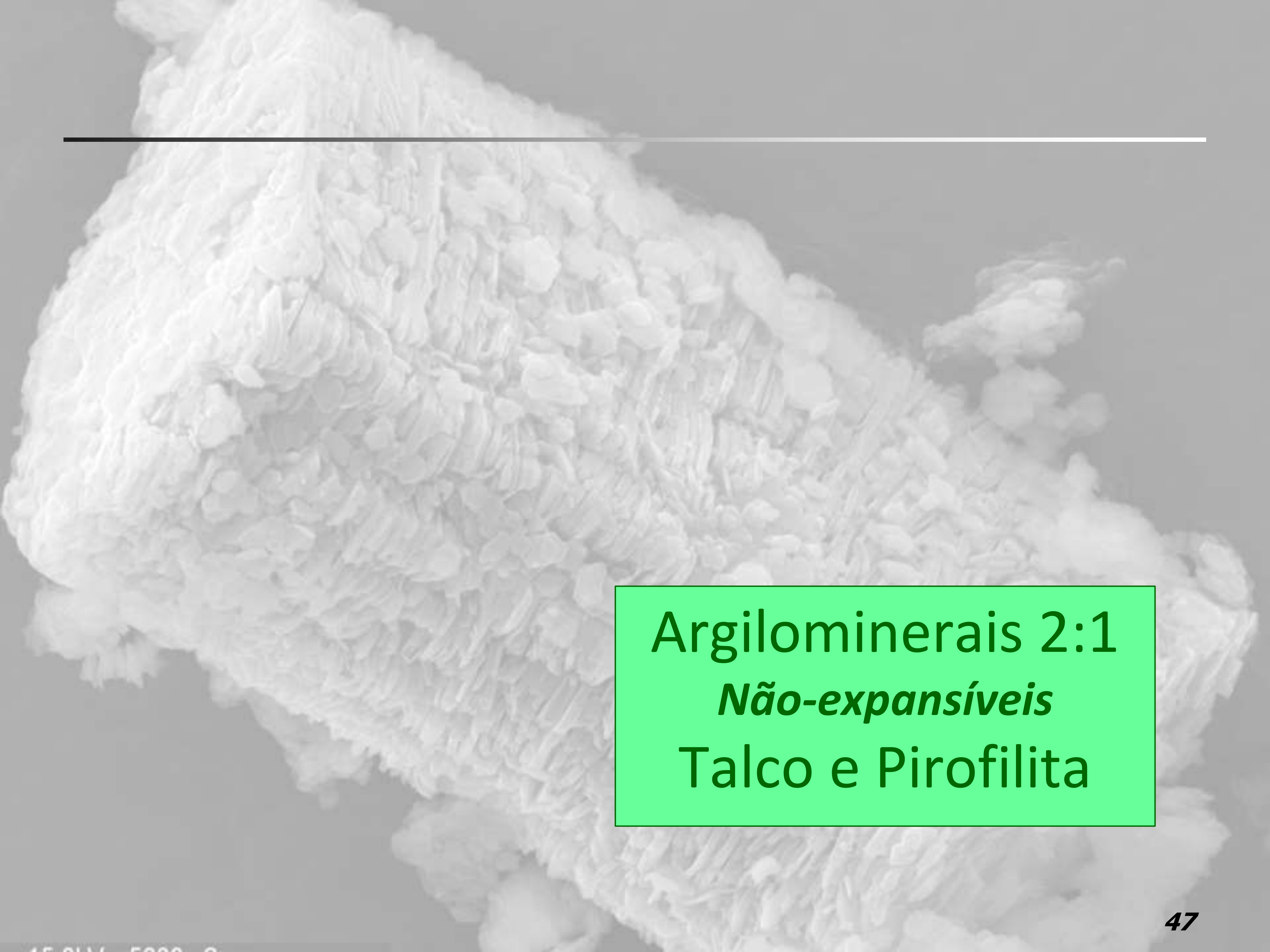
Fig. 9 – Tubes are the most common morphology for halloysite observed using SEM. Planar surface (A) are common. TEM observations of cross-sections of the tubes showed curved shape as well as polygonal shape in the same particle (B). Other cross sections of tubes are polygonal (C). Some unrolled cross sections form plates (D). Also circular cross-sections with pores between the smoothly curved layers (E) were observed.









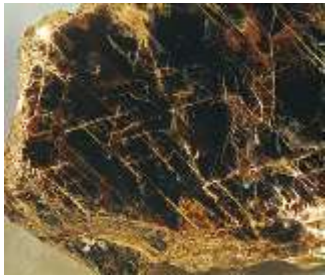


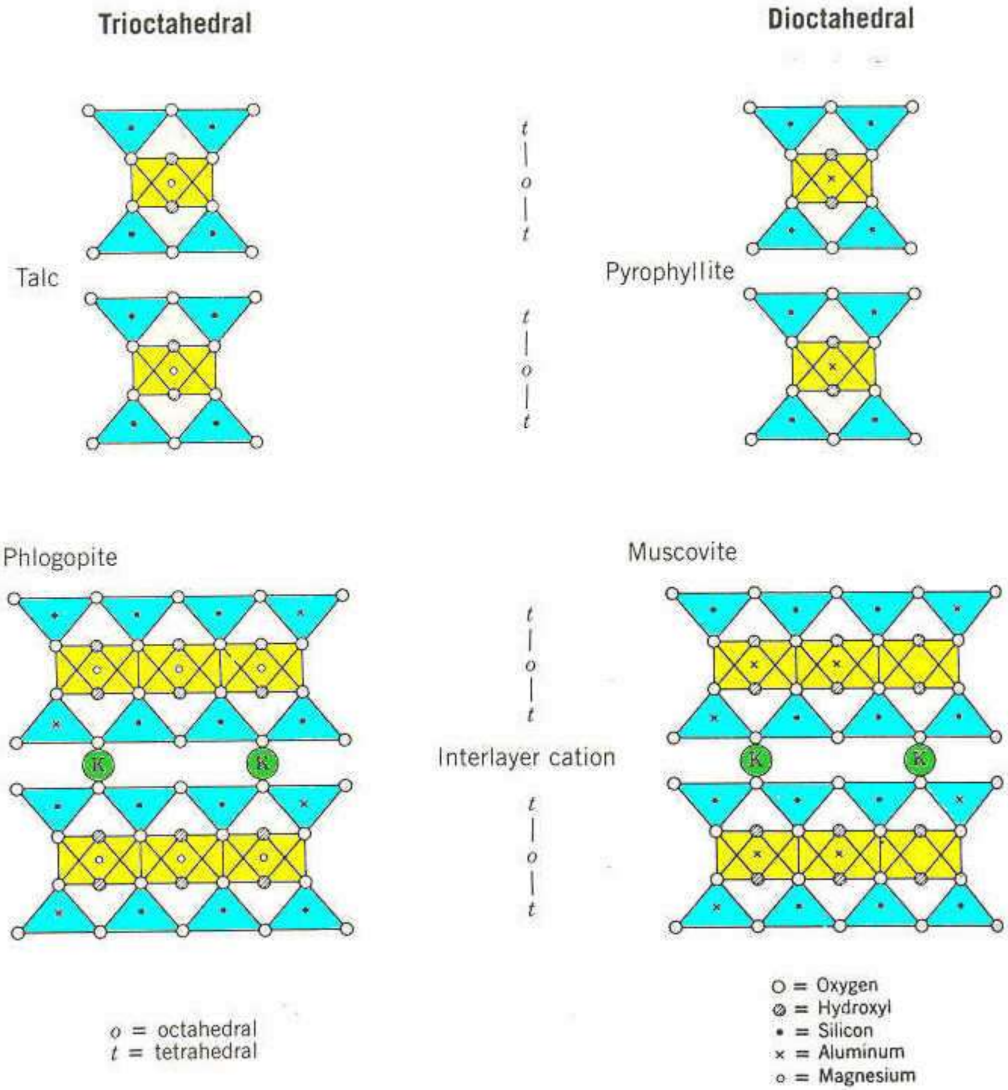
Argilominerais 2:1

Não-expansíveis

Talco e Pirofilita

Estruturas de Argilominerais 2:1



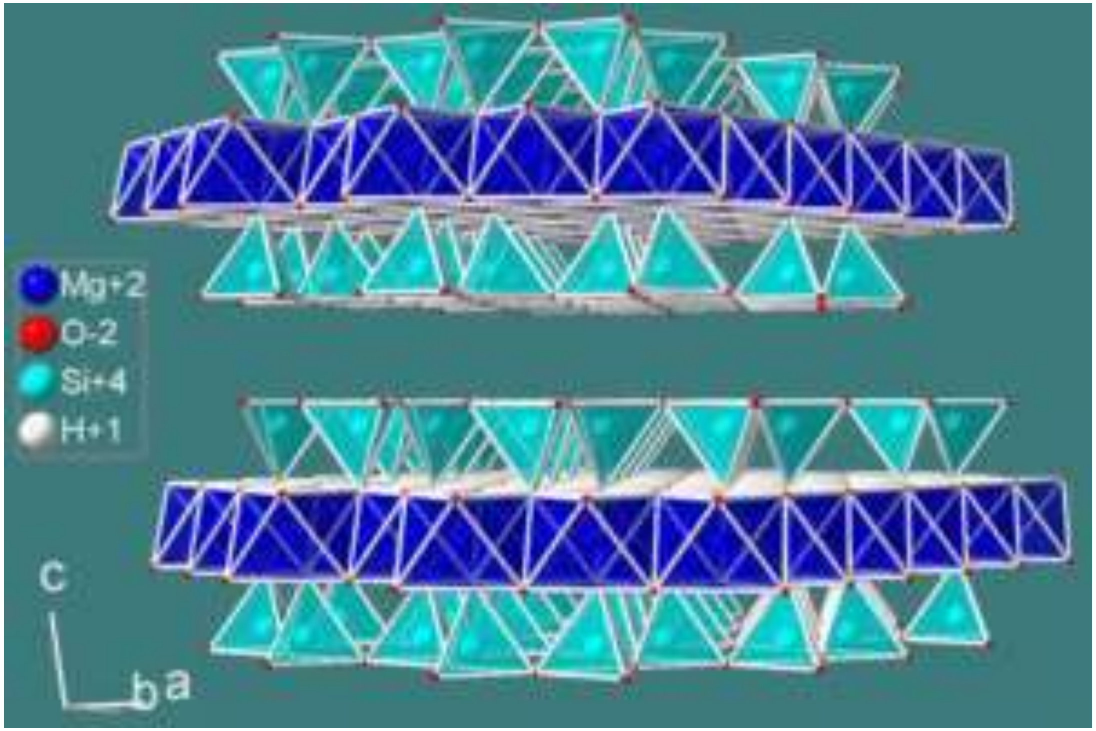


Argilominerais 2:1 - TALCO

Talco - $Mg_6Si_4O_{10}(OH)_8$

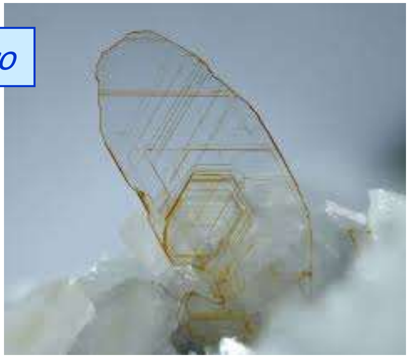
(trioctaédrico)

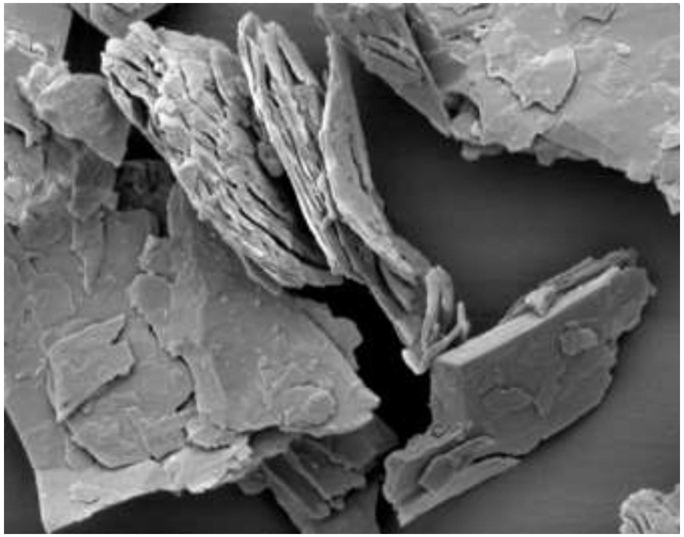
Representação da Estrutura Cristalina do Talco



https://en.wikipedia.org/wiki/Talc

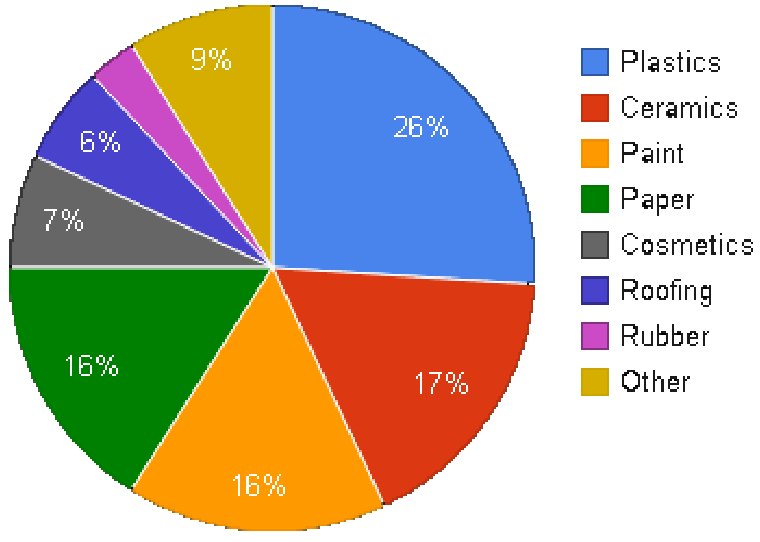
Cristais de talco





https://www.sciencesource.com/archive/Talcum-Powder-SS2201625.html

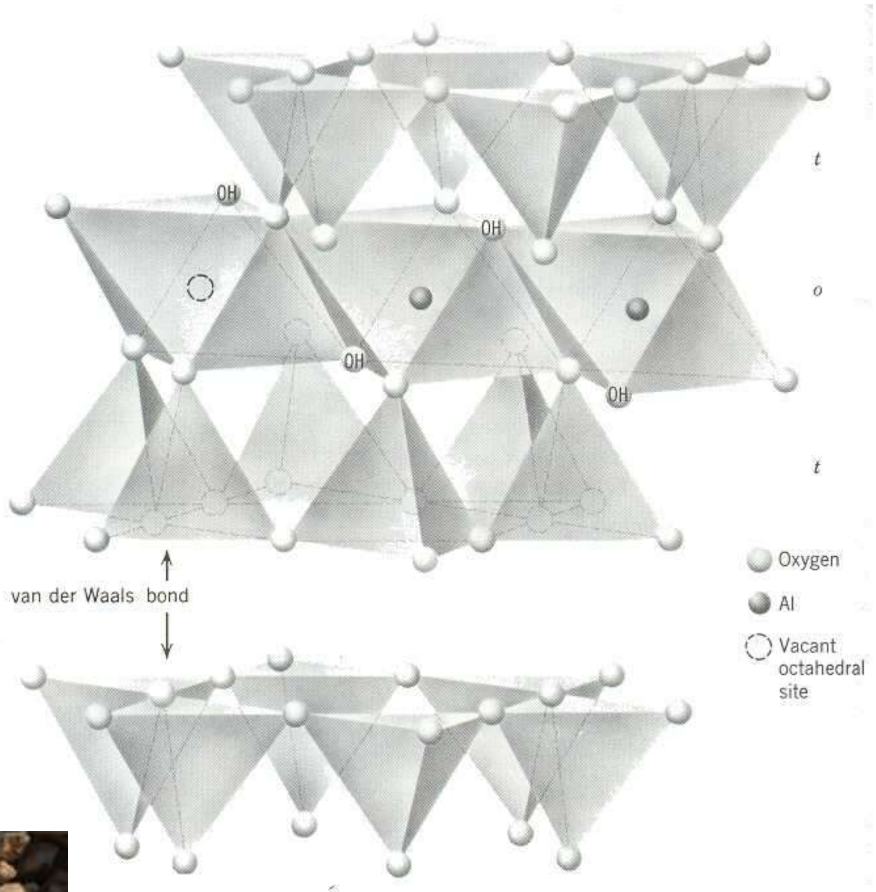
Argilominerais 2:1 - TALCO



https://en.wikipedia.org/wiki/Talc

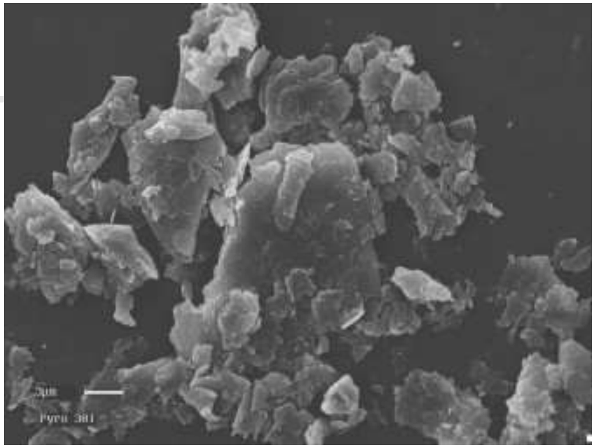
Argilominerais 2:1 - PIROFILITA

Representação da Estrutura Cristalina da Pirofilita



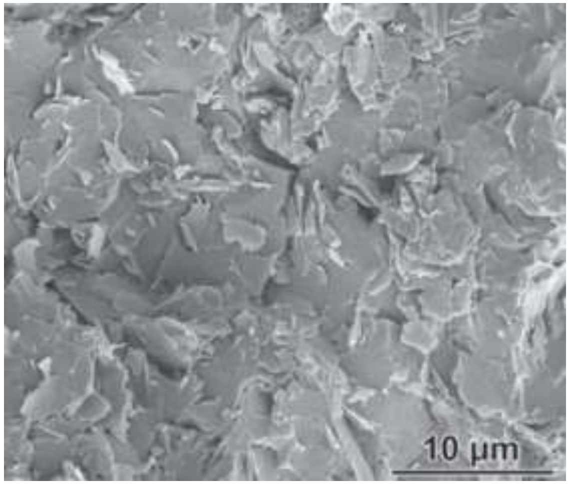
Pirofilita

$Al_4Si_4O_{10}(OH)_8$ *(dioctaédrica)*



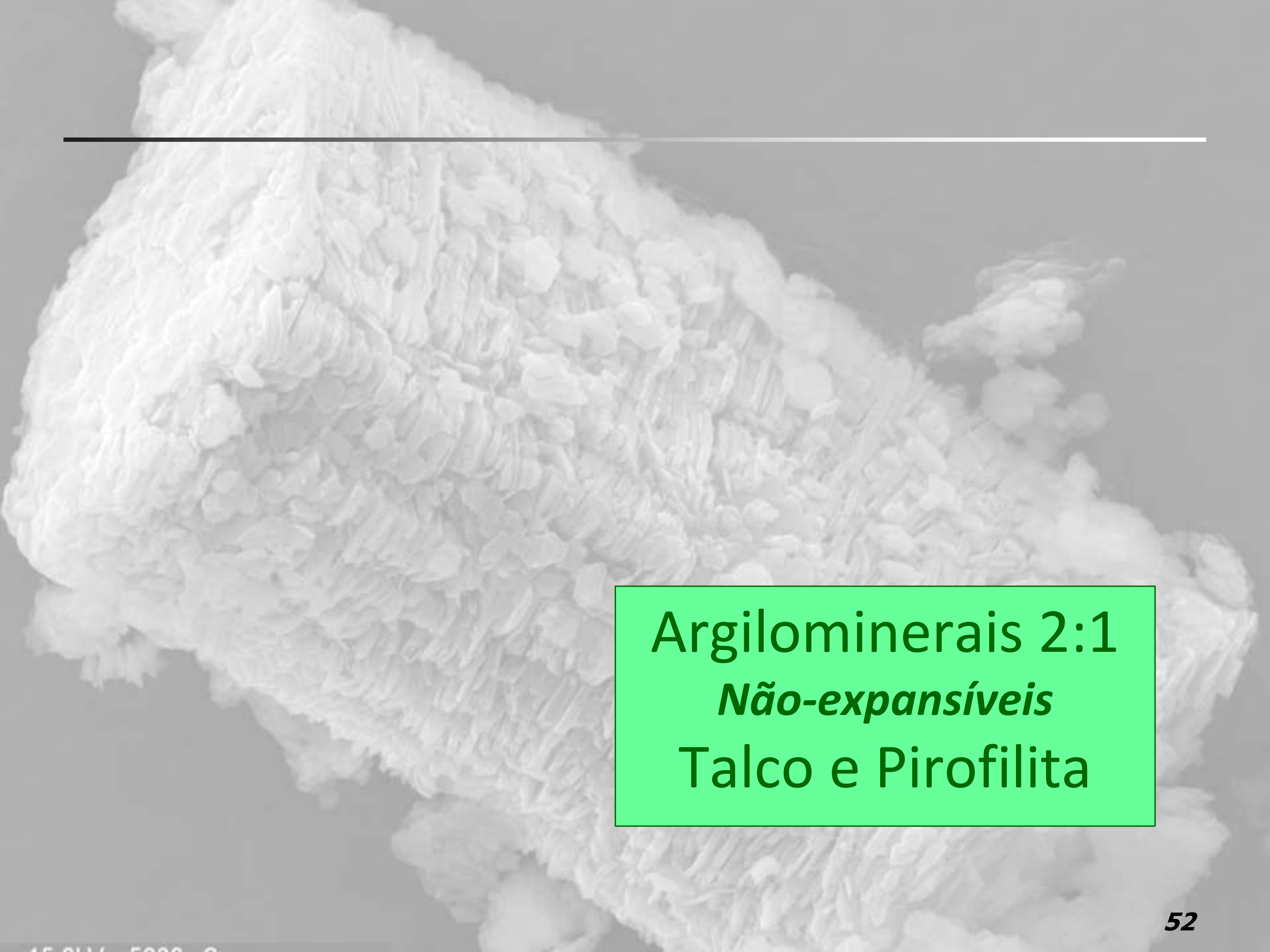
MEV de cristais de pirofilita

Cer. Intern. 36 (3), 909-916 (2010)



MEV de superfície de fratura de pirofilita maciça (Nohwa, Coréia do Sul)

Am. Miner. 91, 1293-1299 (2006)

