Chapter 6
General Data on Clay Science, Crystallochemistry and Systematics of Clay Minerals, Clay Typologies, and Clay Properties and Applications

Celso S. F. Gomes and Michel Rautureau

Abstract Clay and clay minerals are ubiquitous constituents of the Earth's crust, and they are being used by man for therapeutic, cosmetic and many other basic purposes, for instance, in pottery and construction, since prehistoric times. Clay and clay minerals are unique within all other minerals, and as, natural and fine-grained materials they are characterized by singular specific properties such as plasticity and absorption. Also, they are the main constituents of clayey soils and edible clays object of geophagy practices, and of healing mud and peloids used in mud therapy and pelotherapy. This chapter is initiated with relevant information, mainly on clay science, clay and clay minerals' definition, clay typologies, crystallochemical characteristics and properties of clay minerals' species as well as clay typology. Clay minerals' specific properties, such as electric charge (cationic and anionic clay minerals), active sites and functional groups in clay mineral surfaces, basic structural units, planar and non-planar structures and systematic of clay minerals are presented and discussed. The unique properties of certain clays and clay minerals justify their uses for both internal and external applications, in medicines, pharmaceuticals and cosmetics.

C. S. F. Gomes (✉)
Department of Geosciences, Researcher of the Research Unit "GeoBioTec",
University of Aveiro, Aveiro, Portugal
e-mail: cgomes@ua.pt

M. Rautureau
Docteur d'État ès Sciences Physiques, Retired of University of Orléans, Orléans, France
e-mail: mrautureau@wanadoo.fr

C. Gomes, M. Rautureau (eds.), *Minerals* latu sensu *and Human Health*,
https://doi.org/10.1007/978-3-030-65706-2_6

6.1 Introduction to Clay Science

According to Wagner et al. (1998), Carretero et al. (2002, 2006), Wilson (2003) and De Vos (2010), both animals and humans have used *clay*, *clay minerals* and other *minerals* for therapeutic purposes since prehistoric times. Also, cases of *healing clays* have been documented (Droy-Lefaix and Tateo 2006; Carretero et al. 2006; Rautureau et al. 2017). The authors referred to have reviewed the available studies of the beneficial effects of clay and clay minerals on gastrointestinal illnesses attributed to the adsorption of microbes, viruses or their toxins and modification of the mucus lining reinforcing natural defences of the gastric tissue. The beneficial effects could be also favoured by the supply of nutritional *mineral supplements* (e.g. Fe and Cu) that could be provided by certain clay minerals (Aufreiter et al. 1997; Kikouama et al. 2009, Kikouama and Baldé 2010).

Clay, as a natural material, is the main constituent of soils object of *geophagy* practices, also of "*edible clays*", and yet of *healing muds* and *peloids* used in *mud therapy* and *pelotherapy*. Clay is a unique mineral within all minerals. Thorez (2003) has called clays "the mutants of the mineral world" because they are able to change their chemical makeup via ion exchange and readjust to the environment due to their small particle size (<2 μm) and large reactive specific surface area (>100 m^2/g), reactivity due to the electric charge of clay minerals, the clay fundamental constituents.

Some relatively rare natural clays and clay minerals have been identified by their ability to kill a variety of pathogenic bacteria (Williams et al. 2004, Ma'or et al. 2006; Haydel et al. 2008). That is the case, for instance, of the so-called French green clays, mainly composed of *1Md illite* and *Fe-smectite* that successfully have been used to heal *Buruli ulcer*, a necrotizing or "flesh eating" mycobacterial infection (Brunet de Courssou 2002). However, the bactericidal character never happens in clay and clay minerals' dry state, always requiring hydration state. Some other natural clays and clay minerals require adequate manipulation to perform bactericidal properties.

In the literature, we can find interesting references to clay acting as health healing and protector material. Rautureau et al. (2017) report the interesting fact that French soldiers in the First World War who had received mustard (a condiment containing a small quantity of clay as a jellifying agent) in their food ration were less subject to the effects of dysentery and other prevalent diseases within the armies in the field.

Bentonite, *kaolin*, *fibrous clay* (*sepiolite* and *palygorskite*), *French green clay* and *nanoclay* are the most interesting clay types for medical, pharmaceutical and cosmetic applications. Regarding clay, a mineral substance widely used in geopharmacy and geotherapeutics, there is much more or less recent scientific information.

The benefits of clays to human health are well documented in several recently published articles: Robertson (1986, 1996), Novelli (1996, 1998, 2000), Reinbacher (1999, 2003), Viseras and Lopez-Galindo (1999), Veniale (1996, 1998, 1999), Carretero (2002), and Veniale et al. (2004). Also, books of a general scope document too such benefits, and the authors of some of them are herein mentioned: Selinus et al. (2005), Gomes and Silva (2007), Carretero and Pozo (2007), Rautureau et al. (2010, 2017).

All the articles and books referred to disclose important information about properties, applications and functions of clay, clay minerals and clay-based products in human health. Many other studies showing the healing properties of clays and clay minerals are well documented in further topics of this chapter.

The aforesaid justifies the need to provide relevant information, mainly on Clay science, clay and clay minerals' definition, clay typologies, crystallochemical features and systematics of clay minerals and properties of both clay minerals and clays.

Today, when nanotechnology is the hallmark of the scientific world, the so-called nanoclays are fundamental raw materials for several essential technological applications. As a matter of fact, clay of the nanoclay typology has important applications in technological fields, such as *catalysis* (Garrido-Ramirez et al. 2010; Nagendrappa 2011), *food packaging* (Azeredo 2009; Majeed et al. 2013), *textile industry* (Floody et al. 2009; Shahidi and Ghoranneviss 2014) and *high strength materials with thermal and gas barrier properties* (Liu et al. 2011; Wu et al. 2014; Gamelas and Ferraz 2015). Besides these applications, nanoclay has specific and other rather important applications in fields such as *medicine* (Ambre et al. 2010; Suresh et al. 2010), *cosmetics* (Patel et al. 2006; Carretero and Pozo 2009, 2010) and *pharmacy* (Carretero and Pozo 2009, 2010; Khurana et al. 2015). In the particular case of the pharmaceutical industry, clay minerals are widely used as lubricants, desiccants, disintegrants, diluents, thickeners, emulsifiers, binders, pigments, opacifiers, flavour correctors, carriers of active ingredients and anticaking agents.

Other unique clay mineral features are electric charge, specific surface area, dispersivity, hygroscopicity, unctuosity, thixotropy, plasticity, cation exchange capacity, sorption and desorption capacity and varied colour (Khurana et al. 2015). These same authors have synthesized in tables the pharmaceutical activity of certain clay minerals and of certain other minerals; they also propose the corresponding mechanisms of action as well as the applications of natural clay minerals in drug delivery.

Clay minerals need to undergo modification and functionalization of their particle surfaces before incorporation into polymer matrices to develop polymer-clay nanocomposites. As a consequence of clay minerals' electric charge, in general, they show hydrophilic character turning them incompatible with a wide range of polymer types. However, organophilic clay minerals can be produced by ion exchange with an organic cation. For instance, in Na^+*-montmorillonite*, sodium ions can be exchanged for an amino acid such as 12-aminododecanoic acid (ADA) to turn the clay mineral hydrophobic and therefore more compatible with polymers.

Nanoclay high specific surface area is an important factor, since higher surface areas facilitate the interaction clay-polymer. Refining, i.e. going from micro- to nanoscale, and delamination or exfoliation of the platy particles of clay minerals, such as *kaolinite* and *montmorillonite*, could much increase their specific surface areas and consequently the exposure to the polymer matrix. In all applications, nanoclay improves the product quality, costs economy and environment safety.

Khurana et al. (2015) made a special report on clay minerals providing a bird's-eye view of the chemical composition and structure of these minerals and their influence on the release properties of active medicinal agents or drugs. Nanoparticles of other materials are currently available, such as aluminium oxide, copper oxide, iron oxide, titanium dioxide, zinc oxide and calcium carbonate.

According to Rautureau et al. (2017), any science, scientific field or scientific domain requires a well-established and defined object of study, as well as appropriate methodologies to develop the knowledge about that object. However, along the time the definition or concept of the object of study can undergo modifications and adaptations due to science advances, both in theoretical and experimental terms.

Bergaya et al. (2006) consider clay science, i.e. the study of clay, a relatively young discipline initiated about 100 years ago, and the authors enlighten the most remarkable stages of its historical development, and remarkable are too the many references the authors disclose concerned with the subject.

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

Differently of what happens in other sciences, the enormous clay diversity in geological, 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 along this chapter.

Clay science is less than 100 years old, and along its evolution, the definition of clay and clay mineral, the objects of study of this science, has shown significant changes that have been proposed, developed and adopted by several authors and clay groups or clay societies. Such changes were based not only on basic but selective criteria very much dependent upon the particular academic education and professional experience of the authors, for instance, soil scientists, mineralogists, geologists or materials scientists.

