

Original Research Paper

## Clay and Clay Minerals: A Detailed Review

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**Abstract:** In this study, we focused on the presentation of clay minerals, their conditions of formation and their different categories. We also reported the importance of purification in removing impurities and the responses induced by heat treatment of these minerals. Techniques used to detect clay minerals are also exposed. On the other hand, the mineralogical, physicochemical and thermal properties have a direct impact on the field of use of these minerals. These properties differ from one mineral to another, depending on the structure and chemical composition. Moreover, the remarkable properties of smectites make these minerals the most preferred for the industry and also in the environmental field. Due to their brilliant firing properties, illites are suitable for the construction industry. Moreover, the purification by acids (acetic acid and HCl) allows the removal of most associated minerals, and thus a secure access to the clays' characteristics and a very strong sensitization even to the small variation. Finally, the ethylene glycol (EG) swelling test only affects the basal distance of smectites, increasing this distance to 17 Å, but heating to 500°C destroys kaolinite, and closes the basal distance of smectites and vermiculites to 10 Å. Illites and chlorites show no response to these two treatments (EG, heating to 500°C).

**Keywords:** Associated Mineral, Clay Mineral, Ethylene Glycol, Purification, Tetrahedral Sheet.



## 1. Introduction

The science of clays has attracted great interest in recent years, thanks to their capacity to respond to the requirements of the market in several industrial and environmental fields [1]. This science is multidisciplinary, combining geology, mineralogy, crystallography, physics, geotechnology and chemistry [2]. Previously, all civilizations have valued these materials in the fields of construction, pottery, brick making, ceramics, etc. Today, in addition to improving the performance of these minerals in these fields of use, clays have become essential candidates in paints, plastics, rubbers, construction, cosmetics and pharmaceutical industries [3] [4] [5] [6] [7] [8] [9] [10]. The development of characterization, processing, and synthesis methods of these natural resources, expands the field of their use, which will make the future of clay science bright, exciting, and promising.

The great attention given to clay minerals is justified by their abundance in nature, their simple accessibility, their effectiveness and their ecological properties [11] [12] [13]. Moreover, these minerals are indefinitely recyclable, easy to use, and have a unique crystal structure. This crystalline structure and the fine size of the grains ( $< 2\mu m$ ), are responsible for the remarkable physicochemical properties of the clay minerals namely the specific surface (SSA), the surface charge and the cation exchange capacity (CEC) [14] [15] [16] [17] [18]. The later permits the hydration, thixotropy, plasticity and swelling of these materials [19]. These minerals are characterized by other interesting properties, the most important of which are colloidal, mineralogical, mechanical, thermal and rheological properties. These characteristics have aroused considerable interest in many applications, the most promising of which are the development of nano-composites and clay-polymer hybrids [20] [21] [22]. However, the knowledge of these properties is decisive in the production of high quality materials and requires the mastery of processing techniques and the availability of sophisticated equipment. Montmorillonite, kaolinite, bentonite and illite, remain among the most preferred clay minerals by researchers, because of their excellent characteristics [10] [23] [24].

In general, clays have a very heterogeneous composition and usually contain mixtures of clay minerals, which are associated with other minerals and organic products such as quartz, calcite, feldspar, organic matter, etc. These impurities play a significant role in the physicochemical properties of clays, but their presence in large quantities negatively affects the performance of these resources. Thus, purification processes are necessary to concentrate the clay minerals present in the clay fraction [25] [26] [27].

Thanks to their hydrophilic character, provided by the presence of hydrated compensating cations in the interfoliar spaces, the performances of clay minerals are sometimes insufficient, particularly regarding their compatibility with organic substances [28] [29] [30]. To overcome this problem, it is necessary to modify the hydrophilic character of the clay to make it organophilic [31] [32] [33] [34]. These different treatments of clay minerals surface allow the valorization of these materials in other fields and the creation of new materials with much improved characteristics.

On the other hand, the structure of clay minerals is multiscale, the size of agglomerates being of the order of micrometers, while an individual layer has a thickness close to the nanometer. This is why different complementary analysis techniques will be necessary in order to characterize the clay minerals as well as possible and to obtain a large number of information. Generally, the most used characterization techniques are X-ray diffraction (XRD), X-ray fluorescence (XRF), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR), as well as thermal methods such as thermal gravimetric analysis (DTG/TGA) and differential scanning calorimetry (DSC) [8] [35].

This review aims to define clay minerals, their origins and their structures. It also presents the different classification criteria and the important types of clay minerals encountered and their possible uses. It also focuses on the purification process and techniques for determining the clay minerals present in a given clay fraction.

## 2. Literature Review

### 2.1. Clay Definition

In a broader sense, clays and clay minerals are hydrated aluminosilicates belonging to the family of phyllo-silicates, consisting of two-dimensional infinite sheets [13]. The term clay has its origin in the greek word "argilos" which means white. It refers to materials composed mainly of fine grains whose size is less than two microns. At specific water contents, these minerals become plastic and show a hardening when fired or dried.

The term clay mineral covers several concepts depending on the discipline concerned. These notions are related to physical properties, discipline and crystallographic structure. According to the geologist or soil scientist all minerals with a small grain size (between 2 and 4  $\mu\text{m}$ ) are considered clay minerals. Ceramists are interested in the plasticity of clay minerals in the presence of water, while the percentage of minerals in a given clay fraction is the characteristic that attracts the civil engineer, because this mineralogical behavior influences all properties including chemical, physical and thermal properties [19].

## 2.2. Clay Origin

The physicochemical and mineralogical properties and the chemical composition of clays are affected by the formation conditions and the nature of the parent rock. These clayey rocks are abundant on the planet's surface and easily accessible, containing both clay and non-clay minerals. Physical, chemical, and biological alterations influence the parent rocks by several processes to give natural clays with heterogeneous composition. Some minerals are derived from the decomposition of feldspars, others are the result of chemical alterations of volcanic ash [36]. In addition, high temperatures and pressures strongly affect the chemical composition of clays. Indeed, in the zones of low temperatures, the clay minerals obtained are closer to the minerals constituting the parent rock, because the alterations are weak. The clay minerals, illite and chlorite, can exist in this type of climate. Whereas, kaolinites and smectites can be detected in hot and humid conditions where hydrolysis is strong. Finally, a temperate environment encourages the creation of illite, chlorite or vermiculite.

Generally, three processes of clay and clay minerals formation can be distinguished (Fig.1). These processes can be juxtaposed to give heterogeneous clay fractions. Concerning the first process, the formation of clay minerals is done through a simple decomposition of the parent rocks especially in the mountainous massifs under the effect of erosion (rain, wind, freezing, thawing, wave, etc.). In the second mechanism, clays are formed by the combination of substances transported by the soil water, this process serves to transform minerals into clayey rocks under the influence of degradation (loss of soil equilibrium) or aggradation (accumulation of sediments in a water course) of mineral ions [37].