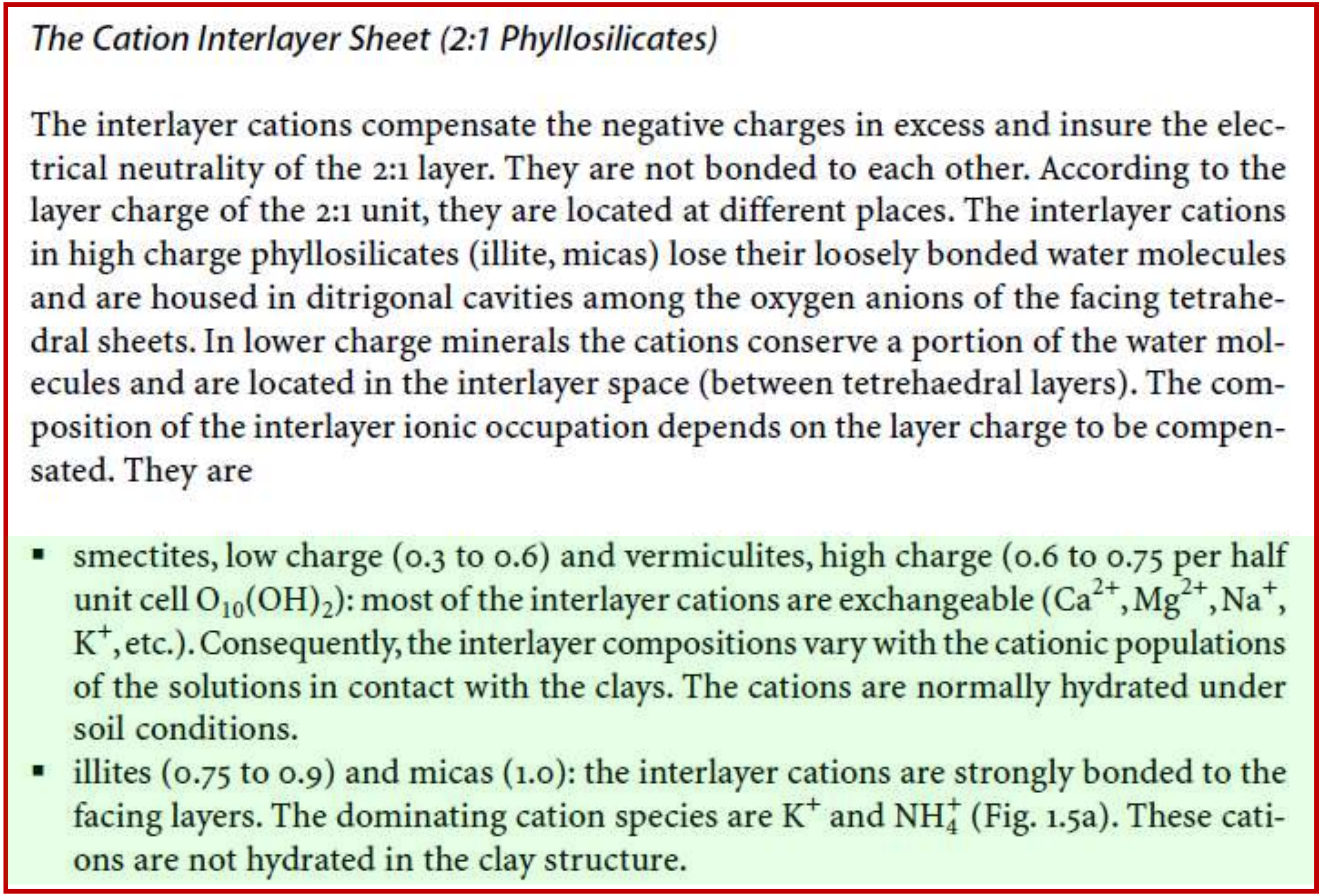


Argilominerais 2:1

Não-expansíveis

Talco e Pirofilita

Argilominerais 2:1 – Carga de Camada



The Cation Interlayer Sheet (2:1 Phyllosilicates)

The interlayer cations compensate the negative charges in excess and insure the electrical neutrality of the 2:1 layer. They are not bonded to each other. According to the layer charge of the 2:1 unit, they are located at different places. The interlayer cations in high charge phyllosilicates (illite, micas) lose their loosely bonded water molecules and are housed in ditrigonal cavities among the oxygen anions of the facing tetrahedral sheets. In lower charge minerals the cations conserve a portion of the water molecules and are located in the interlayer space (between tetrehaedral layers). The composition of the interlayer ionic occupation depends on the layer charge to be compensated. They are

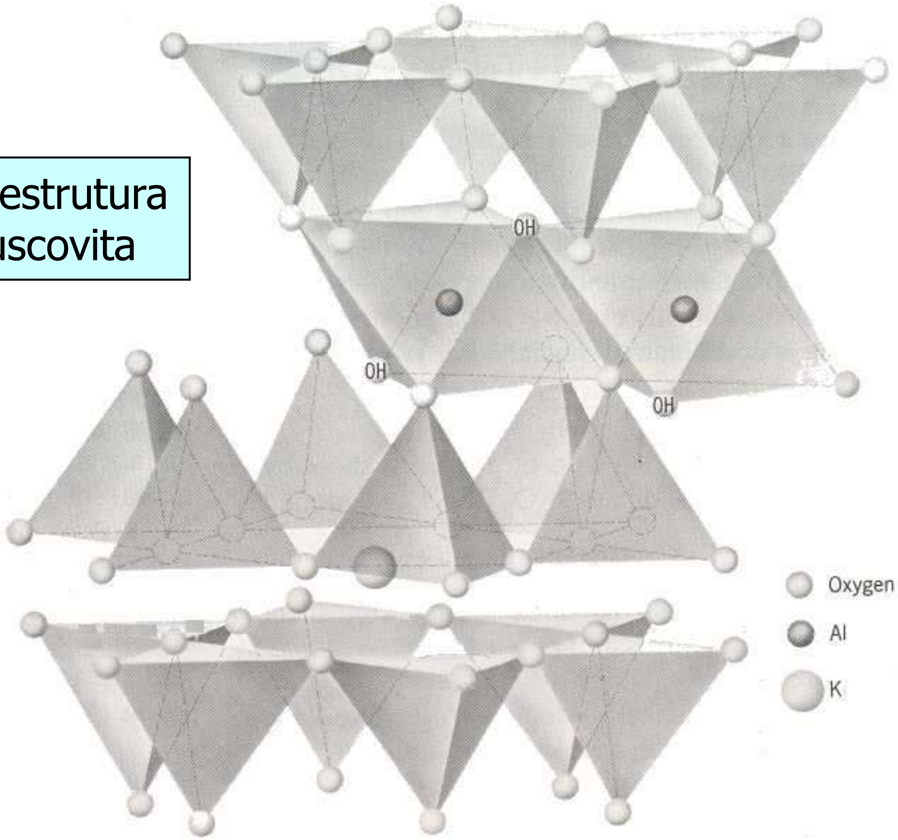
- smectites, low charge (0.3 to 0.6) and vermiculites, high charge (0.6 to 0.75 per half unit cell $O_{10}(OH)_2$): most of the interlayer cations are exchangeable (Ca^{2+}, Mg^{2+}, Na^+, K^+, etc.). Consequently, the interlayer compositions vary with the cationic populations of the solutions in contact with the clays. The cations are normally hydrated under soil conditions.
- illites (0.75 to 0.9) and micas (1.0): the interlayer cations are strongly bonded to the facing layers. The dominating cation species are K^+ and NH_4^+ (Fig. 1.5a). These cations are not hydrated in the clay structure.

Velde, B.; Meunier, A. – The Origin of Clay Minerals in soils and Weathered Rocks. Springer. Berlin. 2008

Estruturas de Argilominerais 2:1 *(continuação)*

Micas

Esquema da estrutura da mica muscovita



(a) Muscovita : $KAl_2(AlSi_3)O_{10}(OH)_2$
(b) Biotita : $K(MgFe)_3(AlSi_3)O_{10}(OH,F)_2$
(c) Lepidolita: $K(LiAl)_2(Si,Al)_4O_{10}(OH,F)_2$
(d) Flogopita: $KMg_3(AlSi_3)O_{10}(OH,F)_2$

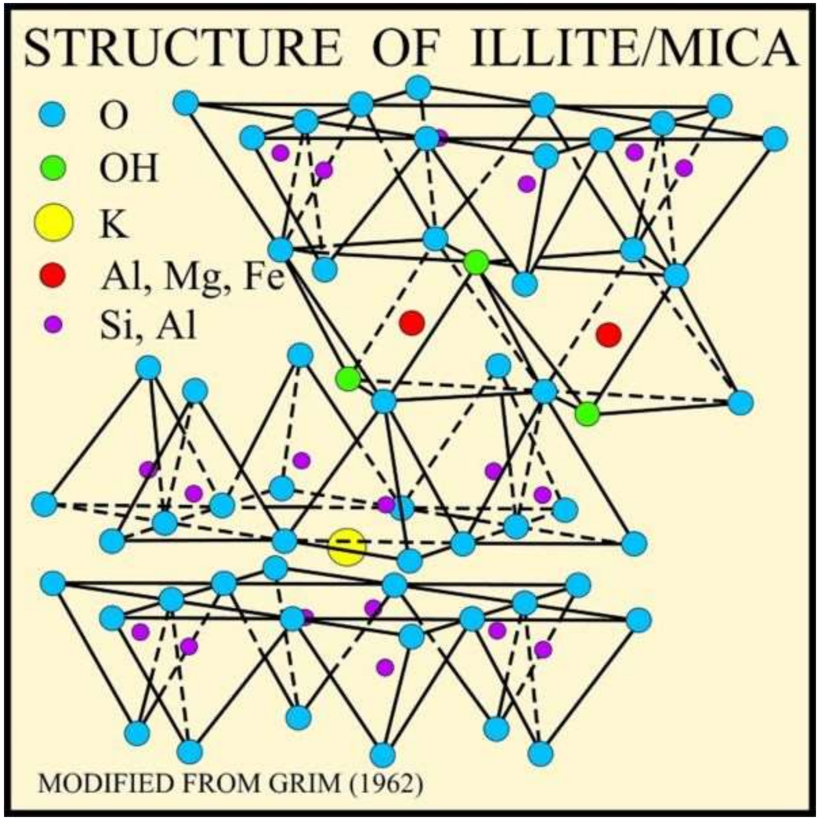
- Muscovita, Lepidolita: dioctaédricas
- Biotita; Flogopita: trioctaédricas

Micas podem existir na forma de cristais macroscópicos muito grandes...

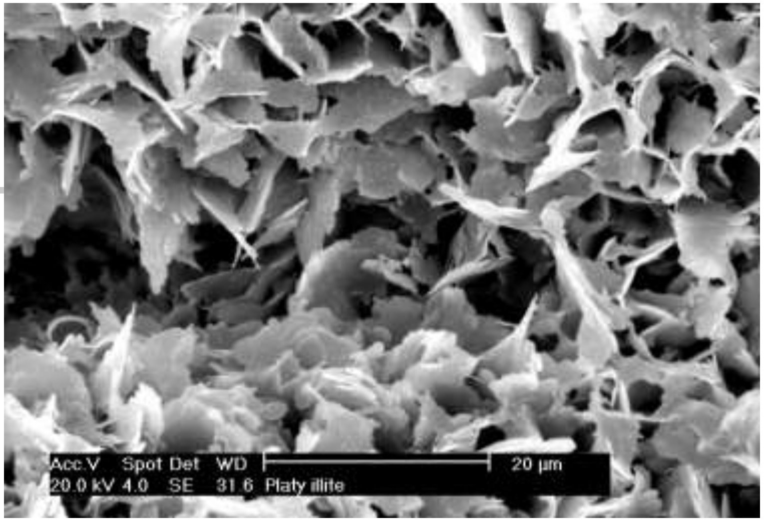
Fig. 11. The largest authenticated *PHYLLOSILICATE* crystal by length. Purdy Mica Mines. Ontario, Canada. This cleavage flake is in the Royal Ontario Museum, Toronto, Canada and the photograph has been supplied by, and is reproduced by permission of, Dr. J. A. Mandarino (Table 1-v_4).

*American Mineralogist **66**, 885-907 (1981)*

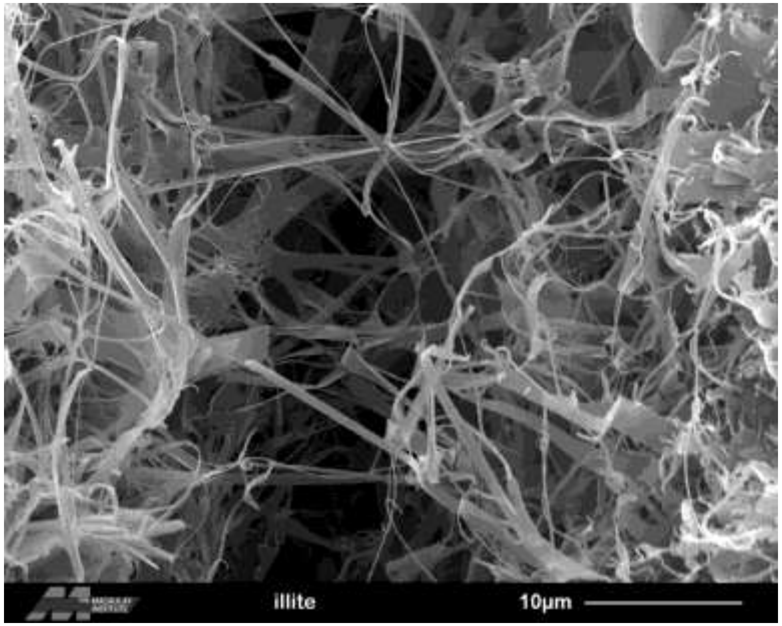
Ilitas



Ilita : $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Dioctaédrica

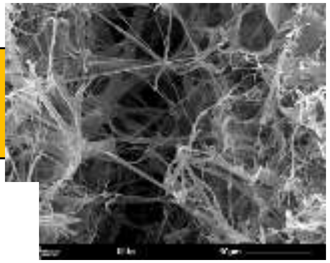


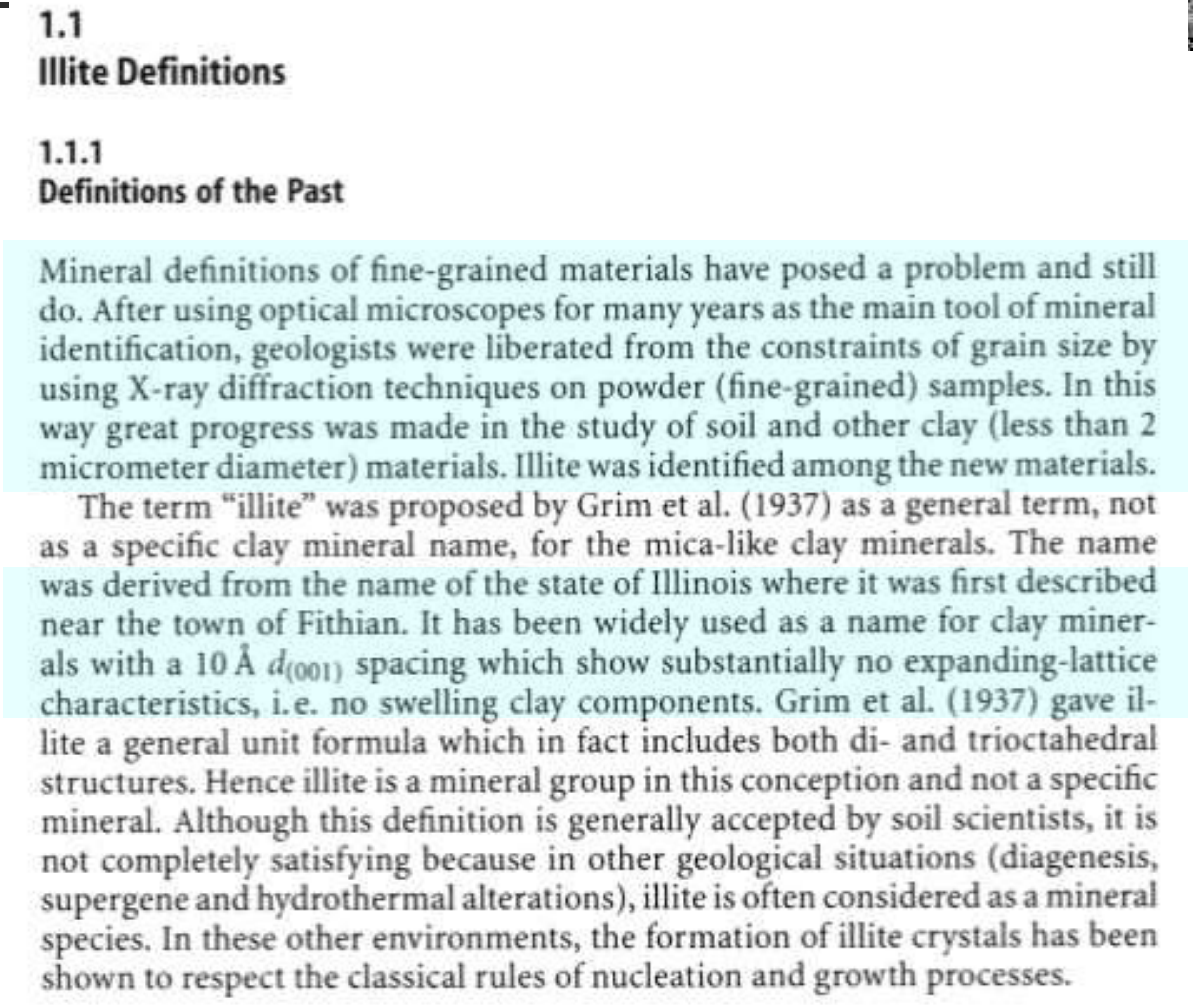
Platy Illite fro the Rotliegend of Northern Germany; M.Roe, Macaulay Institute



Fibrous Illite from Rotliegend, S. North Sea; E. Delbos, James Hutton Institute

Ilitas





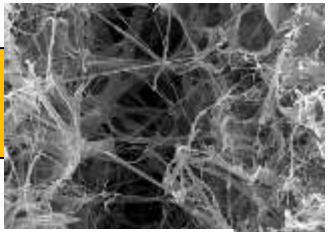
1.1
Illite Definitions

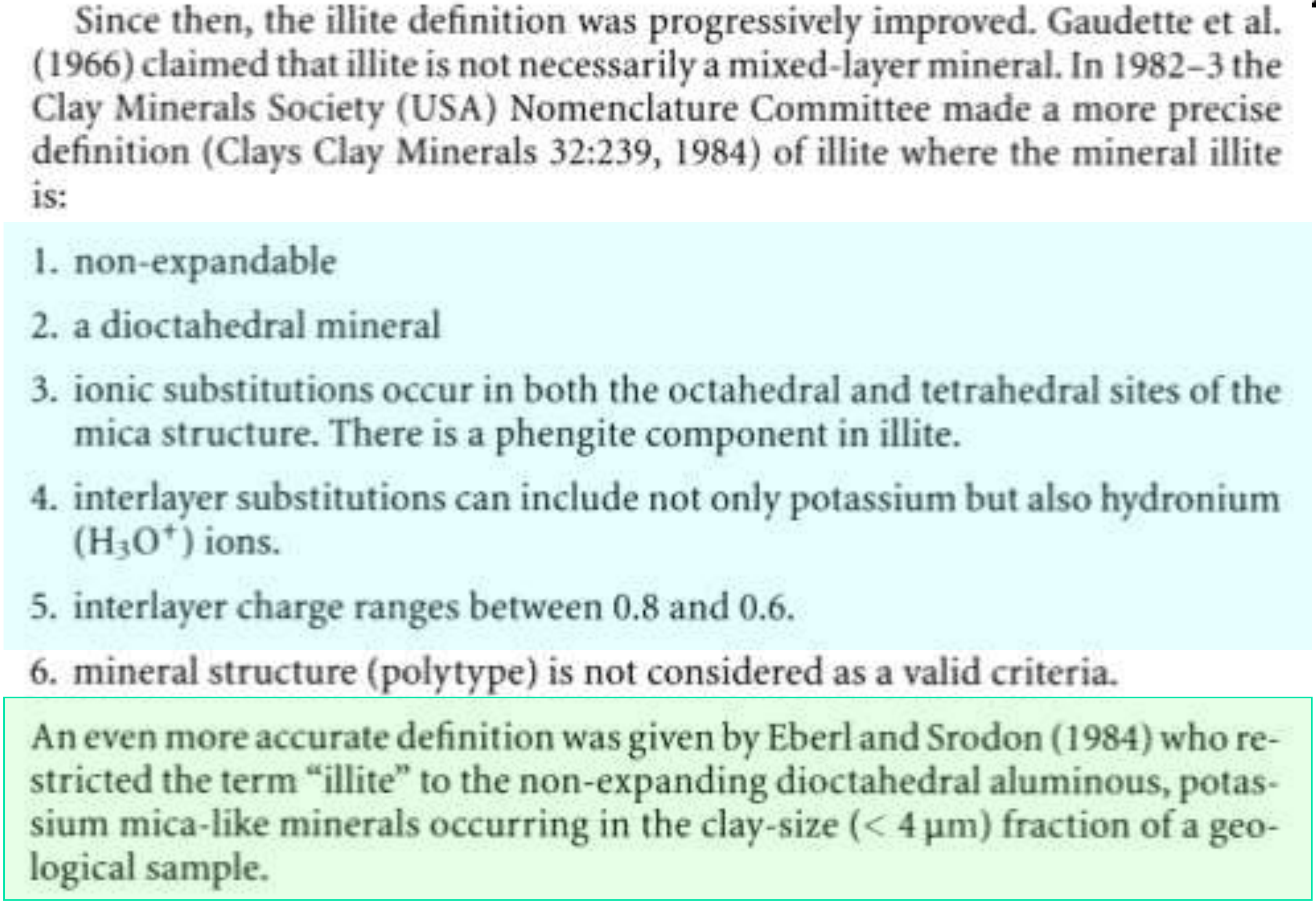
1.1.1
Definitions of the Past

Mineral definitions of fine-grained materials have posed a problem and still do. After using optical microscopes for many years as the main tool of mineral identification, geologists were liberated from the constraints of grain size by using X-ray diffraction techniques on powder (fine-grained) samples. In this way great progress was made in the study of soil and other clay (less than 2 micrometer diameter) materials. Illite was identified among the new materials.

The term "illite" was proposed by Grim et al. (1937) as a general term, not as a specific clay mineral name, for the mica-like clay minerals. The name was derived from the name of the state of Illinois where it was first described near the town of Fithian. It has been widely used as a name for clay minerals with a 10 Å $d_{(001)}$ spacing which show substantially no expanding-lattice characteristics, i.e. no swelling clay components. Grim et al. (1937) gave illite a general unit formula which in fact includes both di- and trioctahedral structures. Hence illite is a mineral group in this conception and not a specific mineral. Although this definition is generally accepted by soil scientists, it is not completely satisfying because in other geological situations (diagenesis, supergene and hydrothermal alterations), illite is often considered as a mineral species. In these other environments, the formation of illite crystals has been shown to respect the classical rules of nucleation and growth processes.