Clay Minerals Society (CMS) with headquarters in Chantilly, Virginia, USA, founded in 1962, has as primary purpose to stimulate research and education and to disseminate information relating to all aspects of clay science and technology. CMS uses to organize annual meetings (AM), which are international multidisciplinary conferences about clay minerals research, applications and technology developments in different disciplines. CMS members include mineralogists, crystallographers, physicists, chemists, geochemists, soil scientists, agronomists, ceramic scientists, civil engineers, petroleum geologists and engineers and industrial scientists. In 2014, the society had about 700 members, one-half of whom are from countries outside the USA. All CMS members belong to the AIPEA (Association

Internationale Pour L'Étude des Argiles) created in 1966, an entity that gathers the individual members of the existing 23 national clay groups from all over the world.

Through the conferences and publications, the journal *Clays and Clay Minerals* and Workshop Lectures Series, CMS provides numerous opportunities for the information exchange and interdisciplinary research collaboration. The last two annual meetings were held, the 55th at the University of Illinois at Urbana-Champaign, and the 56th at the University of Pierre and Marie Curie, in Paris. These conferences, as a rule, are dedicated to particular themes, e.g. "New Visions of Clay Science" in the case of the 55th AM, and 19 thematic sessions covering a broad range of clay sciences: clay mineralogy, crystallography, petrology, materials science, nanosciences, bio-nanoclays in medicine, environmental engineering, soil science, biogeochemistry, industrial technology, isotope geochemistry, cosmogeochemistry, advanced spectroscopies and education, having attracted 240 abstracts. The first proceedings of the AM conferences was issued in 1952. These conferences, as a rule, are attended by hundreds of worldwide clay scientists.

As regards the Workshop Lectures Series, 22 volumes have been already published, the first volume dated of 1989 and entitled "Quantitative Mineral Analysis of Clays", Pevear JR and Mumpton being the editors, and the last volume entitled "Introduction to Oil Sand Clays", Omotoso O and Hockley D being the editors.

In Europe, the Mineralogical Society of Great Britain & Ireland edits the journal *Clay Minerals* in conjunction with the European Clay Groups Association (ECGA). Clay Minerals have continued the *Clay Minerals Bulletin* (1947–1964), and presently the journal produces four issues/year. The Mineralogical Society of Great Britain & Ireland produces monographs too.

Also, in Europe, the national clay groups organize regular scientific meetings, scientific publications being the normal outcome of them. In Europe, the European Clay Groups Association (ECGA) created in 1987 uses to organize quadrennial conferences; the last one, the Euroclay 2019, being organized by the Groupe Francais des Argiles (GFA), was held at the University of Pierre and Marie Curie, in Paris, under the auspices of ECGA and AIPEA (Association Internationale Pour L'Étude des Argiles).

The 56th Annual Meeting of ACS and the 6th Mediterranean Clay Meeting (MCM) were associated to the Euroclay 2019 Conference. The 57th CMS Annual Meeting will be held in Istanbul, Turkey, jointly organized with Turkish Clay Group. The 58th CMS Annual Meeting will take place in Richland, Washington, USA.

The progressive advances on clay science are general or specialized targets and subjects of several publications, books and journals. Within the books, the nine issues or volumes of a series entitled *Developments in Clay Science* are examples of publications that deserve particular appreciation by the clay scientists. A recent article by Zhou et al. (2016) makes clear the highly significant current developments on clay science in China.

Clay occurs where we less expect, not only in rocks of any type (sedimentary, igneous and metamorphic), but also dispersed in atmospheric aerosols, and suspended in the water of oceans, seas, lakes, lagoons and rivers. Naturally and industrially produced dusts that could have deleterious effects on human health can contain clay minerals too.

The basic subject of clay minerals genesis is excellently dealt with in Gálan (2006). Clay minerals are spatially distributed from deep within the Earth's crust to the Earth's surface and to Martian landscapes (Johnston 2010; Milliken and Bish 2011). As a matter of fact, clay minerals are not unique to Earth. The Mars Exploration Rovers, the Mars Phoenix Scout and the Mars Science Laboratory (MSL) have identified hydrous phyllosilicates (clay minerals), sulphates, carbonates, Fe-oxyhydroxides and other minerals at several landing sites. A group of 19 researchers have determined and shown the first X-ray diffraction analyses of clay minerals on Mars; illite and smectite have been identified (Vaniman et al. 2014).

The Mars Science Laboratory rover, named *Curiosity*, carried CheMin, the first X-ray diffraction (XRD) instrument used on a planet other than Earth. With CheMin, the first direct sampling and characterization of clay minerals on Mars could be obtained. Also, in terrestrial laboratories, clay minerals could be identified too in samples of Martian carbonaceous chondrite meteorites.

Clay science, as any science has a past, has a history, and its memory is the required foundation for present and future developments. Within the distinguished and brilliant clay scientists pioneers of clay science. In the 1960s, when one of the authors (CSFG) of this book was just initiating his learning and research in clay science, he had the honour to personally meet, listen and talk with them, particularly during scientific meetings; some of them deceased, are herein remembered: Ralph Grim (1902–1989) from the University of Illinois, Urbana, USA; George Brindley (1905–1983) from the Pennsylvania State University, USA; Jackson ML (1914–2002) from the University of Wisconsin, Madison, USA; Sturges William Bailey (1919–1994) from the University of Wisconsin, USA; William D Keller (1900–2001) from the University of Missouri, USA; Haydn Herbert Murray (1924–2014) from the Indiana University; Robert Mackenzie (1920–2000), Victor Colin Farmer (1920–2006) and Jef Wilson from the Macaulay Institute for Soil Research, in Aberdeen, Scotland; George Brown (1926–1996) from the Soils and Plant Nutrition Department, Rothamsted Experimental Station, Harpenden, England; Simone Caillère (1905–1999) from the Laboratoire de Minéralogie, Muséum National d'Histoire Naturelle, Paris, France; Robert Robertson (1911–1999) from the Cambridge University, England; Georges Millot (1917–1991) from the Université de Strasbourg, France; Carl Wilhelm Correns (1893–1980) from the Kaiser Wilhelm Institute of Physical Chemistry, Berlin, Germany; Karl Jasmund (1913–2003) from the University of Rostock, Germany; Armin Weiss (1927–2010) from the University of Munich, Germany; Toshio Sudo (1911–2000) from the Tokyo University of Education, Japan; Boris Zvyagin (1921–2002) from the Institute of Ore Mineralogy of the Russian Academy of Sciences, Moscow, Russia; Jiri Konta (1922–2017) from the Charles University, Czech Republic; José Serratosa Márquez (1924–2012) from the Instituto de Edafologia del CSIC, Madrid, Spain; Emilio Galán Huertos (1932–2018) from the University of Seville, Spain; Fernando Veniale (1929–2019) from the University of Pavia, Italy; Lisa Heller-Kalai from the Hebrew University, Jerusalem, Israel; Pérsio de Souza Santos from the University of São Paulo, Brazil; Gerhard Lagaly from the University of Kiel, Germany; Maria Franca Brigatti from the University of Modena, Italy; Faïza Bergaya from the University of Orléans, France; Benny Theng from Landcare Research, New Zealand; Peter Komadel from the Institute of Inorganic Chemistry, Slovakia; Jose Luis Pérez Rodriguez from the University of Seville, Spain; Maria Isabel Carretero from the University of Seville, Spain; Alberto Lopes Galindo from the University of Granada, Spain; Fabio Tateo from the Instituto di Ricerca sulle Argille, Italy; Eduardo Ruiz-Hitzky from the Instituto de Ciencia de Materiales de Madrid, Spain; and some others.

When the optical microscope was the only instrumental tool to analyse geological materials, that is, during the last decades of the nineteenth century and the first decades of the twentieth century, clay was defined as an association of fine-grained minerals with particle diameters of less than 2 μm, i.e. beyond the resolution of the optical microscope. Earlier chemical analysis became a fundamental tool to determine the chemical composition of both clays and clay minerals, allowing the establishment of their typology.

Soil science, colloidal chemistry and the development of analytical techniques, such as differential and gravimetric thermal analysis and transmission and scanning electron microscopy, have contributed very much for the identification, quantification and explanation of clay and clay minerals' basic properties.

Starting with the third decade of the twentieth century, X-ray diffraction (XRD) became a powerful tool for investigating the structure of fine-grained materials, clay minerals included, allowing the differentiation of clay mineral structures' achievement fundamental to explain their distinctive properties. As a matter of fact, clay minerals that have been considered essentially amorphous materials, step by step, were found to be structurally ordered and diversified too in physical and chemical properties.

The 60s decade, in particular, really was a golden epoch of clay research due to the dissemination in the USA, Europe and Japan of appropriate analytical systems, in particular based on X-ray diffraction and electron diffraction.

Several other analytical systems soon became available, such as transmission electron microscopy (TEM) with the mode high-resolution imaging (HRTEM), scanning electron microscopy (SEM) associated to X-ray energy-dispersive spectrometry (EDS) to determine the composition of inorganic species, electron energy-loss spectrometry (EELS) to measure the concentration of heavier elements than Li, their oxidation states and chemical speciation; selected area electron diffraction (SAED), electron tomography (ET) to determine 3D particle shapes, and synchrotron X-ray diffraction (SR-XRD).

Modern instrumentation and analysis of clay minerals will play essential roles in modern clay research that is essential to a full understanding of the genesis, role and potential new uses for clays and clay minerals, focused on processing and modifying of clay minerals in order to participate in new adsorbents, catalysts and biomaterials. Indeed, advanced clay-based nanomaterials create great expectations for the use of clay minerals in new approaches to sustainable energy, green environment and human health.