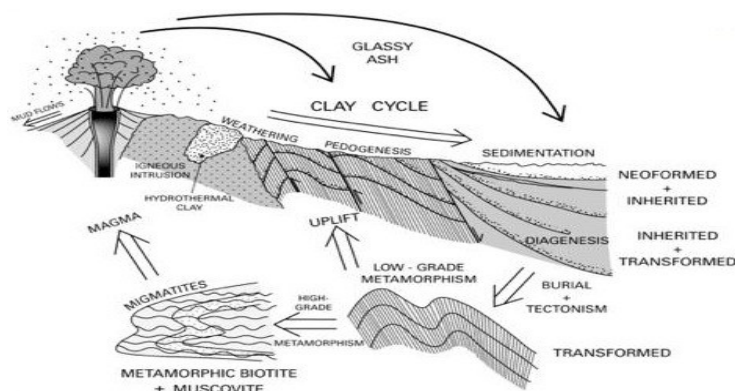


Figure 1. Process of Clay Formation [37]

## 2.3. Structure of Clay Minerals

Clay is a material of double nature, ordered at the microscopic scale and disordered at the macroscopic scale. Regarding the microscopic level, the clay minerals, belonging to the phyllosilicate family, with a structure of two-dimensional sheets stacked on top of each other [38]. These sheets can be tetrahedral or octahedral, linked together by covalent bonds (apical oxygen sharing) [35]. Moreover, the association of two or three sheets forms a layer. These layers are linked together by hydrogen bonds, which are established between the hydroxyl groups of the octahedral sheet of a layer and the oxygen atoms of the tetrahedral sheet of the adjacent layer, or by Vander Waals forces, resulting in a crystallite. The space between two parallel layers is called inter-layer space which can be empty or occupied according to the charge of the sheets. The combination of layer and inter-layer space is called "structural unit", these units are arranged between them to form the clay particles.

### 2.3.1. Tetrahedral Sheet

The tetrahedral sheet, of coordination four, consists of a superposition of elementary tetrahedrons, linked together by the sharing of the three basal oxygens (Fig.2), thus forming a hexagonal or pseudo-hexagonal of six tetrahedrons with a thickness of 3 Å. These tetrahedrons are placed in such a way that their summits are in the same direction and the bases are in the same plane. The fourth oxygen called apical oxygen, allows the connection between the tetrahedral and octahedral sheet. In each tetrahedron, the quarter atoms of oxygens or hydroxyls, forming a tetrahedral cavity whose center is occupied by cations of silicon  $Si^{4+}$ , aluminum  $Al^{3+}$ , or even Iron  $Fe^{3+}$ . The anions formed are respectively  $(SiO_4)^{4-}$ ,  $(AlO_4)^{5-}$  and  $(FeO_4)^{5-}$ . The hexagons formed by the groups of tetrahedrons, have the chemical composition  $Si_4O_6(OH)_4$  in the case of the silicon cation (most encountered) and they are indefinitely linked. On the other hand, substitutions of  $Si^{4+}$ ,  $Al^{3+}$ , or  $Fe^{3+}$  cations by low-valence cations (e.g.,  $Si^{4+}$  by  $Al^{3+}$ ,  $Si^{4+}$  par  $Fe^{3+}$ ) can occur in this sheet, which induces a deficiency of charge. This charge deficiency is compensated by compensating cations in the interlayer space [2] [19] [36] [39] [40].

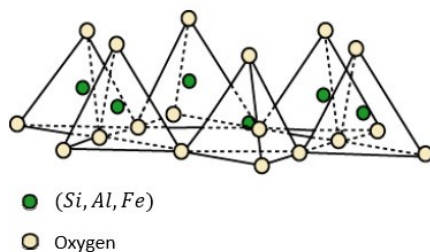


Figure 2. Representation of Tetrahedrons [41]

### 2.3.2. Octahedral Sheet

The octahedral sheet, of coordination six, is constituted by a succession of elementary octahedra, linked together by the sharing of the edges (2 summits) (Fig.3).

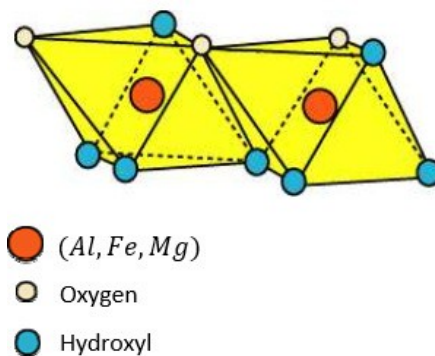


Figure 3. Representation of Octahedra [41]

These octahedra form a sheet of hexagonal or pseudo-hexagonal symmetry, but thicker than the 4 Å tetrahedral sheet. In this sheet, four apical oxygen atoms belonging to the tetrahedral sheet and two hydroxyl groups, give an octahedral configuration in which the cavity is occupied by a trivalent cation ( $Al^{3+}$ ,  $Fe^{3+}$ , etc.) or bivalent cation ( $Mg^{2+}$ ,  $Fe^{2+}$ , etc.). In most cases this cavity is occupied by aluminum and the chemical composition takes the form  $Al_2(OH)_6$ . Thus, when two cavities out of three are occupied by trivalent cations the structure is called di-octahedral  $(Al_2(OH)_6, Fe_2(OH)_6)$ ,

etc.), the third cavity being vacant. Whereas, the tri-octahedral structure ( $Mg_3(OH)_6$ ,  $Fe_3(OH)_6$ , etc.) is constituted when all the octahedral cavities are occupied by divalent metal ions. Finally, isomorphic substitutions that may exist in this octahedral sheet are  $Al^{3+}$  by  $Mg^{2+}$ ,  $Al^{3+}$  by  $Fe^{2+}$ , or  $Mg^{2+}$  by  $Li^+$ . A net negative charge was noted due to this substitution. This charge deficit is balanced by exchangeable cations [19] [36] [38] [40].

### 2.3.3. Layers, Particles and Aggregates

Three structural units can describe the systems of clay minerals namely the layer, the primary particle, and the aggregate. Regarding the layer, it is constituted by two or three layers (tetrahedral, octahedral), linked together by strong bonds. These layers are relatively flexible and deformable and they can be assimilated to a plate or a disc of thickness of approximately 1nm (Fig.4). The lateral dimensions of these layers vary between 1 and 1000 nm and the distance between them is called the interlayer space, which can be empty as well as containing hydrated alkaline and alkaline earth cations. The composition of this layer influences the physicochemical and mineralogical properties of the clay fraction. On the other hand, the superposition of 5 to 10 parallel layers forms the primary particle whose thickness varies between 8 and 10 nm and independent of the inter-layer distance. The stability of this particle is ensured by electrostatic attractive forces of Vander Waals type as well as hydrogen bonds. The third unit is the aggregate which designates a grouping of particles randomly oriented in all directions. The size of this unit varies between 0.1 and 10 microns.

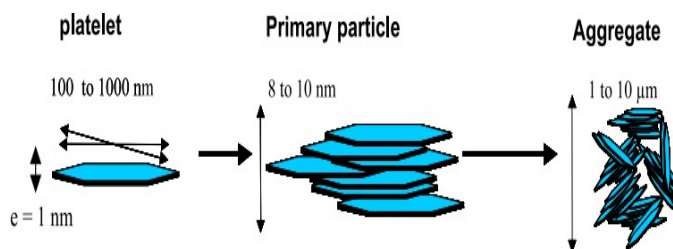


Figure 4. Multiscale Structure of a Clay Mineral [42]

## 2.4. Classification of Clay Minerals

There is a great variety of clay minerals which differ by their molecular crystalline structure and their chemical composition. Indeed, the main criteria of classification of these minerals are based on several parameters such as, the number of tetrahedral and octahedral sheet constituting the layer, the chemical constitution, the spacing of the layers, the type of cations in the octahedron and the tetrahedron, the charge of the sheet, and the nature of the species in the inter-layer space. These main criteria induce several classifications but the most classical one is the one based on the combination of the sheets which allows to distinguish the minerals of type 1:1, 2:1 and 2:1:1. On the other hand, another classification illustrates seven groups (table 1) of clay minerals namely the group of kaolinites which contains kaolinite, halloysite and serpentine. The second group is named the micas whose main minerals are illite and muscovite  $(KF)_2Al_2O_3 \cdot 3(SiO_2) \cdot 6(H_2O)$  [43]. In addition, smectites belong to the third group which includes swelling clay minerals like montmorillonite, bentonite, saponite, etc. The fourth group is called the limited-swelling clays, the best known of which are the vermiculites, without forgetting the group of chlorites. While, talc refers to the group of unfilled minerals such as pyrophyllite and talc. Finally, the group of fibrous minerals which contains palygorskite and sepiolite [30] [44] [45].

