

Clay Composites: Physicochemical Characterization



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Abstract Clay compounds have been used by human societies since time immemorial, because they are abundant in nature, smaller than 4 microns, adherent, plastic, malleable, have ion exchange capacity and affinity with water. Due to their physical and chemical properties, they are used in agriculture, livestock, industry, commerce, tourism and the environment for the development of services and products such as bricks, crockery, paints, pharmaceuticals, agricultural inputs and natural filters. The clay composition of an environment depends on the rock that gave rise to it, weathering and pedogenesis, with the following groups standing out: kaolinite-serpentine, talc-pyrophyllite, mica, vermiculite, smectite, chlorite and sepiolite-palygorskite. Each of these groups has specific physicochemical properties, which will direct them to certain uses. Proper use requires prior characterization, so in this chapter we will discuss the main types of clay compounds, their structure, formation, occurrence, mineralogical and physicochemical characteristics and their environmental importance.

Keywords Clay compounds · Electrostatic interaction · Ion exchange capacity (IEC) · Adsorption

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1 Introduction

Clay minerals are natural compounds, consisting essentially of very small crystalline particles of hydrated aluminum, iron and magnesium silicates, which when moistened with water acquire a certain plasticity. In addition to Al, Fe and Mg, clay minerals can contain other elements in their structure, such as alkaline and earth alkaline, making them diverse and complex.

Clay minerals normally refer to phyllosilicate minerals that occur in clays (less than 4 microns), according to the Wentworth scale [61], and in the clay fraction (less than 2 microns). Some authors restrict the concept of clay minerals to secondary phyllosilicates from soil weathering [39], however, the Clay Minerals Society (CMS) and the Association Internationale pour l'Étude des Argiles (AIPEA) consider that clay minerals comprise phyllosilicate minerals and any other minerals smaller than 4 microns that give clay plasticity and harden by drying or calcination [25, 30], a concept adopted in this chapter.

Clay compounds have been used by human societies since time immemorial, because they are abundant in nature, smaller than 4 microns, adherent, plastic, malleable, have ion exchange capacity and affinity with water. Due to their physical and chemical properties, they are used in agriculture, livestock, industry, commerce, tourism and the environment for the development of services and products such as bricks, crockery, paints, pharmaceuticals, agricultural inputs and natural filters, so it is of interest from various areas of knowledge.

In the Clay Flower scheme (Fig. 1), the interrelationship between clay science (clay mineralogy) and related sciences and clay technologies can be observed. Clay mineralogy studies the morphology, crystallography, chemistry and physics of clay compounds. The knowledge developed by the science of clays subsidizes, for example, geology in the understanding of surface processes such as weathering and erosion, helping to understand the current dynamics of the landscape, in the reconstitution of paleocenes and in the elaboration of future forecasts.

Clay science supports soil science in understanding the genesis and evolution of soils, their morphological, physical and chemical attributes, susceptibility to degradation and mass movements. Such knowledge helps in more efficient and sustainable uses by engineering, environmental sciences and different industrial sectors, such as the oil, chemical, pharmaceutical and space industries.

The clay composition of an environment depends on the original rock, weathering, pedogenesis, stages of stability, transformations and neoformations, highlighting the following groups of phyllosilicates: kaolinite-serpentine, talc-pyrophyllite, mica, vermiculite, smectite, chlorite and sepiolite—palygorskite. Phyllosilicates can be classified according to layer type and charge, interlayer material type, octahedral sheet type and chemical composition (Table 1) [5]. Each of these groups has specific physical and chemical properties, which will direct them to certain uses.

Proper use requires previous characterization, so in this chapter we will discuss the main groups of phyllosilicates, as they are the most common clay compounds, as well as their structure, formation, occurrence, mineralogical, physical, chemical characteristics and their environmental importance.



Fig. 1 Clay flower scheme—interrelationships between clay science, related sciences and clay technologies

2 Fundamentals, Structure and Properties of Phyllosilicates

According to the Clay Minerals Society (CMS), clay minerals are phyllosilicates and other minerals smaller than 4 microns that give clay plasticity. However, as phyllosilicates are the most common clay minerals, our focus will be on them. The word phyllosilicate comes from the Greek phylon, which means leaf, because the constituents of this group have a flattened habit, basal cleavage and the cleavage layers are normally plastic.

The structures of phyllosilicates are basically formed by the superposition of sheets of silicon tetrahedra (SiO_4), where three of the four coordinated oxygens are shared with neighboring tetrahedra, forming the so-called tetrahedral sheet (T) or siloxane (Fig. 2a). Tetrahedral sheets unite with aluminum octahedral sheets of the gibbsite ($\text{Al}(\text{OH})_3$) or brucite ($\text{Mg}(\text{OH})_2$) type (Fig. 2b), giving rise to two families, respectively, trioctahedral and dioctahedral.

Table 1 Classification of phyllosilicates. *Source* Adapted from [9] and [5]

Layer type*	Interlayer	Group ¹	Subgroup ²	Examples
1:1	None or only H ₂ O	Kaolinite-Serpentine (x ~ 0)	Kaolinite (D) Serpentine (T)	Kaolinite, halloysite Chrysotile, lizardite
2:1	None	Talc-Pyrophyllite (x ~ 0)	Talc (T) Pyrophyllite (D)	Talc Pyrophyllite
2:1	Unhydrated cations	Mica (x ~ 1)	Mica (T) Mica (D)	Biotite, phlogopite Muscovite, illite
2:1	Hydrated exchangeable cations	Vermiculite (x ~ 0,6–0,9)	Vermiculite (T) Vermiculite (D)	Vermiculite
2:1	Hydrated exchangeable cations	Smectite (x ~ 0,2–0,6)	Smectite (T) Smectite (D)	Saponite, hectorite, sauconite Montmorillonite, beidellite
2:1:1	Hydroxide blade	Chlorite (x variable)	Chlorite (T) Chlorite (D)	Clinochlore Donbassite
2:1 modulada	H ₂ O	Sepiolite-Palygorskite (x variable)	Sepiolite (T) Palygorskite (D)	Sepiolite Palygorskite

*Refers to the superposition of tetrahedral and octahedral sheets, described in the following item; ⁽¹⁾ x = Layer load per unit structural formula based on half unit cell. ⁽²⁾ D = dioctahedral; T = trioctahedral

These are simplified models to facilitate understanding, as they are actually more complex, as demonstrated by Schulze [50], who identified distortions in models with real structures. There are two reasons why real minerals deviate from ideal structures:

- atoms are not hard spheres whose closest approximation is determined only by the sum of their radii;
- if one tries to join octahedral and tetrahedral sheets constructed with hard spheres, they will not fit together if the spheres representing the oxygen atoms touch each other in the octahedral and tetrahedral sheets. A detailed explanation can be found on pages 25–26 of [50].

The sequence of tetrahedral and octahedral sheets, the existence of ions or compounds between the sheets and the isomorphic substitutions determine the existence of different clay minerals. Clay minerals can be poorly crystallized (allophane) or crystalline, and these can be divided into 1:1 and 2:1 minerals. The union between the layers that form the phyllosilicates occurs by electrostatic bonds between the O and OH ions of adjacent layers in the 1:1 minerals, through cations such as K, Ca and Mg, groups or hydroxy-octahedral sheets positioned in the interlayers of minerals. 2:1 or by van der Waals forces in minerals without net charge [30].