Ilitas



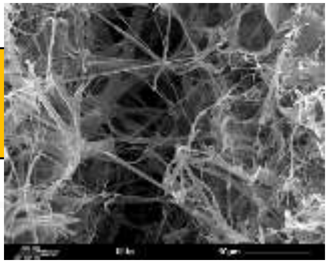


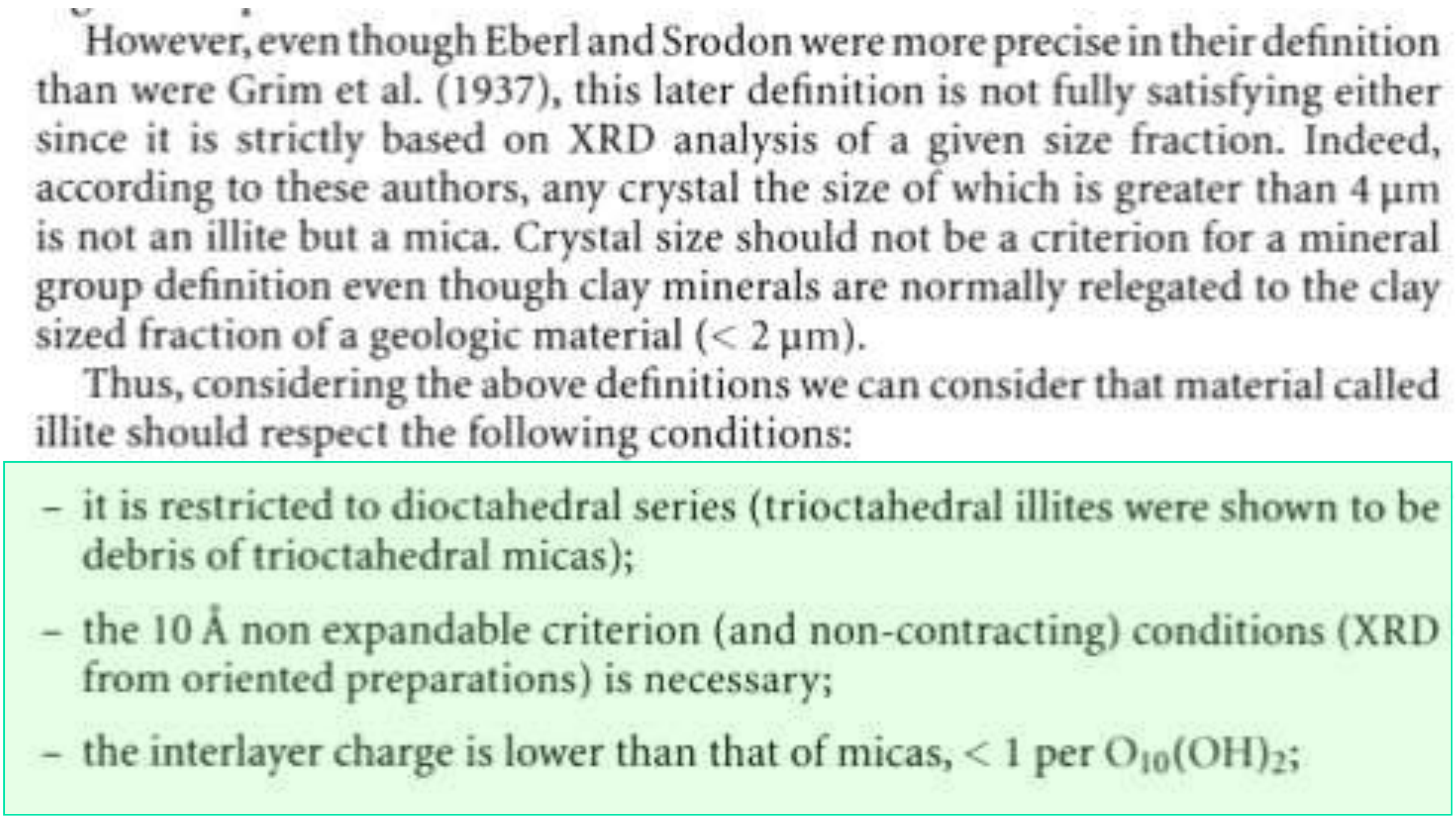
Since then, the illite definition was progressively improved. Gaudette et al. (1966) claimed that illite is not necessarily a mixed-layer mineral. In 1982–3 the Clay Minerals Society (USA) Nomenclature Committee made a more precise definition (Clays Clay Minerals 32:239, 1984) of illite where the mineral illite is:

1. non-expandable
2. a dioctahedral mineral
3. ionic substitutions occur in both the octahedral and tetrahedral sites of the mica structure. There is a phengite component in illite.
4. interlayer substitutions can include not only potassium but also hydronium (H_3O^+) ions.
5. interlayer charge ranges between 0.8 and 0.6.
6. mineral structure (polytype) is not considered as a valid criteria.

An even more accurate definition was given by Eberl and Srodon (1984) who restricted the term "illite" to the non-expanding dioctahedral aluminous, potassium mica-like minerals occurring in the clay-size (< 4 µm) fraction of a geological sample.

Ilitas





However, even though Eberl and Srodon were more precise in their definition than were Grim et al. (1937), this later definition is not fully satisfying either since it is strictly based on XRD analysis of a given size fraction. Indeed, according to these authors, any crystal the size of which is greater than 4 µm is not an illite but a mica. Crystal size should not be a criterion for a mineral group definition even though clay minerals are normally relegated to the clay sized fraction of a geologic material (< 2 µm).

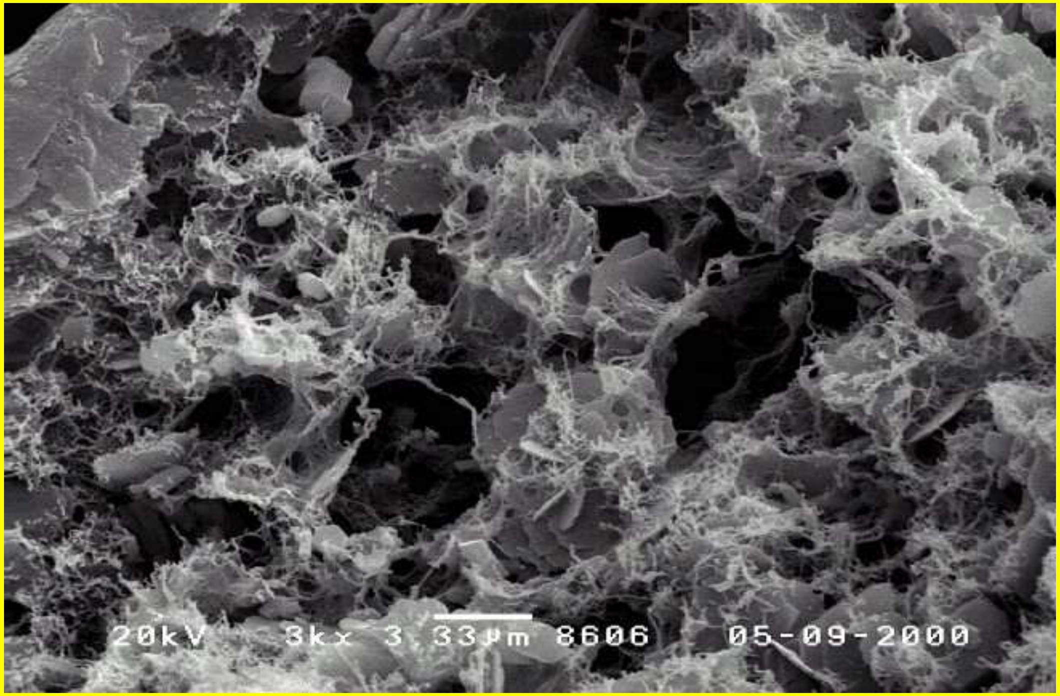
Thus, considering the above definitions we can consider that material called illite should respect the following conditions:

- it is restricted to dioctahedral series (trioctahedral illites were shown to be debris of trioctahedral micas);
- the 10 Å non expandable criterion (and non-contracting) conditions (XRD from oriented preparations) is necessary;
- the interlayer charge is lower than that of micas, < 1 per $O_{10}(OH)_2$;

Ilitas

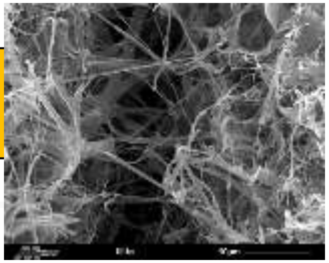
- **Ilita** essencialmente é o nome de um grupo de argilominerais não-expansíveis.
- Segundo Grim (1965), ilita é um nome geral para um material sedimentar de espaçamento basal 10Å para o qual não podem ser obtidos dados precisos sobre pureza, granulometria e composição química; não há, portanto, fórmula estrutural precisa.
- É estruturalmente similar à mica, porém apresentando mais Si, Mg, Fe e água, e ligeiramente menos Al e K interlamelar que a muscovite (Bailey, 1980).

- As ilitas se formam através da ação do intemperismo em feldspatos potássicos, e pela alteração de muscovita (Deer et al., 1975).
- Também podem ser formadas por alteração de esmectitas em ambiente marinho.
- A formação de ilita é geralmente favorecida por condições alcalinas e por concentrações elevadas de Al e K.



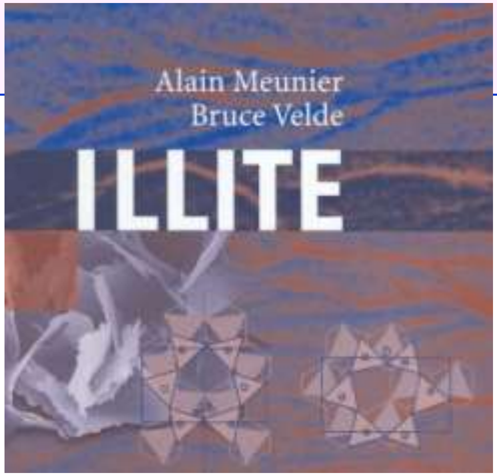
Fibrous illite, North Sea (Sample 'Ill-34': Macaulay Collection)

Ilitas



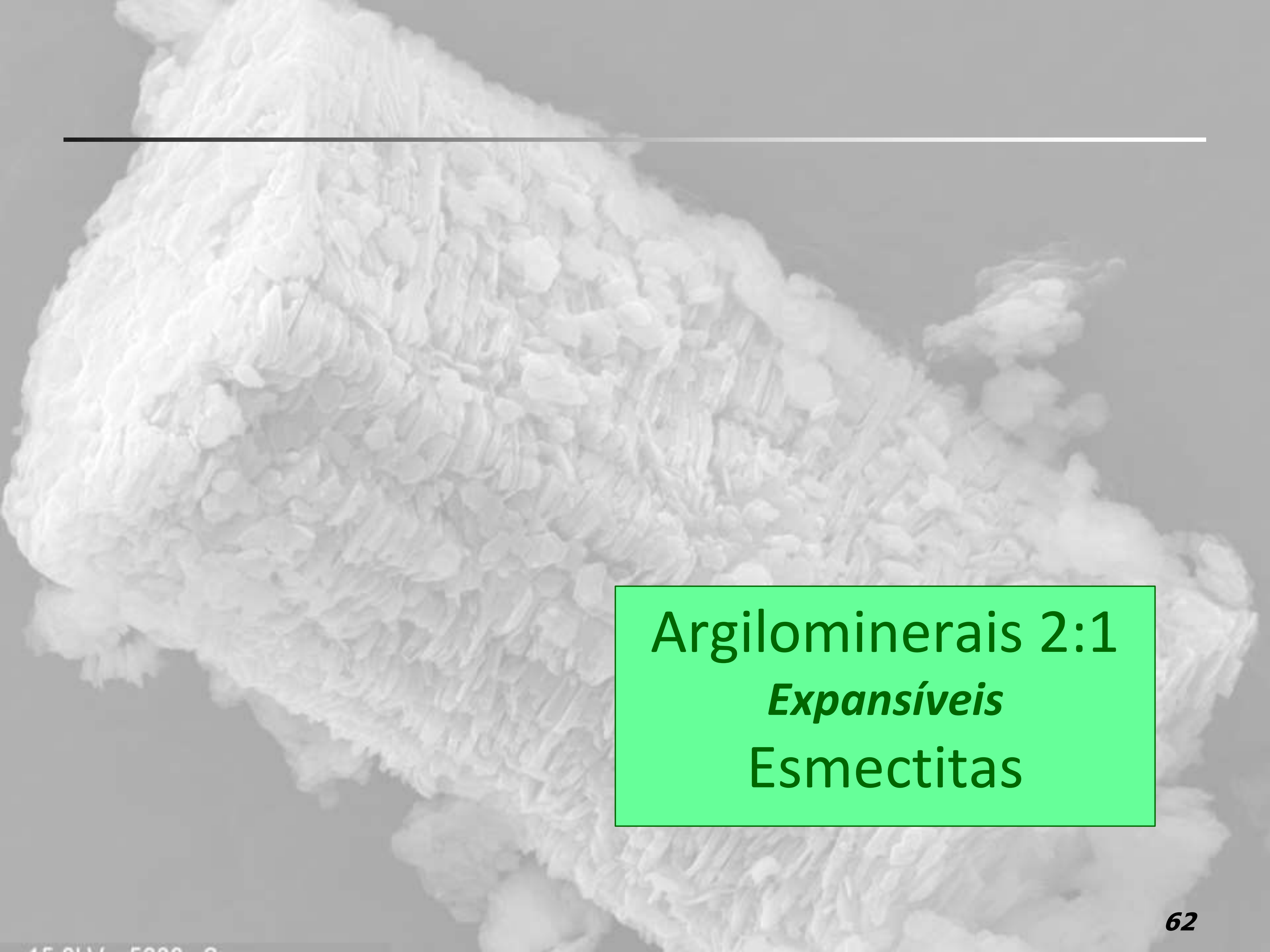
Several questions should be addressed which are not fully answered in the classical definitions of illite:

- what is the extension of the chemical composition range in the dioctahedral phyllosilicate group? What substitutions occur in the tetrahedral, octahedral and interlayer sites?
- are the models of the crystal structure coherent with the crystal growth processes?
- what are the theoretical possibilities of phyllosilicate structures in 3D space and those which are typical of illite?



Alain Meunier
Bruce Velde

ILLITE

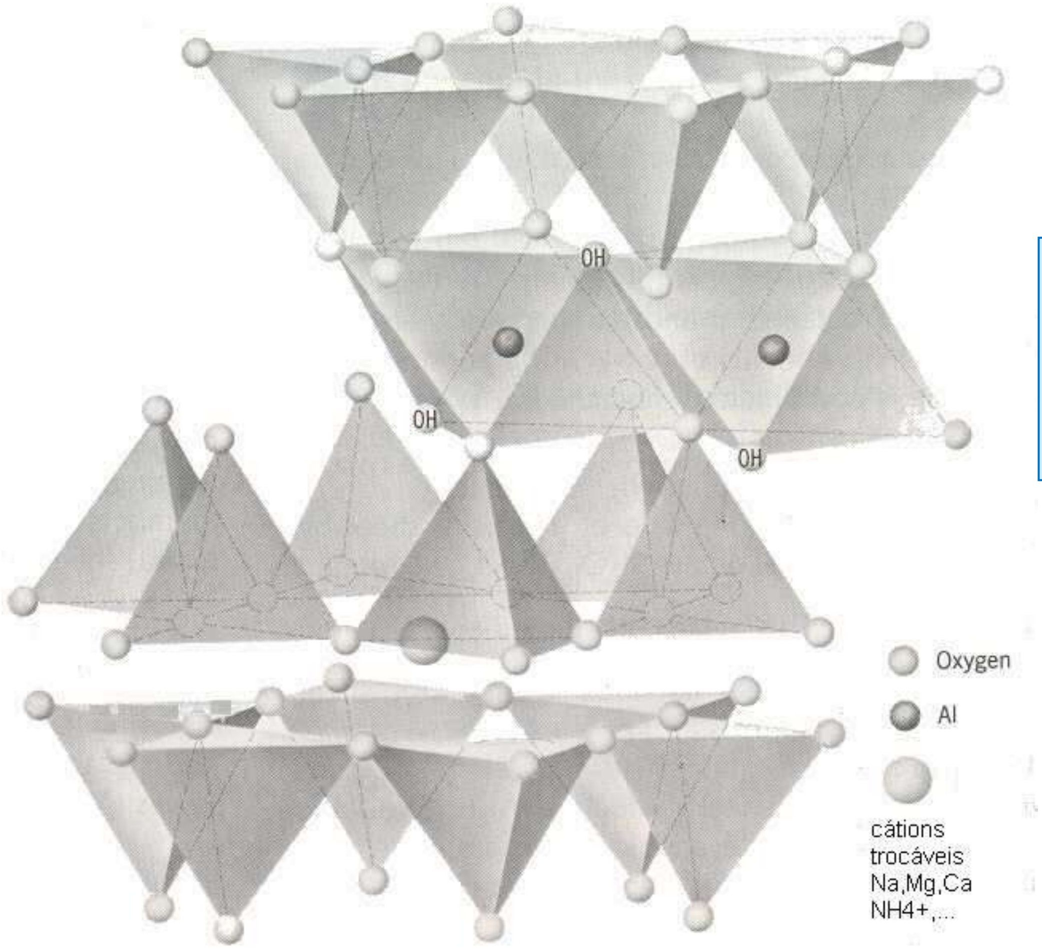


Argilominerais 2:1

Expansíveis

Esmectitas

Estruturas de Argilominerais 2:1 *(continuação)*



ESMECTITAS

- Diversos minerais, dependendo das *substituições isomórficas*

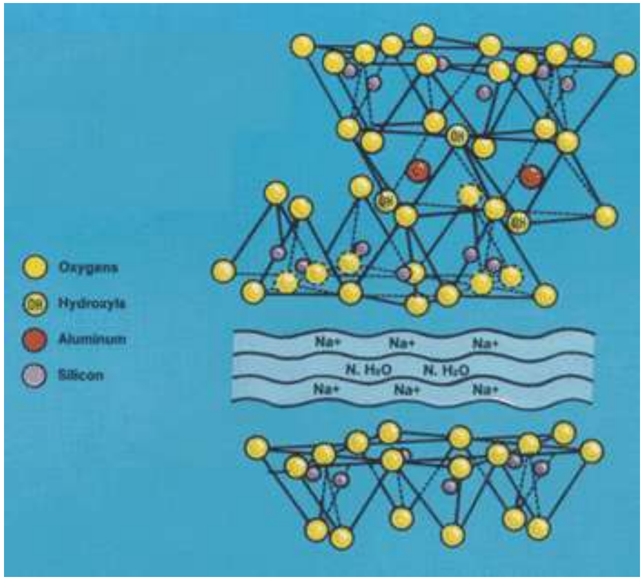
Montmorilonita: $(yM^+)(Al_{2-y}Mg_y)\ Si_4O_{10}(OH)_2.nH_2O$

Nontronita: $(xM^+)\ Fe_2(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$

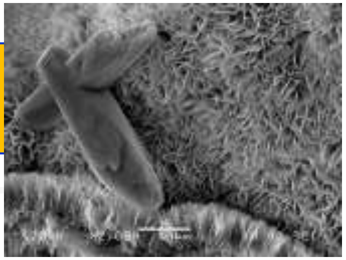
Beidelita: $(xM^+)\ Al_2(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$

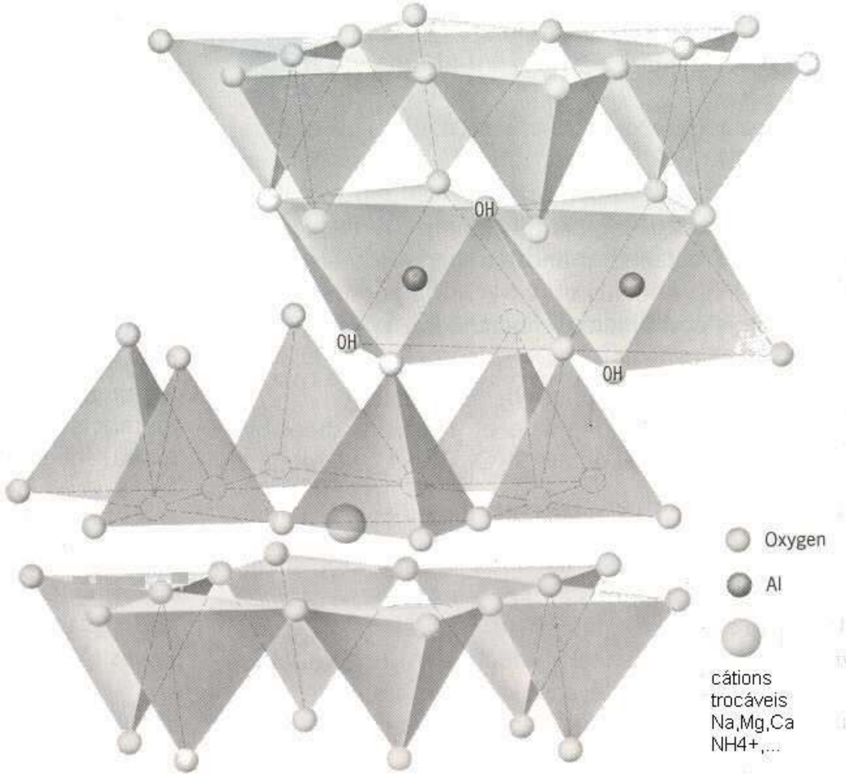
Saponita: $(xM^+)\ Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$

Hectorita: $(yM^+)\ (Mg_{3-y}Li_y)\ Si_4O_{10}(OH)_2.nH_2O$



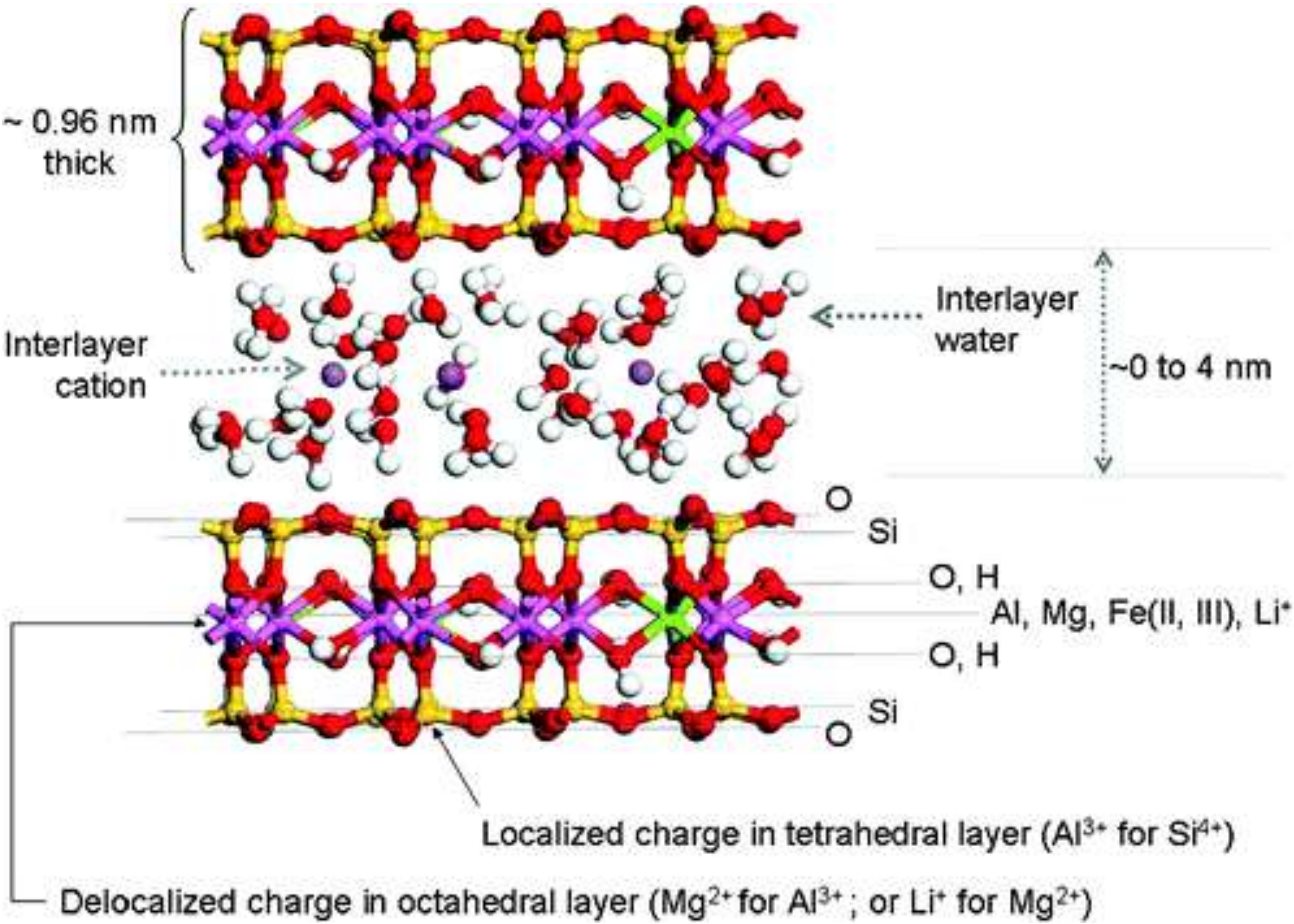
Esmectitas



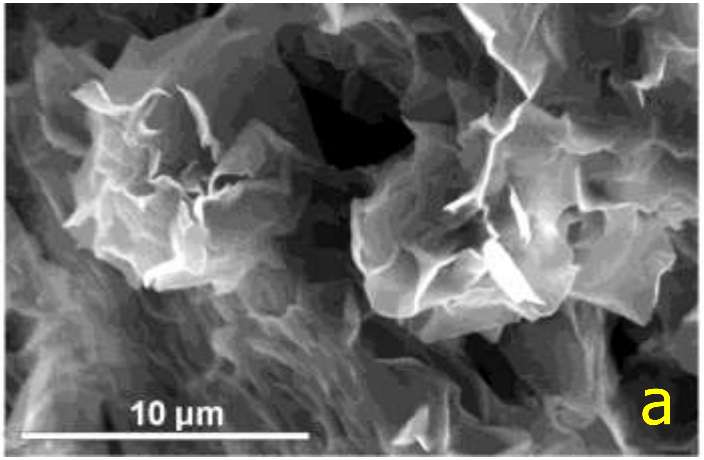


- **$(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$** (metade da cela unitária; **montmorilonita** → dioctaédrica) .
- **$Na_{0,3}(Mg,Li)_3Si_4O_{10}(OH)_2$** (metade da cela unitária; **hectorita** → trioctaédrica).
- Camadas 2:1 não são neutras → carga de camada entre 0,2 e 0,6 por ½ cela unitária
- Espaços interlamelares com cátions hidratados (mono e di-valentes normalmente).
- **Capacidade de troca de cátions elevada** → cátions interlamelares trocáveis.
- Hidratação dos cátions interlamelares varia com as condições ambientes → **inchamento possível,** dependendo dos cátions e das condições ambientais.
- Intercalação de moléculas orgânicas possível.