### 2.4.1. Classification based on Structure

Depending on their structure, the clay minerals are divided into four groups. The first type is the minerals of the 1:1 family, whose structure consists of the association of a tetrahedral sheet and another octahedral one (Fig.5a). The hydrogen bond, which is established between the oxygen atoms of the tetrahedral sheet and the hydroxyl groups of the octahedral sheet, confers a great stability to this structure. This stability prevents the insertion of chemical elements and water molecules into the interlayer space and thus prevents the swelling of these minerals. This gives a low basal distance of

about 7 Å. Among the clay minerals belonging to this category, we can cite as examples kaolinite, halloysite, dickite, etc. On the other hand, when the elementary layer is formed by two tetrahedral sheets surrounding an octahedral sheet, the category is called 2:1 (Fig.5b). The thickness of the layer is about 10 Å, while the basal distance varies between 9 and 15 Å depending on the elements present in the interlayer space. The isomorphous substitutions in the tetrahedral and/or octahedral sheets give a negative charge to the elementary layer. The most important minerals of this family are micas, illites, smectites, vermiculites, etc. In the case of a four-layer stack, the category is called 2:1:1 (Fig.5c). This structure is a special case of the 2:1 structure, except that the interlayer space is occupied by an octahedral layer, resulting in a basal space of about 14 Å. The last type is the inter-stratified minerals whose stacking of the sheets of different natures is more or less regular. The thickness of the sheet of this category is variable. Among the inter-stratified, we can mention, the regular inter-stratified such as corrensite (chlorite-smectite), allevardite and rectorite (illite-vermiculite) while, kaolinite-smectite, chlorite-chlorite and vermiculite-smectite belong to the irregular inter-stratified groups.

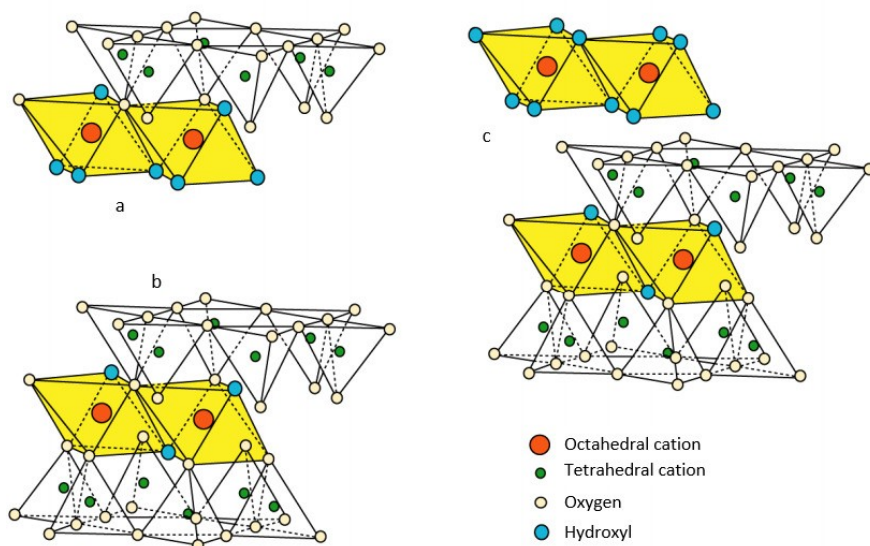


Figure 5. Types of Clay Minerals, (a): 1/1, (b): 2/1, (c): 2/1/1 [41]

## 2.4.2. Classification by Color

The presence of certain ions (Fe, Mg), even in small quantities, influences the color of clay minerals. Indeed, there are clays red, yellow, blue, pink, green, white, etc. Each color allows the valorisation of such a clay mineral in more specific applications. The most popular are the white and green clays.

### 2.4.2.1. Green Clays

This category includes clay minerals with low iron oxide contents. These are generally illites and smectites, in particular montmorillonite. The oxidative properties of these minerals encourage their use to eliminate viruses and bacteria, without forgetting their capacity to attract various pollutants. Moreover, the richness of this category in some oxides allows their valorisation in cosmetics and pharmacy. Finally, the use of green clays in the field of medicine (diarrhoea, enteric infection) is essentially due to their absorbent properties [37].

### 2.4.2.2. White Clays

In the presence of very uniform formation conditions and in an undisturbed environment, clays and clay minerals show a white color. This indicates that the material is devoid of all coloring substances. This property of absence of coloring elements makes these minerals very effective in the field of cosmetics, medicine or in ceramics. Among this category are kaolinite and smectites [46].

As for the red clays rich in iron oxides, they are generally illites. Other illites rich in iron oxides and magnesium takes a yellow color [37] [47].



Table 1. Classification of Clay Minerals

Group	Clay Mineral	Type	Chemical Formula	CEC meq/100g	SSA m <sup>2</sup> /g	Ref
Kaolinite-Serpentine	Kaolinite	1:1	$Al_4Si_4O_{10}(OH)_8$	1-15	10-20	[48]
	Halloysite		$Al_2Si_2O_5(OH)_4 \cdot nH_2O$	5-10	-	[43]
	Nacrite		$Al_2SiO_5(OH)_4$	-	-	
	Dickite		$Al_2SiO_5(OH)_4$	-	-	
	Lizardite		$Mg_3(Si_2O_5)(OH)_4$	-	-	
	Antigorite		$Mg_3(Si_2O_5)(OH)_4$	-	-	
Talc	Talc	2:1	$Mg_3Si_4O_{10}(OH)_2$	-	-	[49]
	Pyrophyllite		$Al_2Si_4O_{10}(OH)_2$	-	-	
	Serpentine		$Mg_3Si_2O_5(OH)_4$	-	-	
Smectite	Mmt	2:1	$Al_{2-x}Mg_x(Si_4O_{10})(OH)_2 \cdot (Na_x \cdot nH_2O)$	10-40	50-100	[40]
	Bentonite		$(Na)_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4 \cdot nH_2O$	-	-	[50]
	Beidellite		$(Na, Ca_{0.5})_{0.3}Al_2(Si, Al)_4O_{10}(OH)_2 \cdot nH_2O$	-	-	[51]
	Nontronite		$Na_{0.3}Fe_2(Si, Al)_4O_{10}(OH)_2 \cdot nH_2O$	-	-	
	Saponite		$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	-	
	Hectorite		$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	80-130	-	
	Sauconite		$Na_{0.3}Zn_3((Si, Al)_4O_{10})(OH)_2 \cdot 4H_2O$	-	-	
Micas	Illite	2:1	$(K, H_3O)Al_2(Si_3Al)O_{10}(H_2O, OH)_2$	10-40	50-100	[40]
	Muscovite		$KAl_2(Si_3Al)O_{10}(OH)_2$	Up to 5	-	[43]
	Phengite		$K(AlMg)_2(OH)_2(SiAl)_4O_{10}$	-	-	
	Biote		$KMg_3(Si_3Al)O_{10}(OH)_2$	Up to 5	-	
Chlorite	Phlogopite		$KMg_3(AlSi_3O_{10})(OH)_2$	-	-	
	Chlorite	2:1:1	$Al_4(Si, Al)_4O_{10}(OH)_8$	10-40	10-20	[52]
	Diocata					
	Chlorite		$(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$	10-40	10-20	
	Triocata					
	Vermiculites		$(Al, Fe, Mg)_2(Si, Al)_4O_{10}(OH)_2$	100-150	10-800	[19]
Fibrous Minerals	Palygorskite	2:1:1	$((Mg, Al)_5(Si, Al)_8O_{20}(OH)_2 \cdot 8H_2O)$	5-30	150-900	[53]
Sepiolite	$Mg_8(H_2O)_4[Si_6O_{15}]_2(OH)_4 \cdot 8H_2O$		10-45	150-900	[54]	