Clay minerals 1:1 are the simplest structures in which only a tetrahedral sheet (Si₂O₅)²⁻ (T) is bonded to a sheet of brucite Mg₃(OH)₆ (O) or a sheet of gibbsite

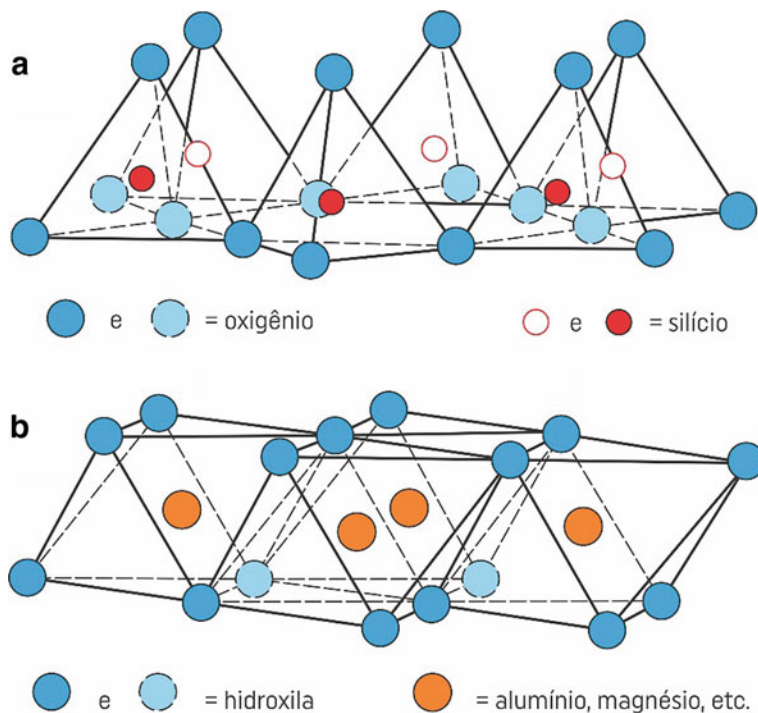


Fig. 2 Models of Si tetrahedrons and Al and Mg octahedrons. **a** Tetrahedrons sharing oxygen and giving rise to the tetrahedral sheet. **b** Octahedrons sharing edges and giving rise to the octahedral blade. *Source* Adapted from [23], pp. 43–44

$\text{Al}_2(\text{OH})_6$ (O), generating a T-O structure. Kaolinite is an example of a 1:1 clay mineral where a siloxane sheet (T) joins a gibbsite type sheet (O), another example is serpentine, where a siloxane sheet (T) joins a sheet of type brucita (O) [50, 64].

The junction of the tetrahedral with the octahedral lamina in 1:1 minerals occurs from the positioning of two oxygens corresponding to the vertices of two unshared tetrahedra of the siloxane lamina, in the place of the positions of two of the three hydroxyls that define faces of the octahedrons in the contact of the octahedral (O) with the tetrahedral (T) blade [40, 50, 64].

The 2:1 clay minerals are formed by the continuous superposition of two tetrahedral sheets for each octahedral sheet, as in the cases of talc and pyrophyllite, where in the first case the structure is trioctahedral and in the second dioctahedral. In these structures, the octahedral lamina is arranged between two tetrahedrals and the coupling occurs by replacing the hydroxyl by oxygen at the apex of the tetrahedrons. Of a total of six hydroxyls of each octahedron, either trioctahedral or dioctahedral, four are replaced by the apical oxygens of the tetrahedrons to form the T-O-T structures [64].

Clay minerals 2:1 can be organized into non-expansive and expansive. The expansive capacity of 2:1 minerals and the expansion intensity are related to the layer charge and its tetrahedral or octahedral origin [50], that is, it is associated with the location of the isomorphic substitution. This explains, for example, the non-expansion of micas, the lower expansion of vermiculite in relation to smectite and the lower expansion of beidellite when compared to montmorillonite, as it has an isomorphic octahedral substitution [49]. According to Kampf and Curi [30], the increase in the charge of the layer and its tetrahedral origin facilitate the contraction of the layers at 1 nm by intercalation with K, improving the organization and decreasing the number of water molecules that can be accommodated in the interlayers.

Clay minerals 2:1 normally occur in poorly weathered soils and environments or from parent materials that contain minerals susceptible to chemical weathering. These clay minerals give soils high cation exchange capacity, high plasticity and stickiness.

Physical and chemical characteristics of phyllosilicates are controlled by the structure of minerals through active sites on the surface of the particles, which interact with other substances or with components of the solution in the environment [64]. During crystal formation, the dominant cation can be replaced by cations with similar ionic radius and different charge, configuring the substitution and isomorphic and giving rise to net charges.

In the formation of tetrahedra, for example, Si^{+4} can be replaced by Al^{+3} , or in the constitution of octahedra, Al^{+3} can be replaced by Mg^{+2} or Fe^{+2} , creating negative electrical charges on the mineral surface. When Al^{+3} , for example, replaces Mg^{+2} or Fe^{+2} at octahedral sites, positive electrical charges are generated. Charges arising from isomorphic substitutions are permanent, independent of pH.

The electrical charges generated by isomorphic substitution produce very important surface phenomena, such as cation exchange capacity (CEC). The CEC of soils plays a fundamental role in the balance of the environment, which is the retention and availability of nutrients for the plants. The anion exchange capacity (AEC) is another important phenomenon originated through isomorphic substitutions, which together with the CTC will mediate control processes (retention and availability) of ions in the environment.

There are electrical charges generated on the surface of minerals that are variable, but these are not related to isomorphic substitution. They result from reactions between H^+ and O^{2-} ions existing on the surface of mineral particles and commonly occur between clay minerals 1:1, Fe and Al oxides, humus and soil solution, varying according to pH. Table 2 summarizes the origin of negative and positive electrical charges in phyllosilicates.

The phyllosilicates strongly influence the physical and chemical properties of sediments and soils, because they are small particles, have high specific surface and cationic and anion exchange properties. Therefore, they are important for understanding many environmental processes and applying strategies for remediation, restoration and environmental control.

The discovery in the early 1920s that clays are crystalline was key to understanding many of the properties of soils and clays. The crystal structures of phyllosilicates

Table 2 Origin of negative and positive electrical charges in phyllosilicates

Constant electrical charges (Negatives)	Variable electrical charges (Positives and negatives)
They result from ionic substitutions of Si for Al or of Al for Mg or Fe(II) in the crystal structure	They result from reactions between H ⁺ and O ²⁻ ions existing on the surface of mineral particles
Occurs only in 2:1 minerals and allophanes	Occurs in clay minerals 1:1, humus, and Fe and Al oxides
Not influenced by environmental conditions or pH dependent	They are influenced by the conditions of the environment and dependent on pH
Internal origin and are always negative	External origin and can be negative or positive

define the different mineral species and are responsible for many of their unique properties [50]. The structural schemes, physical and chemical characteristics and environmental importance of these minerals are discussed in the following items.

3 Major phyllosilicate Groups

The weathering of minerals and phyllosilicates releases nutrients to plants, which are retained by other minerals through adsorption, cation exchanges and precipitation [50]. Clay minerals are weathering indicators, as the presence or absence of specific minerals give clues about the genesis and dynamics of the environment, such as soil formation, dissolution, pollutant concentration, adsorption, absorption or dispersion of nutrients.

