Positive and Negative Interactions of Clay and Clay Minerals with Human Health

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By

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FOREWORD

CELSO GOMES

This book is mainly addressed to upper-level undergraduate, graduate, postgraduate students and researchers doing studies and research, specifically in Geological, Biological, Chemical, Materials, Engineering, Environmental, Pharmaceutical, Cosmetics, and Public Health, all fundamental background scientific fields to accomplish the book´s object – The Positive and Negative Interactions of Clay and Clay Minerals with the Human Health –, because clay and clay minerals are natural or modified nanosized particles, of common interest to all the aforesaid sciences.

The motto of this book is to provide students and researchers worldwide with updated scientific data, generic and specific, of both positive and negative interactions of *minerals latu sensu)* on human *health and living quality*. This book intends to gather, using an integrative mode, most of what is presently known of the significant contributions provided by various scientific and technological sources about the interactions aforesaid referred to. The scientific, historical, and technical references thoroughly disclosed in this book, although numerous, are undoubtedly incomplete. Therefore, our best excuses for the missing references.

This book can be classified as an updated, comprehensive review of the specific natural and modified properties of clays and clay minerals, and their most relevant applications in Health Sciences, especially in Human Health.

Several chapters acknowledge the mainly positive interactions between clay and clay minerals and human health through traditional internal and topical uses and novel applications, such as biomedicine.

Unlike in other sciences, the enormous diversity of clay and clay minerals in compositional (physical, chemical, and physicochemical) and technological terms, as well as the enormous diversity of clay fields of interest and applications, might justify the lack of consensus on clay and clay mineral definitions that will be shown in one chapter of this book.

Clay and clay minerals, whenever used, for example, in therapeutics, pharmaceuticals, and cosmetics, are currently part of formulations administered both orally and topically in various forms, such as patches, pastes, tablets, powders, capsules, emulsions, suspensions, creams, and ointments. They have undergone little or substantial scientific and technical processing and modification for such purposes.

Organoclay, i.e., organically modified natural clay or natural clay mineral, and the organophilic surfaces generated, are efficient sorbents of various types of drugs, such as antibiotics, photosensitizers, disinfectants, and pesticides. Nano clay-reinforced polymer matrix composites incorporating 1-5% of well-dispersed exfoliated nano clay enable the creation of hybrid composite materials with enhanced mechanical, thermal, and electrical conductivity. Flame retardancy, food packaging, and automotive are essential fields of application for these clay-polymer nanocomposites, which can decontaminate and remediate aqueous systems and purify and remediate contaminated soil.

As low-cost adsorptive materials, clays and clay-based materials are used to control environmental pollution, particularly in water and soil resources. Also, mainly since the last decade and as output of scientific and technical developments has increased, the so-called *clay-drug hybrid materials* and *clay-drug delivery systems* are a matter of extensive biomedical research and application both as formulation additives and as drug carriers using a variety of routes, including oral, transdermal, and local administration, drug encapsulation, the formation of antimicrobial surfaces, and the release of active substances.

The so-called biominerals are organic-inorganic hybrid nanocomposites defined as multicomponent compounds having at least one of their organic (biological) and inorganic components in the submicronic and more usually in the nanometric size domain, in which biopolymers (chitin, collagen, other sugars and proteins) are smartly associated with a wide variety of inorganic compounds such as clay minerals, calcium carbonate, calcium phosphates, calcium oxalates, silica, iron oxides.

The first produced organic-inorganic materials were clay-based hybrids. Man’s first achievements regarding organo-mineral hybrid materials are often associated with ancient paintings and frescoes.

Clay nanoparticles can provide unique contributions, such as overcoming hydrogel limitations in recent developments of clay-based nanocomposite hydrogels, emphasizing biomedical applications, with significant interest in three-dimensional (3D) scaffolds. The multifunctionality of clay nanoparticles, combined with the dynamic and structural characteristics of hydrogels, has proven useful across different fields of medicine. This combination synergizes with other materials and enables engineers to create nanocomposites with a broad spectrum of functionalities. The presence of clay particles in nanocomposites provided and enhanced the capacity for structural support necessary for the regeneration of new tissues by improving load-bearing ability, slowing degradation, and controlling the microstructure and network porosity, which influence cell migration and the diffusion of oxygen and nutrients.

Clay and clay minerals, within all minerals, due to their ubiquity at or close to the Earth´s surface and easy extraction and processing, also due to the diversity and crystal-chemical specificities of their essential constituents-clay minerals-, and yet due to their specific physical, chemical and physicochemical properties, are the most acknowledged along the human history regarding the most diverse and valuable studies and applications from geological to health sciences, first on an empirical basis, and later on a scientific basis. In pharmacy and cosmetics, they are active and excipient ingredients; in human health, they are therapeutic agents used for internal and topical applications. Nowadays, it isn't easy to imagine human living standards and civilizational progress without nanotechnologies that require nanomaterials, and clay minerals are fundamental natural nanomaterials that can deliver substantial societal and economic benefits.

Clay science is multidisciplinary, with clay and clay minerals as objects of study, and their properties and applications. It receives important contributions from other sciences or disciplines, such as mineralogy, crystallography, chemistry, geochemistry, sedimentology, geology, soil science, soil mechanics, colloid chemistry, materials science, biology and biotechnology, medicine and public health, pharmacy, geo-engineering, and environmental engineering. As in other sciences, the objects of study required a definition that would deserve general acceptance among all those interested in it, both theoretically and practically, despite the reckoned historical evolution of the concepts.