## 2.5. Categories of Clay Minerals

### 2.5.1. Smectites

Smectites are phyllo-silicates of type 2:1, including montmorillonite, bentonite, nontronite, saponite, etc. The general structure of smectites is of the form  $(M_x + [(AlMg)SiO(OH)] - xnH_2O)$ , with varying contents of Na, Al, Fe and Mg. This group of phyllo-silicates has an intermediate structure between the crystal and the amorphous. This structure is very close to that of pyrophyllite, except that in the case of smectites the compensating cations are hydrated and easily exchangeable, which facilitates their swelling in the presence of water. This possibility of swelling leads to designate smectites by the term of swelling clays, with an inter-layer space that can vary between 10 Å and 21 Å. In contrast, isomorphic substitutions at the interlayer space give these clays a high, permanent, negative and pH-independent charge. These clays also have a high cation exchange capacity. Moreover, soils with high concentrations of smectites can gain 30% of volume under the action of water. In addition, the remarkable plastic, colloidal, swelling, and physicochemical properties allow the introduction of these minerals in a wide range of applications such as pharmaceuticals, drilling fluids, water treatment, ceramics, papermaking and dyes [50] [55] [56] [57] [58]. The most common clay minerals in this family are montmorillonite and bentonite.

Smectite-type clay minerals were incorporated by [59] into an ethylene vinyl acetate (EVA) matrix in order to test the effect of the inorganic phase on the mechanical and thermal properties of the matrix. The surface of the smectites was treated with the organic cations cetyltrimethyl ammonium (CTAB) bromide, and dimethyldistearyl ammonium (DMDSA) bromide, which allows to modify the hydrophilic character of smectites and improves the compatibility with the EVA matrix. According to the published results the thermal and mechanical properties were significantly increased compared to

those of virgin EVA. In another study that focuses on the suitability of a Tunisian smectite to be introduced in the field of pharmaceuticals and cosmetics [6] presented a study regarding this natural clay, performing the necessary tests and calculating the physicochemical properties. The results show that the clay fraction meets the main requirements of the pharmacopoeia and the microbial tests guarantee the safety of the use in the field of pharmacy.

### 2.5.1.1. Montmorillonite

Montmorillonite remains one of the most important and widely used clay minerals in industry. It belongs to the family of di-octahedral smectites and comes from the chemical alteration of volcanic ashes induced by weathering. The structure of montmorillonite consists of an octahedral aluminium sheet sandwiched between two tetrahedral silicon sheets (Fig. 6). Other oxides may exist in the clay mineral such as potassium, magnesium, iron, manganese, etc. Concerning the isomorphic substitutions that can take place at the structural level, we can mention the substitution of  $Si^{4+}$  by  $Al^{3+}$  in the tetrahedral sheet and the substitution of  $Al^{3+}$  ions by  $Mg^{2+}$  in the octahedral sheet. These substitutions produce a negative charge that can be compensated by exchangeable cations in the interlayer space such as  $Na^+$ ,  $Ca^{2+}$ ,  $K^+$ ,  $H^+$ , etc. In addition, the bonds between the layers are weak, which facilitates the penetration of water and other molecules into the interlayer space and thus the swelling of the structure. Montmorillonite is often marketed in green but it also exists in other colors such as grey, white, etc. These brilliant adsorption and swelling characteristics as well as the remarkable physical- chemical properties are the basis for their use in many versatile applications such as pharmaceuticals, oil industry, waste containment, pollutant removal, waste water and oil purification, without forgetting the preparation of nano-composites [36] [40] [54] [60].

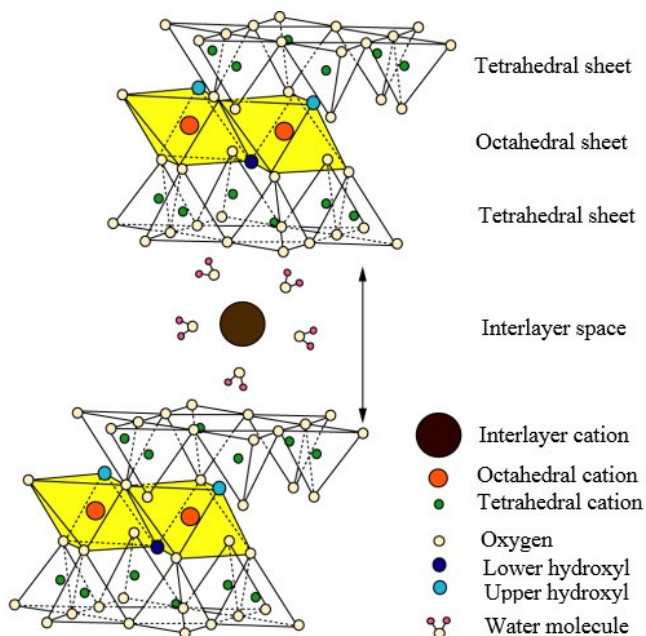


Figure 6. Schematic Representation of the Montmorillonite Structure

In a study, Alwis et al. [61], reported the use of a montmorillonite as a nanofiller to reinforce rubber compounds. According to the characterization techniques (TEM and XRD) the prepared nano-composites show that the interfacial interaction between the rubber and the inorganic phase was significantly improved. This improvement is mainly due to the use of a new method that facilitates the exfoliation of the Mmt layers in the rubber matrix. Another important application of Mmt in controlling hydrophobic drug release was exposed by [62]. The surface of Mmt was made organophilic by using the two modifiers (CTAB, Nonylphenol polyoxyethylene ether (NPE)). This organo-Mmt was combined with alginate and the results reveal that the elaborated material shows remarkable characteristics of controlled drug release.



### 2.5.1.2. Bentonite

The term bentonite was first introduced to describe a plastic, swellable, highly colloidal clay. In their natural state, bentonite deposits are often heterogeneous and may also contain other clay minerals of the smectite type such as montmorillonite and saponite, or smectite/illite and smectite/kaolinite interstratified. Bentonites are of volcanic origin, rich in sodium, calcium and magnesium. Moreover, the surface of this 2:1 mineral (Fig. 7) carries a negative charge due to the iso-morphic substitution of octahedral cations ( $Al^{3+}$ ) by lower valence cations such as  $Mg^{2+}$  and  $Fe^{2+}$ . Similar substitutions can take place in tetrahedral sheets in which  $Si^{4+}$  cations are substituted by  $Al^{3+}$  cations. Exchangeable cations such as  $Na^+$ ,  $Ca^{2+}$ ,  $H^+$ ,  $K^+$ , etc. play the role of compensation for this charge deficit.  $Na^+$  and  $Ca^{2+}$  cations are most present at the interlayer spaces of bentonite. Finally, the importance of bentonite is mainly due to its rheological, swelling, adsorption and other excellent physicochemical properties. In fact, in water, bentonite swells 10 to 15 times its original volume and allows the adsorption of 6.5 times its weight in water. These brilliant properties allow the valorisation of this type of phyllo-silicates in various industrial and environmental fields such as pharmaceuticals, cosmetics, food processing, wastewater treatment, elimination of heavy metals and organic pollutants, decoloration of oils and especially the preparation of nano-composites [36] [40] [56] [57].