These new facilities and the increasing number of clay researchers with education on both fundamental and applied fields of mineralogy, crystallography, physics, chemistry, geochemistry, soil science, agronomy, ceramics, civil engineering, industrial minerals, mineral oil and gas geology and engineering, materials science, nanomaterials, environmental science and health science have contributed for the progressive increase of the number of annual publications.

The identification and characterization of clay minerals based on X-ray analysis (both structural and chemical), thermal analysis (both gravimetric and differential) and infrared spectra analysis have beneficiated of the excellent and indispensable contributions, under the form of textbooks or chapters of books by Grim (1953, 1962, 1968), Kübler (1964, 1968), Jackson (1956), Worrall (1975, 1982), Thorez (1975, 1976), Caroll (1979), Bailey (1980a, b), Caillère et al. (1982, 1989), Brindley and Brown (1980), Chamley (1989, Wilson (1987, 2003, 2013), Velde (1992), Meunier (2005), Brigatti et al. (2006), Murray (2006).

In the fields of clay mineralogy, geology, geochemistry, genesis, properties, as well as in the fields of industrial, environmental and medicinal applications, some relevant textbooks and book chapters are herein mentioned: Kubler (1964), Millot (1970), Worrall (1975, 1982), Grim and Guven (1978), Wilson (1987), Chamley (1989), Veniale (1996), Murray (2006), Christidis (2011).

Wang and Wang (2019), editors of the book *Nanomaterials from Clay Minerals: A New Approach to Green Functional Materials* published by Elsevier, in the book preface after consulting the database of the Web of Science, mention that in 2018 the number of publications involving research on clays and clay minerals was estimated in 8167.

Notwithstanding the Clay science being a recent scientific field, effectively created in the initial years of the twentieth century, counting 15 publications in 1915 and 600 in 1990, it had particularly flourished after 1990. Dozens of periodicals publish the results of the research being produced, the scientific journals *Clays and Clay Minerals*, *Clay Minerals*, and *Applied Clay Science* being the most notorious.

A particular reference deserves the series of handbooks on *Developments in Clay Science* produced by Elsevier Ltd, dealing with various scientific areas and topics of clay science, the first book of a total of nine was issued in 2006, and the last one in 2018.

6.2 Concepts of Clay and Clay Mineral

Both AIPEA and CMS Nomenclature Committees have been involved along 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 several reports with recommendations: Brindley and Pedro (1970, 1976), Bailey et al. (1986), Bailey (1989), Guggenheim et al. (1997), Guggenheim et al. (2002), and Guggenheim et al. (2006).

Recommendations have been proposed too in joint reports of AIPEA and CMS Nomenclature Committees (Guggenheim and Martin 1995, 1997) and by the CMS Nomenclature Committee (Bailey et al. 1971a, b; Bailey et al. 1979; Martin et al. 1991).

Despite the continued efforts of the Nomenclature Committees referred to, the definitions of *clay* and *clay minerals* still are not unanimous. Such could be understood because, for instance, clay being most probably the mineral resource exhibiting the highest variability in geological, textural and mineralogical terms and the most diverse applications, either the professionals, or the disciplines interested on 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 geological 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's crust and the atmosphere, hydrosphere and biosphere as the result of the mechanical and/or chemical alteration of rocks; also, *geologists* classify clays on the basis of their origin and occurrence: residual or primary and sedimentary or secondary (marine, alluvial, glacial, and eolian).
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 on their composition.
3. *Petrologists* consider *clay* as a rock, as a rule weakly consolidated, formed by very fine mineral particles non-identifiable at naked eye or using a magnifying glass.
4. *Sedimentologists* consider *clay* as a granulometric term that identifies the sediment fraction composed of particles with ESD (equivalent spherical diameter) less than 2 μm.
5. *Civil and geotechnical engineers* consider *clay* as the less than 4 μm fraction of the soil and classify clays or clayey soils as swelling or non-swelling, soft or hard, that is selecting the most relevant properties that should be taken into account when the foundation of housing and public construction works is based on them.
6. *Ceramists* consider *clay* as a natural geological 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 on the basis of their plasticity, firing properties and uses: low plasticity, medium plasticity, high plasticity; white burning, red burning, high or low refractory; common clay (brick and roof tile clay and pottery clay); special clay (china clay, fire clay, flint clay, ball clay, bauxitic clay, fibrous clay).
7. *Paedologists* consider *clay* as the active fraction of the soil that comprises particles of colloidal size (<0.1 μm) that results from the action of paedological pro-

cesses 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* as the colloidal fraction of the soil, important in terms of structure, texture and composition for vegetal fixation and growth.
9. Even the *non-educated people* consider *clay* as a type of earth that gets slippery when wet and that could be moulded or shaped.

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

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

Clay is "a natural material, mostly composed by fine-grained minerals, mainly hydrated phyllosilicates the so-called clay minerals; clay, in general, exhibits plastic behaviour and hardens after drying or firing; associated to 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, responsible for clay plasticity and hardening after drying and firing".

Clayey materials or clay-bearing materials are "those geological materials, such as shale, slate, phyllite, marl, marly limestone, lapilli tuff, hyaloclastite 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".

Distinctive parameters for clay and clay mineral should be taken into account in their concepts, well summarized by Bergaya and Lagaly (*in Handbook of Clay Science*, Elsevier, 2006):

> For clay: "Natural; fine-grained (<2 μm or <4 μm); 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".

Very recently, Moreno-Maroto and Alonso-Azcárate (2018), soil specialists, state that particle size criterion is not proper to differentiate clays, clayey materials and non-clayey soils while plasticity is. Plasticity is defined as "the ability of a material to be molded to any shape". Plasticity is a fundamental property in the processing of clay- based materials since it defines the technical parameters to convert a ceramic mass into a given shape by application of pressure (Moore 1965). Plasticity in clay-water systems is defined as the "property of a material which allows it to be repeatedly deformed without rupture when acted upon by a force sufficient to cause deformation and which allows it to retain its acquired shape of the removal of the applied force (Perkins 1995). Several measuring techniques and devices can be used to determine the plasticity of clay-water systems, such as: Atterberg method, Pfefferkorn method, penetration methods, Capillary rheometer method, Torque rheometer method (Andrade et al. 2011). Mineralogical composition, particle size distribution, water nature and content, and organic substances nature and content are the major conditioning factors of clay-water plasticity.

Guggenheim and Martin (1995) state that in the case of clays, the plasticity is provided by clay minerals. It is well known that different species of clay minerals provide different plasticities, and such determines the minimum clay minerals' total content (as a rule >10%) that allows the classification of a geological material as a clay.

Moreno-Maroto and Alonso-Azcárate (2018) have put forward a new definition of *clay* based on plasticity, the ratio plasticity index/liquid limit (PI/LL) being a great indicator that soil and clay scientists could use to classify soil textures based on PI/LL ratio and sand percentage. A fine-grained material can be defined as a *clay* when PI ≥ LL/2 and a moderately or slightly clayey material if LL/3 < PI < LL/2 (LL being the Atterberg liquid limit). The authors propose the following definition for clay:

"A naturally occurring material composed primarily of fine-grained minerals whose PI is equal to or higher than LL/2, so that a 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, so that a clayey material is slightly or moderately plastic at those water contents located 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".

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

The only factor able to definitively distinguish clay from non-clay geological materials is the existence of clay minerals in clay. But an important and decisive question remains concerning the clay concept. What is the less clay minerals' content able to allow the classification of a geological material as *clay*? Mineralogical composition, grain size and plasticity are complementary factors that could help to solve the question. With regard to clay minerals' definition, classification and nomenclature, over the times there has been some controversy too.

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 the human life in particular. Clay minerals are defined as "fine-grained hydrous phyllosilicates, 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".

Clay 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.

What really characterizes and distinguishes mineral species, clay mineral species included, is their specificity in terms of chemical composition and 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 happens with the clay minerals *dickite* and *nacrite*, both polymorphs of *kaolinite*. As a rule, individual crystals of clay minerals exhibit micrometric sizes; in spite of some clay minerals, such as true micas, vermiculites and chlorites, they could exhibit millimetric and centimetric sizes.

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

Clay by definition is a geomaterial of natural occurrence mainly composed of fine-grained minerals, and within these minerals, the so-called clay minerals are essential or fundamental constituents. *Clay minerals* by definition are hydrous phyllosilicates that as a rule are characterized by plasticity exhibition, property observable as far as water is added to them in sufficient quantity, and by the property of getting hard after drying and firing.

Besides clay minerals, clay could contain silicates such as *quartz*, *feldspar* and *mica*; carbonates such as *calcite* and *dolomite*; iron and aluminium 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* and *ferrihydrite*; and amorphous iron hydroxides.

Man has used clay since the Neolithic initiated, approximately, at 10,000 years ago, period represented by polished stone and pottery. Ceramics is indeed the traditional field of clay application. The "Venus of Vestonice" found in 1920 in Dolní Vestonice, Moravia, Czech Republic, is the oldest known piece of baked clay, around 10 cm tall, and dated 23,000 years old. Within clay-based fragments of statuettes portraying wolves, horses, foxes, birds and women, the "Venus of Vestonice" is one of these prehistoric female figures that have remained almost undamaged. Another piece made of baked clay is the most recent archaeological find, the well-preserved bison found in the caves of Tuc d´Audoubert, in France, dated 12,000 years old.