Clay Science is less than one hundred years old. Along with its evolution, the definition of clay and clay mineral, one of the objects of this science, has shown significant changes that have been proposed, developed, and adopted by several authors individually and by National and International Clay Groups or Clay Societies. Such changes were based not only on essential but selective criteria very much dependent upon the authors' education, academic background, and professional experience, for instance, soil scientists, mineralogists, geologists, or materials scientists.

Novel scientific and applied fields for clays and clay minerals are being developed, mainly through particle surface modification, employing methods of thermal activation, acid and alkali activation, and organic intercalation and activation. Clay particle nano-size, particularly clay particle surfaces, which are naturally hydrophilic, can be turned into hydrophobic, a promising modification in studies and applications in environmental protection and biomedicine.

There is a growing interest in mineral additives in animal feed. Commercial-grade clays such as bentonite, kaolin, and sepiolite, which are characterized by high adsorption capacity and non-toxicity, are used as feed additives for all animal species (beef and dairy cattle, poultry, pigs, etc.), acting, for instance, as *mycotoxins binders*. The primary function of clay-based feed additives is to bind toxic metabolites and *mycotoxins* without being detrimental to animal health.

Clay and clay minerals can play essential roles in environmental protection, in general, and in improving drinking water quality and in rehabilitating metal-polluted soil, in particular.

Climate change and the role of clay and clay minerals in it are being investigated through the capture and storage of CO_2 emissions that cause the greenhouse effect.

Presumably, clay-organic hybrid nanocomposites were spontaneously formed in nature, assuming that clay minerals, particularly the swelling species, can accommodate organic species in the interlayer spaces. Such hybrid clay-organic intercalates could have played an essential role in the hypothetical abiogenesis process that led to life's origin around 3.8 Ga. Processes involving clay, whether suspended in shallow sea waters of warm coastal areas or formed in submarine and continental hydrothermal systems, have been the focus of much research on life´s origin. Life’s origin is an enigma so much discussed so much but not yet revealed.

CHAPTER 1

CLAY AND CLAY MINERAL DEFINITIONS

CELSO GOMES

1.1. Background

Both AIPEA (Association Internationale Pour L´Étude des Argiles) and CMS (Clay Minerals Society) Nomenclature Committees have been involved over the years in the definition, classification, and terminology of clays, clay minerals, related materials, and specific properties. For instance, the AIPEA Nomenclature Committee has proposed, over the years, some reports with recommendations: Pedro 1970; Brindley and Pedro, 1970, 1972, 1976; Bailey *et al.*,1982,1986; Bailey, 1980, 1989; Guggenheim *et al.*, 1997; Guggenheim *et al.*, 2002; and Guggenheim *et al.*, 2006.

Recommendations have been proposed, for instance, in Joint Reports of AIPEA and CMS Nomenclature Committees: Guggenheim and Martin, 1995, 1996; and by the CMS Nomenclature Committee: Brindley *et al.*,1968; Bailey *et al.*, 1971a, 1971b; Bailey *et al.*,1979; and Martin *et al.*,1991.

Despite continued efforts by the Nomenclature Committees, the definitions of clay and clay minerals remain contentious. Such can be understood because, for instance, clay is most probably the mineral resource exhibiting the highest variability in geologic, textural and mineralogical terms, as well as the most diverse applications, either the professionals or the disciplines interested in clay try to enhance in its definition the property or properties of clay which are relevant for a particular application, situations well expressed in Gomes (1988, 2002) and in Rautureau *et al.*, (2017):

1 - *Geologists* consider *clay* as a geologic product of generalized occurrence and of fine granularity that occurs at the surface or near the surface of the Earth, and that is formed at the interfaces between the Earth crust and the atmosphere, hydrosphere, and biosphere as the result of the mechanical and/or chemical alteration of rocks; also *geologists* classify clays based on their origin: residual or primary and sedimentary or secondary, and their occurrence: marine, alluvial, glacial, aeolian, etc;

2 - *Mineralogists* consider *clay* as an aggregate or mixture of minerals of fine granularity, consisting principally of clay minerals, which are hydrous phyllosilicates based on Si, O, OH, and H_2O, and elements such as Al, Mg, Fe, K, Ca, and Mg can participate in their composition.

3 - Petrologists consider clay a rock, generally weakly consolidated, formed by very fine mineral particles that are non-identifiable to the naked eye or even with a magnifying glass.

4 - Sedimentologists consider clay a granulometric term that identifies the sediment fraction composed of particles with an e.s.d (equivalent spherical diameter) less than 2µm.

5 - Civil and geotechnical engineers consider clay to be less than a 4µm fraction of the soil and classify clays or clayey soils as swelling or non-swelling, soft or hard**,** electing the most relevant properties that should be considered when the foundation of housing and public construction works is based on them.

6 - *Ceramists* consider *clay* as a natural geologic material that, whenever mixed with water in adequate quantity, becomes plastic, allowing its workability and shaping, and that hardens and maintains the acquired shape after drying or firing; ceramists classify clays based on their plasticity, firing properties and uses: low plasticity, medium plasticity, high plasticity; white-burning, red-burning, high or low refractory; common clay (to manufacture construction or structural products, such as brick and roof tile, and pottery clay; special clay (China clay, fire clay, flint clay, ball clay, bauxitic clay, fibrous clay).

7 - *Pedologists* consider *clay* as the active fraction of the soil that comprises particles of colloidal size (<0.1µm) resulting from the action of pedological processes upon rocks and which are responsible for the reversible fixation of cations and anions, such as NH_4^+, K^+, PO_4^{3-} and NO_3^-)*,* etc.

8 - Agronomists consider clay the colloidal fraction of the soil, which is important in terms of structure, texture, and composition for vegetal fixation and growth.