The physical and chemical characteristics of clay minerals are also important for urban planning, construction and maintenance of buildings, roads and airports. They are inputs for industry, in addition to being used to adsorb organic and inorganic environmental pollutants, attenuating their movement in the environment or preventing their absorption by plants [30, 50]. Knowing phyllosilicates, their influence on soils and interactions with fungi, bacteria and plants is essential for the creation of phytoremediation strategies and recovery of degraded areas [1, 2, 3, 4, 42, 47].

Schulze [50] points out that some minerals are pollutants themselves and can cause serious environmental problems when exposed to weathering. Therefore, understanding phyllosilicates is also often the key to solving environmental problems. Next, the main classes of phyllosilicates are presented, highlighting their physical, chemical, structural characteristics, genesis and environmental importance.

3.1 Kaolinite-Serpentine Group

The kaolinite-serpentine group is composed of two subgroups: (a) kaolinite subgroup—composed of dioctahedral minerals, mainly kaolinite and halloysite; (b) serpentine subgroup—composed of trioctahedral minerals, mainly chrysotile and antigorite (Table 1).

Kaolinite is a phyllosilicate formed by a sheet of siloxane (T) joined to a sheet of the type gibbsite (O), structure 1:1, it is presented in the form of plates due to the stacking one above the other of the sheets T-O. Kaolinite is dioctahedral and contains Al^{3+} at octahedral sites and Si^{4+} at tetrahedral sites (Fig. 3). The 1:1 layer is electrically neutral, and the adjacent layers are held together by hydrogen bonds between the basal oxygens of the tetrahedral sheet and the surface plane hydroxyls of the adjacent octahedral sheet [50].

Kaolinite has a basal spacing of 0.72 nm, chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, the specific surface area varies from 10 to 20 $\text{m}^2 \text{g}^{-1}$, and the cation exchange capacity varies from 3 to 15 $\text{cmol}_c \text{dm}^{-3}$ (Table 3), being pH dependent because of the hydroxyls along the edges of the mineral. Depending on the H^+ or OH^- of the soil solution or the environment, hydroxyls can be protonated or deprotonated and give rise to positive or negative charges, reflecting, respectively, the anion exchange capacity or cation exchange capacity [40].

Kaolinite can form in soils from Al and Si released by the weathering of primary and other secondary minerals, such as feldspars from igneous rocks. In addition, it can be inherited from other soil source materials, such as sedimentary rocks. Kaolinites extracted from mineral deposits are widely used in industrial applications, such as fillers for plastics, ceramics and paper coatings [50].

The 1:1 layer has little or no permanent charge due to the low amount of substitution in the tetrahedral or octahedral sheets, and most kaolinites are close to ideal for the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Therefore, exchange capacities and surface areas

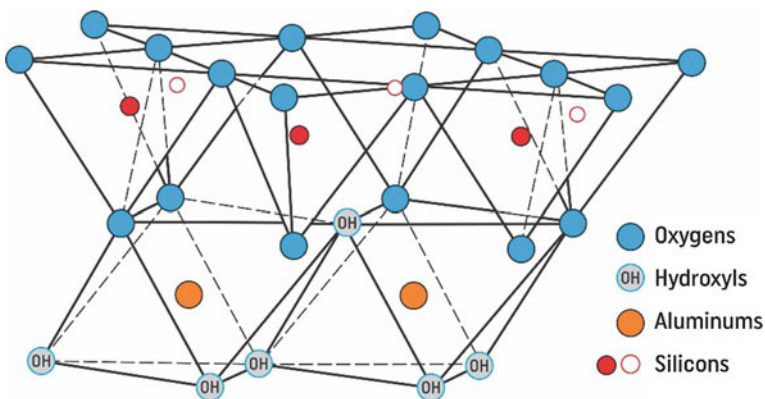


Fig. 3 Schematic of the structure of kaolinite. *Source* Adapted from [23, p. 46]

Table 3 Cation exchange capacity (CEC) and specific surface of materials (SS)

Phyllosilicates	CEC (cmol _c dm ⁻³)	SS (m ² g ⁻¹)	References
Vermiculite	115–250	~800	[21, 38]
Smectite	50–160	600–800	[11, 48]
Chlorite	10–40	26–45	[30, 32]
Illite	5–15	*	[30, 58]
Palygorskite	5–30	~800–900	[55]
Sepiolite	20–45		
Kaolinite	3–15	10–20	[9, 23, 40, 50, 62]
Talc-pyrophyllite	~2	~10–43,7	[65]

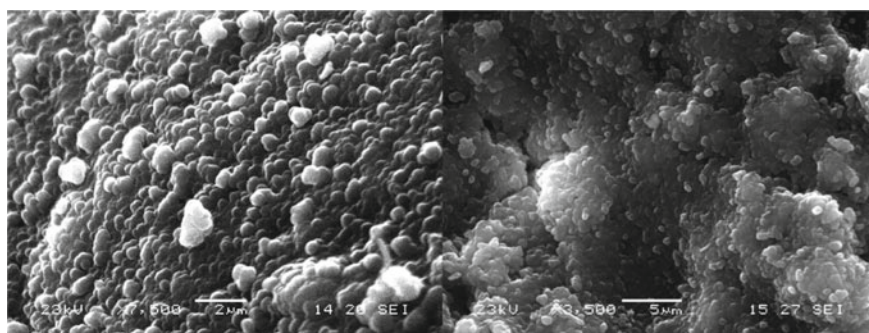
*Information on illite specific surface (SS) is scarce and existing information is not consistent for soils

are low, giving soils low chemical fertility when compared to soils dominated by 2:1 clay. Kaolinite is a common mineral in soils, being normally abundant in highly weathered soils, such as Ultisols and Oxisols [50].

Kaolinites interfere with several physical and chemical processes in soils, such as aggregate formation, increased porosity, water retention, drainage, cation and anion exchange reactions, among others [40]. In hypoferric soils, kaolinites are associated with the formation of block structure and cohesive horizons present in soils developed from the Barreiras Formation, a geological unit found throughout the Brazilian coast [44].

The cohesive horizons developed in soils of the Barreiras Formation are dense subsurface horizons, which are hard when dry and friable when wet. This behavior is probably due to the transport of small kaolinites from the surface horizons of soils and subsurface precipitation, and the mechanisms involved in the process are detailed in the works of [17] and [44] (Fig. 4).

Halloysite has a similar crystallographic structure to kaolinite; however, the 1:1 sheets are separated by a layer of H₂O molecules (Fig. 5) and generally

**Fig. 4** SEM photomicrograph of kaolinite in a cohesive horizon

occur as tubular or spherical particles. Halloysite is usually found in soils formed from volcanic deposits (volcanic ash and obsidian) such as Andisols. Halloysite is formed at the beginning of the weathering process, being less stable than kaolinite, transforming into it over time [50].

The phyllosilicates of the kaolinite subgroup perform important environmental functions, as summarized in Table 4 in final considerations. In soils, they are responsible for several physical and chemical processes that interfere, for example, in the formation of aggregates, especially subangular ones, and in the increase in porosity, they are responsible for retaining anions at acidic pH and cations at high pH and have the possibility of retaining nitrates at acidic pH.