Ceramics defined as man-made "nonmetallic inorganic solids" (Kingery et al. 1976) is classified into two classes: *traditional ceramics* and *advanced ceramics*, the first one based on baked or fired clay or pottery ware, the second one considered to be generally developed within the last 100 years.

Pottery ware is divided into two types: vitrified ware and nonvitrified ware, and within these divisions, we have distinct types: red paste pottery, and white paste pottery (earthenware, stoneware, porcelain of soft-paste and hard-paste, and bone china).

Advanced ceramics, also referred to as “special”, “technical” or “engineering” ceramics, exhibit superior mechanical properties, corrosion/oxidation resistance or electrical, optical and/or magnetic properties.

6.3 General Notes on Crystallochemistry and Systematics of Clay Minerals

By definition, as aforesaid, clay minerals are hydrous phyllosilicates of fine granularity and planar or non-planar structure that can provide plasticity to the clay in which they participate, if the right amount of water is added and afterwards dried and fired.

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

In the ionic state, the chemical elements referred to above resemble small spheres that can be arranged or organized 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 picometres (1 pm ± 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 crystallochemical 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 in their crystallochemical structures:

Anions:

O^{2-}, 140 pm; OH^{-}, 141 pm; F^{-}, 136 pm

Cations in the structural tetrahedral sheets:

Si^{4+}, 40 pm; Ti^{+4}, 68 pm; Al^{3+}, 51 pm; Fe^{3+}, 64 pm; Cr^{3+}, 69 pm

Cations in the structural octahedral sheets:

Mg^{2+}, 66 pm; Ca^{2+}, 99 pm; Fe^{2+}, 74 pm; Mn^{2+}, 80 pm; Zn^{2+}, 74 pm; Cu^{2+}, 72 pm

Interlayer cations:

Na^{+}, 97 pm; K^{+}, 142 pm; Li^{+}, 68 pm (interlayer spaces can be occupied too by cations that usually occupy *octahedral sites*)

6.3.1 Electric Charge of Clay Minerals

In clay minerals, as in other minerals, however to a greater degree and extent, justified by the conditions of their formation in terrestrial/hydrosphere/atmosphere/biosphere, interface environments characterized by large metastability, an electric charge is developed in their particles. Two types of electric charge exist in minerals: (1) a permanent charge resulting from higher valence cations replaced by lower valence cations or from atomic omissions in crystals 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 in particular produces the appearance of an overall negative *electric charge* on the basal surfaces of clay particles whose value per unit cell varies according to 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 *electric charge*, a little higher than zero, because the isomorphous atomic substitution is almost absent in this clay mineral of very simple chemical composition; the clay mineral *montmorillonite*, $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2nH_2O$, relative to kaolinite has a more complex chemical composition, and the electric charge shows values between 0.45 and 0.6; and the clay mineral called *illite* shows the highest value of electric charge, about 1.

Figure 6.1 shows a schematic representation of the electric charge distribution on clay mineral surfaces.

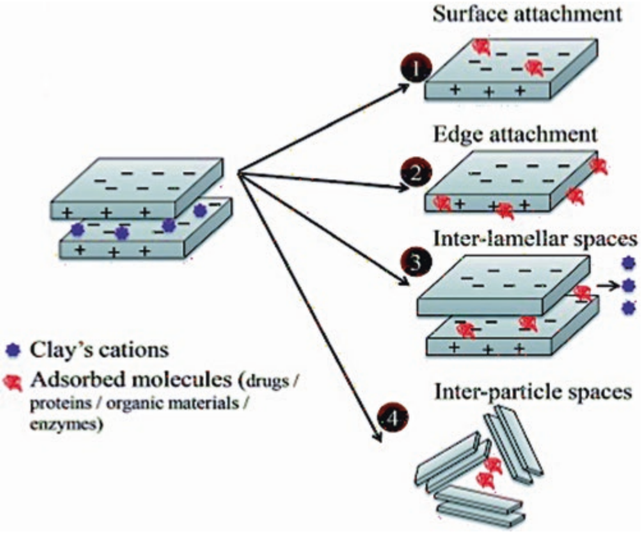


Fig. 6.1 Schematic representation of electric charge distribution in clay mineral surfaces (*In*: Ghadiri et al. 2015)

When dispersed in water, the electric charge distribution on clay mineral surfaces is very much influenced by the pH of the dispersion medium. Low pH turns particle edges positively charged and particle basal faces negatively charged conditions favourable to interparticle attraction. High pH turns particle edges negatively charged and particle basal faces negatively charged too, conditions favourable to interparticle repulsion. Neutral pH creates negative and positive charges on particle edges and negative charges on particle basal faces, conditions favourable to interparticle attraction and repulsion. The three situations referred to naturally control the stability or instability of clay/water dispersions.

Electric charge, particle size and particle shape are the fundamental properties of clay minerals, the other properties being dependent on them.

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

1. The group 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 electric charge z ≈ 0 (as a rule, particularly in kaolinite, the electric charge value is little above zero due to very limited isomorphous substitution of Al for Fe or Mg, and Si for Al)
2. The group of high activity clay minerals, type 2:1 or T:O:T, named *illite/vermiculite/smectite group*, the electric charge z, as a rule, being less than 1

In group 1 the distribution of the basic chemical elements and the electric charge in the structural unit layer of kaolinite is shown in Table 6.1a.

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 electric charge in the case of *montmorillonite* structural unit layer is shown in Table 6.1b.

In real kaolinite and in the smectite group of clay minerals that includes *montmorillonite*, as well as in other clay minerals, the electric charge always exists due to

Table 6.1a Electric charge distribution in the structural unit layer of *kaolinite*

Electric 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

Table 6.1b Electric charge distribution in the structural unit layer of *montmorillonite*

Electric 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

various types of crystal defects, those due to isomorphous substitution being the determinant ones.

Konta (1998) also on the basis of *electric charge*, but not only, considers five groups of clay minerals:

1. Low-medium electric 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 electric charge clay minerals, in the case of *dioctahedral* and *trioctahedral micas*, which include unsolvated intercalated cations and having 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 pseudocode structures, *palygorskite* and *sepiolite*, which have four different types of water, large microchannels and high absorbent capacity.
5. Amorphous or almost amorphous clay minerals, such as *allophane* and *imogolite*, which have high chemical reactivity and anionic adsorption.

The *electric charge* is usually determined in the clay minerals with expansive structure (*smectites* and *vermiculites*) by two methods:

1. One based on the exchange capacity of the alkylammonium cation.
2. Other based on the structural formula calculation.

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

1. *Cationic clay minerals* (cationic CM) which possess a general negative electric charge and are widespread in nature (e.g. *kaolinite* and *montmorillonite*).
2. *Anionic clay minerals* or layered double hydroxides (LDH) which possess a positive electric charge and are rarely found in nature, but rather simple and economical to synthesize.

From the applied point of view, the cationic clay minerals are much more interesting than the 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).

6.3.2 Active Sites and Functional Groups in Clay Mineral Surfaces

The electric charge of clay minerals of type 2:1, besides being a very important criterion used in the systematic 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 by the high water retention capacity for many clays and 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 certain clays (Chap. 7, item 7.5 of this book).

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 electric 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 nonreactive 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 isomorphous 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, Mg, 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 when in the state of maximum oxidation (e.g. Cu^{2+} and Fe^{3+}, which being reduced can form organic cations) occupy exchange cationic sites.
4. Sites where water molecules envelop by solvation and coordinate the exchange cations becoming polarized and functioning 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 (e.g. 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 electric charge both in polar liquids such as water by two mechanisms:

1. First by atomic isomorphous substitutions both in tetrahedral and octahedral sheets, situations that 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 being 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).

But according to the same authors, clay minerals can acquire electric charge in non-aqueous apolar liquids by the addition of surfactants usually used to improve the stability of the mineral dispersion, the charging being the result of the acid-base mechanism of interaction between the clay particles and the suspending medium.

The location of the isomorphous, octahedral or tetrahedral substitution sites has a great influence on the adsorption of polar organic molecules. On the other hand, the OH groups of the crystalline edges of the clay minerals constitute strongly active sites and are responsible for the electric charge of pH-dependent clay and clayey soils. At low pH, the mentioned sites develop a positive charge due to the adsorption of protons and can interact with organic acids and oxyanions. Increasing the pH shows a certain value for which the electric charge is neutral (point of zero charge or PZC) and from this value the charge becomes negative. In clay minerals with very low electric 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 crystallochemical 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.

6.3.3 Basic Units of Clay Mineral Structures

The basic structural components of clay minerals, in increasing order of complexity, are the following: *ions*, *atomic planes* or *structural planes*, *structural sheets*, *structural layers* and *structural unit* (Fig. 6.2).