9 - Even the non-educated consider clay a type of earth that gets slippery when wet and can be shaped.

1.2. Clay and Clay Mineral Definitions: Discussion

From the aforesaid clay concepts, concepts in science can be expressed differently by people from different educational backgrounds and experiences. Concepts can also evolve.

Gomes (2002) has distinguished three fundamental concepts in the field of clay science: *clay*, *clay mineral*, and *clayey geologic material* or *clay-bearing geologic material*, as follows:

Clay is *"a natural material, mostly composed of fine-grained minerals, mainly hydrated phyllosilicates the so-called clay minerals; clay, in general, exhibits plastic behaviour and hardens after drying or firing; associated with clay minerals other minerals and non-minerals (inorganic and organic cryptocrystalline or amorphous compounds) can occur in clay".*

Clay minerals are *"phyllosilicates, essentially hydrous aluminosilicates, fundamental constituents of clay and accessory constituents of clayey rocks and clayey soils, particularly responsible for clay plasticity and hardening after drying and firing".*

Clayey materials or clay-bearing geologic materials are "*those geologic materials, such as shale, slate, phyllite, marl, marly limestone, lapilli tuff, hyalloclastic tuff, and soils that could bear clay minerals in significant quantity; despite of some of these materials do not exhibit plasticity in the natural state they could be used, for instance, as ceramic raw materials after being finely ground or blended with other adequate minerals".*

According to Moore (1996), clay is used as a mineral, a grain or particle size term, and a *rock term*.

In sedimentology, independent of the presence or absence of clay minerals, the sediment with the size fraction less than 2µm size is named *clay fraction.*

Paquet and Clauer (1997) classified clays into three groups: low-, intermediate-, and high-activity. This classification was based on the electrical charge (z) of the structural unit cell, and they have defined kaolin, represented principally by kaolinite, "*as low-activity clay, having a low layer charge, nearly zero*".

Distinctive parameters for clay and clay minerals should be considered in their concepts, all well summarized by Bergaya and Lagaly (*In:* Handbook of Clay Science, Elsevier, 2006):

For *clay*: "*Natural*; *fine-grained (<2µm or <4µm)*; *phyllosilicates as main constituents*; *plastic*; *hardens on drying or firing"*.

For *clay mineral*: *"Natural and synthetic*; *any size*; *may include non-phyllosilicates*; *plastic*; *hardens on drying or firing"*.

Bergaya and Lagaly (2006) established the distinction between *clay* and *clay minerals* based on the following parameters: genesis, granularity, mineralogy, plasticity, and behaviour on drying or firing (in Table 1.1).

Table 1.1. Distinction of clay and clay mineral (Bergaya and Lagaly, 2006)

Clay	*Clay mineral*
Natural	Natural and synthetic
Fine-grained (<2µm or <4µm)	No size criterion
Phyllosilicates as principal constituents	May include non-phyllosilicates.
Plastic (except flint clays)	Plastic
Hardens on drying or firing	Hardens on drying or firing

The term synthetic clay mineral - an inorganic, crystalline hydrous phyllosilicate produced in the laboratory - could well be added to the term modified clay mineral, which is the analogue of natural clay mineral (see Chapter 8 in this book).

AIPEA Nomenclature Committee (Guggenheim *et al.*, 1997) endorses the use of both commercial names and synthetic names to the nomenclature established by the IMA Commission on New Minerals and Names (CNMMN) (Nickel, 1996). Therefore, synthetic minerals should be referred to by enclosing the name in quotation marks unless the synthetic mineral has been recorded as a trademark, in which case the name starts with a capital letter.

Regarding the distinction between clay and clay mineral, the actual position of the JNCs (Joint Nomenclature Committees) of AIPEA and CMS (2006) on the use of clay as a rock term remains indeterminate. Nevertheless, the literature often uses the term clay for clay minerals, such as kaolin instead of kaolinite, because the former name is shorter and less cumbersome.

Guggenheim and Martin (1995) state that clay minerals, hydrous phyllosilicates, provide the plasticity in clays. Because minerals are not defined based on their crystalline size, appropriate phyllosilicates of any grain size may be considered “clay minerals.”

It is well known that different species of clay minerals provide different plasticity, which determines the minimum total clay mineral content (as a rule >10%) that allows the classification of a geologic material as clay.

Very recently, Moreno-Maroto and Alonso-Azcárate (2018), soil specialists, stated that the particle-size criterion is not appropriate for differentiating clays, clayey materials, and non-clayey soils, whereas plasticity is. The authors have proposed a new definition of *clay* based on plasticity, the ratio *Plasticity Index* / *Liquid Limit* (*PI* / *LL*) being an excellent indicator for soil and clay scientists to use to classify soil textures based on PI / LL ratio and sand percentage. *Plasticity* is defined as “the ability of a material to be moulded to any shape”.

A fine-grained material could be defined as *clay* when PI ≥ LL/2 and a moderately or slightly clayey material if LL/3 < PI < LL/2 (LL being the *Atterberg Liquid Limit*).

Moreno-Maroto and Alonso-Azcárate (2018) propose the following definition of clay:

> “*A naturally occurring material composed primarily of fine-grained minerals whose PI is equal to or higher than LL /2 so that clay is plastic or highly plastic at those water contents located between the LL and PL. A moderately or slightly clayey material is a naturally occurring material composed primarily or partially of fine-grained minerals whose PI value is between LL /3 and LL /2. A clayey material is slightly or moderately plastic at those water contents between the LL and PL. Both clayey materials will harden when dried or fired, being this effect more pronounced as the value PI / LL increases*”.

In sedimentology, independently of the presence or absence of clay minerals, a sediment fraction less than 2 µm is called a *clay fraction*.