Esmectitas

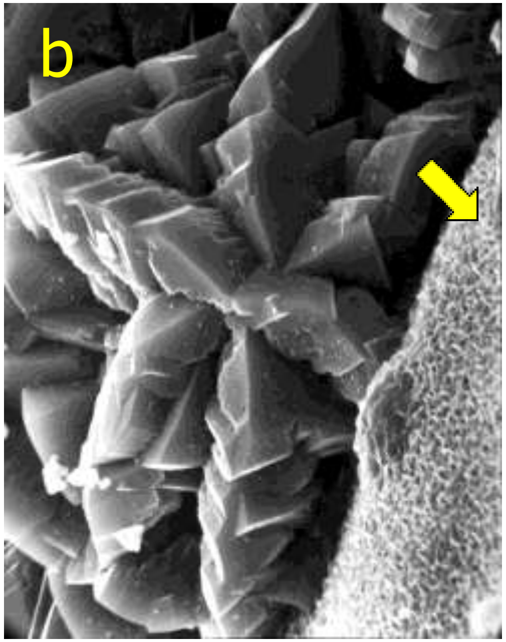

~ 0.96 nm
thick
Interlayer
cation
Interlayer
water
~0 to 4 nm
O
Si
O, H
Al, Mg, Fe(II, III), Li+
O, H
Si
O
Localized charge in tetrahedral layer (Al3+ for Si4+)
Delocalized charge in octahedral layer (Mg2+ for Al3+ ; or Li+ for Mg2+)

Esmectitas

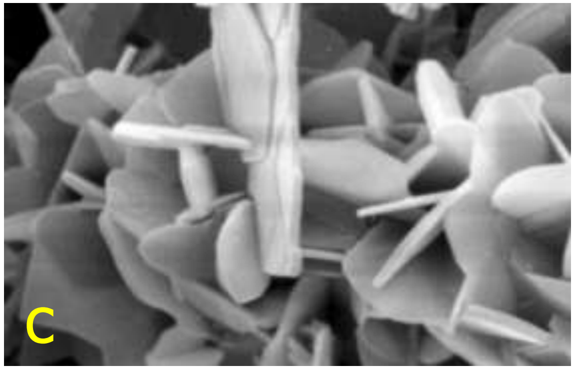


Montmorillonite showing a rose like texture, Miocene arkose, Madrid Basin, Spain

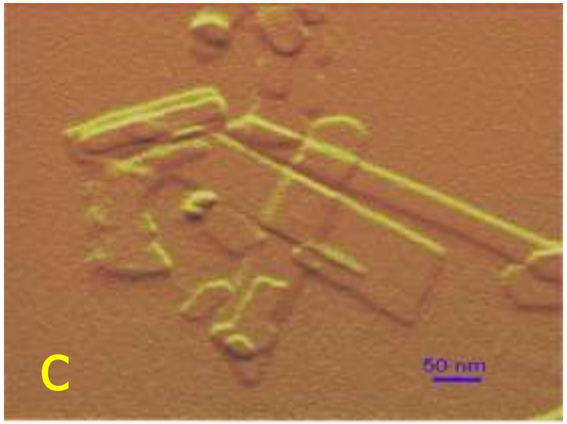
Hectorita natural (EUA)



SEM image of chabezite and smectite (magnesium-iron **saponite**) in an altered clast collected from the debris-avalanche deposit, Washington,1980



"Card-house" structure of **synthetic** fluoro **hectorite** (from melts, K. Beneke)



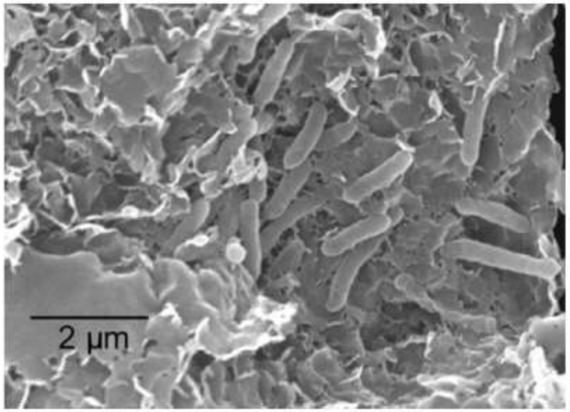
Scanning force microscopy image of overlying 1 nm thick **hectorite** clay minerals

(a) Montmorilonita: $(yM^+)(Al_{2-y}Mg_y)\ Si_4O_{10}(OH)_2.nH_2O$

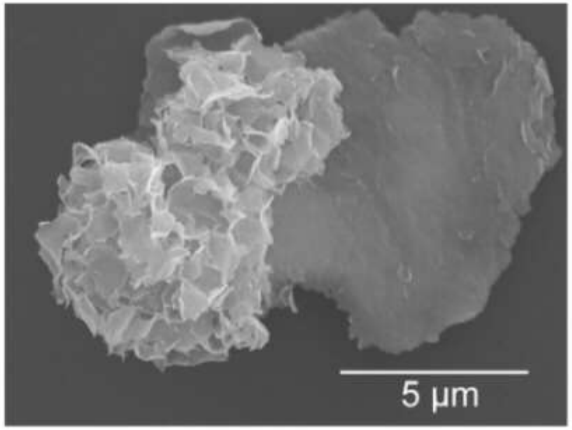
(b) Saponita: $(xM^+)\ Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$

(c) Hectorita: $(yM^+)\ (Mg_{3-y}Li_y)\ Si_4O_{10}(OH)_2.nH_2O$

Esmectitas



Secondary electron image showing bacteria in association with smectite.



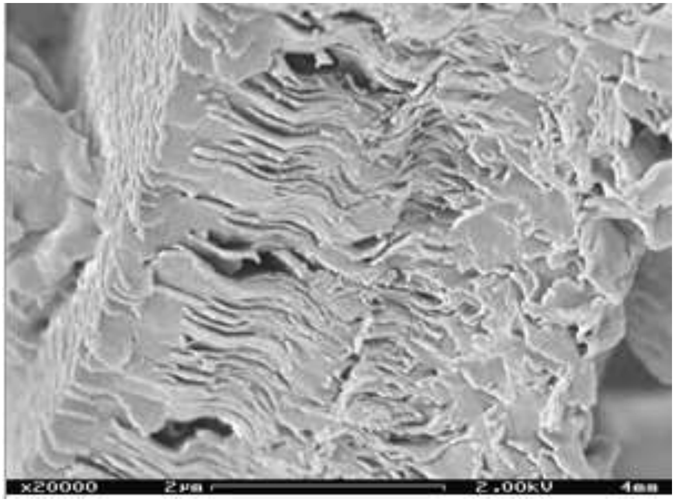
Secondary electron image showing mineral transformation from the oxidized, unaltered smectite (dark sheet on the right) to the biogenic smecite (euhedral crystals on the left).

Alteração biogênica de esmectita rica em ferro

Nontronita , Linópolis,
Divino das Laranjeiras, MG

Nontronite
Higher magnification view of smectite microboxwork in a saprolitized clinopyroxenite from Koua Bocca, Ivory Coast, West Africa

Nontronita , Eslováquia



Nontronita: $(xM^+)\ Fe_2(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$

Esmectitas

Imagem de MET de uma esmectita brasileira

Imagem de MEV de esmectita + quartzo

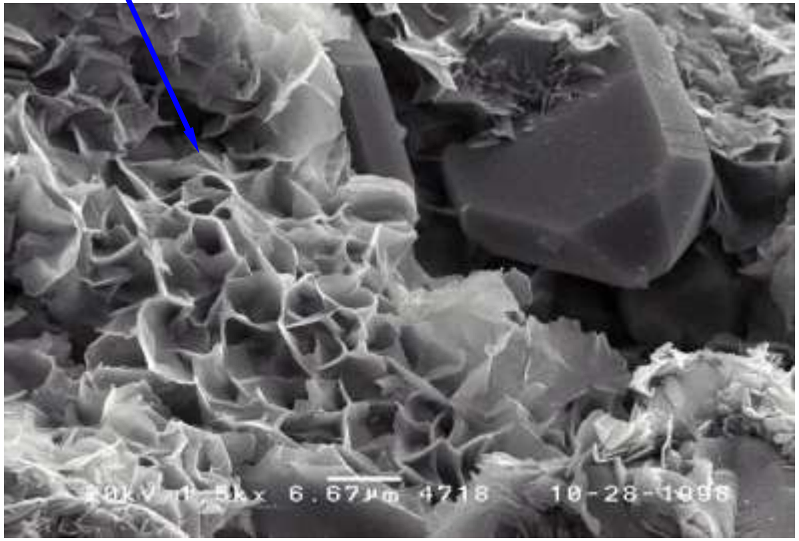
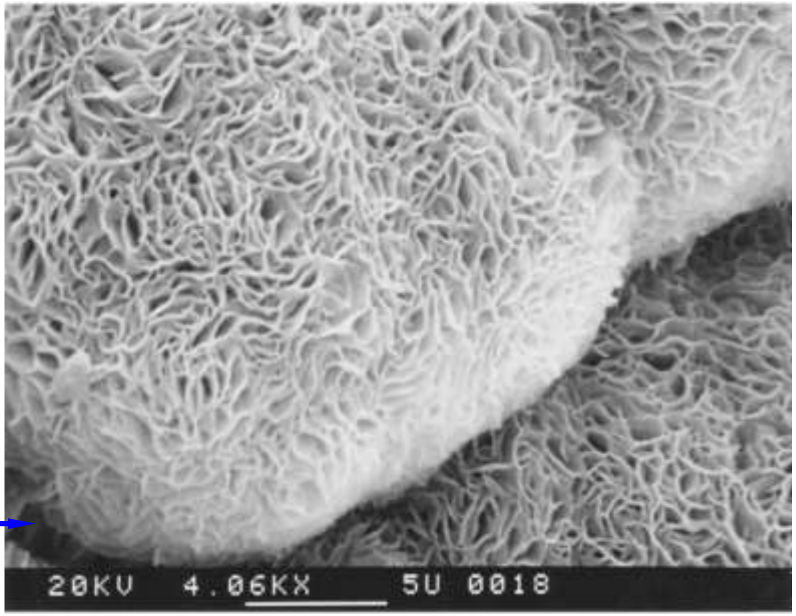


Imagem de MEV de uma esmectita dos EUA (Yucca Mountain, Nevada)

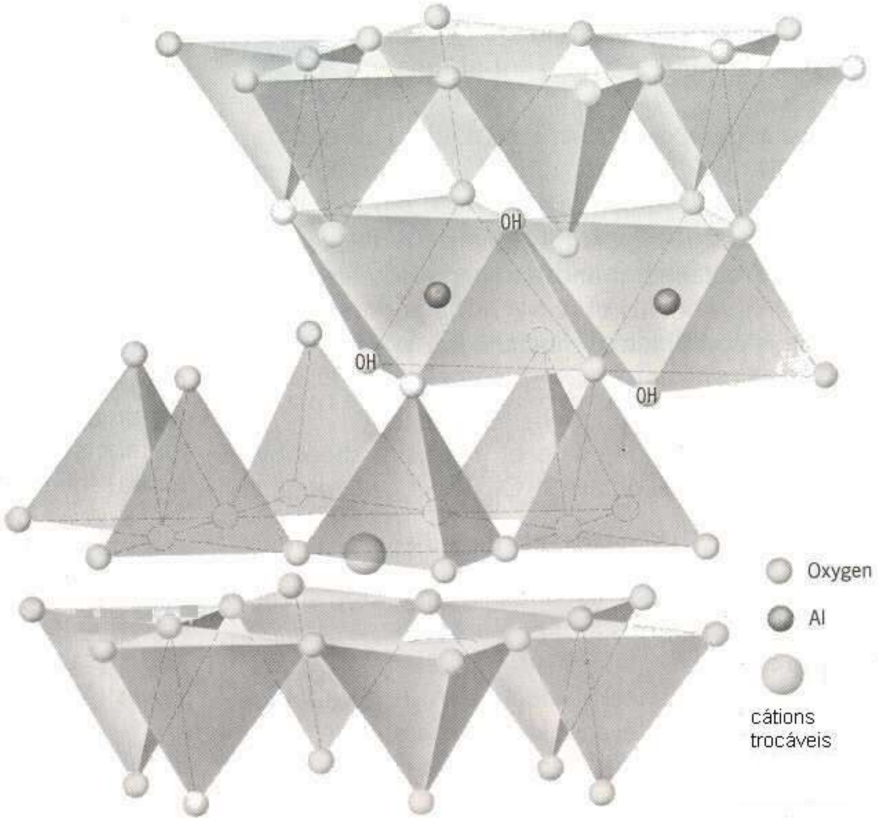


Argilominerais 2:1

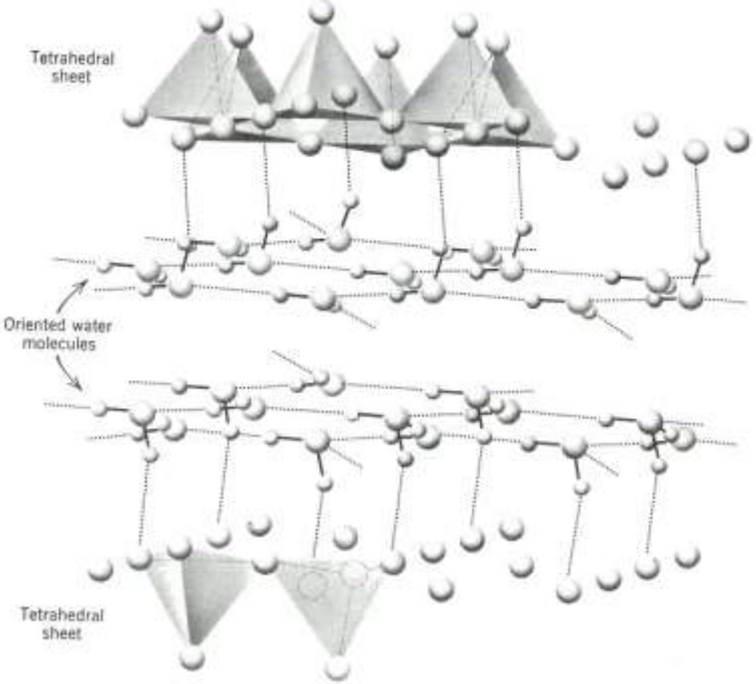
Expansíveis

Vermiculitas

Estruturas de Argilominerais 2:1



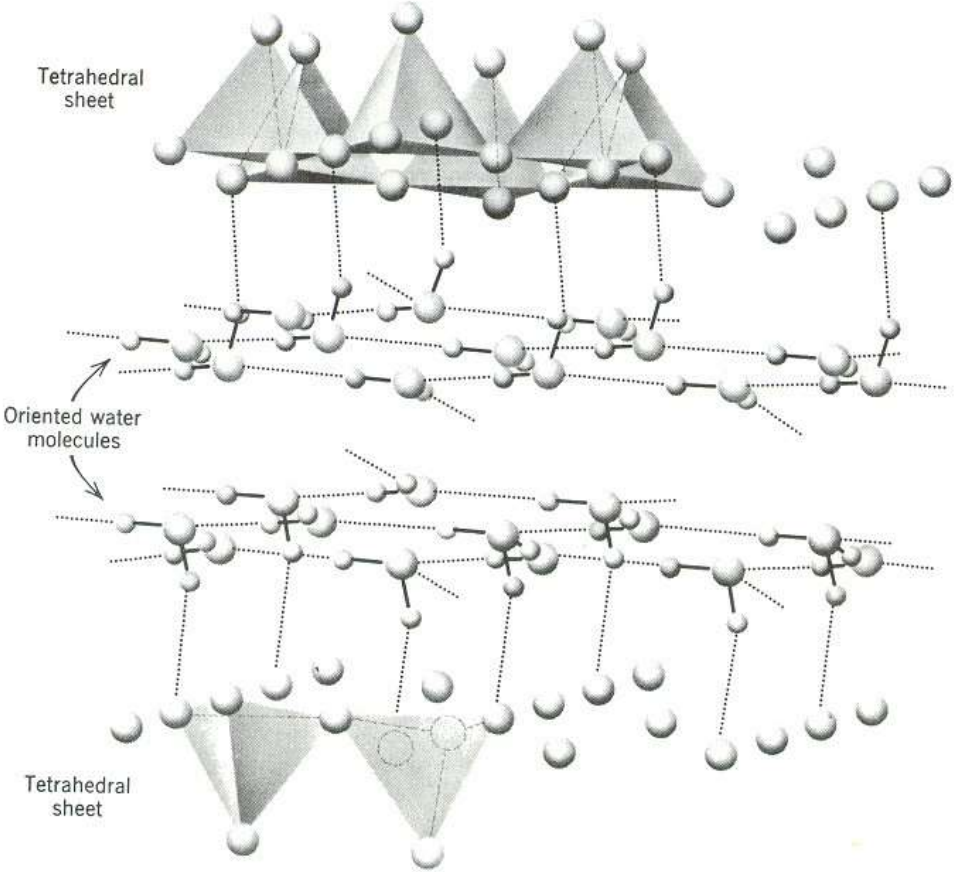
Vermiculitas



- CTC bastante elevada.
- Cátions trocáveis: Ca^{2+},Mg^{2+}.
- Piroexpansíveis.

Vermiculita: $(Mg,Ca)_{0,3}(Mg, Fe,Al)_3 (Al,Si)_4O_{10}(OH)_2.4H_2O$
geralmente Trioctaédrica

Vermiculitas



- **$(Mg,Fe^{++},Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4(H_2O)$** (metade da cela unitária).
- Camadas 2:1 não são neutras → carga de camada entre 0,6 e 0,9 por ½ cela unitária.
- Espaços interlamelares com cátions hidratados (mono e di-valentes normalmente).
- **Capacidade de troca de cátions elevada** → cátions interlamelares trocáveis.
- Macrovermiculitas → **piroexpansíveis.**
- Microvermiculitas → importantes componentes dos solos.