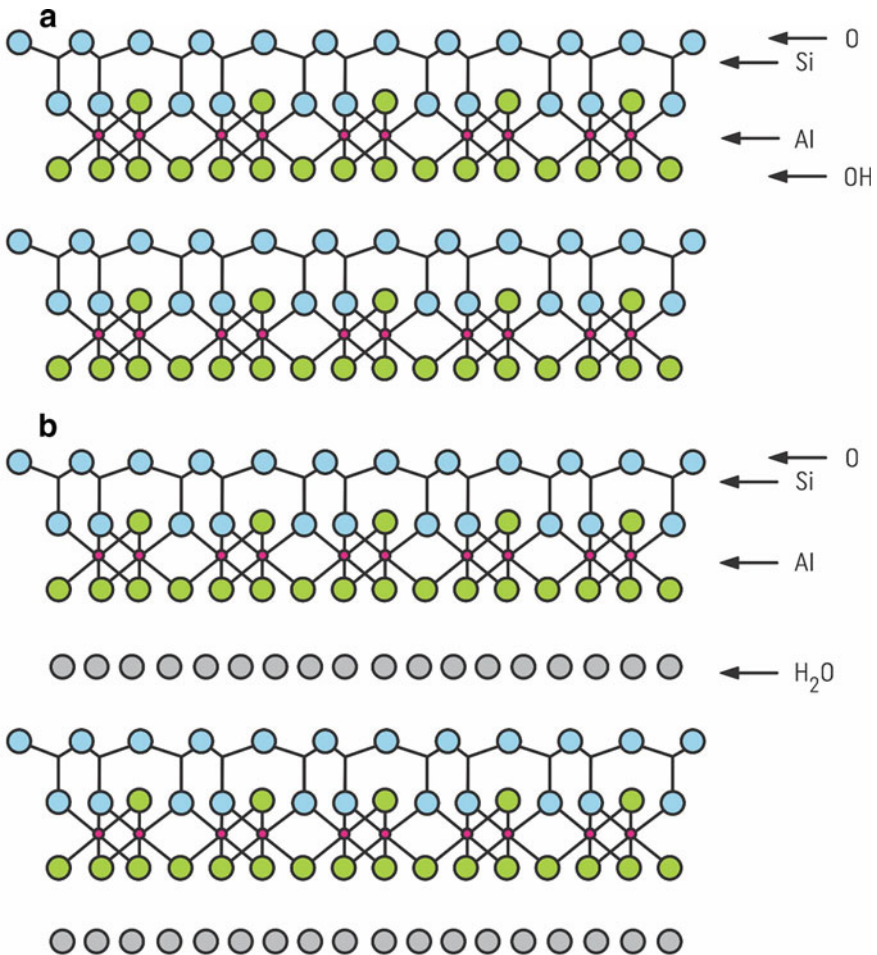


Fig. 5 Schematic of the structure of kaolinite and halloysite. Source Adapted from [51]

Table 4 Environmental importance of phyllosilicates

Phyllosilicates	Environmental importance	References
kaolinite and halloysite	Retention of anions at acidic pH and cations at high pH; possibility of retention of nitrates in acidic pH; greater physical stability, less plasticity, greater water retention capacity, confers less erodibility to the soil, low expansion/contraction capacity, less dispersibility, weak sorption and less metals when compared to phyllosilicates 2:1, when associated with iron oxides can favor the sorption of metals and anions, can be used to adsorb radionuclides, such as Cs and Ra, as well as oil residues from oil extraction, spills and other disasters in the marine environment; can be used to mitigate problems related to hazardous organic pollutants even in small concentrations, such as phenols; they have a lower ability to buffer acidification when compared to smectites, the interaction between kaolinite, iron oxides and organic matter (SOM) favors a decrease in the rate of SOM decomposition, favors the adsorption of organic molecules; are good environmental indicators, especially in more weathered environments	[8, 12, 16, 19, 27, 29–31, 37, 50, 56, 60, 62]
Serpentine	As they are formed from the weathering of ultramafic rocks, their presence together with the predominance of magnesium in the exchange sites can hinder calcium adsorption and plant development, as well as concentrate high levels of heavy metals	[30, 62]

(continued)

Table 4 (continued)

Phyllosilicates	Environmental importance	References
Talc and pyrophyllite	They are sources of potassium (K), non-expandable, soft and have poor cohesion. They are rare in soils, but when present they indicate that the soil is poorly weathered. They are soft, foliated morphology, inertia, purity, whiteness, high melting point, high thermal conductivity and low electrical conductivity and low chemical reactivity	[30, 50, 65]
Mica	Most common sources of potassium (K) in soils; its alteration can generate vermiculite, smectite and interstratified, which are also macronutrient reserves; can be used to adsorb radionuclides, such as Cs and Ra, as well as oil residues from oil extraction, spills and other disasters in the marine environment	[30, 35, 41, 50, 54, 58]
Vermiculite	Increases the cation exchange capacity of the soil; adsorbs radionuclides and heavy metals, such as Cs, Ra and Cu; selectively adsorbs cations preferentially K^+ , NH_4^+ , Rb^+ and Cs^+ ; favors cationic exchange of ions that have high hydration energy, such as Ca^{+2} and Mg^{+2}	[30, 38]
Smectite	They confer high fertility to the soils; organic compounds adsorption, herbicides and pesticides; enhanced anionic polymer adsorption; it has a high potassium (K) fixation potential; high potential for fixing toxic elements, such as heavy metals; are very useful in waste dumps when used properly, especially due to their high expansion pressure, low hydraulic conductivity and high CEC	[18, 30, 33, 34, 48, 50, 53, 57]

(continued)

Table 4 (continued)

Phyllosilicates	Environmental importance	References
Chlorite	It is capable of adsorbing heavy metals and radioactive elements such as Cr and Cs; has selectivity for cations with low hydration energies, such as K^+ , NH_4^+ e Rb^+	[32]
Sepiolite-Palygorskite	Used as gelling agents to keep other solids in suspension; in oil well drilling; in asphalt-based coatings, sealing and paving; in the handling and distribution of liquid fertilizers; as oil adsorbents; for pharmaceutical purposes; as supports for biocides; for absorption and adsorption of animal waste; to cover the floor of herd-carrying wagons	[30, 55]

The phyllosilicates of the kaolinite subgroup provide greater physical stability, less plasticity, greater water retention capacity and less soil erodibility. They have low expansion/contraction capacity, lower dispersibility, weak sorption and lower capacity to buffer acidification when compared to 2:1 phyllosilicates, such as smectite. When associated with iron oxides, kaolinitic minerals can favor the sorption of metals and anions; in addition, it can favor the reduction of the decomposition rate of organic matter.

Minerals from the kaolinite family are good indicators of hot and humid environments, especially kaolinite. In addition, they can be:

- (a) used in the recovery of degraded areas and/or contaminated by heavy metals and organic compounds [16, 22, 29, 37, 60],
- (b) in the adsorption of oil residues from oil extraction, spills and other disasters in the marine environment [6, 19, 56] and,
- (c) as physical and chemical barriers against emerging pollutants such as microplastics (MPs), already commonly identified in the atmosphere, lakes, rivers, seas, glaciers, living beings and in the soil-groundwater system.