Flint clay, also called *hard clay*, can contain around 95% of clay minerals, especially kaolinite, and even so, it does not exhibit natural plasticity unless it is very finely ground and mixed with an adequate content of water. Hence, the sole existence of clay minerals is essential, but it is not a determining factor for a geologic material to be classified as clay. Besides mineralogy, geologic history and diagenesis are also conditioning factors.

The only factor that can definitively distinguish clay from non-clay geologic materials is the existence of clay minerals in clay. However, an important and decisive question remains concerning the clay concept. What is the minimum clay mineral content allowing the classification of a geologic material as clay? Mineralogical composition, grain size, and plasticity are complementary factors that could help to solve the question. Regarding clay minerals' definition, classification, and nomenclature, there has also been some controversy over the years.

Clay minerals occur in rocks of all lithologies and ages. Also, clay minerals are common and important constituents of the fine fraction of *clay* as well as of the fine fraction of soils, which are fundamental for life in general and for human life in particular.

Clay, associated with clay minerals, may contain other materials that impart plasticity and harden when dried or fired. Clay minerals are not defined *a priori* as fine-grained minerals because clays are fine-grained materials, but rather they may be of any crystallite size so that the term *clay mineral* is consistent with the *definition of mineral*, which is unrelated to crystallite size. The particle-size issue has been separated from the *clay mineral definition*. As a rule, individual crystals of *clay minerals* exhibit micrometric sizes, despite some *clay minerals*, such as true micas, vermiculites and chlorites, which could exhibit millimetric and centimetric sizes. Natural aggregates of such coarse-size phyllosilicates do not show any plasticity unless, after being finely ground, the reason why the term *clay* should not be applied to those natural aggregates.

Clay minerals are defined as: "*Hydrous phyllosilicates and hydrous iron minerals of planar or non-planar structures which could impart plasticity (if the right amount of water is added) and hardening (if dried or fired) to the clay in which they occur"*.

What really characterizes and distinguishes mineral species, clay mineral species included, is their specificity in terms of chemical composition and internal organization or structure (the way the constituent chemical elements, like building blocks, are spatially organized). However, the same chemical elements can be organized in different structures, the so-called polymorphs, as is the case with the clay minerals *dickite* and *nacrite*, both of which are polymorphs of *kaolinite*.

About 70 (seventy) *clay mineral species* are identified and acknowledged. As is well established for standard mineral species, clay minerals can show chemical and structural varieties if their basic building elements are partially replaced by other elements present in the formation environment, provided the isomorphous substitution rules are met and changes occur in their internal order-disorder. For example, in the clay mineral species - *kaolinite,* characterized by simple chemical composition and structure, in a few structural sites, Al can be replaced for Ti and Fe, and various degrees of internal order called crystallinity can occur. The amount and degree verified in both parameters can differentiate the individual particles or crystals of a particular mineral species in a particular clay.

Any clay has its own *clay fraction* in which the clay-size particles and clay minerals - the essential constituents of clay - are more concentrated. Conventionally, some disciplines set a maximum size for clay particles: *edaphology* or *pedology* < 2µm; *geology*, *sedimentology,* and *geoengineering* < 4µm; *colloid science* < 1µm. However, the upper limit on the size of an individual clay mineral particle or crystal has not been established.

Besides clay minerals, clay could contain silicates such as *quartz*, *feldspar,* and *mica*; carbonates such as *calcite* and *dolomite*; iron and aluminum oxides and hydroxides such as *hematite*, *goethite* and *gibbsite*; X-ray amorphous organic materials such as organic matter constituted of several organic compounds; quasi-amorphous inorganic X-ray materials, such as *opal A*, *goethite*, and *ferrihydrite*; and amorphous iron hydroxides. Like phyllosilicates, these quasi-amorphous and amorphous iron hydroxides, particularly those characterized by planar structures, can impart plasticity to clay. Thus, the definition of clay mineral cannot be limited to phyllosilicates.

Despite the complexity of the topic dealt with, the author of the present book defends the importance of concepts in science, both fundamental and applied, and defends that the concepts deserve the maximum acceptance, proposes the following definitions for *clay* and *clay mineral*:

Clay is: "*A geomaterial of natural occurrence mainly composed of fine-grained minerals and within these minerals the so-called clay minerals as essential or fundamental constituents, sometimes associated to coarse-grained minerals, to amorphous or quasi amorphous compounds, as well as to organic matter, geomaterial that could show plasticity (if the right amount of water is added to it), hardening (if dried or fired), and other specific physicochemical properties*".

Clay mineral is: "*A hydrous phyllosilicate of planar or nonplanar structure, or a hydrous quasi-amorphous or amorphous compound of planar structure* *(particularly iron-bearing), of any grain or crystal size, that is either a major or a minor constituent of both natural clay and modified clay".*

CHAPTER 2

CLAY MINERALS STRUCTURAL CHARACTERIZATION AND SYSTEMATICS

CELSO GOMES

2.1. Basic notes

As aforesaid, clay minerals are hydrous phyllosilicates of fine granularity and planar or non-planar structure that can provide plasticity when the right amount of water is added and harden when dried and fired.

As phyllosilicates, the respective chemical formulas are based on the radical or anion $(Si_4O_{10})^{4-}$ or more simply $(Si_2O_5)^{2-}$, which may be associated with cations such as Al^{3+}, Fe^{3+}, Fe^{2+}, Ca^{2+}, Na^{+}, K^{+}, and Li^{+}. As hydrated phyllosilicates, water participates in the form of HO- groups and/or H_2O water molecules in the respective chemical formulas.