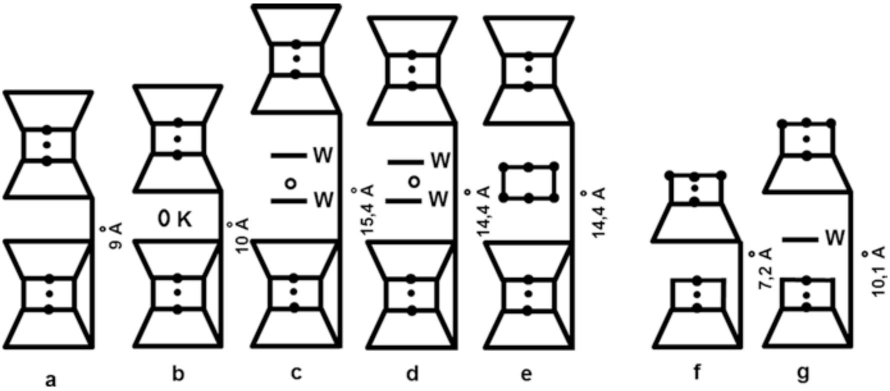
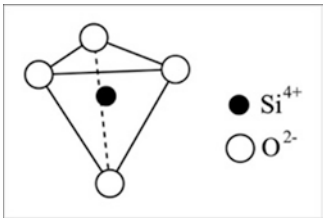


Fig. 6.2 Schematic representation of structures and respective basal spacings $d_{(001)}$ of the main clay mineral species: • octahedral cations; ◦ exchange cations; OH groups; 0 interlayer cations; w, water layers; (**a**) pyrophyllite; (**b**) mica; (**c**) montmorillonite; (**d**) vermiculite; (**e**) chlorite; (**f**) kaolinite; (**g**) fully hydrated halloysite

Fig. 6.3 Tetrahedron [SIO_4]



The *atomic planes* comprise the atoms on their ionic form that are arranged in the structure of the clay mineral. The *structural sheets* are groupings of atoms distributed through several atomic planes, atoms that constitute polyhedric configurations, *tetrahedron* or *octahedron* (Figs. 6.3 and 6.4), which in turn associate and form tetrahedral structural sheets and octahedral structural sheets (Figs. 6.5 and 6.6).

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 ion coordinates are O^{2-} and HO^{1-}.

Both tetrahedral and octahedral units are linked together in planar developments, 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 getting organized 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 general composition T_2O_5, where T represents the tetrahedral cation, i.e. with 4 (four) or tetrahedral coordination. The

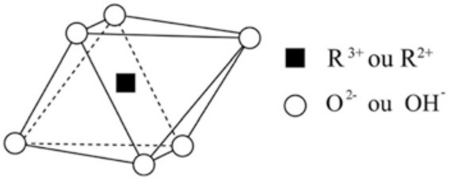


Fig. 6.4 Octahedron [(R^{2+} or R^{3+}) O_6], R^{3+} = Al, Fe^{3+}; R^{2+} = Mg, Fe^{2+}

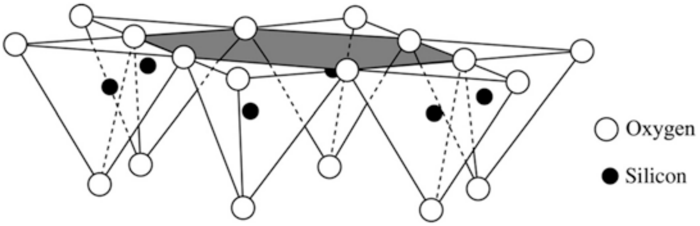


Fig. 6.5 Diagram of the tetrahedral structural sheet showing the hexagonal "hole" represented by the grey colour

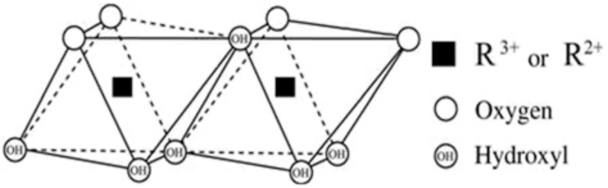


Fig. 6.6 Diagram of the octahedral structural sheet

tetrahedral cation which as a rule is Si can be partially replaced by Al and/or Fe. Also, Si occupies the tetrahedra centres, while the vertices are occupied by oxygens. Each tetrahedron connects to adjacent tetrahedra by sharing the three coplanar 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 octahedra are connected laterally to each other, they have the respective centre occupied by an octahedral cation, 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 number of 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 by symmetrical and periodic repetition originates the entire structure of the clayey mineral, which comprises the representation of the basic structural layer and the content of space, when there are structural interlayers. The *unit chemical formula* expresses the chemical composition of the *structural unit*. It is the organization of the *structural unit*, more precisely the number and nature of the structural tetrahedral (T) and octahedral (O) sheets, that make up the *structural unit*, and what 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 6.2 shows, schematically, the various structures and their respective characteristic basal spacings identified on X-ray diffraction patterns of the main clay mineral species.

The basal spacing $d_{(001)}$ of a 1:1 structure is slightly higher than 7 Å (angstrom) or 0.7 nm (nanometre), while the basal spacing $d_{(001)}$ of a 2:1 structure is about 10 Å, i.e. about 1 nm, 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 take values between 7 Å and 18 Å depending on the type of the structural layer that is the basic component of the *structural unit* and the occupation of the structural interlayers by certain chemical species: cations, water and hydroxyls.

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

$$7\ \overset{\circ}{A} = O_5\left(OH\right)_4 = 14^{e-}$$

$$10\ \overset{\circ}{A} = O_{10}\left(OH\right)_2 = 22^{e-}$$

$$14\ \overset{\circ}{A} = O_{10}\left(OH\right)_8 = 28^{e-}$$

Figures 6.3 and 6.4 show the fundamental or basic units, tetrahedron and octahedron, the building blocks of clay mineral structures.

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

Table 6.3 Classification of *hydrous phyllosilicates* or *clay minerals* of planar structure (*In:* Guggenheim et al. 2006)

Layer type	Interlayer material[a]	Group	Octahedral character	Species[b]
1:1	None or H_2O only (x~0)	Serpentine-kaolin	Trioctahedral Dioctahedral Di,trioctahedral	Lizardite, berthierine, amesite, cronstedtite Kaolinite, dickite, nacrite, halloysite (planar) Odinite
2:1	None (x~0)	Talc-pyrophyllite	Trioctahedral Dioctahedral	Talc, willemseite, kerolite, pimelite Pyrophyllite, ferripyrophyllite
	Hydrated exchangeable cations (x~0.2–0.6)	Smectite	Trioctahedral Dioctahedral	Saponite, hectorite, sauconite, stevensite, swinefordite Montmorillonite, beidellite, nontronite, volkonskoite
	Hydrated exchangeable cations (x~ 0.6–0.9)	Vermiculite	Trioctahedral Dioctahedral	Trioctahedral vermiculite Dioctahedral vermiculite
	Hydrated mono- or divalent cations (x~ 0.6–0.85)	Interlayer-deficient mica	Trioctahedral Dioctahedral	Wonesite[c] None
	Non-hydrated monovalent cations (≥50% monovalent, x~ 0.85–1.0 for dioctahedral)	True (flexible) mica	Trioctahedral Dioctahedral	Phlogopite, siderophyllite, aspidolite Muscovite, celadonite, paragonite
	Non-hydrated divalent cations (≥50% divalent, x~1.8–2.0)	Brittle mica	Trioctahedral Dioctahedral	Clintonite, kinoshitalite, bityite, anandite Margarite, chernykhite
	Hydroxide sheet (x = variable)	Chlorite	Trioctahedral Dioctahedral Di,trioctahedral Tri,dioctahedral	Clinochlore, chamosite, pennantite, nimite, baileychlore Donbassite Cookeite, sudoite None
2:1	Regularly interstratified (x = variable)	Variable	Trioctahedral Dioctahedral	Corrensite, aliettite, hydrobiotite, kulkeite Rectorite, tosudite, brinrobertsite
1:1, 2:1			Trioctahedral	Dozyite

[a] x is the net layer charge per formula unit, given as a positive number

[b] Not an exhaustive list of species; in general, listed in order of abundance

[c] Net layer charge may be <0.6, but this is an exception

Table 6.4 Classification of *clay minerals*, hydrous phyllosilicates, of non-planar structure (*In*: Guggenheim et al. 2006)

Layer type	Modulated component	Linkage configuration	Unit layer, c sinβ value	Traditional affiliation	Species
Modulated structures					
1:1 Layer	Tetrahedral sheet	Strips Islands Other	7 Å 7 Å	Serpentine Serpentine None	Antigorite, bementite Greenalite, caryopilite, pyrosmalite, manganpyrosmalite, ferropyrosmalite, friedelite, megillite, shallerite None
2:1 Layer	Tetrahedral sheet	Strips Islands Other	9.5 Å 12.5 Å 9.6–12.5 Å 12.3 Å 14 Å	Talc Mica Mica/complex Other Chlorite	Minnesotaite Ganophyllite, eggletonite Zussmanite, caryopilite, manganopyrosmalite, ferropyrosmalite, friedelite, megillite, schallerite, nelenite Bannisterite Gonyerite
	Octahedral sheet	Strips	12.7–13.4 Å	Pyribole	Sepiolite, loughlinite, falcondoite, palygorskite, yofortierite
Rolled and spheroidal structures					
1:1 layer	None	Trioctahedral	-	Serpentine	Chrysotile, pecoraite
		Dioctahedral	-	Kaolin	Halloysite (non-planar)

6.3.4 *Crystallochemistry and Systematics of Clay Minerals*

Presently about 70 species of clay minerals are known, species distinguished by their crystallochemical specificities, which as a rule, based on common structural and chemical features, can be gathered into two main groups (see Tables 6.3 and 6.4, and Guggenheim et al. 2006):

1. *Planar hydrous phyllosilicates*, i.e. *planar clay minerals.*
2. *Non-planar 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).