As phyllosilicates are important components of the soil-groundwater system, [63] performed an experiment on the mobilization of MPs, notably polystyrene nanoparticles in quartz sand mixed with kaolinite, montmorillonite and illite on the mobility of MPs in groundwater and suggest that kaolinite has a greater effect on inhibiting the mobility of MPs, but montmorillonite and illite also play this role. This is because the change in ionic strength can change the surface charge of MPs and clay minerals, affecting the interaction energy. The findings of [63] can help to understand the transport mechanisms of microplastics in porous media and provide subsidies to simulate microplastic contamination in groundwater.

In recent decades, many hazardous and toxic organic pollutants have been detected in soils, surface waters, groundwater and even drinking water, arising from conventional or emerging activities and products, such as additives incorporated into MPs. Additives are chemical products that have heavy metals added to the plastic to color, provide transparency, improve mechanical, thermal and electrical resistance and degradation by ozone, light radiation, mold, bacteria and moisture and include inert or reinforcing fillers, plasticizers, antioxidants, ultraviolet light stabilizers, lubricants, dyes and flame retardants [26]. Such additives and the degradation of organic compounds that make up MPs can pose a threat to human health, some of them even in low concentrations, such as phenolics.

Phenolics are chemicals that pose a threat to human health even in low concentrations and can enter the human body through the skin or esophagus and cause damage to the protein structure of our body [7, 36, 66].

According to Senthilvelan et al. [52], 700 million tons of phenol are produced annually as a raw material in the petroleum and chemical industries. That's why we need to develop technologies for the efficient treatment of wastewater to protect ourselves. Wang et al. [60] developed a new low-cost carbon catalyst that is efficient in removing phenol from the carbonization of halloysite at different temperatures (600, 700, 800 and 900 °C), showing the importance of this group of phyllosilicates in the environmental area.

The abundance, geochemical stability and physical and chemical characteristics of clay minerals from the kaolinite family favor their use in the biogeoenvironmental industry applied to environmental management, which includes the development and application of techniques for area recovery and contaminant control, as well as such as monitoring environmental resources such as soil and water.

The serpentine subgroup consists of 1:1 trioctahedral phyllosilicates, similar in structure to kaolinite but containing a variety of cations in the octahedral sheet, such as Fe II, Fe III, aluminum, magnesium, manganese, nickel and zinc. Serpentine normally occurs in large grains, but appears as small plaques and fibrous structures, as is the case with chrysotile, widely used in the past as a constituent of asbestos, a carcinogenic material [62].

The serpentine subgroup minerals do not have a significant permanent charge, so it is inferred that the cation exchange capacity is mainly due to the variable charge at the edges of the crystals and the values are similar to those of kaolinite.

The serpentines are formed from the weathering of ultramafic rocks, so it can favor the concentration of heavy metals in the soil. The presence of minerals from this subgroup has a predominance of magnesium in the exchange sites, which hinders calcium absorption and impairs plant development. They are indicators of poorly weathered soils and have several environmentally unfavorable characteristics, such as occurrence in shallow soils that are more prone to erosion [30, 62].

3.2 Talc and Pyrophyllite

The talc-pyrophyllite group is composed of two subgroups: (a) talc subgroup—composed of trioctahedral minerals, mainly talc; (b) pyrophyllite subgroup—composed of dioctahedral minerals, mainly pyrophyllite (Table 1). The simple structures of talc and pyrophyllite are good starting points for discussing the structures of 2:1 phyllosilicates (Fig. 6).

Talc and pyrophyllite consist of 2:1 layers stacked on top of each other, with the former having Mg^{2+} at the octahedral sites and the latter having Al^{3+} at the octahedral sites. The tetrahedral sheets of both minerals have only Si^{4+} , the talc formula being $Mg_3Si_4O_{10}(OH)_2$ and from pyrophyllite $Al_2Si_4O_{10}(OH)_2$ [50]. In both subgroups, the charges are balanced within the 2:1 layer, making them electrically neutral. Adjacent 2:1 layers are held together by weak van der Waals forces, which can be easily separated, which explains their tendency for prominent basal cleavage, high softness, and low hardness (from 1 to 2) on the Mohs scale.

They have a basal spacing of 0.92–1.0 nm, specific surface area of ~10 to 43.7 $m^2 g^{-1}$ and very low cation exchange capacity ($\sim 2 cmol_c dm^{-3}$) (Table 3). Only the edges of the layers provide potentially reactive sites, which are pH dependent and also influenced by particle size. The ions (cations and anions) that bind to the edges of talc-pyrophyllite probably do so through a specific adsorption (chemisorption) or inner sphere binding mechanism [65].

Talc and pyrophyllite are used industrially as ingredients in paints, ceramics, plastics, papers and cosmetics, so when they are found in river and estuarine environments, they are indicators of industrial activity, if there is no proximal geological source [50].

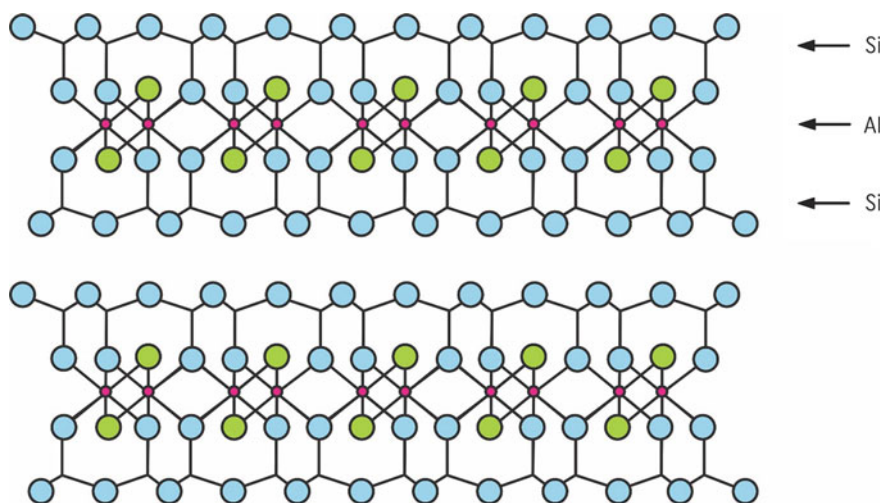


Fig. 6 Schematic of the structure of talc-pyrophyllite. Source Adapted from [51]

The most important physical and chemical characteristics of talc-pyrophyllite are softness, foliated morphology, inertia, purity, whiteness, high melting point, high thermal conductivity, low electrical conductivity and low chemical reactivity, because they are practically electronically neutral [65]. They are non-expansive sources of potassium (K), rare in soils, but when present, they indicate that the soil is poorly weathered [30].