A research [23] showed that ultrafiltration membranes prepared from a bentonite, were very efficient in the removal of cationic and anionic dyes. According to the authors, this type of membrane could be used in the treatment of regenerated wastewater in the textile industry.

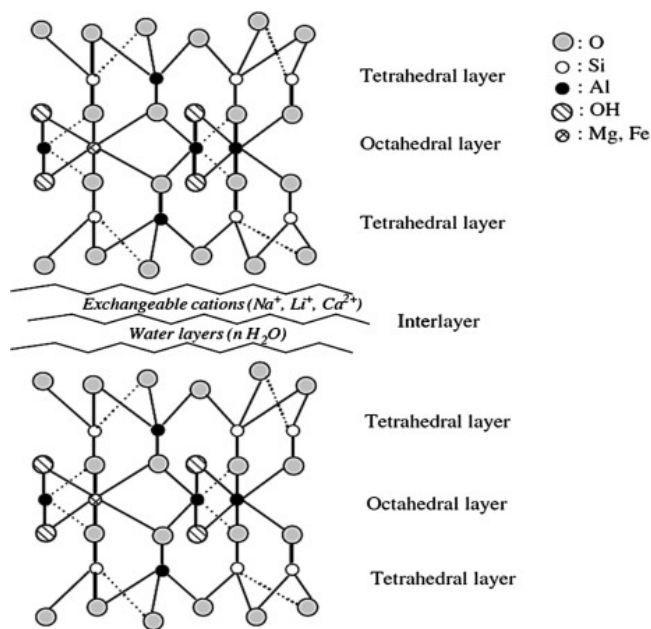


Figure 7. Schematic Representation of the Bentonite Structure

### 2.5.1.3. Illite

The alteration of potassium feldspars or muscovite, gives rise to illite. This clay mineral has a 2:1 structure, comprising an octahedral sheet centered on aluminum surrounded by two tetrahedral sheets centered on silicon (Fig. 8). It is poor in magnesium, but rich in iron and calcium. The fundamental difference between smectites and illite lies in the low exchangeability of potassium compensating cations present in the interlayer space of illite. These large cations ( $K^+$ ) provide ionic bonding of adjacent layers and block the basal distance at 10 Å.

Regarding the isomorphous substitutions for this type of clay minerals,  $Si^{4+}$  cations are replaced by  $Al^{3+}$  cations in the tetrahedral sheet. This generates a negative surface charge compensated in most cases by  $K^+$  ions or sometimes by other cations such as  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , etc. The hydration properties of the  $K^+$  ions make the illites non-swelling and therefore small amounts of water are enclosed between the layers [36] [40] [57].

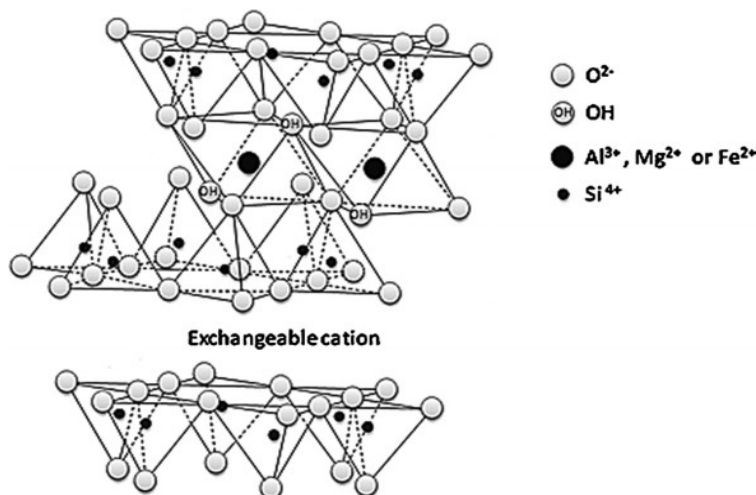


Figure 8. Schematic Representation of Illite Structure [40]

The main use of illite is the manufacture of bricks for construction. In this context, a study conducted by [10] showed that illite can be valorized in the production of high performance bricks. This suitability was verified by comparing the results obtained with reference values suitable for construction. The products tested are durability, strength and vapor permeability.

#### 2.5.1.4. Kaolinite

Kaolinite is a clay mineral formed by the alteration of aluminum-rich silicates such as feldspars and muscovite. It has a 1:1 structure, composed of a tetrahedral sheet, whose elementary tetrahedron is centered by the  $Si^{4+}$  cation, and an octahedral sheet whose elementary octahedron is centered by a  $Al^{3+}$  cation (Fig. 9). In this structure the aluminum ions ( $Al^{3+}$ ) occupy two thirds of the available cavities in the octahedral sheet, the other cavities remain empty. This clay generally takes a white color, but it can be colored by iron hydroxides in yellow or green. It is also soft, refractory and rich in silica. Furthermore, the basal distance of kaolinite varies between 7 Å and 7.4 Å. The kaolinite sheet is neutral because the negative charge of the anionic backbone is fully compensated by the positive charge of the cations centered in the tetrahedral and octahedral cavities. It is a non-swelling clay mineral with absence of exchangeable cations in the interlayer space. This confirms its low specific surface and low cation exchange capacity. This material is mainly used in the production of porcelain and ceramics. Similarly, the high absorption capacity encourages the introduction of these minerals in the purification of wastewater and other environmental fields, without forgetting their great importance in the pharmaceutical, medical and paper production sectors [14] [36] [40] [54] [57].

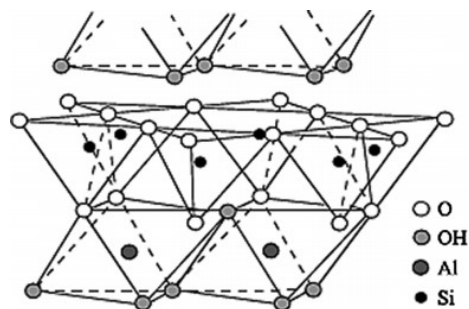


Figure 9. Schematic Representation of the Kaolinite Structure [40]

With the aim of valuing kaolinite in the environmental field, a study was presented by Jawad & Abdulhameed [63]. In this study, the authors investigated the ability of an Iraqi red kaolin clay in the adsorption of methylene blue dye. The results obtained reveal the possibility of introducing this clay mineral in the treatment of wastewater and the adsorption of dyes such as methylene blue. A similar study was conducted by Karim et al [64] in which they tested the capacity of a natural clay from the Safi region in Morocco in the removal of the dye Basic Red 46. The kaolinitic phase (29%) was more predominant in the clay fraction than illite (18%). It appears from the results obtained that the clay was effective in the elimination of the dye with an efficiency that can reach 95%. The maximum adsorption capacity of this dye was 54 mg/g. In another very important application, kaolinite has been used by Bouna et al. [65] for the synthesis of mesoporous geopolymer materials with high dye adsorption capacity. The measurement of the physico-chemical properties, in particular the specific surface, shows an improvement compared to pristine clay. In addition, the efficiency of dye removal shows a significant increase, which encourages the use of this type of new material in environmental applications.