All the groups referred to will be described below; those clay minerals with health interest and application, as are the cases of *kaolin* and *smectite*, deserved a more detailed treatment.

Non-planar phyllosilicates comprise clay mineral species whose particles exhibit fibrous, tubular and spheroidal shapes, and with these characteristics, two groups of clay minerals are defined: *halloysite*, *chrysotile*, *antigorite*, *sepiolite*, *palygorskite*, *allophane and imogolite*.

Sepiolite, *palygorskite* and *halloysite* due to their health interest and application deserved a more detailed treatment.

The underdescribed characterization of clay minerals gives particular development to those clay minerals recognized as having more interaction with human health.

6.3.4.1 Clay Minerals with Planar Structures

6.3.4.1a: Kaolin-Serpentine Group of Clay Minerals

Kaolinite and *halloysite* are dioctahedral T:O or 1:1 clay mineral, and they are the most representative species of the Al-rich *kaolin subgroup*, and their ideal chemical compositions are $Al_2Si_2O_5(OH)_4$ for *kaolinite* and $Al_2Si_2O_5(OH)_4.2H_2O$ for *halloysite*.

Dickite and *nacrite* are two other species of the *kaolinite subgroup*, really polytypes of kaolinite. Unlike *kaolinite*, *dickite* and *nacrite* whose particles exhibit platy shapes, *halloysite* particles can exhibit platy, tubular and spheroidal shapes.

Lizardite, *antigorite* and *chrysotile* are trioctahedral T:O or 1:1 clay mineral, and they are the most representative species of the *serpentine subgroup*, and being Mg rich, $Mg_3Si_2O_5(OH)_4$ is the expression of their ideal chemical composition.

Figures 6.5 and 6.6 schematically show the tetrahedral and octahedral sheets which are the basic components of the crystallochemical structures of the *kaolin-serpentine* group of clay minerals.

Figure 6.7 shows schematically the structure of the clay mineral *kaolinite*.

$R^{3+} = Al^{3+}, Fe^{3+}\ldots$ $R^{2+} = Mg^{2+}, Fe^{2+}, Ni^{2+}\ldots$

In kaolinite, R^{3+} is aluminium Al^{3+}.

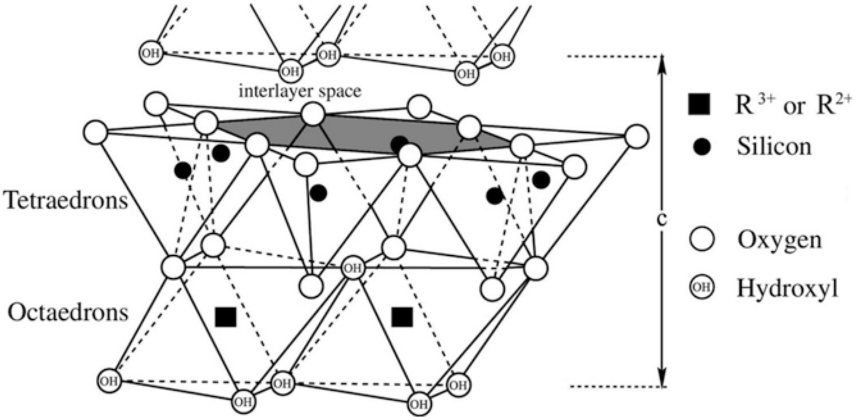


Fig. 6.7 Diagram of the T:O, OR TE:OC, OR 1:1 *kaolinite* structure

The name “kaolin” is derived from “Gaoling”, the Chinese word meaning “High Ridge”, a Chinese village near Jingdezhen in south-eastern China, Jiangxi Province. The name entered the English in 1727 from the French version of the word *kaolin*, following François Xavier d’Entrecolles’s reports on the making of Jingdezhen porcelain.

Kaolinite subgroup minerals have a permanent dipole moment due to their structural asymmetry, the structural unit showing two distinct surfaces.

The theoretical chemical formula of *kaolinite*, structurally triclinic, is $Al_2Si_2O_5(OH)_4$, that means SiO_2-46, 54%; Al_2O_3-39, 50%; and structurally bonded hydroxyls, -13.96% (value corresponding to the weight loss on ignition).

The OH groups are very important constituents of the *kaolin subgroup minerals* (kaolinite, dickite and nacrite). There are two types of OH groups: structural OH coordinated to Al and surface OH positioned at the layer broken edges. The structural OH groups through hydrogen bonds OH…O condition the layer stacking.

A typical crystal of kaolinite has a thickness of the order of 50 to 100 nm, the thickness of a single kaolinite structural layer being 0.7 nm, which means that the typical crystal before referred to consists of 70–200 individual layers stacked on top of each other Layers are stacked along the c axis by hydrogen bonding interaction. The electrical charge of the layer unit is near to zero.

Exposed surface OH groups, especially under-coordinated OH groups positioned at the broken edges, exert great influence on clays’ rheological properties as well as on their ability to bind metals and oxyanions. Water molecules are always associated with clay minerals due to the small particle size, large external and internal surface area and electric charge of clay minerals.

Intercalation of certain polar molecules (e.g. K-acetate, urea, hydrazine, dimethyl sulphoxide and formamide) in *kaolinite* interlayer spaces is an important property of *kaolinite*, and it can take place when the bonding energy of the intercalate compound overcomes the original interlayer energy. The molecules referred to have the ability to interact favourably with both the siloxane and surface hydroxyls and to overcome the existing interlayer forces. Although direct intercalation is limited to small intercalate molecules, larger molecules can be introduced indirectly into the interlayer space following the formation of “primary intercalates” (Johnston 2010).

Chemical intercalation associated to ultrasonication can be used for kaolinite delamination, important for certain kaolinite applications. Kaolinite delamination can be achieved by grinding and high-pressure extrusion. In *kaolinite*, the bonding between adjacent structural layers is made through hydrogen H–O bonds and van der Waals bonds, naturally weak chemical bonds, reason why *exfoliation* in kaolinite as well as in other *kaolin minerals* requires low energy. In *kaolinite*, the interlayer space (Fig. 6.7) is almost inexistent.

Kaolinite normally occurs as stacked pseudohexagonal platelets frequently exhibiting booklet-like shape (Fig. 6.8). Each *kaolinite platelet* is an association of several structural layers, each layer consisting of one tetrahedral sheet bond to one octahedral sheet.

Like in other clay minerals, structural order-disorder occurs in kaolin subgroup minerals. For instance, various order-disorder degrees can be found in kaolinite,

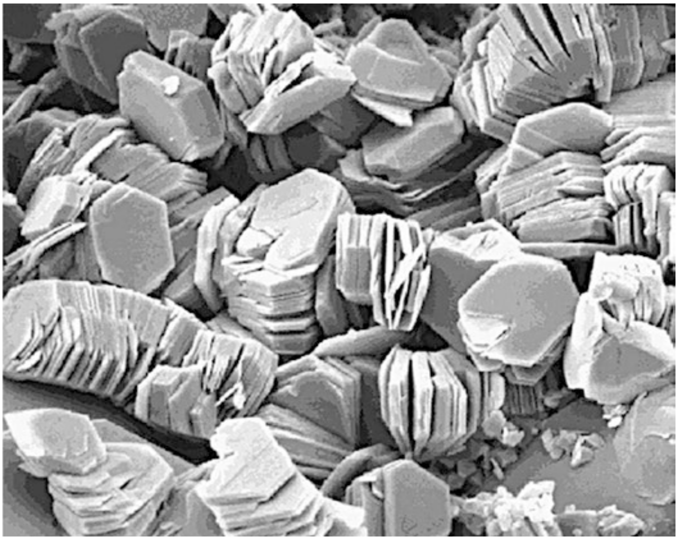


Fig. 6.8 "Booklets" of pseudohexagonal platy particles of *kaolinite*

which can condition, for instance, rheological properties and chemical activity (Plançon and Thchoubar 1977a, b; Plançon 2001; Johnston et al. 2008).

Kaolinite is very resistant to chemicals (chemical inertness over a wide range of pH 4–9) and to heat (melting point at 1785 °C). In raw kaolin, *kaolinite* is associated to minerals considered as impurities such as *quartz*, *feldspar*, *mica*, *anatase*, *rutile* and iron oxides and hydroxides (*hematite*, *goethite*).

Each *kaolinite layer* is considered a strong dipole: the *siloxane surface* being hydrophobic is dominated by negative charges; the *aluminol surface* being hydrophilic is dominated by positive charges. Such explains why *kaolinite* individual layers are strongly bonded by hydrogen and dipolar interactions.

Kaolin and kaolinite are classified as eco-friendly mineral resources with important applications in biomedicine, energy and electronics. Most applications require the modification and transformation of kaolinite crystallochemistry, through thermal activation, acid activation, alkaline activation, mechanical activation and organification activation.

A reference is due to a very recent work of Cheng et al. (2019) on "Kaolinite Nanomaterials: Preparation, Properties and Functional Applications" that is Chap. 6 of the book entitled *Nanomaterials from Clay Minerals: A New Approach to Green Functional Materials* edited by Wang A and Wang W and issued by Elsevier. The main reserves of kaolin and kaolinite occur in the USA, Brazil, England, France, Germany and China.