3.3 Mica

The mica group is composed of two subgroups, one composed of trioctahedral minerals, mainly represented by biotite and phlogopite, and the other composed of dioctahedral minerals, represented by muscovite and illite (Table 1). Mica have the 2:1 layer structure described for talc and pyrophyllite (Figs. 7, 8 and 9), but with two important differences, according to [50]:

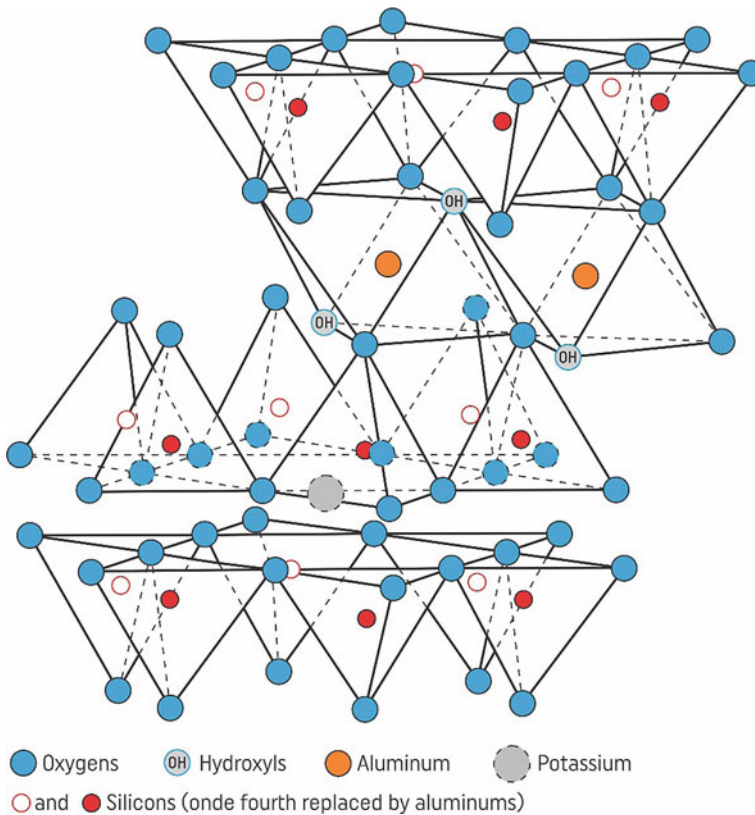


Fig. 7 Schematic of the structure of muscovite. *Source* Adapted from [23], p. 66

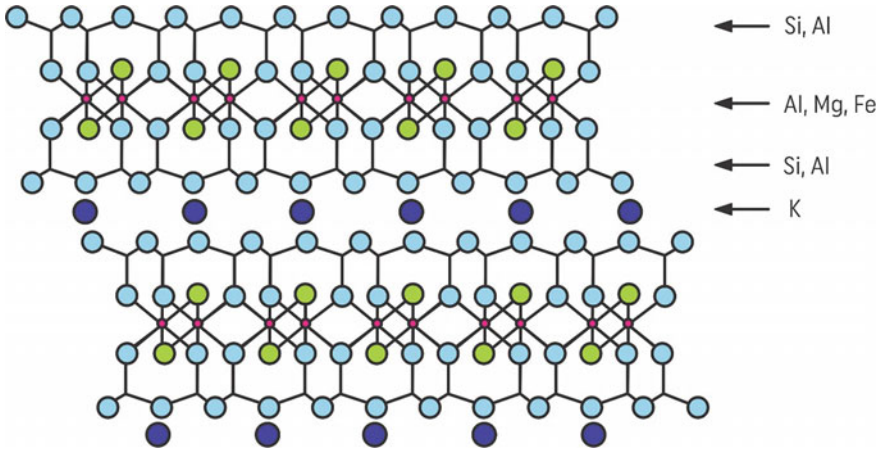


Fig. 8 Structural scheme of dioctahedral mica. *Source* Adapted from [51]

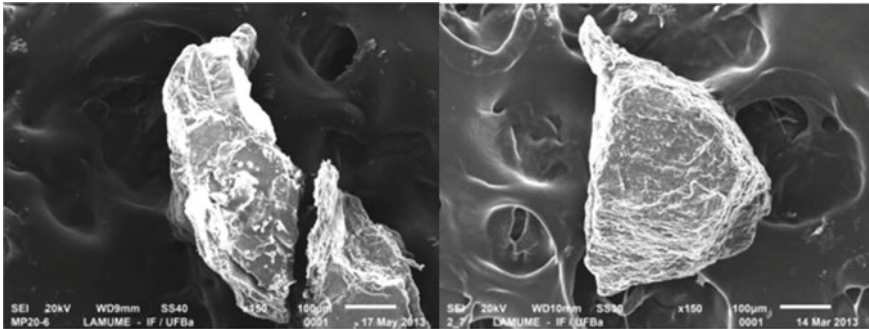


Fig. 9 Photomicrograph of biotite. Images kindly provided by Gileno Moreira dos Santos

- (a) instead of having only Si^{4+} at the tetrahedral sites, a quarter of the tetrahedral sites are occupied by Al^{3+} . Because of this substitution, there is an excess of one negative charge per formula unit in the 2:1 layer;
- (b) excess negative charge is commonly balanced by K^+ , which occupy intermediate sites between two 2:1 layers. Therefore, the ideal formula for a mica mineral with Al at the octahedral sites is $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$.

Mica can be dioctahedral or trioctahedral, because Fe^{2+} and Fe^{3+} can replace Mg^{2+} and Al^{3+} in the octahedral sheet and Na^+ and Ca^{2+} can replace K^+ in the middle layer [58]. Mica in soils is inherited from the parent rock, usually those derived from igneous or metamorphic rocks or from sediments derived from these rocks.

Muscovite, biotite and phlogopite are the most common minerals, and all have K^+ in the middle layer; however, they differ in the composition of the octahedral sheet

and whether they are di- or trioctahedral [50]. In soils, the most common micas are muscovite and illite, because the dioctahedral ones are more resistant to weathering.

Mica has a basal spacing of the layer+interlayer (structural unit) of 1.0 nm, high specific surface area (between 65 and 100 m² g⁻¹) and low cation exchange capacity of the clay fraction (illite), between 5 and 15 cmol_cdm⁻³ (Table 3). Values of up to 40 cmol_cdm⁻³ reported for illite and glauconite in the literature are due to inter-bedding, mainly of illite-smectite [30].

Mica are environmentally significant because they are the most common sources of potassium (K) in soils, in addition to being sources of Fe (II) and because they facilitate the fixation of weakly hydrated cations, such as NH₄⁺, Rb⁺ and radionuclides such as Cs⁺ [58]. Mica weathering can generate vermiculite and smectite. When present in soils, they may indicate that they are poorly weathered. Micaceous minerals, such as illite, can also be used to inhibit the mobility of MPs [63].

3.4 Vermiculite

The vermiculite group is composed of two subgroups, one trioctahedral and the other dioctahedral (Table 1). Vermiculite has a similar 2:1 layer structure to mica, but instead of having a layer charge of ~1 per formula unit and K⁺ at interlayer positions, it has a layer charge of 0.9–0.6 and contains cations, mainly Ca⁺² and Mg⁺², in the middle layer (Fig. 10) [38].

It has the ability to expand in water like smectite, but not as extensively because of the presence of only two planes of water molecules surrounding the hydrated cations in the interlayer space. It has the following ideal formulas: (a) trioctahedral vermiculite: [nH₂O, Mg_x(Mg₃) (Si_{4-x}Al_x)O₁₀(OH)₂]—originated from the transformation of biotite; (b) dioctahedral vermiculite: [nH₂O, Mg_x(Al₂) (Si_{4-x}Al_x)O₁₀(OH)₂]—originated from the transformation of muscovite [30].

The high charge per formula unit gives vermiculite a high cation exchange capacity (CEC), ranging from 115 to 250 cmol_cdm⁻³ [21] and the specific surface around ~800m² g⁻¹ [38]. They have the ability to selectively adsorb cations with low hydration energy, such as K⁺, NH₄⁺, Rb⁺ e Cs⁺. In addition, it favors cationic exchange of ions that have high hydration energy, such as Ca⁺² e Mg⁺².