### 2.5.1.5. Chlorite

Chlorites have a 2:1:1 structure (Fig. 10) with a basal spacing of 14 Å. The basal spacing of chlorite remains unchanged after ethylene glycol treatment and shows no decrease in the case of heating to 500°C [66]. This structure is very similar to that of illite and smectite, with the presence of a stable hydroxide (magnesium, iron, aluminum) sheet in the interlayer space. The silicon of the tetrahedral sheet can be substituted by the cation  $Al^{3+}$  or  $Fe^{3+}$ . In addition, the strong bonding produced between the hydroxyls makes the chlorites thermally stable. The disadvantages of this type of clay mineral are the lack of swelling capacity and the difficulty of detection.

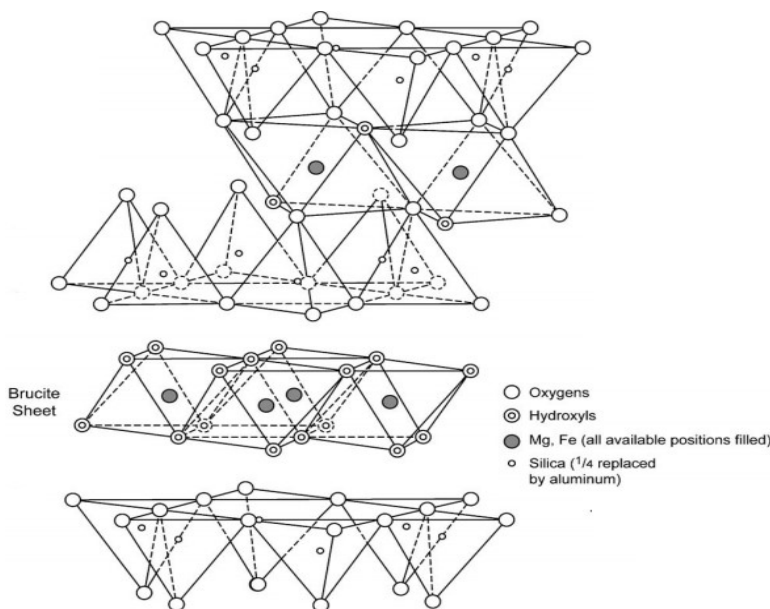


Figure 10. Schematic Representation of Chlorite Structure [66]

### 2.5.1.6. Vermiculite

The vermiculites present a family of phyllo-silicates of type 2:1, characterized by the presence of hydrated compensating cations  $Mg^{2+}$  or  $Ca^{2+}$  at the level of the inter-layer space without forgetting the presence of water molecules. The origin of this material is essentially volcanic, formed by the hydration of basaltic minerals. On the other hand, it can be formed by the alteration of illite or muscovite, which gives a di-octahedral vermiculite. In addition, a tri-octahedral vermiculite may be the origin of the alteration of chlorites. Structurally, vermiculite is similar to smectites except that

vermiculites have a larger charge deficit. The properties of dilatation to the heating and the lightness of this material make it very useful in the field of the construction as insulating without forgetting their importance in the preparation of nano-composites [37].

Júnior et al. [33], preferred to test the influence of the presence of vermiculite in a poly(hydroxybutyrate)/ poly(ethylene) glycol (PHB/PEG) mixture. The organo-vermiculite was elaborated by cation exchange with an alkyl quaternary ammonium and then inserted into the PHB/PEG matrix by casting. The thermal characterization of the prepared nano-composites shows an improvement of the thermal stability of the matrix at low vermiculite contents. According to the authors, vermiculites can be valorized in packaging and medical devices.

### 2.5.1.7. Fibrous Clays

This family of clays includes sepiolite and palygorskite. They have a fibrous structure formed by ribbons and not swelling in the presence of water. These ribbons are stacked alternately and are not superposed, which allows water molecules and exchangeable cations to fit into the empty spaces. The pseudo-sheets are formed by hexagonal planes constituted by the oxygen atoms. The structure of the fibrous clays comprises two tetrahedral plans surrounding two discontinuous octahedral plans, whose tops are occupied by the oxygen and hydroxyl atoms. The discontinuity of these octahedra forms ribbons (Fig. 11). Indeed, the number of octahedrons in each ribbon allows to distinguish palygorskite and sepiolite. Moreover, the fibrous structure and the size of the particles, give to these minerals large specific surfaces, great capacity of water adsorption, specific rheological and colloidal properties. This allows the valorisation of these materials in various industrial fields without forgetting the ability to produce inorganic-organic nano-composites [53] [67] [68].

Palygorskite, also called attapulgite, which contains 5 octahedra in each ribbon, is a clay mineral of the silicate family rich in magnesium and aluminum. Regarding the isomorphic substitutions, a substitution of  $Al^{3+}$  by  $Fe^{2+}$  can be noted at the level of the octahedral pseudo-sheet. Whereas the substitutions of  $Si^{4+}$  by  $Al^{3+}$  at the level of the tetrahedral pseudo-sheet are limited. The diversified structure of palygorskite, contains two types of water one zeolitic ( $H_2O$ ) contained at the level of rectangular channels and the other of crystallization ( $OH_2$ ) bound to the edges of the ribbons. This type of fibrous minerals takes an important place in several fields such as oil decoloration, water purification, paper making, oil-water separation [54,60]. On the other hand sepiolite contains eight octahedra in each ribbon. In addition, the orthorhombic crystal structure contains two tetrahedral pseudo-sheets enclosing an octahedral pseudo-sheet of magnesium. These materials are rich in magnesium and do not swell in the presence of water, but they possess adsorption power, which encourages their introduction in decolorization, filtration, drilling fluids and other applications requiring thermal insulation [14] [54] [57].

The ability of sepiolite was tested by [69] in an attempt to adsorb the antibiotic oxytetracycline (OTC). The clay mineral was treated by the combination of two modifiers one cationic (CTAB) and the other anionic which is sodium dodecyl sulfonate (SDBS). The results show that sepiolite was able to effectively remove CTAB from water.

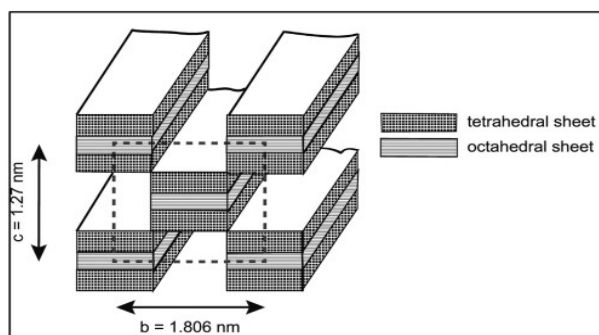


Figure 11. Arrangement of the sheets of a fibrous clay [53]