Vermiculitas

Vermiculita da Carolina do Norte (EUA)

Vermiculita piroexpandida

Vermiculita da Pensilvânia(EUA)

Vermiculita de Libby, Montana (EUA)

Vermiculita brasileira (Paulistana, PI)

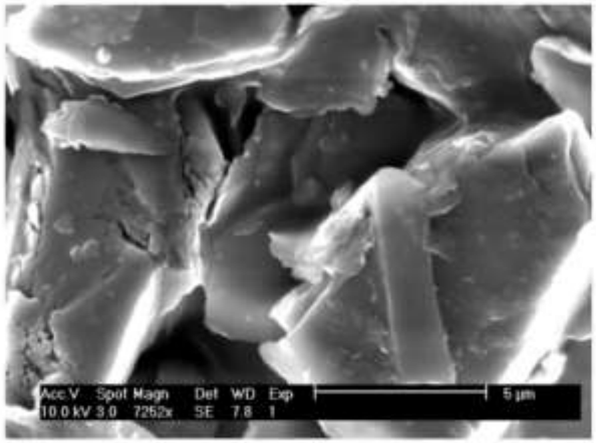
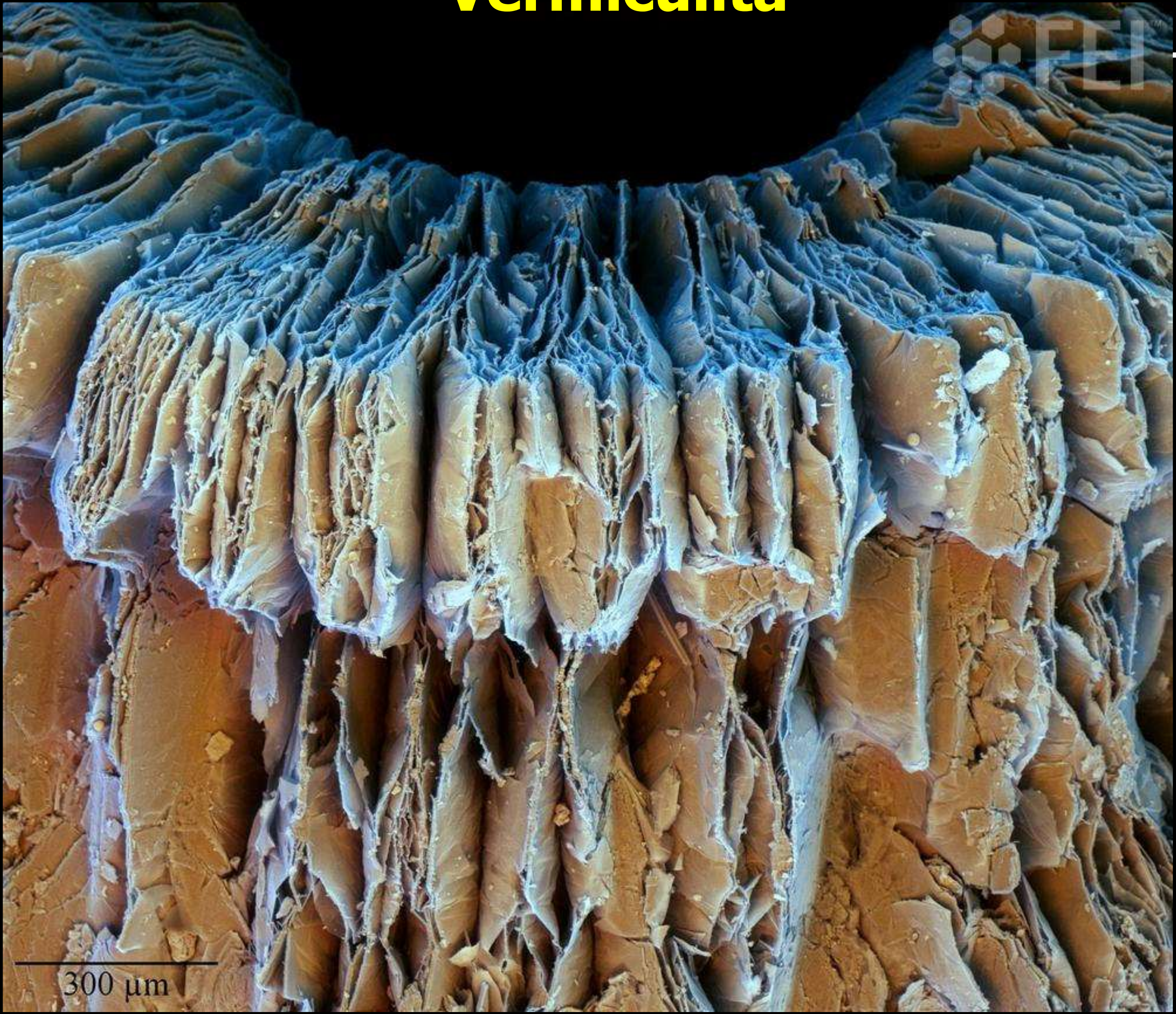


Imagem de MEV de cristais de **vermiculita**

Vermiculita



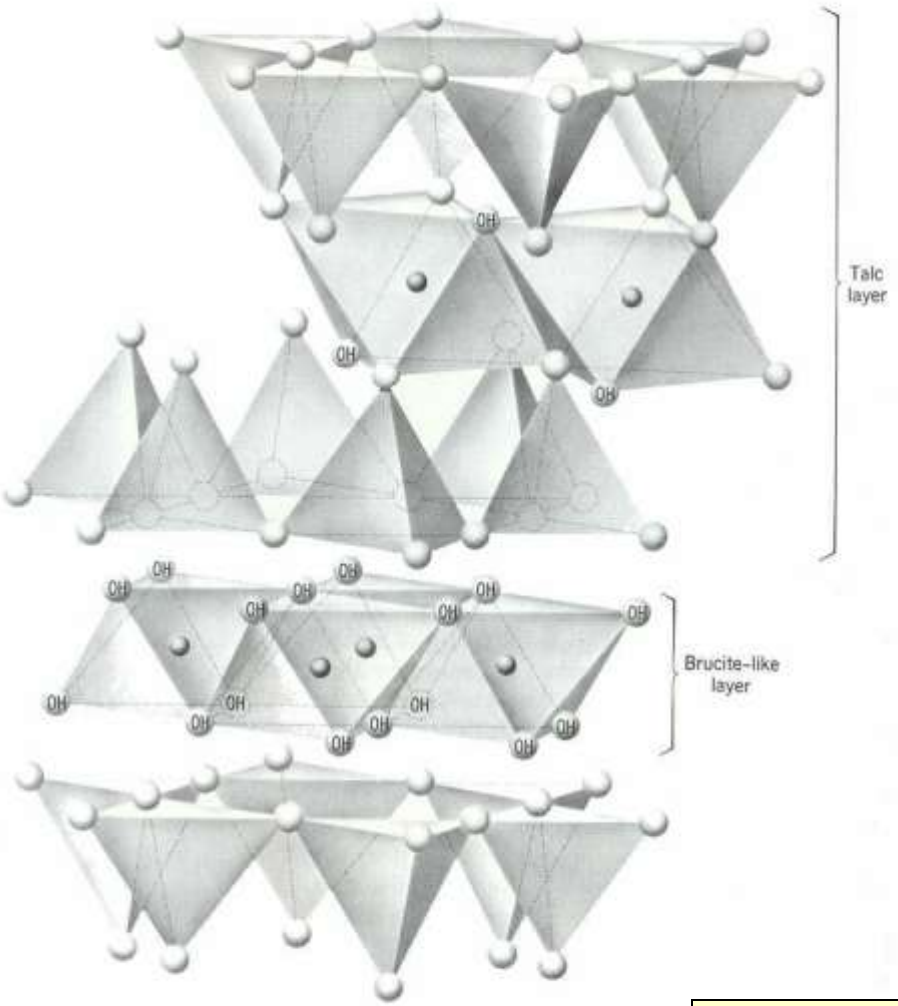
Argilominerais “2:1:1”

Não-Expansíveis

Cloritas

Estruturas de Argilominerais 2:1

Cloritas



- A estrutura da clorita é composta pelo empilhamento, ao longo do eixo c , de camadas 2:1 intercaladas com camadas octaédricas completas. As camadas estão ligadas entre si por pontes de hidrogênio.
- Bailey (1980) dividiu as cloritas em quatro subgrupos:
  - Cloritas trioctaédricas: tanto a camada 2:1, quanto a camada octaédrica intercalada, são trioctaédricas → são as mais comuns.
  - Cloritas dioctaédricas: tanto a camada 2:1, quanto a camada octaédrica intercalada, são dioctaédricas.
  - Cloritas di-trioctaédricas: a camada 2:1 é dioctaédrica, enquanto a camada octaédrica intercalada é trioctaédrica.
  - Cloritas tri-dioctaédricas: a camada 2:1 é trioctaédrica, enquanto a camada octaédrica intercalada é dioctaédrica.

Bailey, S.W. Structure of layer silicates, in Brindley, G.W.; Brown, G (eds.) Crystal Structures of Clay Minerals and Their X-Ray Identification. Mneralogical Society. Londres. 1980.

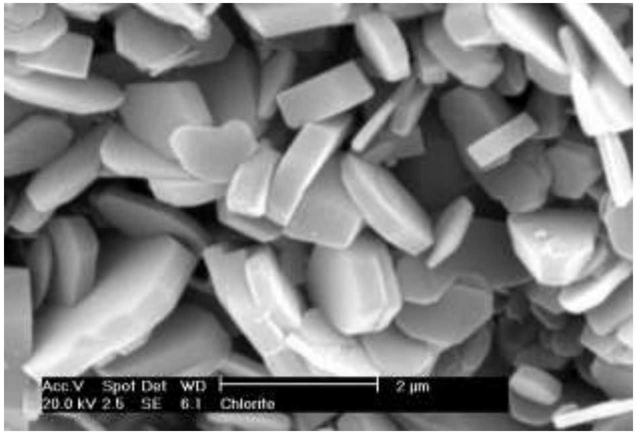
Cloritas

- As cloritas não são expansíveis.
- Bailey (1975) introduziu uma nomenclatura para as cloritas trioctaédricas, baseada em cinco *"end-members"* :

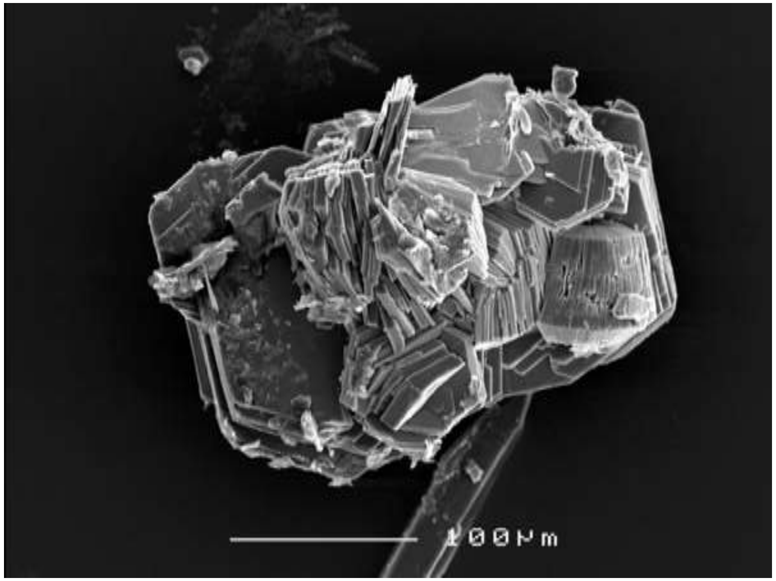
CLORITAS TRIOCATÉDRICAS

Clinocloro: $(Mg_5Al)(Si_3Al)O_{10}(OH)_8$
Chamosita: $(Fe^{2+}{}_5Al)(Si_3Al)O_{10}(OH)_8$
Pennantita: $(Mn^{2+}{}_5Al)(Si_3Al)O_{10}(OH)_8$
Nimita: $(Ni_5Al)(Si_3Al)O_{10}(OH)_8$
Baileyclore: $(Zn_5Al)(Si_3Al)O_{10}(OH)_8$

- Composições intermediárias e a presença de outros cátions são identificados pela adição de um prefixo ao nome do *"end-member"*:
  - Um clinocloro com alguma substituição isomórfica de Mg por Cr é chamado de "clinocloro magnesiano".

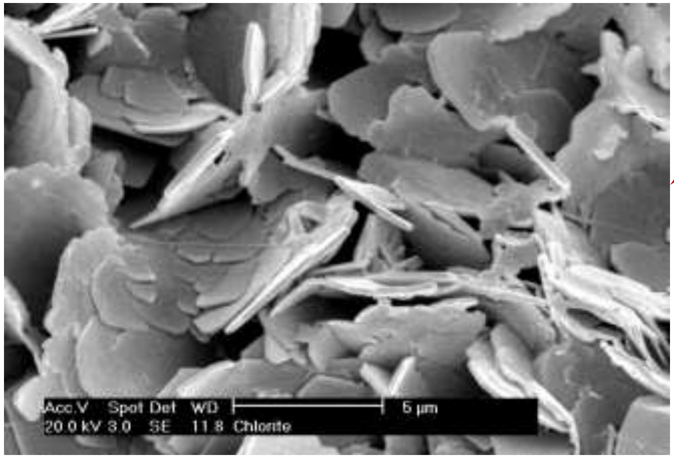


Clorita rica em Fe *(Spiro Sandstone, Arkoma Basin, Oklahoma, USA)*

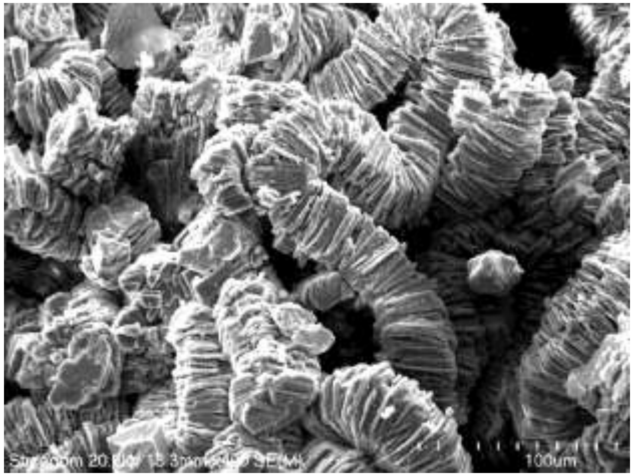


Chamosita *(Lyndseys Leap Quarry, Newcastle, Co. Down, Northern Ireland)*

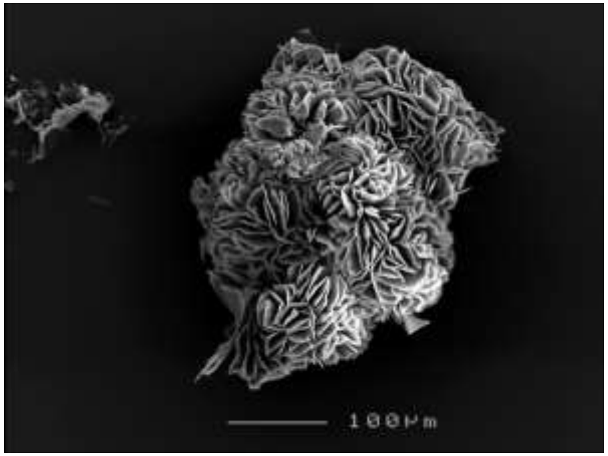
Cloritas



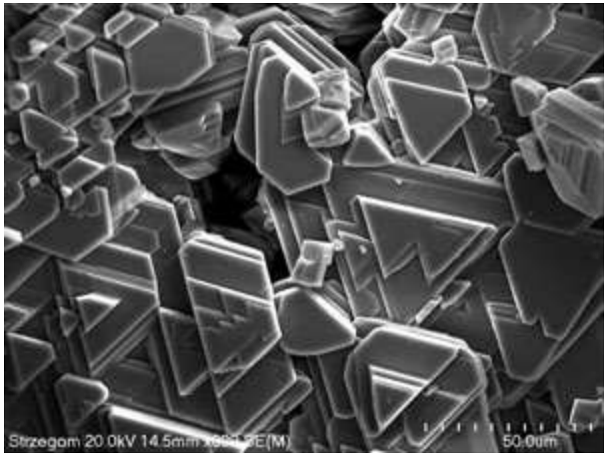
Clorita rica em Mg *(Rotliegend, Northern Germany)*



Clorita vermiforme rica em Al e Fe *(em um pegmatito de Strzegom, Polônia)*

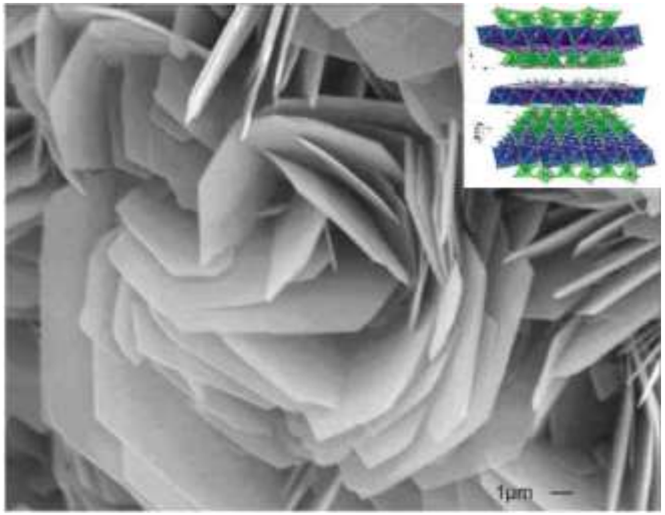


Clorita *(Eas a Brahdain, Loch Ainort, Isle of Skye, Irlanda*)



Clorita rica em Al e Fe *(em um pegmatito de Strzegom, Polônia)*

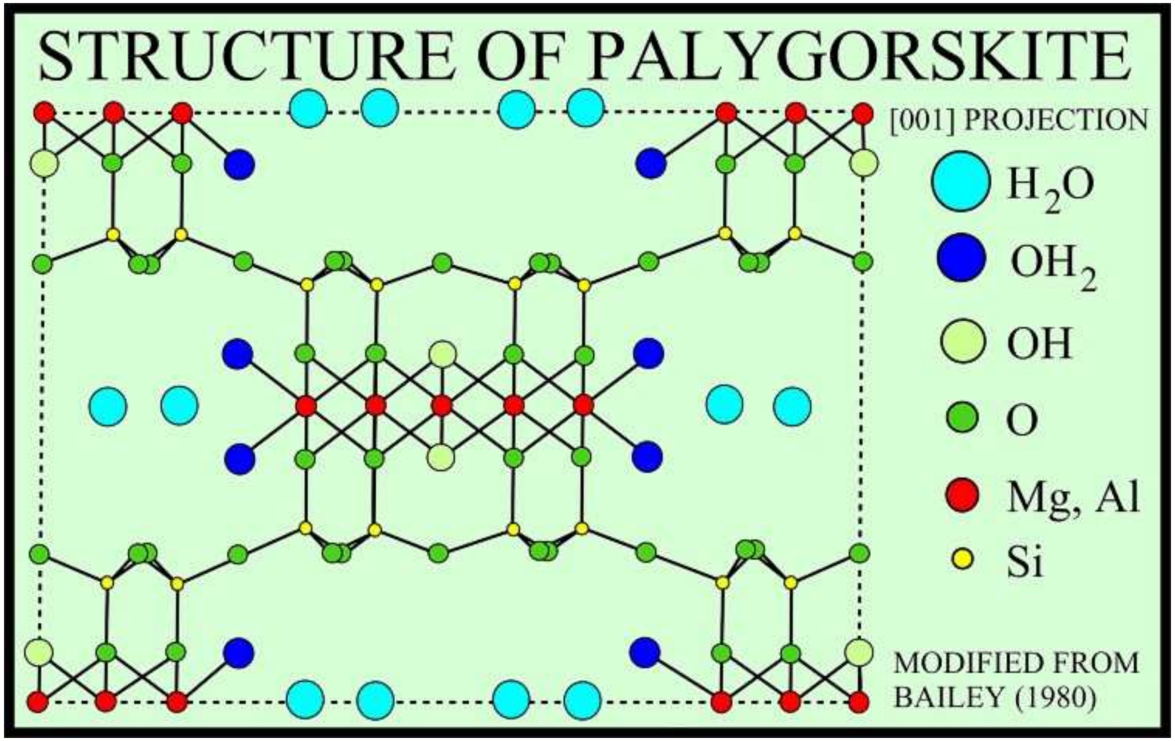
Cloritas

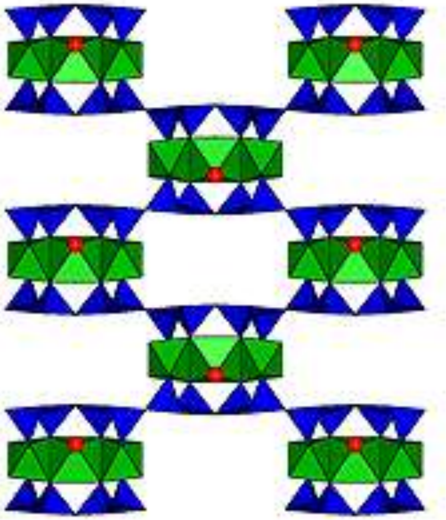


Baileychlore	$(Zn,Fe^{+2},Al,Mg)_6(Al,Si)_4O_{10}(O,OH)_8$
Chamosite	$(Fe,Mg)_5Al(Si_3Al)O_{10}(OH)_8$
Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$
Cookeite	$LiAl_4(Si_3Al)O_{10}(OH)_8$
Donbassite	$Al_2[Al_{2.33}][Si_3AlO_{10}](OH)_8$
Gonyerite	$(Mn,Mg)_5(Fe^{+3})_2Si_3O_{10}(OH)_8$
Nimite	$(Ni,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$
Odinite	$(Fe,Mg,Al,Fe,Ti,Mn)_{2.4}(Al,Si)_2O_5OH_4$
Orthochamosite	$(Fe^{+2},Mg,Fe^{+3})_5Al(Si_3Al)O_{10}(O,OH)_8$
Pennantite	$(Mn_5Al)(Si_3Al)O_{10}(OH)_8$
Ripidolite	$(Mg,Fe,Al)_6(Al,Si)_4O_{10}(OH)_8$
Sudoite	$Mg_2(Al,Fe)_3Si_3AlO_{10}(OH)_8$

Argilominerais 2:1
“Hormitas”

Paligorsquita e Sepiolita – *"Hormitas"*

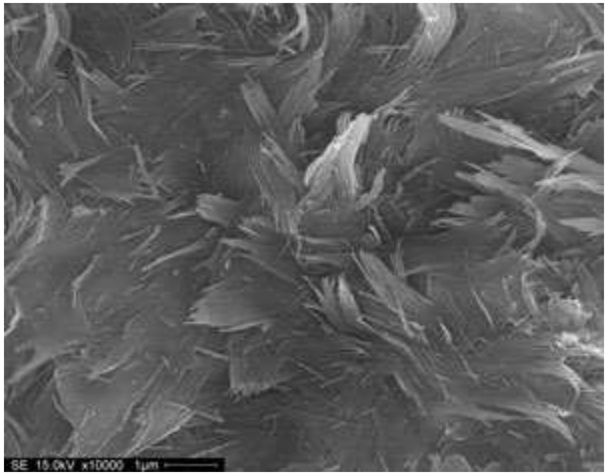




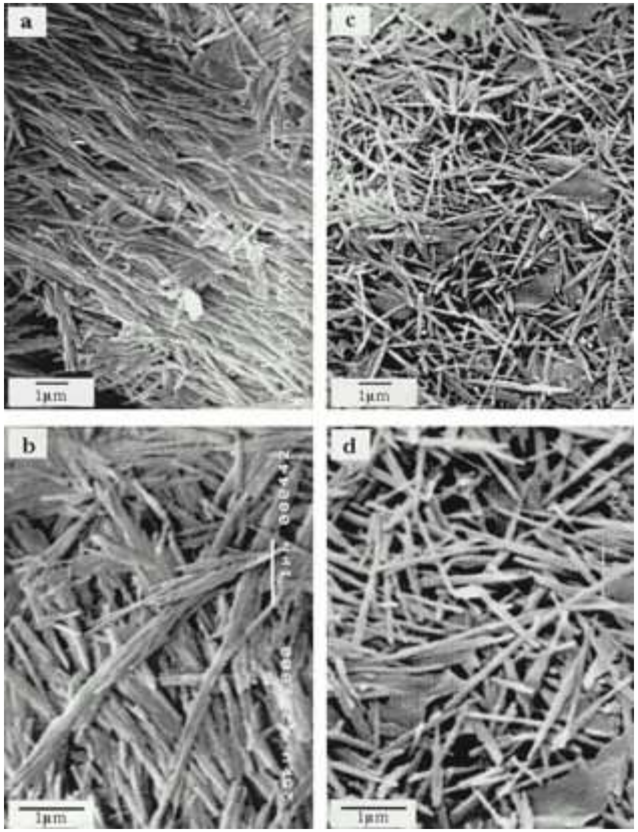
Paligorsquita *("Atapulgita")* :
$(Mg,Al)_4(Si,Al)_8O_{20}(OH)_2.8H_2O$

Paligorsquita

Large agglomerate of **Palygorskite** (Attapulgite) fibres *(Attapulgus, Georgia, USA)*



Paligorsquitas do Negev *(Israel)*

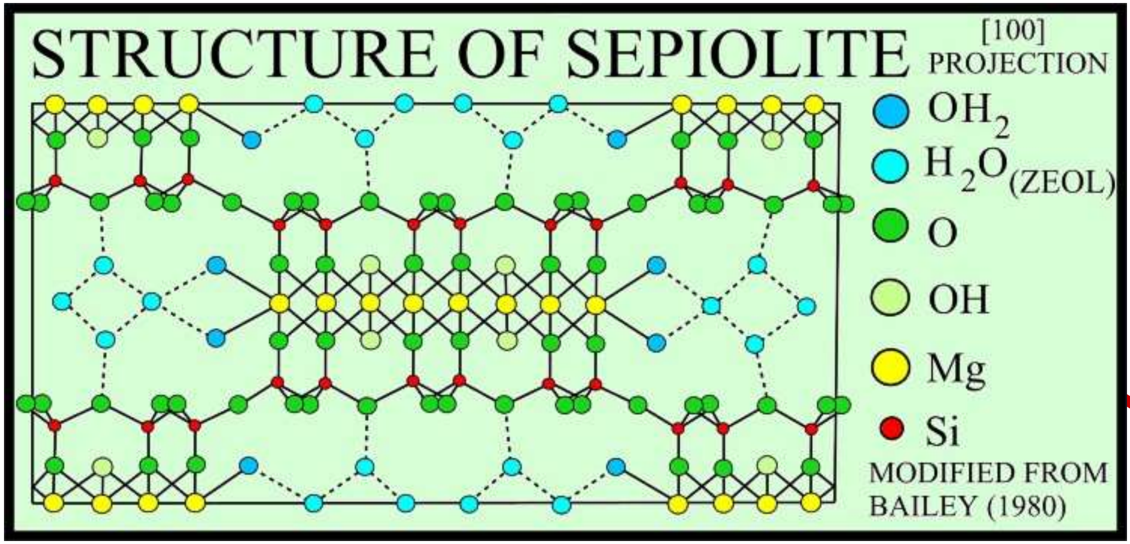


Paligorsquita (Guadalupe, PI)