In the ionic state, the chemical elements referred to above resemble small spheres that can be arranged into seven distinct three-dimensional structural models, characterized by a markedly two-dimensional development of the phyllosilicates. The ionic radii of the main anions and cations forming the clay minerals are generally expressed in picometers (1pm ± 10-12 m), with the values of the ionic radii being the conditioning factors of the isomorphous substitution both between cations and between anions in the structures of the clay minerals.

At least some basic crystal-chemical information is fundamental for an adequate understanding of the specific properties of clays and clay minerals, starting with the radii sizes of the principal chemical elements, anions, and cations, which participate and much determine the position in their crystal-chemical structures:

Anions:
O^{2-} - 140pm, OH^-- 141pm, F^-- 136pm.

Cations in the structural tetrahedral sheets:
Si^{4+} - 40pm, Ti^{+4}- 68pm, Al^{3+}- 51pm, Fe^{3+} - 64pm, Cr^{3+} - 69pm.

Cations in the structural octahedral sheets:
Mg^{2+}- 66pm, Ca^{2+}- 99pm, Fe^{2+} - 74pm, Mn^{2+} - 80pm, Zn^{2+} - 74pm, Cu^{2+} - 72pm.

Interlayer cations:
Na^+ - 97pm, K^+ - 142pm, Li^+ - 68pm; interlayer spaces can also be occupied by cations that usually occupy *octahedral sites*.

2.2. The Electrical Charge of Clay Minerals

Clay minerals, like other minerals, develop an electrical charge on their particles to a greater extent, as justified by the conditions of their formation at the terrestrial/hydrosphere/atmosphere/biosphere interface environments characterized by large metastability.

Two types of electrical charge exist in minerals:

1. A permanent charge resulting from higher valence cations replaced by lower valence cations or from atomic omissions in the crystal structure.

2. A variable charge resulting from dissociation and/or association of protons by surface hydroxyl groups (Van Olphen, 1963).

The so-called *isomorphous atomic substitution* produces an overall negative *electrical charge* on the basal surfaces of clay particles, with a value per unit cell that varies with the structure of the clay mineral species. For example, the clay mineral called *kaolinite*, $Al_2Si_2O_5(OH)_4$, shows the lowest value of *electrical charge*, higher than zero, because the isomorphous atomic substitution is almost absent in this clay mineral of very simple chemical composition; the clay mineral *montmorillonite*, $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2nH_2O$, relatively to *kaolinite* has a more complex chemical composition. The electrical charge typically ranges from 0.45 to 0.60. The clay mineral illite shows the highest electric charge, about 1.

Figure 2.2a shows a schematic representation of the electrical charge distribution on clay mineral surfaces.

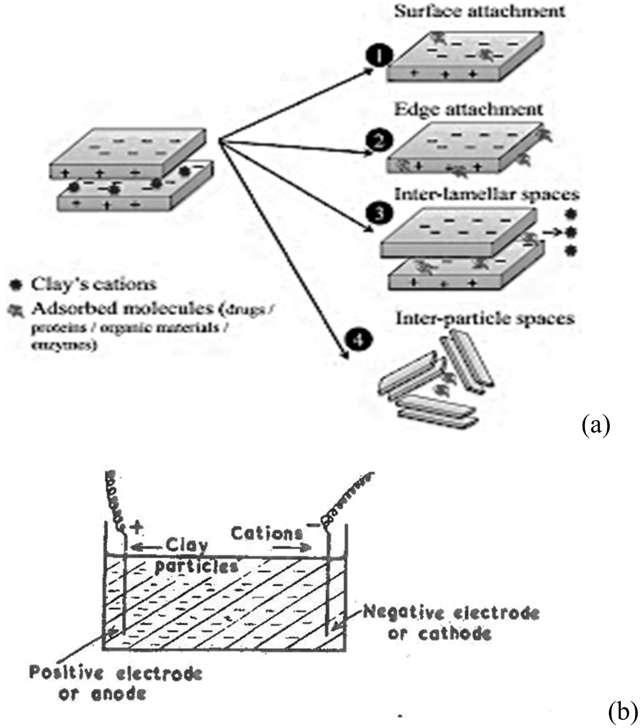

Figure 2.2 – (a) Schematic representation of electrical charge distribution in clay mineral surfaces. (*In*: Ghadiri *et al.*, 2015); (b) Global negative electrical charge of clay particles demonstrated by electrophoresis. (Gomes, 2002).

The global negative electric charge of natural clay particles can be easily demonstrated using electrophoresis, schematically shown in Figure 2.2b. In a very diluted clay/water suspension contained in a small transparent glass tank, clay particles can be observed moving towards the positive electrode. The relative speed of particle movement distinguishes clay mineral species: higher for clay minerals with a high electrical charge, e.g., montmorillonite and vermiculite, and lower for clay minerals with a low electrical charge, e.g., kaolinite.

When dispersed in water, the pH of the dispersion medium greatly influences the electrical charge distribution on clay mineral surfaces.

Low pH turns particle edges positively charged, and particle basal faces negatively charged, conditions favorable to interparticle attraction. High pH turns particle edges and basal faces negatively charged, conditions favorable to interparticle repulsion. Neutral pH creates negative and positive charges on particle edges and negative charges on particle basal faces, conditions favorable to interparticle attraction and repulsion.

The three situations referred to are naturally controlling the stability or instability of clay/water dispersions.

Electrical charge, particle size, and particle shape are the fundamental properties of clay minerals, and the other properties depend on them. These properties justify several important applications of clays in natural and modified forms, such as acting as adsorbents to remove heavy metals from aqueous solutions (Bourliva *et al.*, 2013; Uddin, 2017).