## 2.6. The Accessory Minerals of Clays

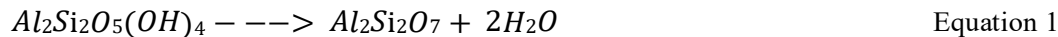
In their natural state, clays and clay minerals have a heterogeneous composition which gathers clay minerals as well as other non-clay minerals. Indeed, sometimes the presence of these impurities, especially in small quantities, can improve certain properties such as plasticity, shrinkage during firing, coloring, etc. On the other hand, some impurities can be harmful, in particular for the physico-chemical properties, when they are in notable quantities. Among these associated minerals, we can mention silica as a mineral often present in clay fractions. This tectosilicate can be detected in three crystallized forms such as quartz ( $SiO_2$ ), tridymite and cristobalite. It helps to decrease the plasticity of very fat clays and reduce the shrinkage during firing. Other poorly crystallized and hydrated forms of silica can be detected in the form of silix. Iron oxides and hydroxides are other impurities that may exist in the clay mass, they are responsible for the coloring of these minerals as well as the reinforcement of their mechanical properties. Minerals of this type of the most famous impurities are hematite ( $\alpha Fe_2O_3$ ), maghemite ( $\gamma Fe_2O_3$ ), magnetite ( $Fe_3O_4$ ), goethite ( $\alpha FeOOH$ ), lepidocrocite ( $\gamma FeOOH$ ), limonite ( $Fe_2O_3 \cdot 3H_2O$ ). In addition, iron sulfide can also be detected as an associated mineral in the form of pyrite or marcasite, it allows clays to take on a green color. The presence of large amounts of iron sulfide can be harmful to the clay mineral. Another type of associated minerals that we can meet are carbonates in the form of calcite ( $CaCO_3$ ), dolomite ( $Ca, Mg)(CO_3)_2$ , aragonite, magnesite ( $MgCO_3$ ), siderite, etc. Calcite and dolomite are the most frequently encountered in clays without forgetting impurities such as gibbsite, titanium oxides, feldspar ( $K_2O)(SiO_2)_6(Al_2O_3)$  [70] and manganese dioxide. The feldspars react with the lime in very alkaline medium to give the hydrated calcium silicates. Finally, the presence of the organic matters (pollens, spores, amorphous matters, etc.), confer to the clays the gray, brown, black, veil, etc. colors. In addition, they can increase the plasticity of clay minerals. The origin of these organic materials is generally the decomposition of plants. One of the best techniques to detect these impurities is X-ray diffraction (XRD). Table 2 shows the different peaks of impurities detected by XRD [5] [8] [9] [49] [71] [72] [73] [74].

## 2.7. Heat Treatment of Clay Minerals

The internal structure of clays and clay minerals confers different types of molecules and groups of molecules as the case of the hydroxyl group (OH) and the water molecules. Indeed, the increase of the temperature generates thermal transformations at the level of this structure. These transformations are linked to physical phenomena, detected during the firing of clay minerals. These phenomena have a great importance on the properties of use and the physicochemical properties of the final product.

Therefore, understanding the source of all thermal transformations is a decisive step to improve the quality of elaborated products. Generally, these phenomena reveal peaks, representing in the case of clay minerals, water loss as well as structural reorganization. We distinguish four types of water that can be present in the structure of clay minerals. The first type is the water physically adsorbed on the surfaces of the sheets. Another type of water molecule, which are strongly bound with the compensating cations, is called intercalary water. Without forgetting the zeolitic water which can be present within the structure of clay minerals of fibrous type (palygorskite, sepiolite). The last type is the crystalline water, which results from the dehydroxylation of groups (-OH) in the octahedral sheet. In the temperature range  $80 - 400^\circ C$ , the phenomena that can occur are the dehydration of the physisorbed water as well as the degradation of the organic matter. Above  $200^\circ C$ , we can observe the departure of water bound to the compensating cations potassium ( $200^\circ C$ ), calcium ( $230 - 250^\circ C$ ).

This resistance of this type of water is probably due to the formation of hydrogen bonds with the atoms of clay minerals. In the case of smectites the phenomenon of water departure can be recorded even at  $250^\circ C$  for the water molecules trapped between the sheets. The zeolitic water evaporates between  $150$  and  $200^\circ C$ . However, in the temperature range  $400 - 750^\circ C$  several events can occur, in particular the dehydroxylation of some clay minerals like kaolinite and illite as well as the transformation of quartz. This phenomenon of dehydroxylation breaks the hydroxyl groups ensuring the cohesion between the octahedral and the tetrahedral sheet. The dehydroxylation temperature of an ordered kaolinite is about  $600^\circ C$  while that of a disordered kaolinite is lower ( $450 - 550^\circ C$ ). The increase in temperature leads to a progressive amorphization transforming the kaolinite into meta-kaolinite according to the following reaction:



Dehydroxylation of illite generally occurs at temperatures between  $550$  and  $650^\circ C$ . At about  $573^\circ C$

quartz shows an allotropic transformation from quartz  $\alpha$  to hexagonal  $\beta$ . Carbonates, especially calcium carbonate ( $CaCO_3$ ) decompose in the temperature range  $750^\circ C$  to  $850^\circ C$  to give lime ( $CaO$ ). In this temperature range we also note the dehydroxylation of smectites at about  $850^\circ C$ . Above  $850^\circ C$ , a structural reorganization, due to the demixing of meta-kaolinite into silica or alumina rich micro-domains, is observed around  $950^\circ C$  and a spinel structure or mullite seeds may appear. In this temperature range the non-calcareous clays show a liquid sintering giving to the final materials a structure bound by a glassy phase. Whereas, this glassy phase is absent in the case of calcareous clay minerals [5] [71] [73] [82] [83] [84].

Table 2. The Main Associated Minerals Detected in the Clays

Minéral Argileux	Pays	Minéral Associé	$2\theta(^{\circ})$	Dhkl (Å)	Réf
Argile naturelle	Morocco	quartz	26	3.42	[22]
Bentonite	Cameroon	quartz	26.47	3.36	[11]
Natural clay	Nigeria	quartz	26.4	3.37	[75]
Palygorskite	Senegal	quartz	26.5	3.36	[53]
Bentonite	Cameroon	quartz	21.97	4.04	[11]
Argile naturelle	Cameroon	quartz	26.7	3.33	[17]
palygorskite	China	quartz	26.7	3.33	[76]
Raw clay	Burkina Faso	quartz	26.66	3.34	[70]
Smectite	USA	quartz	20.88	4.25	[77]
Raw clay	Morocco	quartz	20.78	4.27	[78]
Unmodified Mmt	Scotland	quartz	20.78	4.27	[79]
Natural clays	Morocco	quartz	20.90	4.24	[80]
Smectite	USA	quartz	26.66	3.34	[77]
Smectite	USA	quartz	50.36	1.81	[77]
Raw clay	Morocco	quartz	36	2.49	[81]
Raw clay	Morocco	quartz	67.7	1.38	[78]
Argile naturelle	Morocco	calcite	29.5	3.02	[22]
Raw clay	Morocco	calcite	29	3.07	[81]
Raw clay	Morocco	calcite	26	3.42	[81]
Raw clay	Morocco	calcite	39	2.30	[81]
Raw clay	Morocco	calcite	29.4	3.03	[78] [80]
Organo-Mmt	Scotland	calcite	29.5	3.02	[79]
Raw clay	Morocco	calcite	23.1	3.84	[78]
Raw clay	Morocco	calcite	39.5	2.27	[78]
Bentonite	Cameroon	Muscovite	21.24	4.18	[11]
Bentonite	Cameroon	Muscovite	51.05	1.78	[11]
Bentonite	Cameroon	Muscovite	54.95	1.67	[11]
Raw clay	Morocco	Muscovite	8.92	9.9	[80]
Raw clay	Morocco	Muscovite	8.88	9.95	[80]
Smectite	USA	Calcium sulfate	11.62	7.6	[77]
Smectite	USA	Calcium sulfate	20.72	4.28	[77]
Smectite	USA	Calcium sulfate	29.16	30.6	[77]
Raw clay	Burkina Faso	goethite	36.8	2.44	[70]
Raw clay	Burkina Faso	hematite	33.26	2.69	[70]
Raw clay	Morocco	dolomite	32	2.79	[81]
Palygorskite	Senegal	dolomite	30.98	2.88	[53]