There are clay minerals of the *kaolin group* which particles do not show platy morphology; indeed, they commonly exhibit tubular shapes and rarely spherical shapes.

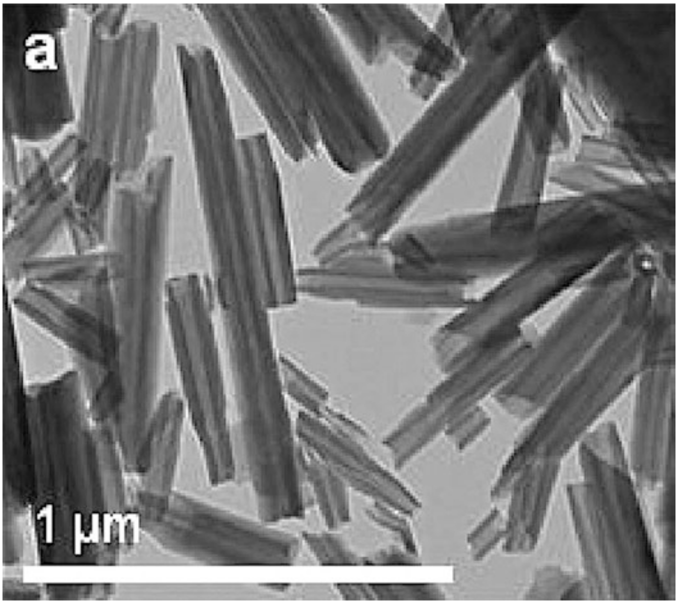


Fig. 6.9 Rolled and tubular particles of *halloysite*

Figure 6.9 shows the tubular shape that, as a rule, is exhibited by *halloysite* crystals, *halloysite* being a species that belongs to the *kaolin subgroup* of clay minerals characterized by dioctahedral T:O structures.

The name *halloysite* was dedicated by Berthier in 1826 to Baron Omalius d'Halloy who investigated this mineral found in dissolution cavities of Carboniferous limestone, in the region of Liège, Belgium. *Halloysite* may be considered as being a *hydrated kaolinite*, water being present in the interlayer space, hence justifying the general chemical formula $Al_2Si_2O_5(OH)_4.2H_2O$, characterized by a layer periodicity of 10 Å, i.e. $d_{(100)} = 10$ Å. Comparatively to *kaolinite* which $d_{(100)} = 7.2$ Å, *halloysite* has an additional water monolayer between the adjacent layers.

Brigatti et al. (2006, 2013) and Detellier and Schoonheydt (2014) propose explanations for the change of *kaolinite* platelets into *halloysite* rolls. The substitution of Fe^{3+} for Al^{3+}, the first larger than the second, the distribution of vacant sites in the octahedral sheet and the orientation of hydroxyl groups could contribute for that change. *Halloysite rolls* or *tubes* are formed as a result of strains caused by lattice mismatch between adjacent tetrahedral and octahedral sheets.

Hydrated halloysite has a layer periodicity or basal spacing very close to 10 Å, reason why it is called *halloysite 10 Å*. The interlayer water can be easily removed at 70–100 °C, and the dehydrated form having a basal spacing of 7.2 Å is called *halloysite 7 Å*, although the name *metahalloysite* is sometimes used.

According to Churchman et al. (1972), the dehydration process is progressive. Natural *halloysite* may exhibit intermediate degrees or levels of hydration.

The collapse of the *halloysite* structure occurs at approximately 400 °C, i.e. at lower temperature than the one required for kaolinite structure collapse.

Pure kaolinite and halloysite are white minerals. In case they exhibit other colours (yellowish to brown), such is due to isomorphous substitution of Si^{4+} or Al^{3+} by metal ions, such as Fe^{3+}, Cr^{3+} and Ti^{4+}.

Differences in ion size and other structural defects (e.g. ion vacancies) may cause the weakening of the interlayer hydrogen bonds and consequently the rolling of the multilayer *halloysite* structure. The mechanism of halloysite curling is still a matter of discussion. Kirkman (1981) has proposed a curling mechanism based on crystal internal dislocations. Dimensions of the *halloysite* tubes vary depending on the natural occurrence, the tubes length in the range of 0.5–2.0 μm, the outside diameter in the range of 50–200 nm and the internal lumen diameter in the range of 10–50 nm.

One of the important features of *halloysite* tubes is the different surface chemistry of the inner and outer sides of the tubes: silica sheets occur on the external surfaces of the tubes and exhibit a negative charge above pH 1.5, whereas alumina sheets make up the inner surfaces involving tubes lumen showing a positive charge up to pH 8.5. The difference in tubes surface charges allows for the selective modification of inner and external surfaces of *halloysite nanotubes* and selective loading of negatively charged molecules within halloysite internal lumens.

Halloysite nanotubes can be selectively modified at external or internal sides by using silanes or polyphosphates. *Halloysite nanotubes* can be loaded with a broad variety of substances, from simple organic and inorganic molecules to high-molecular-weight polymers and biologically active substances, including drugs and enzymes (Price et al. 2001; Lvov et al. 2008; Lvov 2008; Levis and Deasy 2003; Kelly et al. 2004).

Churchman and Pasbakhsh (2015) discuss the current trends in research and application of natural mineral nanotubes. *Halloysite* nanotubes can be successfully loaded with various types of active agents including pharmaceutical agents and antibacterials. Lumen loading capability and controlled release are important features in what concerns biomedical applications. The release from halloysite lumen could last from several hours to days depending on molecular mass, structure and solubility of the active agent in the release medium (Lvov and Abdullayev 2013; Abdullayev and Lvov 2013).

A significant number of studies involving active agents encapsulated by halloysite nanotubes have been reported, such as *ibuprofen*, *curcumin*, *resveratrol*, *ofloxacin*, *gentamicin* and *mercaptobenzothiazole*.

Only two high-grade *halloysite* deposits are known in the world: one in Northland, New Zealand, from weathered rhyolite, and the other in the Tintic district of Utah, USA.

Wilson and Keeling (2016) describe the characteristics of most known commercial, or potentially commercial, *halloysite* deposits, in terms of both their geological settings, and also some of the main commercially important properties of the *halloysites* being mined, properties which include purity, composition, shape, colour and associated minerals. Hillier et al. (2016) describe systematic relationships between features in their X-ray diffraction patterns and infrared spectra that reflect variations in the size, shape and other physical characteristics of the halloysite nanotubes (HNTs).

Not all halloysites exhibit particle tubular shape. Cunningham et al. (2016) describe the novel occurrence in vermicular "book" form of *halloysite* in tuffs from New Zealand. The authors propose a mechanism for their formation that involves transformations from spherical, tubular and also platy forms.

Spheroidal or onion-like morphology of *halloysite* crystals is much rare than the tubular morphology, but in general they can coexist in the same deposit, situation recently well exemplified in *halloysite* deposits from Rio Negro, Patagonia, Argentina (Cravero et al. 2016), in which *halloysite*/*kaolinite* concentration ratio ranges from 75–25 to 100–0, *halloysite* and *kaolinite* being formed from weathering of volcanic-pyroclastic rocks.

The formation process of *spheroidal halloysite* is still a matter of discussion. Some authors consider that *spheroidal halloysite* results from the fast dissolution of volcanic glass yielding supersaturated solutions which favour the formation of this particular shape (Quantin et al. 1988; Adamo et al. 2001; Churchman et al. 2016).

The medicinal interest of *tubular halloysite* has only raised after 2005, in particular as drug carrier.

Recently, Hanif et al. (2016) have reviewed HNTs as a delivery system with applications in anticancer therapy, sustained and controlled release drug delivery systems, cosmetics, delivery of proteins, vaccines and genes. The authors have identified some characteristics of HNTs that are relevant to their use in these applications along with some of the methods for loading the tubes.

The use of *tubular halloysite* as drug carrier and deliver will be dealt with in Chap. 10 of this book. Unlike *tubular halloysite*, no medical applications have been found for *spheroidal halloysite*.

Some other authors propose that the origin of *spheroidal halloysite* is related to transformation of *allophane* (Askenasy et al. 1973; Sudo and Yotsumoto 1977; Quantin et al. 1988; Adamo et al. 2001).

6.3.4.1b: Pyrophyllite-Talc Group of Clay Minerals

There are clay minerals which structures are based on T:O:T or 2:1 structural layer, an octahedral sheet sandwiched by two tetrahedral sheets. There are clay minerals exhibiting such structure and simple chemical composition; they form the *pyrophyllite*/*talc group*, *pyrophyllite* $Al_2Si_4O_{10}(OH)_2$ being the dioctahedral species and *talc* $Mg_3Si_4O_{10}(OH)_2$ being the trioctahedral species.

The ideal structural layers of *pyrophyllite* and *talc* are nearly electrically neutral, and then no charge-balancing cation is present in the interlayer space. Isomorphous atomic substitutions are very limited, of Al^{3+} for Si^{4+} in *pyrophyllite* and of Al^{3+} or Fe^{3+} for Mg^{2+} in *talc*. Therefore, contiguous layers are held together mainly by van der Waals bonds, reason why crystal exfoliation requires very low energy.