Paquet and Clauer (1997), established a simple systematic clay mineral, based on the *electrical charge* z of the structural unit, which comprises two main groups:

1. The **group 1** of low-activity clay minerals, type 1:1 or T:O (one tetrahedral sheet linked to one octahedral sheet in each structural layer), named *kaolinite group*, with electrical charge $z \approx 0$ (as a rule, particularly in kaolinite, the electric charge value z is little above zero due very limited isomorphous substitution of Al for Fe or Mg, and Si for Al.

2. The **group 2** of high activity clay minerals, type 2:1 or T: O: T, named *illite/vermiculite/smectite group*, the electrical charge z, as a rule, being less than 1.

Table 2.2a shows the distribution of the basic chemical elements and the distribution of electrical charge in the structural unit layer of kaolinite in group 1.

Table 2.2a - Electrical charge distribution in the structural unit layer of *kaolinite*

Electrical charge distribution in the structural unit layer of *kaolinite*		
Ion	Number of ions	Total charge
O^{2-}	6	-12
Si^{4+}	4	+16
$O^{2-} + (OH)^-$	$4\ O^{2-} + 2(OH)^-$	-10
Al^{3+}	4	+12
$(OH)^-$	6	-6

Note: The plane of ions $O^{2-} + (OH)^-$ is shared by both tetrahedral and octahedral structural sheets

In turn, **group 2** comprises three categories:

a) Category with high electric charge (z = 0.8-0.9), represented by *illite*;

b) Category with intermediate electric charge z = 0.45-0.8) represented by *vermiculite*.

c) Category with low electric charge (z <0.45) represented by *smectite*.

In **group 2,** the distribution of the basic chemical elements and the electrical charge in the case of *montmorillonite* structural unit layer is shown in Table 2.2b.

Table 2.2b - Electrical charge distribution in the structural unit layer of *montmorillonite*

Electrical charge distribution in the structural unit layer of *montmorillonite*		
Ion	**Number of ions**	**Total charge**
O^{2-}	6	-12
Si^{4+}	4	+16
$O^{2-} + (OH)^-$	$4\ O^{2-} + 2(OH)^-$	-10
Al^{3+}	4	+12
$O^{2-} + (OH)^-$	$4\ O^{2-} + 2(OH)^-$	-10
Si^{4+}	4	+16
O^{2-}	6	-12

Note: The two planes of ions $4O^{2-} + 2(OH)^-$ are shared by the octahedral structural sheet and the two structural sheets

In real *kaolinite* and in the smectite group of clay minerals which includes *montmorillonite*, as well as in other clay minerals, the electrical charge always exists due to various types of crystal defects, those due to isomorphous substitution being the determinant ones.

Konta (1998), also based on *electrical charge*, but not only, considers 5 (five) groups of clay minerals:

1. Low-medium electrical charge clay minerals with structures of type 2:1 or T: O: T; the minerals of this group, including smectites (low filler) and vermiculites (medium filler), incorporate solvated intercalated cations and have high absorbent capacity.

2. High electrical charge clay minerals, such as dioctahedral and trioctahedral micas, include non-solvated intercalated cations and have selective absorbing properties.

3. Uncharged or almost uncharged clay minerals: 1:1 or T:O; 2:1 or T: O: T; and 2:1:1 or T:O:T:O types of ores, such as *talc*, *pyrophyllite*, *kaolinite*, *serpentine,* and *chlorite*, characterized by moderate absorbent and catalytic capacities.

4. Clay minerals with no electric charge with pseudo-layered structures, *palygorskite* and *sepiolite*, which have four different types of water, large microchannels, and high absorbent capacity.

5. Amorphous or almost amorphous clay minerals like allophane and imogolite have high chemical reactivity and anionic adsorption.

The *electrical charge* is usually determined in clay minerals with expansive structures (*smectites* and *vermiculites*) by two methods (Laird, 1994):

1. One based on the exchange capacity of the alkylammonium cation.

2. Other, based on the structural formula calculation.

Based on their *electrical charge,* clay minerals can be divided into two main groups:

1. *Cationic clay minerals* (cationic-CM), which possess a general negative electric charge and are widespread (e.g., *kaolinite* and *montmorillonite*).

2. *Anionic clay minerals* or Layered Double Hydroxides (LDH) possess a positive electric charge and are rarely found in nature but are relatively simple and economical to synthesize.

From the applied point of view, cationic clay minerals are much more interesting than anionic clay minerals. In this regard, cationic clay minerals, both unmodified (natural and synthetic) and modified (clay-drug hybrid, organoclay, clay-polymer hybrid), have diverse applications in the fields of biological or biomedical systems, for example, in pharmaceuticals (as active ingredient for instance as drug carrier or as excipient), in cosmetics (for sunscreens and topical personal care), in biomaterials, in biosensors, and in medical devices (Ghadiri *et al.*, 2015).

2.3. Active Sites and Functional Groups in Clay Mineral Surfaces

The electrical charge of clay minerals of type 2:1 besides being a fundamental criterion used in the systematics of this type of clay minerals, is also a property responsible for the chemical reactivity of its surfaces with certain organic and inorganic compounds and the higher water retention capacity of many clays and is also indicative of the ability to set cations and adsorb water and several polar organic molecules. The said interactivity is concentrated on the surfaces of the crystals in the so-called active sites or functional groups, which, for example, are decisive for the bactericidal character attributed to certain clay minerals and clays.