Vermiculite in soils is believed to form almost exclusively from the weathering of micas and chlorites. The weathering of micas to vermiculite (or smectite) probably occurs by substitution of K⁺ at the interlayer sites by hydrated exchangeable cations. The integrity of the 2:1 layer is preserved, but there is a reduction in layer load [50].

Vermiculite plays an important role in regulating nutrient dynamics for plants, sometimes even acting as a source or sink for various elements. Due to its high cation exchange capacity (CEC) together with the ability to fix certain ions, it is suitable for removing contaminants, including heavy metals, radionuclides and grounded nuclear waste [20, 38, 59].

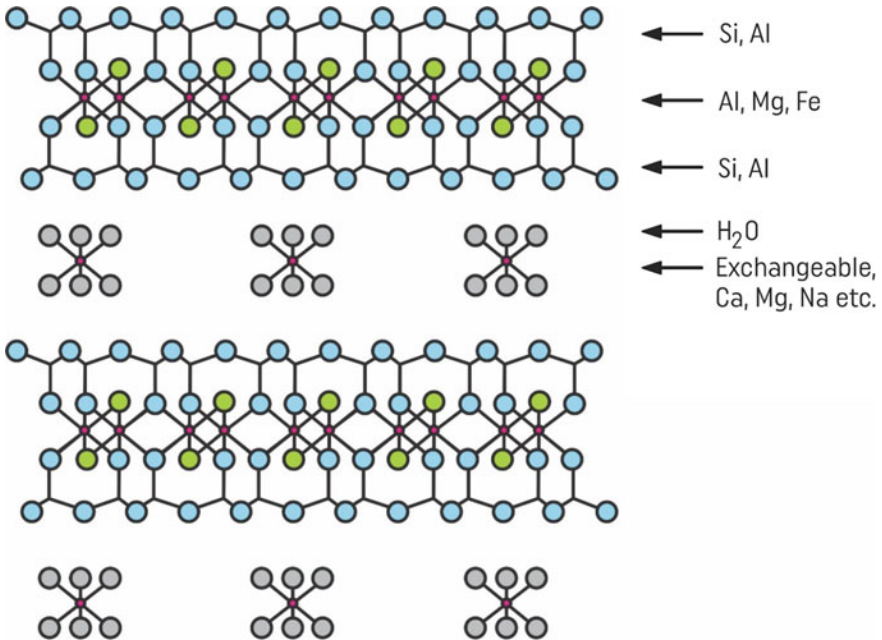


Fig. 10 Schematic of dioctahedral vermiculite and smectite structural units with interlayer hydrated cations. *Source* Adapted from [51]

Its ability to expand and exfoliate at high temperatures makes it useful in many industrial applications such as horticultural potting media, thermal insulation materials, soil conditioners and substrates [38, 50].

3.5 Smectite

The smectite group is composed of two subgroups, one composed of trioctahedral minerals, mainly represented by saponite, hectorite and saunonite, and the other composed of dioctahedral minerals, represented by montmorillonite and beidellite (Table 1). The smectite group consists of 2:1 minerals (Fig. 11), with an intermediate layer containing exchangeable cations and a charge ranging from 0.6 to 0.25.

Dioctahedral smectites are more common in soils than trioctahedral ones, the main representatives being montmorillonite, beidellite and nontronite, which differ in tetrahedral composition and in octahedral sheets [48]. Smectites do not fix K⁺ as readily as vermiculite because they have a lower layer charge; however, they are more expansive [50].

Smectites contract when dry and expand when wet, leading to cracking and displacement problems when houses, roads and other structures are built on smectitic

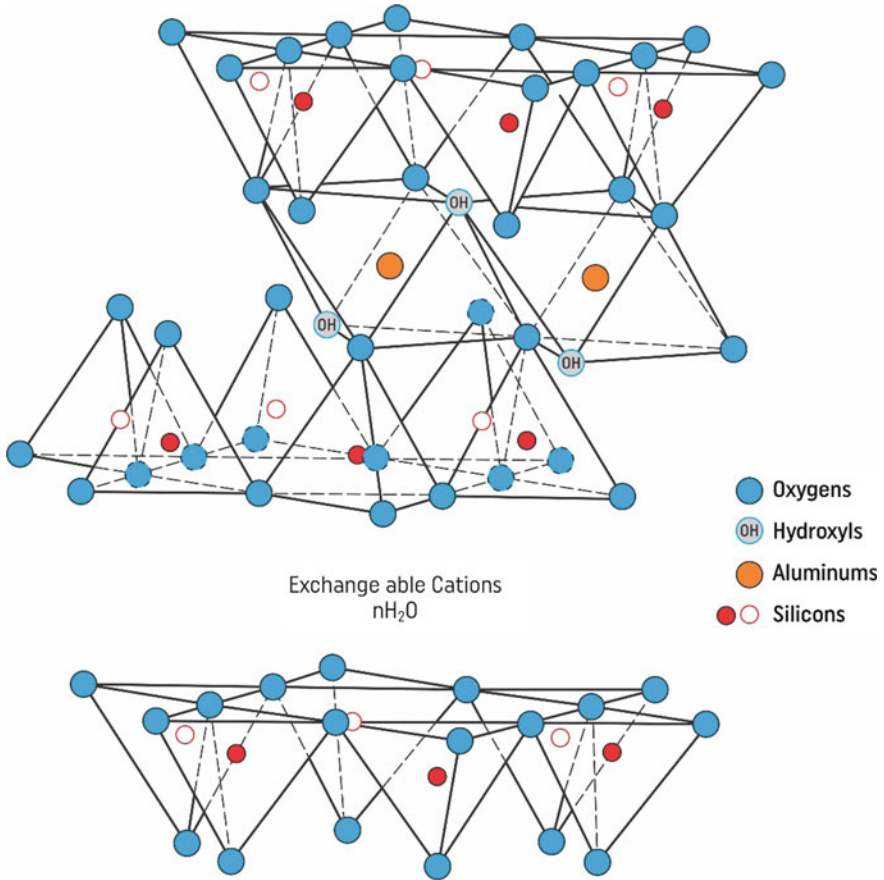


Fig. 11 Schematic of the structure of montmorillonite. *Source* Adapted from [23], p. 56

soils such as Vertisols [50]. As the expansive capacity of 2:1 minerals and the intensity of this expansion are related to the charge of the layer and its tetrahedral or octahedral origin, this explains why montmorillonite is more expansive than beidellite, as it has an isomorphic octahedral substitution.

Due to high specific surface area (600 a $800 \text{ m}^2 \text{ g}^{-1}$), its adsorptive properties and high cation exchange capacity (47 a $162 \text{ cmol}_c \text{ dm}^{-3}$) (Table 3), smectites are used as catalysts, adsorbents for spills of liquid substances and oils, as sealants for ponds and wells, in drilling fluids for oil wells and in landfill linings [50].

The smectite group has important implications for agriculture, engineering and environmental purposes, as they are expansive, the specific surface area and the cation exchange capacity are high [48]. Therefore, they provide good soil fertility, are good reservoirs of macronutrients, adsorb organic compounds, herbicides, pesticides, have a high potential for fixing potassium (K) and a high potential for fixing toxic elements, such as heavy metals.