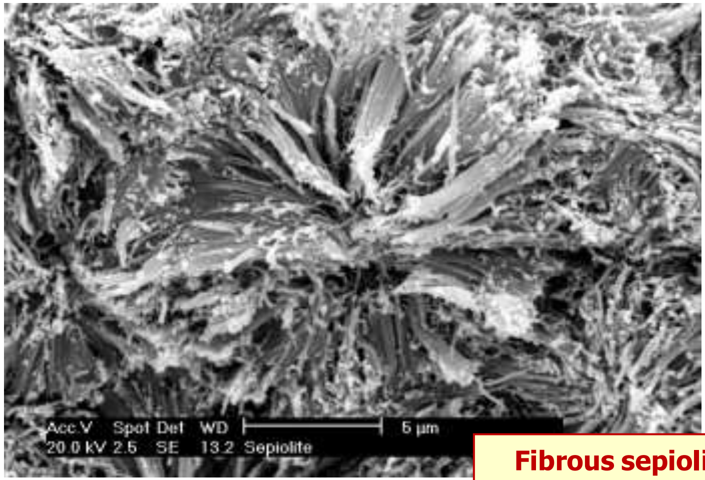
Sepiolita

Vicalvaro Quarry – Madrid *(TOLSA)*

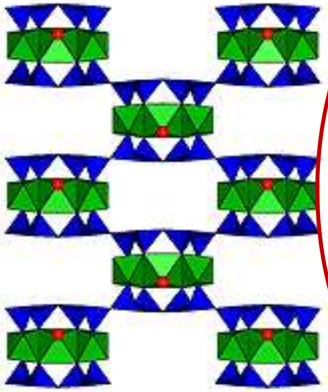
Sepiolita: $Mg_4Si_6O_{15}(OH)_2.6H_2O$



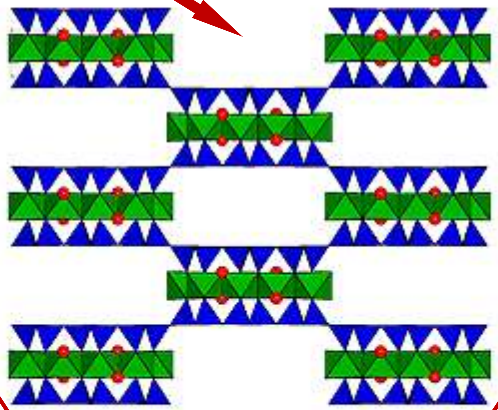
MODIFIED FROM BAILEY (1980)



Fibrous sepiolite *(Eskisehir, Turkey)*

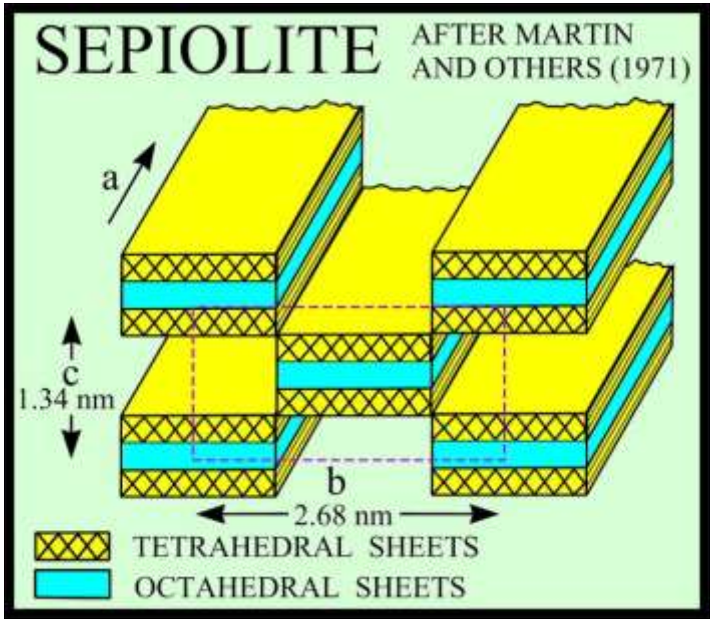


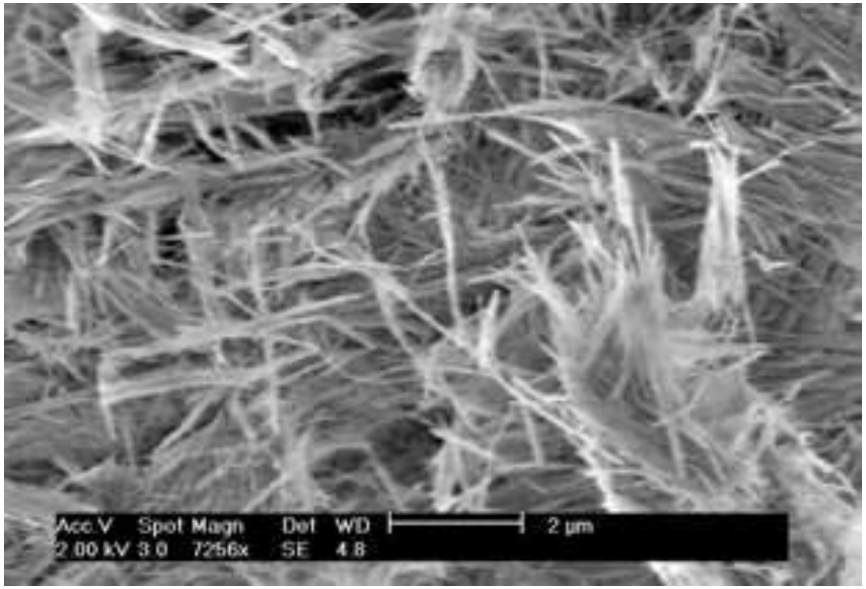
Paligorsquita

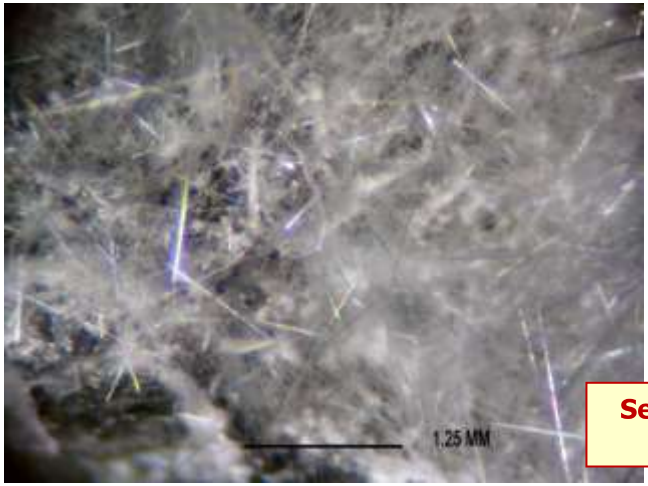


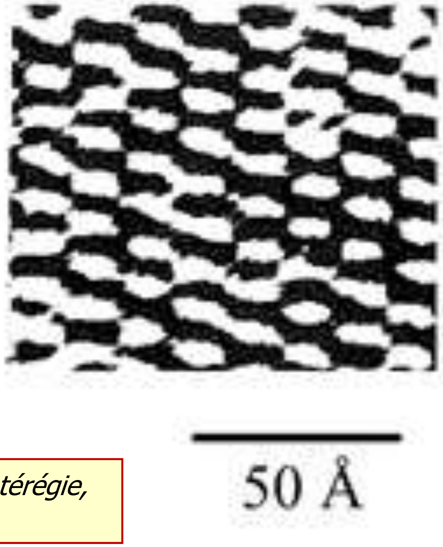
Sepiolita

Sepiolita



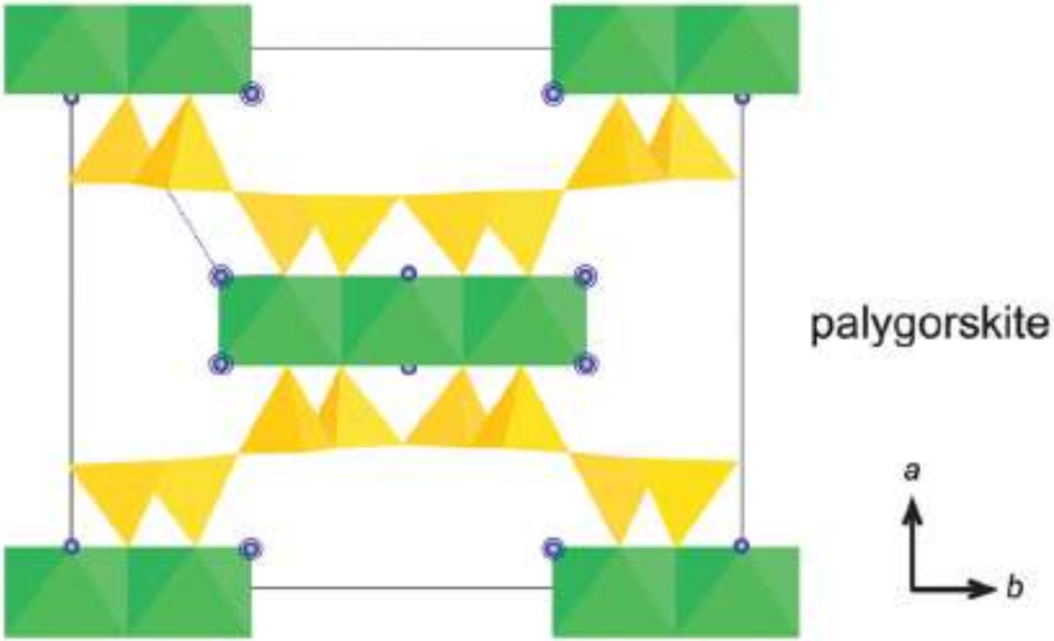


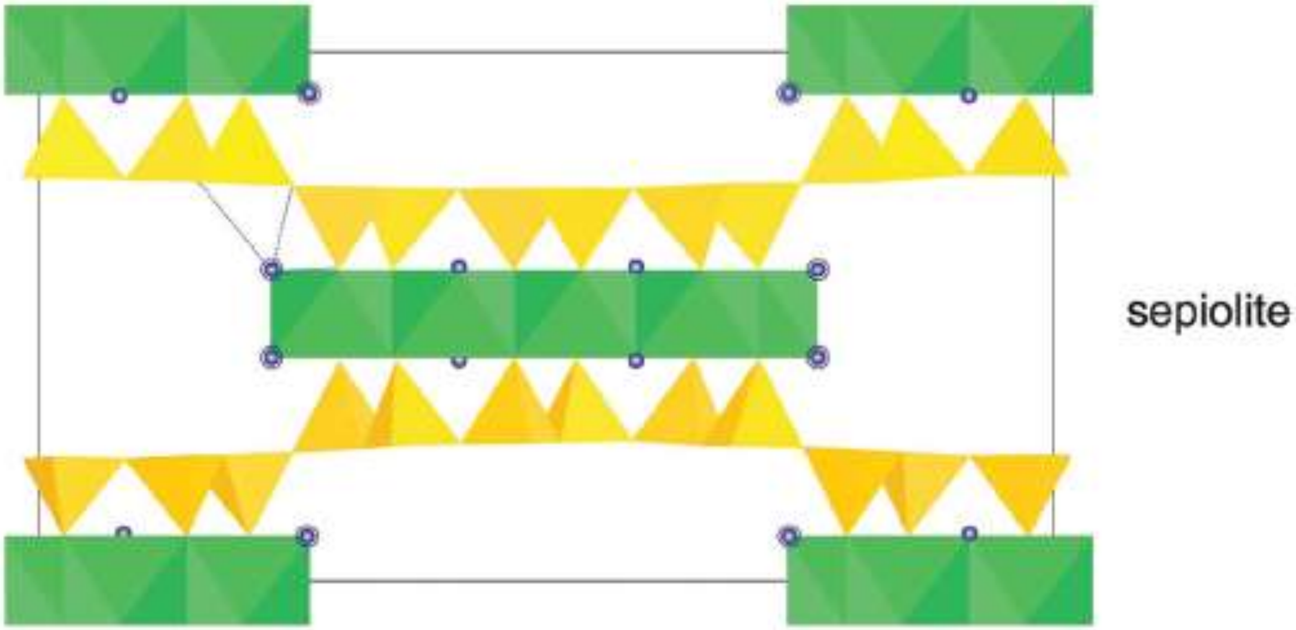




Sepiolita *(Poudrette quarry, Mont Saint-Hilaire, Montérégie, Québec, Canada)*

Paligorsquita e Sepiolita

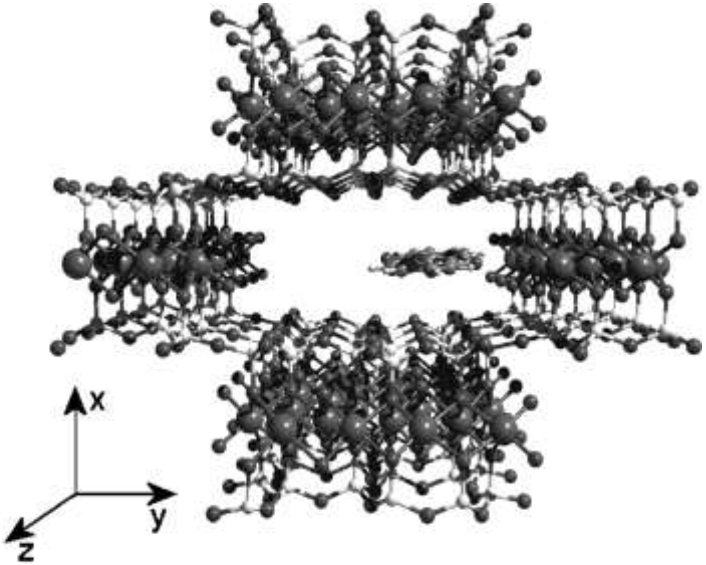




Curiosidades : Azul Maya

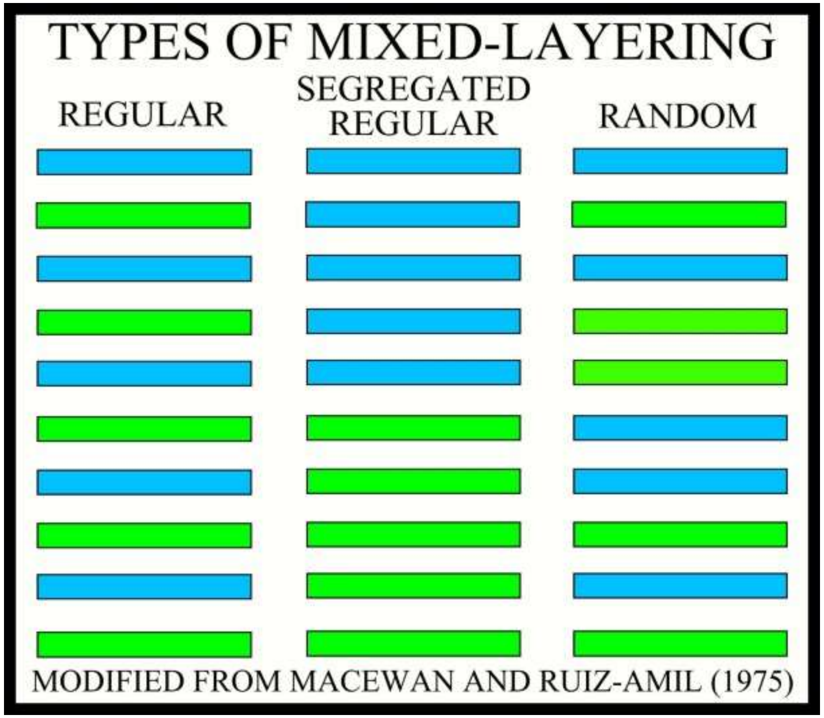
Maya Blue
(#73C2FB)

- The *Maya blue* pigment is a composite of organic and inorganic constituents, primarily indigo dyes derived from the leaves of añil (*Indigofera suffruticosa*) plants combined with palygorskite, a natural clay. Smaller trace amounts of other mineral additives have also been identified.



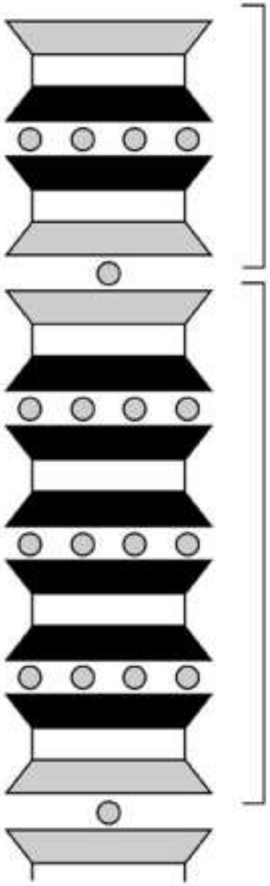
Argilominerais Interestratificados

Argilominerais em Camadas Mistas (Interestratificados)

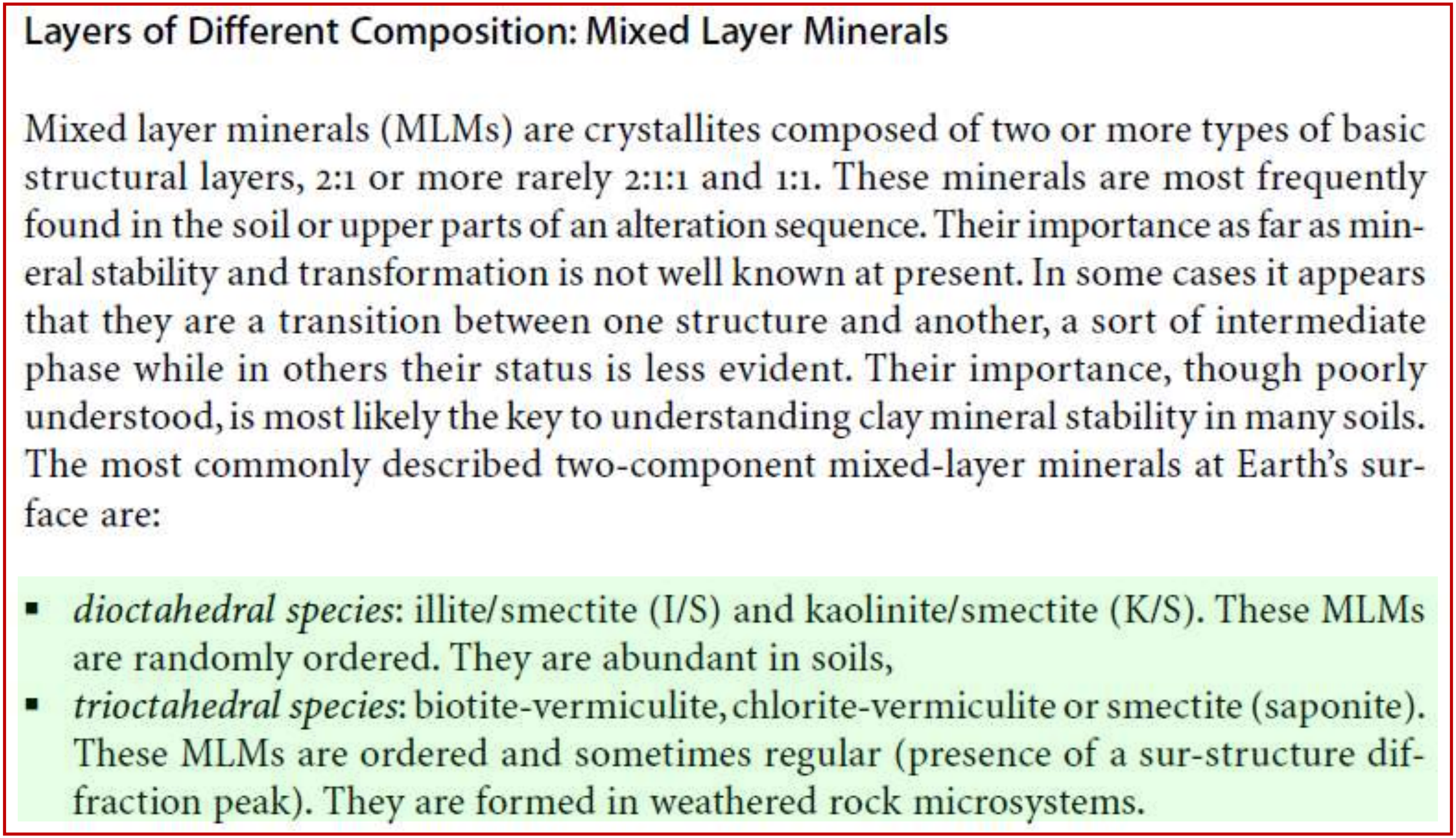


MODIFIED FROM MACEWAN AND RUIZ-AMIL (1975)

Corrensita – argilomineral regularmente interestratificado *(A mass of pinkisk Corrensite in Mn-oxides from the Bölet mine, Västergötland, Sweden)*



Argilominerais em Camadas Mistas (Interestratificados)



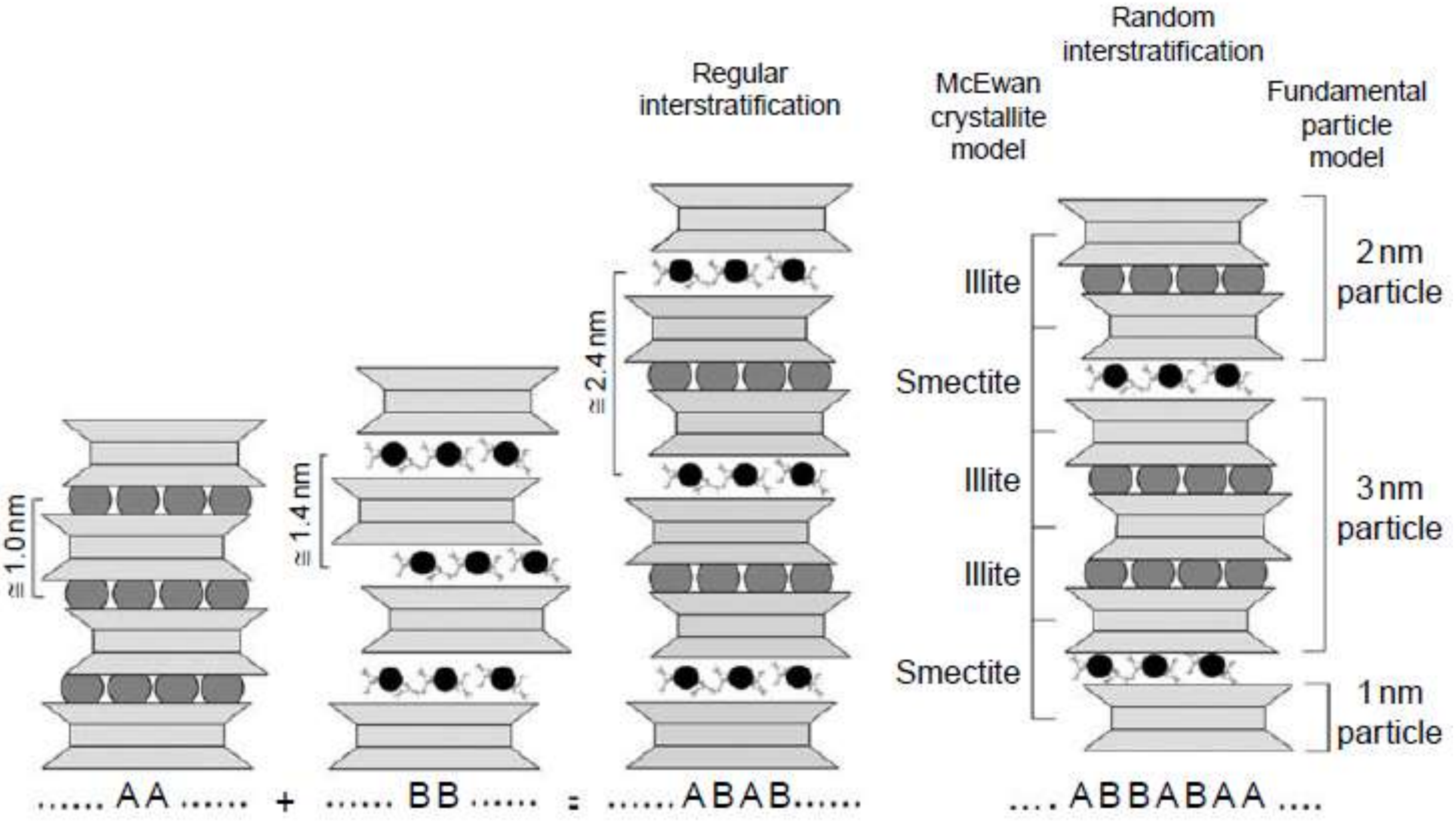
Layers of Different Composition: Mixed Layer Minerals

Mixed layer minerals (MLMs) are crystallites composed of two or more types of basic structural layers, 2:1 or more rarely 2:1:1 and 1:1. These minerals are most frequently found in the soil or upper parts of an alteration sequence. Their importance as far as mineral stability and transformation is not well known at present. In some cases it appears that they are a transition between one structure and another, a sort of intermediate phase while in others their status is less evident. Their importance, though poorly understood, is most likely the key to understanding clay mineral stability in many soils. The most commonly described two-component mixed-layer minerals at Earth's surface are:

- *dioctahedral species*: illite/smectite (I/S) and kaolinite/smectite (K/S). These MLMs are randomly ordered. They are abundant in soils,
- *trioctahedral species*: biotite-vermiculite, chlorite-vermiculite or smectite (saponite). These MLMs are ordered and sometimes regular (presence of a sur-structure diffraction peak). They are formed in weathered rock microsystems.