Johnston (1996), considers six types of active sites or functional groups in clay minerals:

1. "Siloxane" type surfaces in neutral hydrated phyllosilicates because they have an electrical charge equal to zero or close to zero, being 2:1 (e.g., *pyrophyllite* and *talc*) or 1:1 type (e.g., *kaolinite*), surfaces which although considered non-reactive due to the strong bonds between Si and O atoms, are predominantly hydrophobic and function as weak Lewis bases and can provide free electron pairs of surface oxygen for chemical bonds.

2. Sites related to isomorphic atomic substitution (e.g., Al *per* Mg or Si *per* Al), characterized by permanently negative electric charge and where the load deficit is compensated by the inorganic exchange cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) or organic (being organic preferentially adsorbed compared to inorganic), sites that can occur in both the tetrahedral structural sheets and the octahedral structural sheets.

3. Sites of the structural interlayer spaces where cations of certain alkaline, alkaline-earth, and transition metals in the state of maximum oxidation (e.g.,

Cu^{2+} and Fe^{3+}, which, being reduced, can form organic cations) occupy exchange sites cationic.

4. Sites where water molecules are enveloped by solution and coordinate, the exchange cations become polarized and function as sources of Bronsted acidity, yielding electrons.

5. Hydrophobic sites of the structural interlayer surfaces of the crystals of clayey minerals after the adsorption of organic molecules by these surfaces (for example, when alkylammonium cations replace inorganic cations in smectites, so-called organic clays, creating hydrophobic surfaces, serving the organic cations of molecular pillars that allow the adsorption and absorption of organic molecules).

6. Sites on the edges of lamellar crystals where broken links occur or where silanol and aluminol groups are exposed (either exposed structural groups or OH^- groups derived from the reaction of Si^{4+} and Al^{3+} ions not completely coordinated with water molecules and thus complete the respective coordinates).

Clay minerals acquire an electric charge in polar liquids such as water by two mechanisms (Ponto and Berg, 2018):

1. First, by atomic isomorphic substitutions in tetrahedral and octahedral sheets, situations create a permanent negative charge on the surfaces of clay mineral particles.

2. Second, by broken -OH functional groups at the edges of the particles, the electric charge is dependent on water pH; at low pH values, -OH groups are protonated and acquire a positive charge, whereas, at high pH values, they are deprotonated and acquire a negative charge.

However, according to the same authors, clay minerals can acquire an electric charge in non-aqueous, non-polar liquids by adding surfactants, which are usually used to improve the stability of mineral dispersion. Charging results from the acid-base interaction mechanism between the clay particles and the suspending medium.

The location of isomorphous, octahedral, or tetrahedral substitution sites significantly influences the adsorption of polar organic molecules. On the other hand, the OH groups on the crystalline edges of the clay minerals constitute strongly active sites. They are responsible for the electrical charge of pH-dependent clay and clayey soils. At low pH, the mentioned sites acquire a positive charge through proton adsorption, which can interact with organic acids and oxyanions. Increasing the pH shows a pH value at which the electrical charge is neutral (zero load point, or PZC), and beyond this value, the charge becomes negative. In clay minerals with very low electrical charges, such as *kaolinite*, these pH-dependent sites are the main source of reactivity.

The very small particles of the clay minerals, because they present a greater number of crystallo-chemical defects, are those that present a greater number of active sites of the mentioned type related to structural point defects (atomic isomorphous substitution and atomic omission) and other defects of planar and volumetric nature.

2.4. Basic Units of Clay Mineral Structure

The basic structural components of clay minerals and hydrous phyllosilicates, in increasing order of complexity, are ions, atomic planes or structural planes, structural sheets, structural layers, and structural units.

The *atomic planes* comprise the *atoms* in their *ionic form* arranged in planes in the clay mineral's structure. The *structural sheets* are groupings of atoms distributed through several atomic planes, atoms that constitute polyhedric configurations, *tetrahedron* or *octahedron* (Figures 2.4a and 2.4b), which in turn associate and form tetrahedral structural sheets and octahedral structural sheets (Figures 2.5 and 2.6).

The basic building units of the clay mineral structures have configurations represented by tetrahedra in which the coordinating ion is Si^{4+} and the coordinated ion is O^{2-}, and octahedra in which the coordinating ion is either Al^{3+} or Mg^{2+}, and the ions coordinates are O^{2-} and HO^{1-}.

In planar developments, both tetrahedra and octahedra units are linked together in the so-called structural sheets - tetrahedral sheet (T) and octahedral sheet (O) -, which in turn establish links between them, either through van der Waals bonds or through intercalation cations and organize them into the so-called *structural layers*.

The *structural layers* can be classified into three main types: T:O or 1:1, represented by the clay mineral *kaolinite*; T: O: T or 2:1, represented by the clay mineral *illite*; and T:O:T:O or 2:1:1, represented by the clay mineral *chlorite*.

The tetrahedral structural sheets have a general composition of T_2O_5, where T represents the tetrahedral cation, i.e., with 4 (four) or tetrahedral coordination. The tetrahedral cation, which, as a rule, is Si, can be partially replaced by Al and/or Fe. Also, Si occupies the tetrahedra centers, while the vertices are occupied by oxygen. Each tetrahedron connects to an adjacent tetrahedron by sharing the three co-planar basal vertices occupied by oxygens, constituting the so-called *tetrahedral structural sheet* - the structural plane of the three basal oxygens is a two-dimensional hexagonal arrangement - while the fourth apex of each tetrahedron occupied by apical oxygen is part of the *octahedral structural sheet.*

In the octahedral structural sheets, the octahedrons are connected laterally to each other. An octahedral cation occupies its respective center, that is, with 6 or octahedral coordination, and the octahedral cation can be Al^{3+}, Mg^{2+}, Fe^{3+} or Fe^{2+}, the six vertices of the octahedra being occupied by oxygens and/or hydroxyls.