The high expansiveness of the smectite group, especially montmorillonite, can hinder agricultural uses and management and their use as borrowing materials for the construction of roads, buildings and houses, for example. They can present geotechnical risks, such as cracks and ruptures in engineering works; however, they are very useful in waste deposits when used properly, especially due to their high expansion pressure, low hydraulic conductivity and high CEC.

Recent research also points out that smectites can be used to inhibit the mobility of emerging contaminants, such as PMs and contaminants associated with them [63].

3.6 Chlorite

The chlorite group is composed of two subgroups, one composed of trioctahedral minerals, mainly represented by clinocllore, and the other composed of dioctahedral minerals, represented by donbassite (Table 1).

Chlorite has a 2:1 layer structure with excess negative electrical charge, the excess charge being balanced by a positively charged interlayer hydroxide sheet [32] (Fig. 12). Any octahedral sheet, whether part of the 2:1 layer or the hydroxide interlayer, can be di- or trioctahedral and contain Mg^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Al^{3+} , Fe^{3+} e Cr^{3+} , giving rise to different types of minerals [50].

The union between the 2:1 layer and the hydroxide layer occurs through hydrogen bonding, resulting in a fixed basal spacing of 1.4 nm. As they do not expand, they have a low specific surface ($26\text{--}45\text{ m}^2\text{ g}^{-1}$) [32] and the cation exchange capacity between 10 and $40\text{ cmol}_c\text{ dm}^{-3}$ (Table 3) [30]. Part of the CEC is pH dependent and is associated with $Al(OH)_3$ groups at the edge of the minerals. Chlorite group minerals are rare in soils, and when they occur, they are inherited from metamorphic rocks, igneous rocks or hydrothermally altered sediments. Chlorite group minerals transform into vermiculite and smectite and are sensitive to chemical weathering [50].

Chlorite has aroused environmental interest because it is capable of adsorbing heavy metals and radioactive element ions, such as chromium and cesium. In addition, it has selectivity for cations of low hydration energies, such as K^+ , NH_4^+ e Rb^+ , and can adsorb anions at the exposed edges of the mineral, because they generate pH-dependent charges.

3.7 Sepiolite and Palygorskite

The sepiolite-palygorskite group is composed of two subgroups, the sepiolite, which is trioctahedral, and the palygorskite, which is dioctahedral (Table 1). Sepiolite and palygorskite minerals are considered phyllosilicates, but are structurally distinct from typical 1:1 and 2:1 layer structures in that they have continuous tetrahedral sheets, but with adjacent bands of tetrahedra within a tetrahedral sheet that point in two

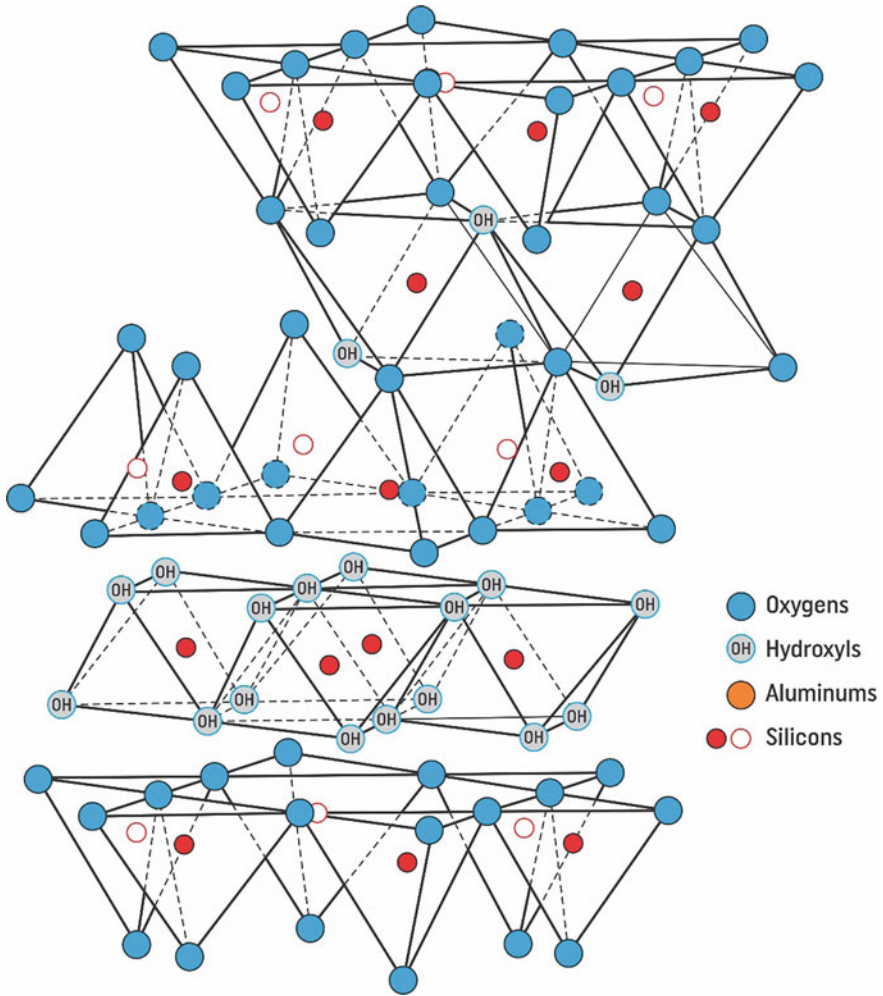


Fig. 12 Schematic of the structure of chlorite. *Source* Adapted from [23], p. 70

opposite directions. Water molecules occur in the spaces between the leaves, with the 2:1 leaves being wider in sepiolite than in palygorskite [50].

Sepiolite is a low aluminum trioctahedral magnesium silicate with ideal formula $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$, while palygorskite is intermediate between di- and trioctahedral, with ideal formula $\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$ [55], and having equal proportions of Al and Mg [30]. Minerals have low CEC, ranging from 5 to 30 $\text{cmol}_c\text{kg}^{-1}$ to the palygorskite and from 20 to 45 $\text{cmol}_c\text{kg}^{-1}$ to the sepiolite [55], both have high specific surface (Table 3).

They are mostly found in soils in arid and semi-arid environments, have a fibrous morphology and apparently consist of aggregates or bundles of thin laths, oriented

in parallel and with a width of 10–35 nm and a thickness of 5–10 nm [55]. Due to their fibrous morphology, the suspension of these clays can form thick gels even at low concentrations of solids. Therefore, they are used industrially as gelling agents to keep other solids in suspension [50].

Sepiolite and palygorskite can also be used as thixotropic agents in oil well drilling in saline regions, for asphalt-based coatings, sealing and paving, in the handling and distribution of liquid fertilizers, as oil adsorbents, and for pharmaceutical purposes, as substrate primers for biocides, for absorption and adsorption of animal excrement and for covering the floor of cattle transport wagons.

4 Final Considerations

The physical and chemical characteristics of phyllosilicates play important roles in the dynamics of the environment, as expressed throughout the chapter. The knowledge of such properties can favor their use to stop or mitigate the contamination of degraded areas by different types of substances, whether organic, mineral or radioactive. A summary of the environmental importance of phyllosilicates is presented in Table 4.

The table summarizes the importance of phyllosilicates in environmental management and, in a way, signals the importance of expanding research to improve the techniques that use them as absorbing and adsorbing agents for contaminants. New horizons are approaching, signaling the importance of deepening knowledge about phyllosilicates and other clay minerals as actors to safeguard the environment.

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