Velde, B.; Meunier, A. – The Origin of Clay Minerals in soils and Weathered Rocks. Springer. Berlin. 2008

Argilominerais em Camadas Mistas (Interestratificados)



Regular and random interstratified clay minerals. A and B are layers with different periodicity along the *c* direction. The 'McEwan crystallite model' and the 'Fundamental particle model' are also indicated.

Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

Arg. em Camadas Mistas

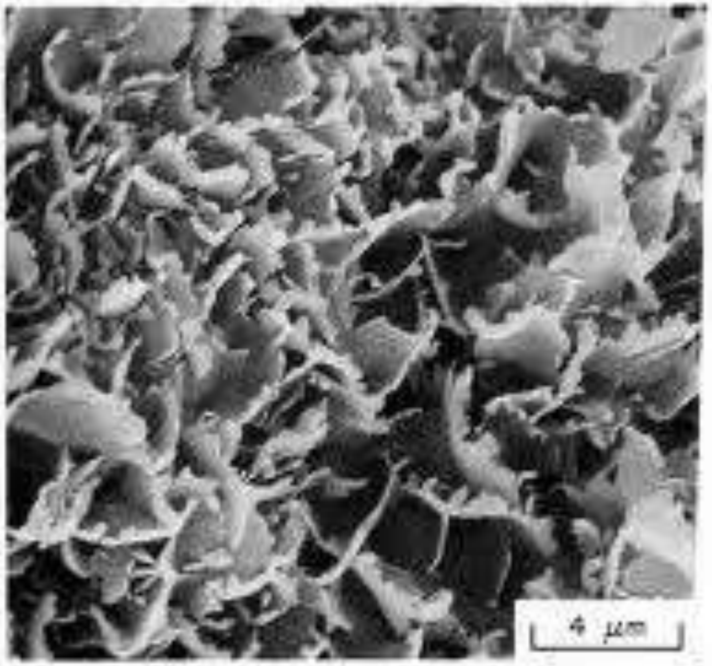


FIG. 18.—Authigenic mixed-layer smectite/illite. Mixed-layer clay minerals appear to take on the characteristics of the participating minerals. This example resembles the illite shown in Figure 16B. Distinguishing mixed-layer smectite/illite from illite or smectite may be unreliable if only the SEM is used. Cretaceous Mesaverde Group, Colorado.

Desenvolvimento da i**interestratificação ilita-esmectita** (irregular) em processo de alteração hidrotermal em rocha vulcânica *(Murakami et al., CCM* ***51*** *(5), 440-451, 2003)*

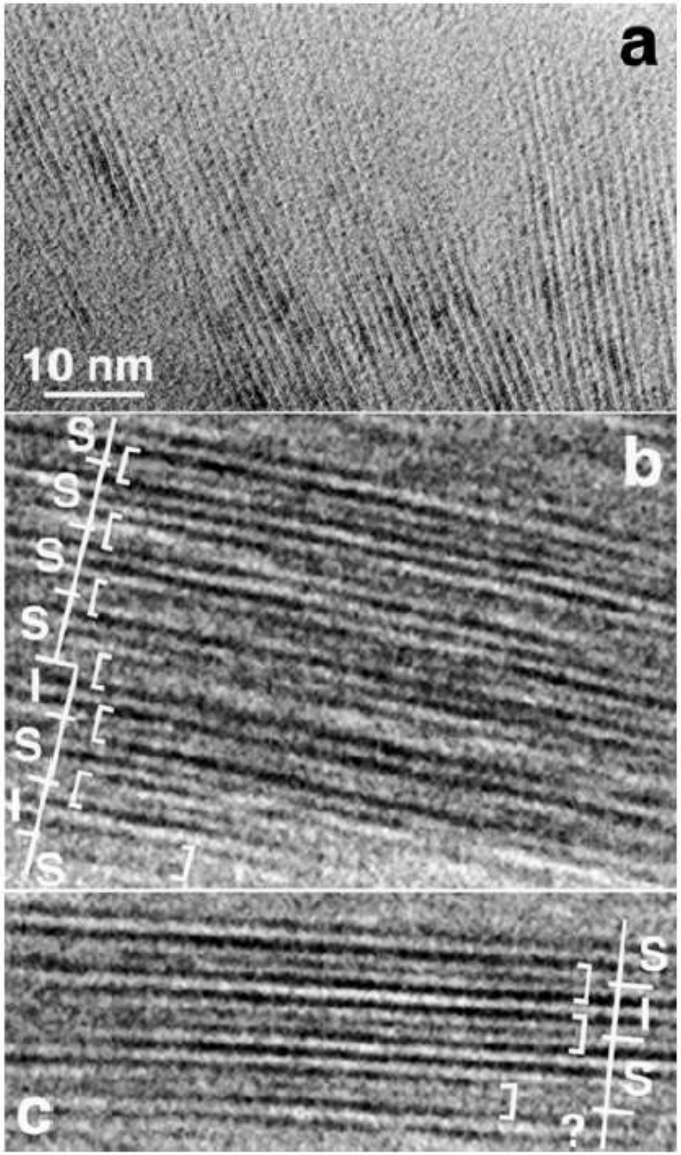
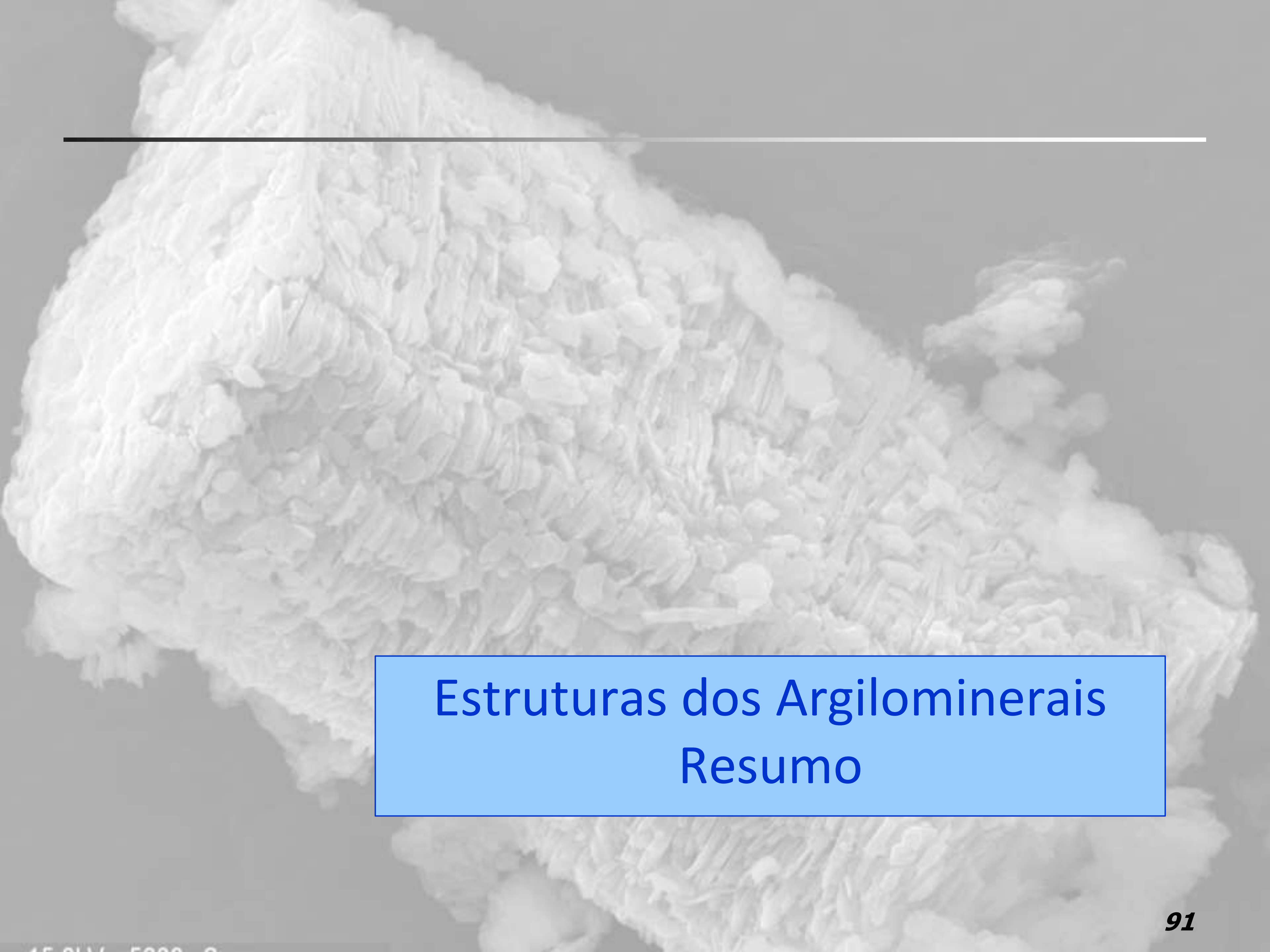
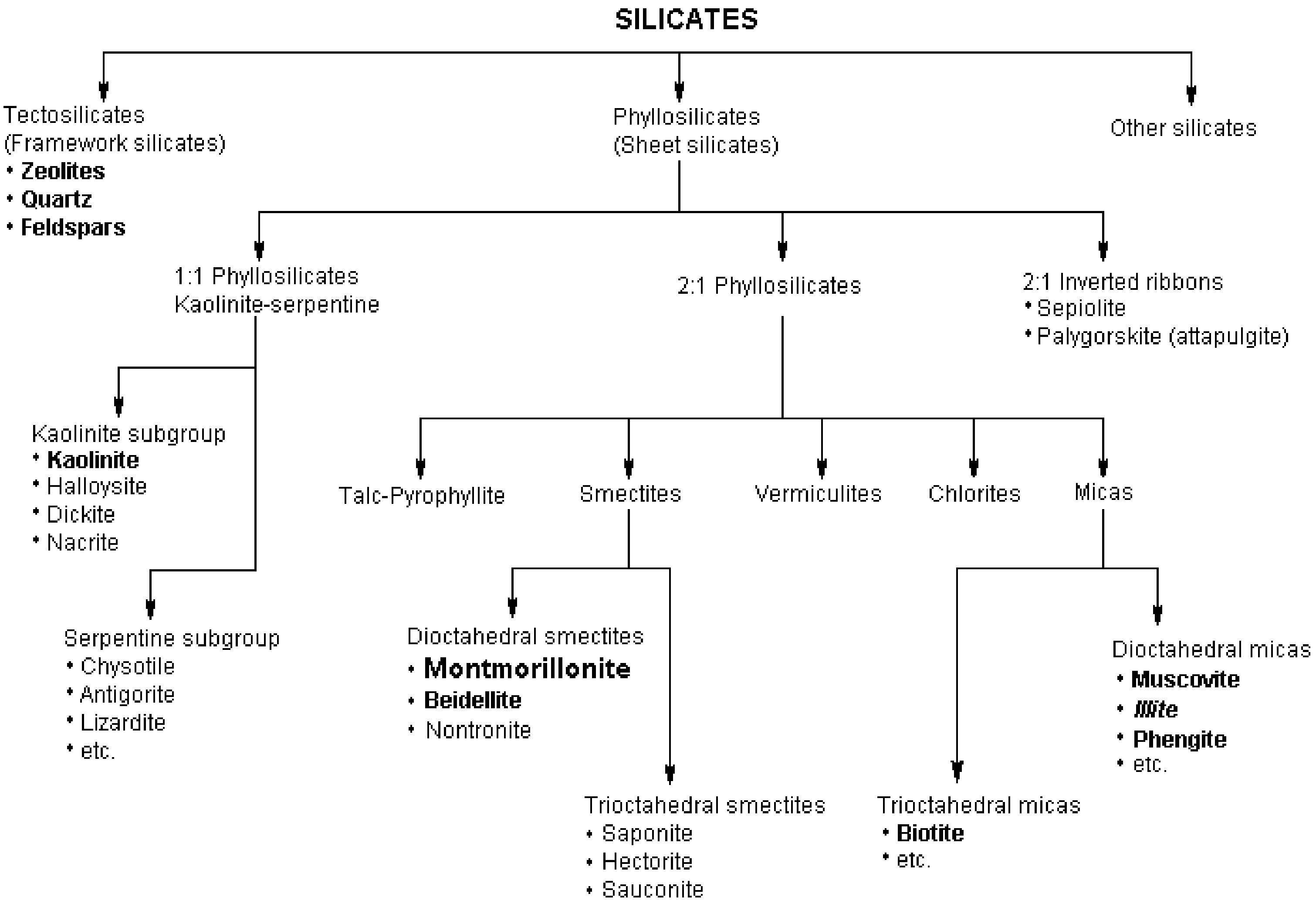


Figure 4. TEM images of sample 435 at low magnification (a) and at high magnifications (b and c). Each bracket shows one *T-O-T* silicate layer; I accompanied by a pair of bars indicates one illitic layer and S with a pair of bars one smectitic layer. Each bar near I or S is located at the center of an octahedral cation plane. A question mark, ?, indicates an area with ambiguous lines. The distance between a pair of bars with I is 1.0 nm.



Estruturas dos Argilominerais Resumo

Argilominerais : Resumo



SILICATES

Tectosilicates
(Framework silicates)
- **Zeolites**
- **Quartz**
- **Feldspars**

Phyllosilicates
(Sheet silicates)

Other silicates

1:1 Phyllosilicates
Kaolinite-serpentine

2:1 Phyllosilicates

2:1 Inverted ribbons
- Sepiolite
- Palygorskite (attapulgite)

Kaolinite subgroup
- **Kaolinite**
- Halloysite
- Dickite
- Nacrite

Serpentine subgroup
- Chysotile
- Antigorite
- Lizardite
- etc.

Talc-Pyrophyllite

Smectites

Vermiculites

Chlorites

Micas

Dioctahedral smectites
- **Montmorillonite**
- **Beidellite**
- Nontronite

Trioctahedral smectites
- Saponite
- Hectorite
- Sauconite

Dioctahedral micas
- **Muscovite**
- ***Illite***
- **Phengite**
- etc.

Trioctahedral micas
- **Biotite**
- etc.

Argilominerais 1:1

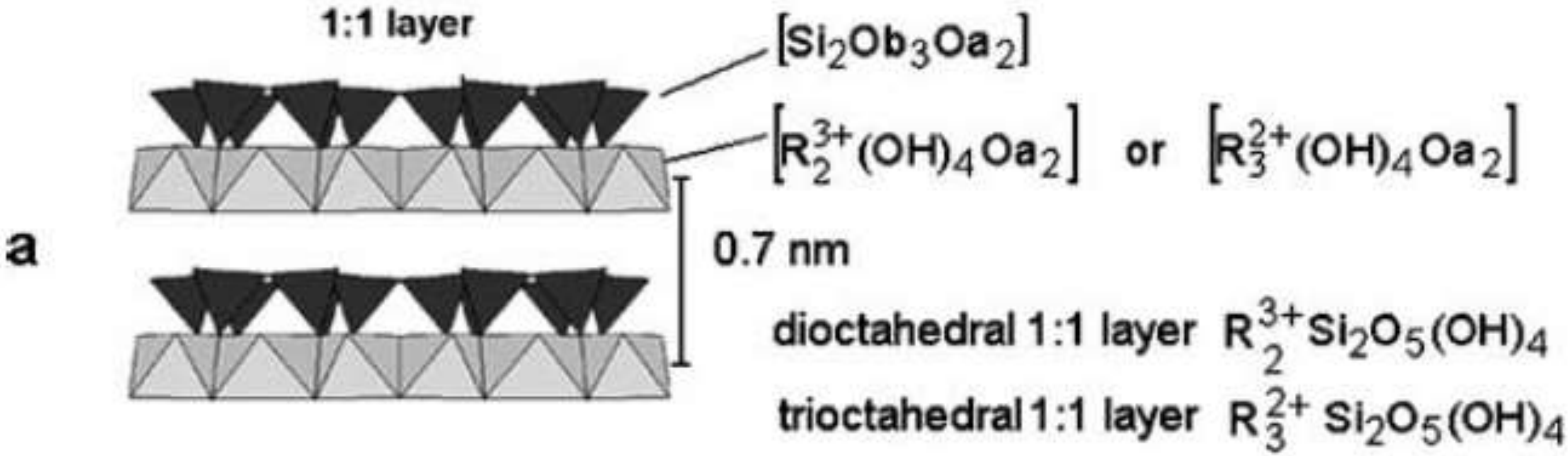


Fig. 2.5. Different layer structures: (a) 1:1 layer (i.e., kaolinite- and serpentine-like layer); (b) 2:1 layer (i.e., pyrophillite- and talc-like layer); (c) 2:1 layer with anhydrous interlayer cations (i.e., the mica-like layer); (d) 2:1 layer with hydrated interlayer cations (i.e., smectite- and vermiculite-like layer); (e) 2:1 layer with octahedrally coordinated interlayer cations (i.e., chlorite-like layer).

Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

Argilominerais 2:1

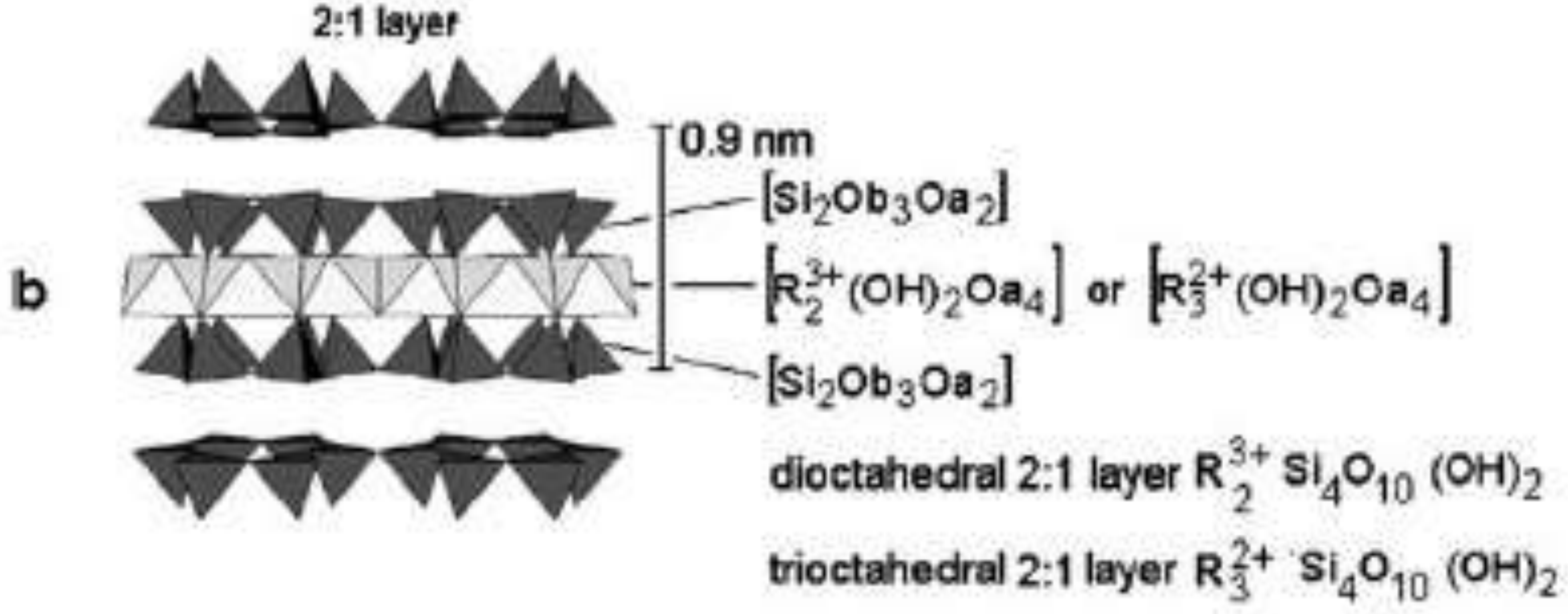


Fig. 2.5. Different layer structures: (a) 1:1 layer (i.e., kaolinite- and serpentine-like layer); (b) 2:1 layer (i.e., pyrophillite- and talc-like layer); (c) 2:1 layer with anhydrous interlayer cations (i.e., the mica-like layer); (d) 2:1 layer with hydrated interlayer cations (i.e., smectite- and vermiculite-like layer); (e) 2:1 layer with octahedrally coordinated interlayer cations (i.e., chlorite-like layer).

Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

Argilominerais 2:1 *(continuação)*

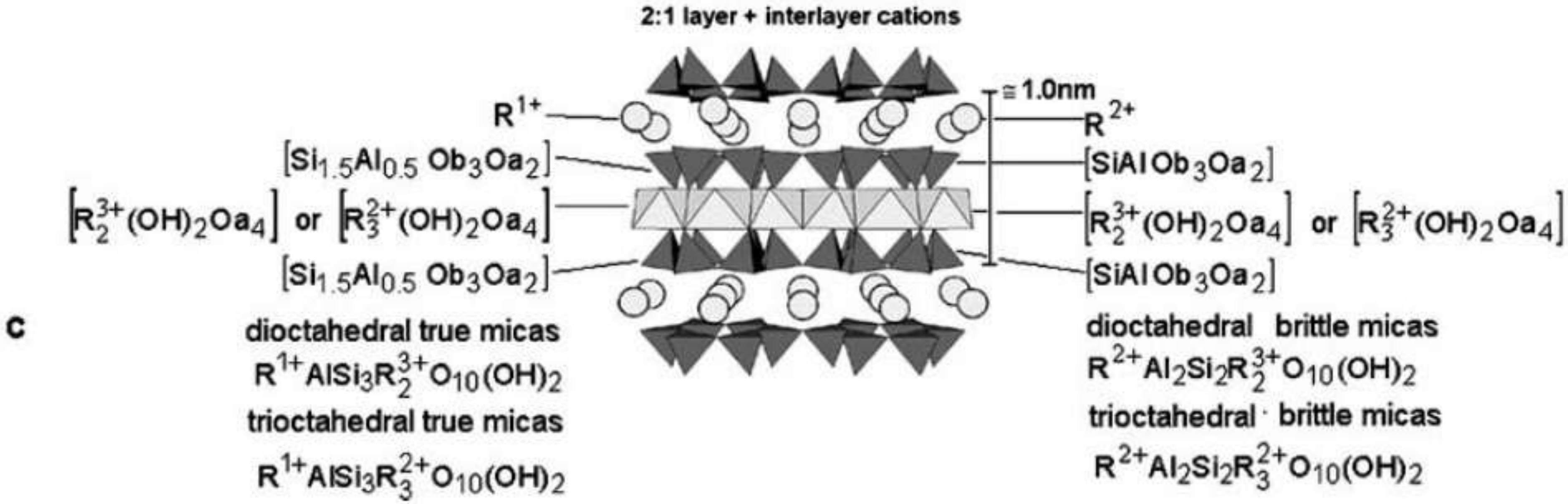
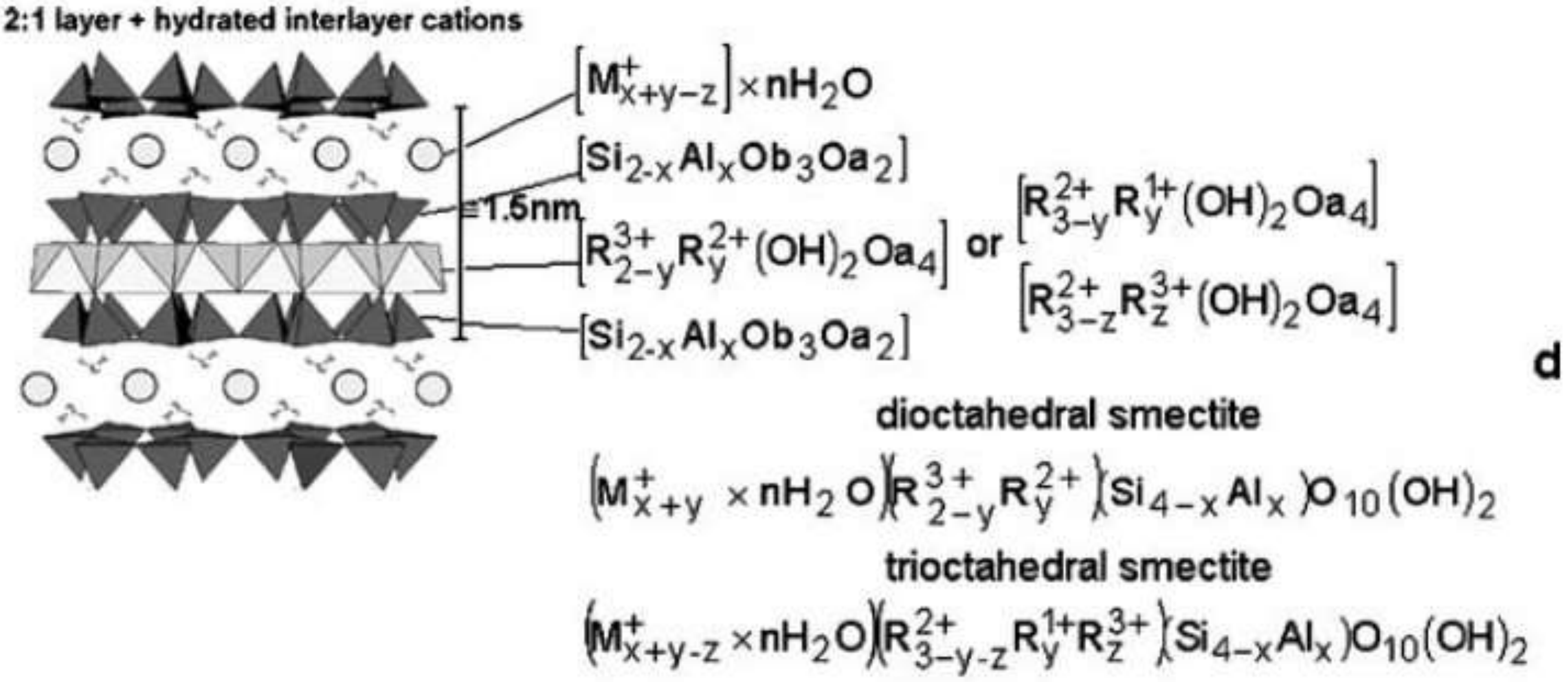


Fig. 2.5. Different layer structures: (a) 1:1 layer (i.e., kaolinite- and serpentine-like layer); (b) 2:1 layer (i.e., pyrophillite- and talc-like layer); (c) 2:1 layer with anhydrous interlayer cations (i.e., the mica-like layer); (d) 2:1 layer with hydrated interlayer cations (i.e., smectite- and vermiculite-like layer); (e) 2:1 layer with octahedrally coordinated interlayer cations (i.e., chlorite-like layer).

Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

Argilominerais 2:1 *(continuação)*



dioctahedral smectite

$$(M^{+}_{x+y} \times nH_2O)(R^{3+}_{2-y}R^{2+}_y)(Si_{4-x}Al_x)O_{10}(OH)_2$$

trioctahedral smectite

$$(M^{+}_{x+y-z} \times nH_2O)(R^{2+}_{3-y-z}R^{1+}_yR^{3+}_z)(Si_{4-x}Al_x)O_{10}(OH)_2$$

Fig. 2.5. Different layer structures: (a) 1:1 layer (i.e., kaolinite- and serpentine-like layer); (b) 2:1 layer (i.e., pyrophillite- and talc-like layer); (c) 2:1 layer with anhydrous interlayer cations (i.e., the mica-like layer); (d) 2:1 layer with hydrated interlayer cations (i.e., smectite- and vermiculite-like layer); (e) 2:1 layer with octahedrally coordinated interlayer cations (i.e., chlorite-like layer).

Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

Argilominerais 2:1

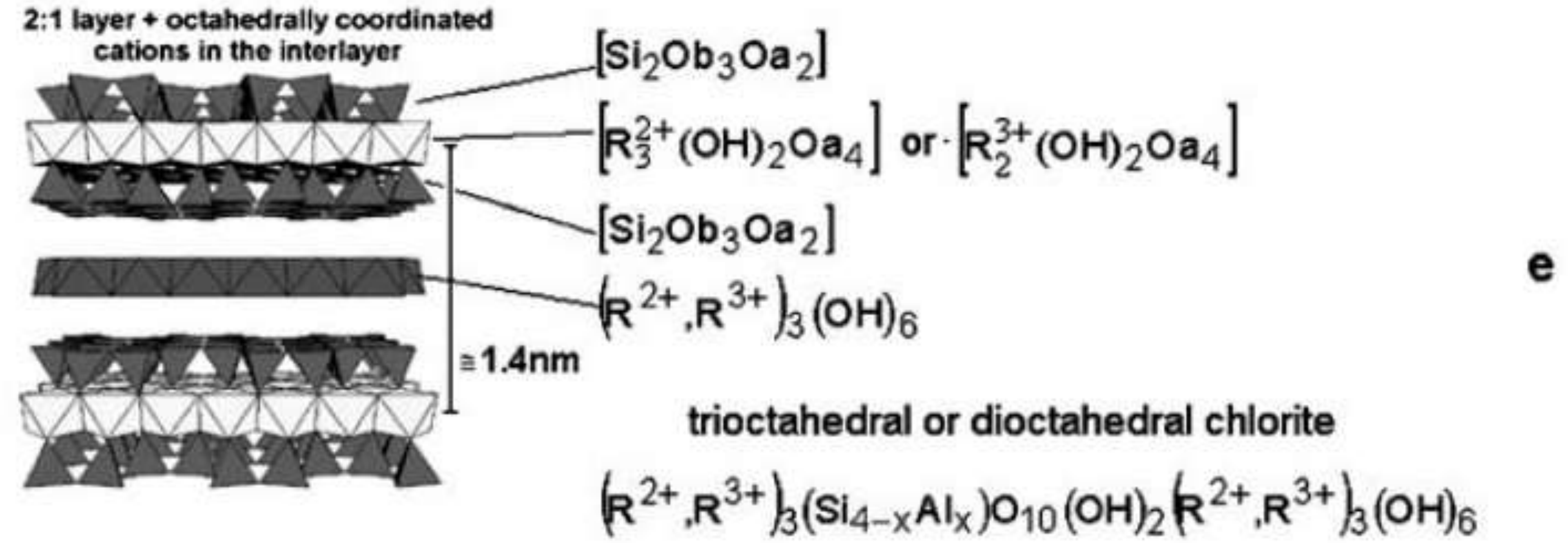
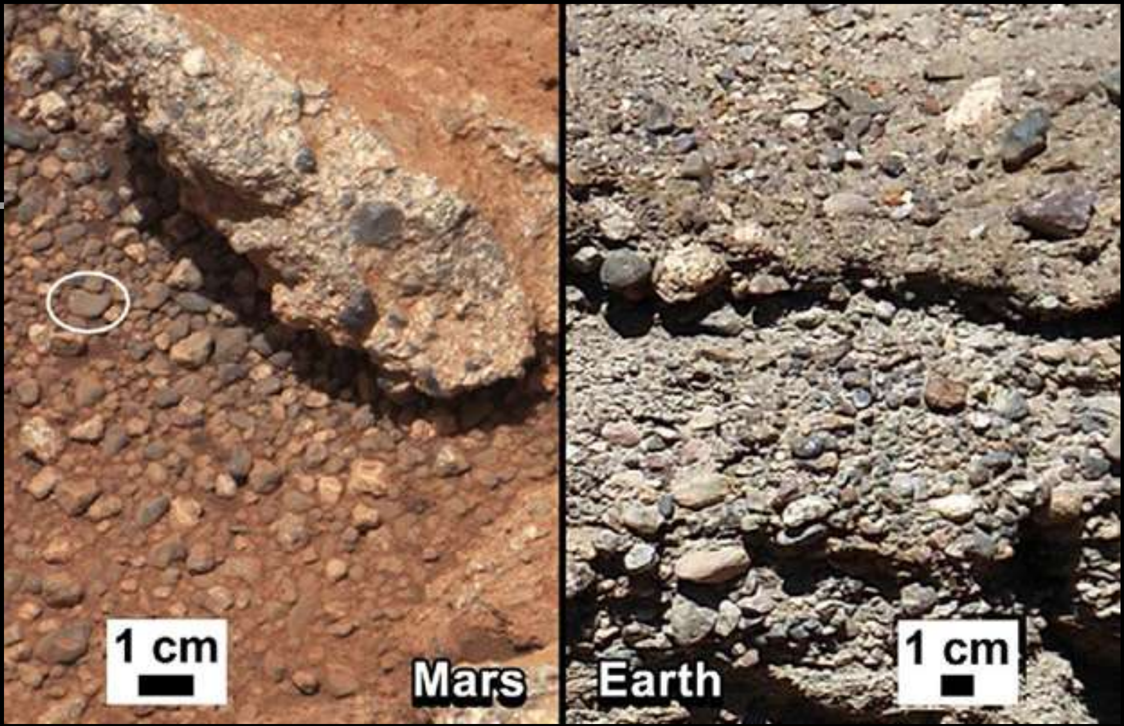


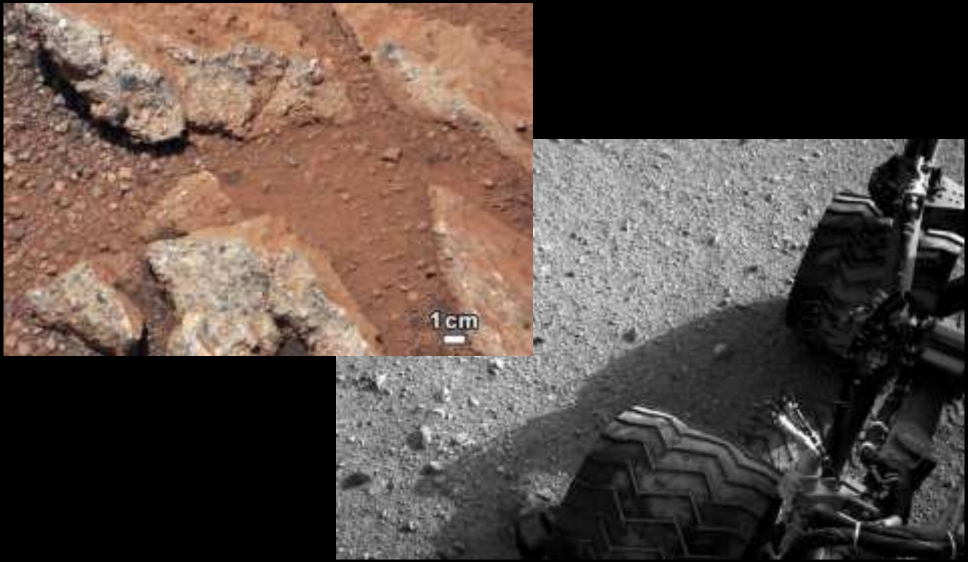
Fig. 2.5. Different layer structures: (a) 1:1 layer (i.e., kaolinite- and serpentine-like layer); (b) 2:1 layer (i.e., pyrophillite- and talc-like layer); (c) 2:1 layer with anhydrous interlayer cations (i.e., the mica-like layer); (d) 2:1 layer with hydrated interlayer cations (i.e., smectite- and vermiculite-like layer); (e) 2:1 layer with octahedrally coordinated interlayer cations (i.e., chlorite-like layer).

Bergaya, F.; Lagaly, G. (Eds.)– Handbook of Clay Science. 2ª Ed. Elsevier. Amsterdam. 2013

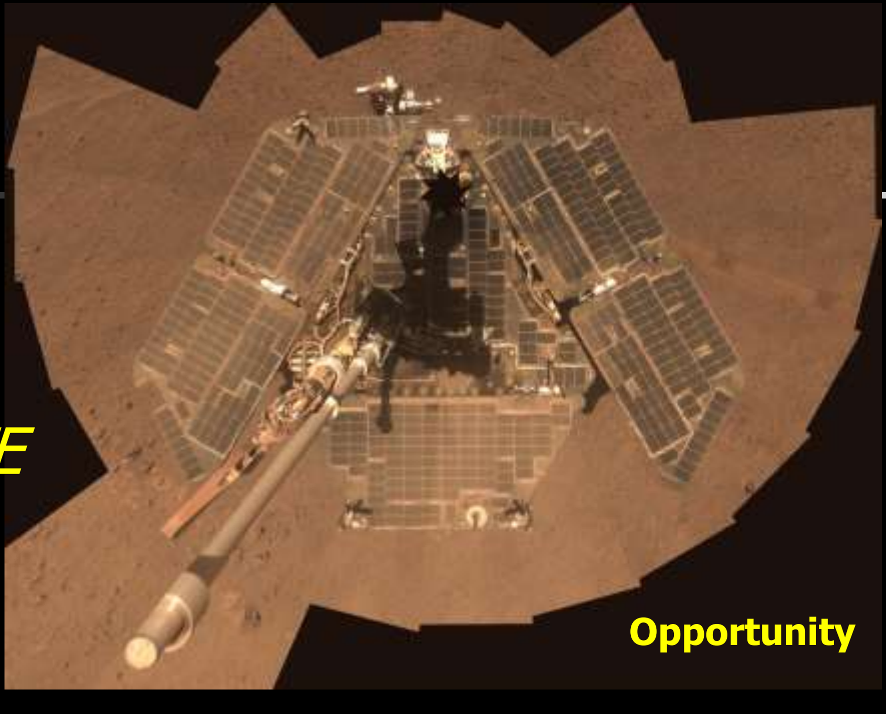
MARTE

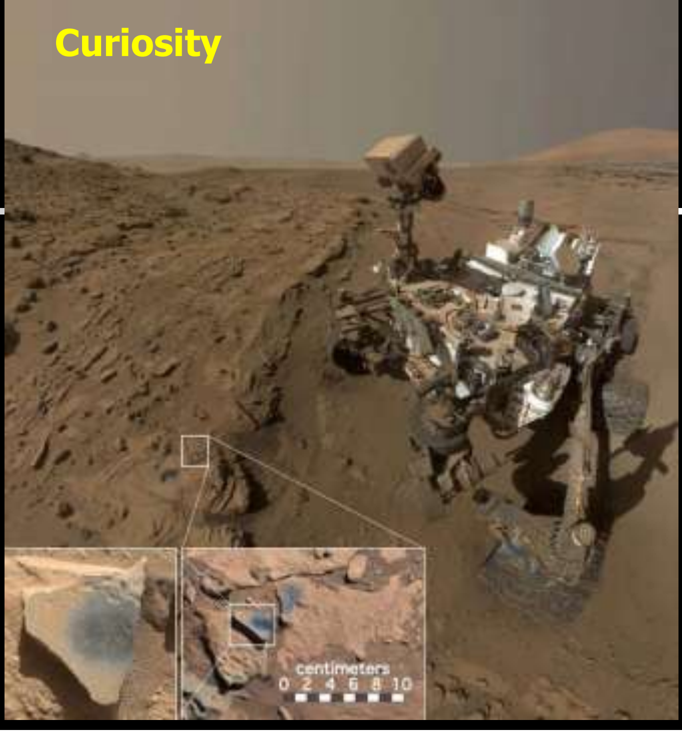
Imagens obtidas pela câmera de alta definição da sonda Curiosity

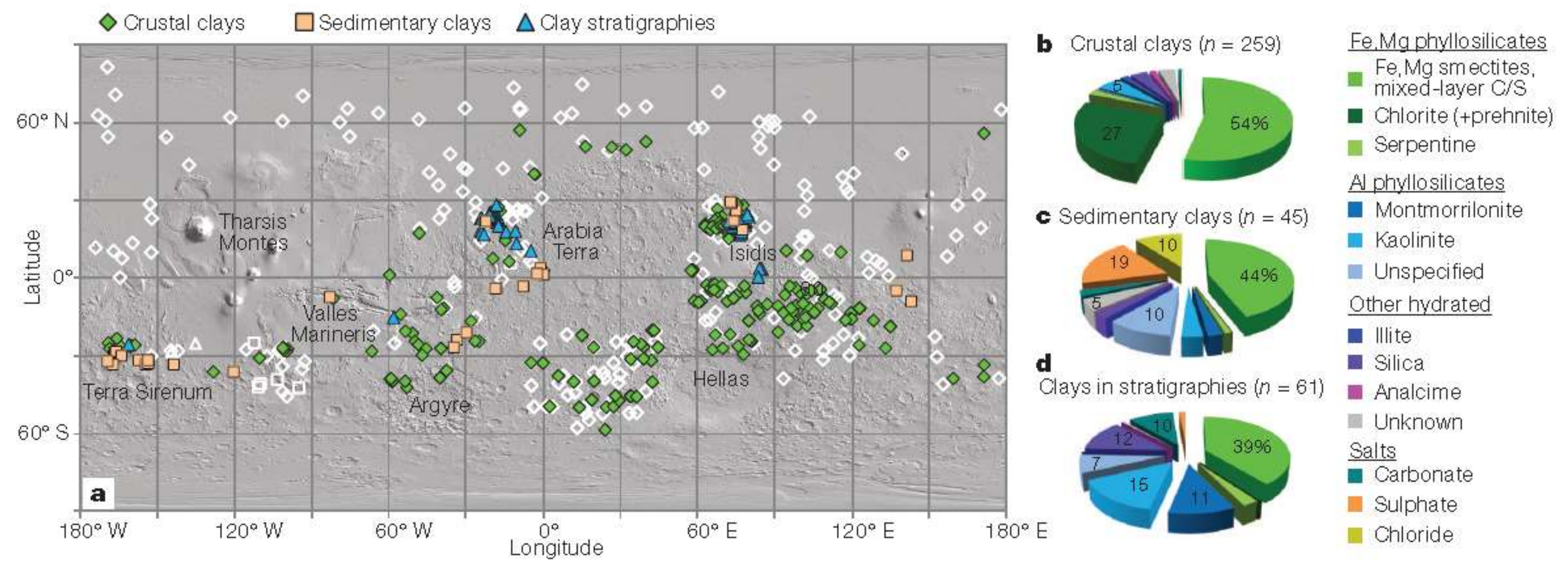




MARTE


Opportunity


Curiosity
centimeters
0 2 4 6 8 10


Crustal clays
Sedimentary clays
Clay stratigraphies
60° N
0°
60° S
Latitude
Tharsis Montes
Arabia Terra
Isidis
Valles Marineris
Terra Sirenum
Argyre
Hellas
a
180° W
120° W
60° W
0°
60° E
120° E
180° E
Longitude
b Crustal clays (n = 259)
5
27
54%
c Sedimentary clays (n = 45)
10
19
44%
5
10
d Clays in stratigraphies (n = 61)
10
12
7
15
11
39%
Fe,Mg phyllosilicates
Fe,Mg smectites, mixed-layer C/S
Chlorite (+prehnite)
Serpentine
Al phyllosilicates
Montmorrilonite
Kaolinite
Unspecified
Other hydrated
Illite
Silica
Analcime
Unknown
Salts
Carbonate
Sulphate
Chloride

Referências

- Bergaya, F.; Lagaly, G. (Eds.) – Handbook of Clay Science. 2ª Ed. Developments in Clays Science vol.5. Elsevier. Amsterdam. 2013. Cap. 2-3.
- Schroeder, P.A. Clays in the Critical Zone. Cambridge University Press. 2018. Cap. 1.
- Meunier, A. – Clays. Springer-Verlag. Berlim. 2005. Cap. 1.
- Velde, B. (Ed.) – Origin and Mineralogy of Clays. Springer-Verlag. Berlim. 1995. Cap. 1.
- Velde, B.; Meunier, A. – The Origin of Clay Minerals in Soils and Whethered Rocks. Springer-Verlag. Berlim. 2008. Cap. 1.
- Souza Santos, P. – Ciência e Tecnologia de Argilas. 2ª Ed. Edgard Blucher. São Paulo. 1989. Caps. 3-6.
- Gomes, C.S.F. – Argilas, o Que São e Para Que Servem. Fundação Calouste Gulbenkian. Lisboa. 1988. Caps. 1-3.
- Meunier, A. – Illite: Origins, Evolution and Metamorphism. Springer-Verlag. Berlim. 2013.
- ...na web: Curso “ GEOL 8550 Clay Mineralogy”, Dr. Paul Schroeder, University of Georgia , < *http://clay.uga.edu/courses/index.html* >.