The *structural layers* are groupings of a few structural tetrahedral and octahedral sheets and are the basic building blocks of the structures of the various clay minerals.

Finally, the *structural unit* is the basic motif that, through symmetrical and periodic repetition, gives rise to the entire structure of the clayey mineral. This comprises the representation of the basic structural layer and the spatial content when structural interlayers are present.

The *unit chemical formula* expresses the chemical composition of the *structural unit*. The organization of the structural unit, more precisely the number and nature of the structural tetrahedral (T) and octahedral (O) sheets, makes up the structural unit and determines the three basic structural types of clay minerals previously referred to: 1:1 or T:O; 2:1 or T: O: T; and 2:1:1 or T:O:T:O.

Figure 2.3 schematically shows the various structures and their respective characteristic basal spacings identified on the X-ray diffraction patterns of the main clay mineral species.

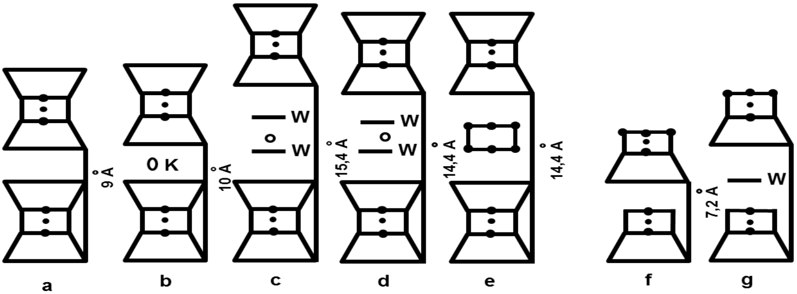

Figure 2.3 - Schematic representation of structures and respective basal spacings $d_{(001)}$ of the main clay mineral species: • octahedral cations; ◦ exchange cations; OH groups; 0 interlayer cations; w -water layers; a - pyrophyllite; b - mica; c - montmorillonite; d - vermiculite; e - chlorite; f - kaolinite; g - fully hydrated halloysite. (Gomes, 2002).

The basal spacing $d_{(001)}$ of a 1:1 structure is slightly higher than 7 Å (angstrom) or 0.7 nm (nanometer). In comparison, the basal spacing $d_{(001)}$ of a 2:1 structure is about 10 Å, i.e., about 1nm, and the basal spacing $d_{(001)}$ of a 2:1:1 structure is slightly higher than 14 Å, i.e., about 1.4 nm.

However, these basal spacings can deviate from the above values and range from 7 Å to 18 Å depending on the type of structural layer, which is the basic component of the *structural unit* and the occupation of the structural interlayers by particular chemical species: cations, water, and hydroxyls.

In the structural formula of a clay mineral, the global electrical charge of the cations is compensated by the global electrical charge of the anions. The latter, less affected by isomorphous atomic substitution, serves as the basis for calculations of crystallo-chemical formulas. Thus, for clay minerals with basal spacings with values 7 Å, 10 Å, and 14 Å, the following anionic loads corresponding to half of the structural unit are as follows:

7 Å = $O_5 (OH)_4 = 14^{e-}$
10 Å = $O_{10} (OH)_2 = 22^{e-}$
14 Å = $O_{10} (OH)_8 = 28^{e-}$

Figures 2.4a and 2.4b show the fundamental or basic units, tetrahedron and octahedron, the building blocks of clay minerals structures.

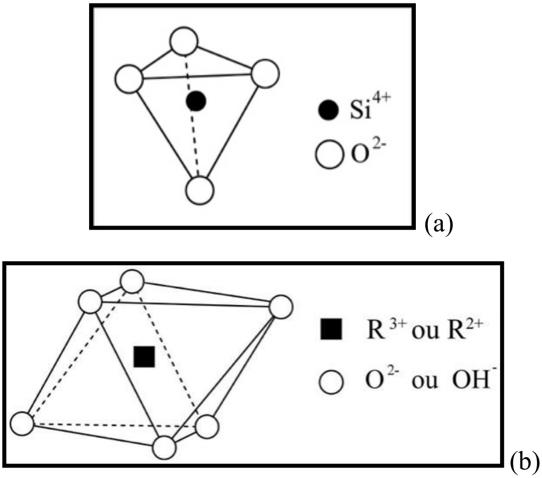

Figure 2.4 – (a) Tetrahedron [SiO_4]; (b) Octahedron [(R^{2+}or R^{3+}) o_6], R^{3+}= Al, Fe^{3+}; R^{2+}=Mg, Fe^{2+}

Each of these basic units, tetrahedron and octahedron, can be associated with linking to adjacent tetrahedra and octahedra, forming continuous two-dimensional patterns called tetrahedral and octahedral sheets. These sheets, in turn, can be related to the formation of different three-dimensional layer organizations or structures of varying complexity, namely clay mineral structures.

2.5. Crystallochemistry and Systematics of Clay Minerals

Presently, about seventy (70) species of clay minerals are known, species distinguished by their crystallo-chemical specificities, which as a rule, based on common structural and chemical features, can be gathered into two main groups (see Table 2.3 and Table 2.4, and Guggenheim *et al*., 2006):

1. *Planar hydrous phyllosilicates,* i.e*., planar clay minerals*.

2. *Nonplanar hydrous phyllosilicates,* i.e*., non-planar clay minerals*.

Planar hydrous phyllosilicates comprise nine groups: *kaolin-serpentine*; *pyrophyllite-talc; smectite*; *true or flexible mica*; *interlayer deficient mica*; *brittle mica*; *vermiculite*; *chlorite*; and *regularly interstratified* (*In:* Guggenheim *et al*., 2006).