## 2.8. Detection of Clay Minerals by XRD

The diversified chemical composition, the structural disorder and the great structural diversity make the characterization of clay minerals very difficult. Indeed, the X-ray diffraction technique has become more and more one of the most introduced techniques to analyze qualitatively and quantitatively these minerals [85]. It is most preferred for researchers over any other technique, such as FTIR and TEM [86]. In order to simplify the distinction between clay minerals present in a given clay fraction, purification is desirable in order to concentrate these minerals and have intense peaks sensitive to small variations under specific treatment applied. The principle of the distinction by XRD is based mainly on the calculation of the basal distance of the planes (hkl). In addition, the interaction with the applied treatment differs from one clay mineral to another. In this context, Bergaya et al. [2], presented four specific tests that help to distinguish between clay minerals, based on the evolution of the inter-layer distance. The first test aims to have a reference diagram, by drying the slide in the air. This treatment is called the normal test from which we can judge the displacements recorded in the other tests. On the other hand, the identification of swelling clay minerals requires a treatment with ethylene glycol (EG), this test is used to place the blade in an atmosphere of EG for a given period. The third test is based on the principle of heating the blade to 300 or 500°C. The choice of this test is justified on the one hand by the possibility of distinguishing the kaolinitic phase which disappears at about 500°C. On the other hand, the closure of vermiculites and smectites at 10 Å in the case of their treatment at 500°C, simplified the identification of these two phases. This test can also be used to identify inter-stratified minerals containing vermiculite or smectite. For the determination of kaolinitic interlayers, heating the mineral between 100 and 350°C is the most efficient because it does not destroy the kaolinite and hydrates the smectite and vermiculite family in a reversible way. This treatment dehydrates the halloysites into metahalloysites. Finally, the distinction between kaolinite and chlorite requires the combination of another test with the 500°C heating test. The hydrazine-mono-hydrate treatment is the most appropriate, because it allows the swelling of the kaolinite without influence on the structure of the chlorite, and thus the distinction between the two phases, based on the peak located at 7 Å. Table 3 represents the displacements undergone by the different clay minerals when exposed to these treatments [66] [87] [88] [89].

## 2.9. Purification

The increasing introduction of clay minerals in the manufacture of advanced materials requires the mastery of different purification and enrichment steps. These processing steps are also necessary to study the different properties of clay minerals and allow a secure access to their characteristics. Indeed, sometimes even small quantities of these associated materials can strongly influence the mechanical, colloidal and rheological physicochemical properties of clays. For example, the presence of silica in large quantities can prevent the swelling and dispersion of clay minerals. In addition, these organic and inorganic materials can make mineralogical identification difficult. Several studies have shown that particle size fractionation of clays often provides more accurate information than could be obtained by characterizing the raw clay.

Table 3. Reactions of Clay Minerals with Some Specific Treatments

Traitement	Normal			EG			Heating à 490°C			Ref
	(001) Å	(002) Å	(003) Å	(001) Å	(002) Å	(003) Å	(001) Å	(002) Å	(003) Å	
Illite	10	5	2.8	10	5	2.8	10	5	2.8	[5]
Smectite	12-15	-	-	17	-	-	10	-	-	[87]
(Mg <sup>2+</sup> , Ca <sup>2+</sup> )										[89]
Kaolinite	7	3.5	2.3	7	3.5	2.3	Disappearance of the Mineral			[90] [91]
Vermiculite	14	-	-	14	-	-	10	-	-	[92]
Chlorite	14	7	3.5	14	7	3.5	14	7	3.5	
Palygorskite	10.4	-	-	10.4	-	-	10	-	-	
Sepiolite	12	-	-	12	-	-	10	-	-	

In addition, despite the development of the technology and the tools of purification we cannot achieve more than 90% [2]. Generally, the purification operation to be applied to a given clay fraction differs according to the elements present in the source rock. Firstly, natural clays must be crushed using a specific mortar (agate mortar), which avoids contamination of the chemical composition. The sieving of the powder obtained helps to eliminate large particles (quartz, carbonates, etc.) and facilitates the purification process. Then, if the sample contains organic matter, the clay fraction must be attacked with hydrogen peroxide. The estimation of the presence of organic matter is based on the color of the rock or by the X-ray diffraction technique. This technique also helps to test for the presence of carbonates, the removal of which requires treatment with acid solutions such as acetic acid. This attack serves to liberate and extract the clay particles embedded between the carbonate crystals. Carbonates can also be detected by a chloride acid test. Sometimes treatment with acetic acid does not allow complete removal of carbonates, so treatment with HCl is desirable especially in the case of calcareous samples. During this operation, one must be careful to avoid local overconcentration of the acid. In addition, when the PH paper indicates a pink color, the carbonates are completely dissolved. Finally, the purified clay fraction was recovered after a series of washing by centrifugation [6] [27].

### 3. Discussion

The diversification of the production sources of the clay minerals allows to produce minerals with varied structures and thus of chemical composition and versatility. This versatility gives to these minerals different behaviors when they are subjected to thermal, mechanical and rheological tests, etc. The polyvalence of the chemical composition also allows these minerals to interact differently with other organic and inorganic substances. The valorisation of such a clay mineral in a given field depends strongly on the mineralogical composition as well as the physico-chemical properties. For example, to introduce a clay mineral in the removal of pollutants and intercalation of substances at a level of the interlayer space, researchers prefer swelling clay minerals with high cation exchange capacity such as smectites, vermiculites and fibrous clays. Illites show a remarkable firing behavior, which encourages the incorporation of these minerals in the field of construction. Moreover, the richness of clay minerals in some specific oxides (e.g. Mg) encourages their use in pharmacy and cosmetics. On the other hand, the color of clay minerals can be a decisive element in the choice of such a mineral for such applications. Regarding the associated minerals, the studies show that quartz, calcite and feldspar are the most encountered and their presence in the structure remains among the criteria taken into account in the selection of minerals for such an application. According to the literature, the response of clay minerals to the tests carried out differs from one mineral to another, which facilitates the distinction between minerals. Indeed, smectites are the only clay minerals that show swelling in the case of EG treatment. Moreover, heating to about 500 °C destroys kaolinite and facilitates its detection in the clay fractions. The latter tests hydrate clay minerals of the 2:1 family, especially smectites and vermiculites. The peak related to these minerals blocks at 10 Å after heating to 500°C. Illites and chlorites do not react to these tests. Finally several purification processes have been reported in the literature. These processes are a function of the impurities associated to these minerals. Therefore, a preliminary sieving considerably reduces the quantity of these associated minerals and facilitates the purification operation.

### 4. Conclusion

The present literature review was interested in the presentation of clay minerals, their definition, their origins and their structures. Then, the focus was put on the criteria of classification of these minerals and the important categories met in nature without forgetting their possible applications. In another part, this article demonstrated the advantages and disadvantages of the associated minerals often detected in the clay fraction. The response to heat treatment, the techniques used to detect the minerals are also exposed in this work. Finally, the last part clarified the importance of the purification processes and the steps to follow to achieve better results.

The diversification of the sources and the climates of production of clays and clay minerals gives rise to different structures and categories of clays. We have distinguished three structures which are 1:1, 2:1 and 2:1:1 whose properties differ from one type to another. Smectites remain among the most employed minerals due to their remarkable properties (absorption, swelling, CEC, etc.). The illites also present interesting properties in the field of construction. Therefore, the properties presented by

each mineral determine the field of valorisation. In addition, fibrous clay minerals are also an important category due to their brilliant properties, especially in the construction and environmental field. On the other hand, the removal of associated minerals remains a challenge for researchers and therefore purification is desirable. This purification operation is a function of the quantity and quality of impurities present. Finally, the swelling test by EG and the heating at 500°C remain among the most suitable treatments for the distinction between the clay minerals constituting a clay mass. Indeed, the EG test swells only the smectites to 17 Å, but heating to 500°C destroys the kaolinite and decreases the basal distance of the smectites and vermiculites to 10 Å. The other minerals remain unchanged when these tests are applied.

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