Dehydration, that is, the loss of hydroxylic water, occurs in *pyrophyllite* above 800 °C. Talc-like minerals are *kerolite* (hydrated variety), *minnesotaite* (Fe-rich variety) and *willemesite* (Ni-rich variety). According to Harvey and Lagaly (2013), *talc* and *pyrophyllite* are important filler materials for polymer and rubber.

Talc is also used extensively in cosmetic and pharmaceutical powders. Talc is the softest known mineral. *Talcum powder* is made of pulverized talc. When it is finely ground, talc creates a smooth and silky powder that absorbs moisture, reduces odours and cuts down on friction. Those properties make it an ideal ingredient in baby powder, deodorant, makeup and hundreds of other consumer products. Talc dust can cause significant harm if it is swallowed or inhaled. Current research indicates that pure talc does not cause mesothelioma. However, if talc is contaminated with *asbestos* and *asbestiform minerals*, it could lead to the development of *mesothelioma*.

6.3.4.1c: True or Flexible Mica Group of Clay Minerals

There are clay minerals still based on T:O:T or 2:1 layer characterized by more complex chemical composition; they form the *group of true or flexible mica*, the *group of brittle mica*, the *group of interlayer-deficient mica*, the *group of smectite*, the *group of vermiculite* and the *group of chlorite*, all having in common a similar structural model. In each of these groups, there are dioctahedral and trioctahedral species.

The *group of true* or *flexible mica* and the *group of brittle mica* are distinguished from the *group of smectites* just in the interlayer space. Unlike the second group of clay minerals, the first group of clay minerals has non-hydrated exchangeable cations in the interlayer space.

True or *flexible mica* is distinguished from *brittle mica* because the interlayer of *true mica* is occupied by non-hydrated monovalent cations such as K^+ or Na^+ and the electric charge is x~0.85–1.0, whereas the interlayer space of *brittle mica* second is occupied by non-hydrated divalent cations such as Ca^{2+} and the electric charge is x~1.8–2.0.

Three representative species of *true* or *flexible mica* are identified and expressed by their structural chemical formula as follows:

Muscovite, $KAl_2(Si_3,Al)O_{10}(OH)_4$, known as white mica, is K and Al rich and dioctahedral true mica most widespread in the Earth's crust.

Biotite, $(K_{0.78}Na_{0.16})(Mg_{1.68}Fe^{2+}{}_{0.71}Fe^{3+}{}_{0.19}Ti_{0.34}Al_{0.19}Mn_{0.01})Si_{2.86}Al_{1.14})O_{10}(OH_{0.71}F_{0.29})$, known as black mica, is Mg and Fe rich and trioctahedral true mica most widespread in the Earth's crust.

Phlogopite, $(K_{0.93}Na_{0.04}Ca_{0.03})(Mg_{2.77}Fe_{0.10}Ti_{0.11})(Si_{2.88}Al_{1.12})O_{10}(OH_{1.49}F_{0.51})$, is the magnesium end member of the biotite solid solution series.

6.3.4.1d: Brittle Mica Group of Clay Minerals

Margarite, $CaAl_2(Al_2Si_2)O_{10}(OH)_2$, is the dioctahedral species, and *clintonite*, $Ca(Mg_2Al)(Al_3Si)O_{10}(OH)_2$, is the trioctahedral species, both the most representatives of *brittle micas*. The detailed classification of the mica group has been proposed by Rieder et al. (1998).

6.3.4.1e: Interlayer-Deficient Mica-Like Group of Clay Minerals

Illites, known as clayey micas, are the most abundant clay minerals in the Earth's crust, continental and marine. *Illite* is a dioctahedral interlayer-deficient series name to describe certain micas after only optical microscopic data become available.

Other dioctahedral interlayer-deficient micas of a series type are *glauconite* and *brammallite*.

There are *dioctahedral illite* and *trioctahedral illite*, the first crystallochemically close to *muscovite*, the second crystallochemically close to *biotite*, differentiated by much smaller crystal size, more degraded structure, little less Al content in the octahedral sheet, little less K content and little higher H_2O content in the interlayer space.

According to Brigatti and Guggenheim (2002), the term *illite* is applied to very fine 2:1 clay mineral which shows a non-expandable layer and a wide variety of chemical compositions.

Figure 6.10 shows the crystallochemical features of *illite/mica* (Grim 1962).

The chemical composition of *illite* differs from the composition of muscovite in having heterovalent isomorphous substitution (Al^{3+} for Si^{4+} and Fe^{2+}, Mg^{2+} for Al^{3+}) as well as homovalent isomorphous substitution (Fe^{3+} for Al^{3+}) and a layer charge between 0.6 and 0.9.

The diffraction maxima, on the X-ray diffraction patterns, are not as sharp in *illite* as in *muscovite*. Unlike in most of 1:1 clay mineral represented by *kaolinite*, in 2:1 clay mineral, the interlayer space between structural layers exists with a fixed value in micas and illite and with a variable value in *smectites* dependent upon the solvation capacity of the interlayer cation, Na^+ or Mg^{2+}.

In smectites, the nature of the interlayer cation very much conditions the smectites swelling capacity, highly dependent on the atomic substitution that mainly occurs in the inner octahedral structural sheets. Swelling is justified by the weak electrostatic energy existent between adjacent structural layers. Unlike in *smectites*, in *micas* and *illites*, the atomic substitution mainly occurs in tetrahedral sheets, i.e. in the outer sheets of the structural layers, reason why it is high the electrostatic energy of the bonds between adjacent structural layers.

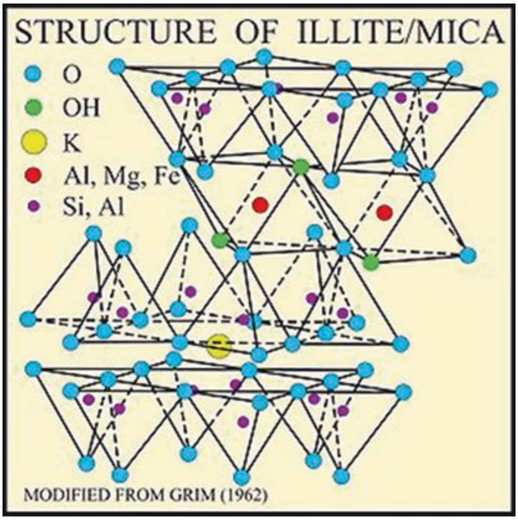


Fig. 6.10 Schematic representation of *illite/mica* structure

Within clay minerals, *illite* is the most common in the Earth's crust, being the major constituent of shales. In geological studies, illite "crystallinity" is a crystallochemical parameter used to classify low-grade metamorphic activity in pelitic rocks (Abad 2003). Determining the "illite crystallinity index" allows geologists to designate what metamorphic facies and metamorphic zone the rock was formed in and to infer what temperature the rock was formed.

According to Merriman and Peacor (1998) three kinds of data are useful to deduce the sedimentary-basin maturity what is of paramount importance, for instance, to determine the hydrocarbon potential of a sedimentary basin:

1. Clay mineral assemblages
2. Quantification of mixed-layer clay minerals
3. Clay minerals "crystallinity"

The Kübler index (KI) introduced by Kübler (1964) for petroleum exploration purposes is the preferred index to be used in illite crystallinity studies based on its reproducibility and simplicity. The KI measures the changes in the shape of the first X-ray diffraction basal reflection (d_{100}) of illite-muscovite that corresponds to a spacing of approximately 10 Å and is experimentally determined by measuring the full width at half maximum height.

Prior to the introduction of the Kübler index, there were two other indices used to classify illite crystallinity in low-grade metamorphic rocks: Weaver index and Weber index. The KI is a valid tool, successfully applied to many fine-clastic metasedimentary sequences to detect the anchizonal limits in sedimentary basins and in the outer fold-and-thrust zones of orogenic belts.

6.3.4.1f: Smectite Group of Clay Minerals

Smectite group of clay minerals are 2:1 hydrous phyllosilicates with a total negative layer charge between 0.2 and 0.6 per *formula unit* (FU) or half *unit cell* (UC).

Except for the layer charge and hydration of the interlayer cations, smectite structure is similar to that of other 2:1 hydrous phyllosilicates already described.

The octahedral sheet may be dominantly occupied either by trivalent cations e.g. Al(III) or FE(III), in the case of *dioctahedral smectites* or by divalent cations e.g. Mg(II), in the case of *trioctahedral smectites*. *Dioctahedral* and *trioctahedral smectites* are two subgroups of the *smectite group of clay minerals*.

Commonly Si^{4+}, Al^{3+} and Fe^{3+} occupy the tetrahedral sites, and substitution of Al^{3+} and/or Fe^{3+} for Si^{4+} creates an excess of negative charge on the three basal oxygens and the apical oxygen affecting the total layer charge as well as the local negative charge at the layer surface. Commonly too, Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Li^{+} occupy the octahedral sites. The negative electrical charge of the layers is balanced by hydrated exchangeable cations, mostly Ca^{2+}, Mg^{2+} and Na^{+} located in the interlayers spaces.

In *dioctahedral smectites* (*montmorillonite*, *beidellite*, *nontronite* and *volkonskoite*), substitution of divalent cations for trivalent cations creates an excess of negative layer charge, whereas substitution of trivalent cations for divalent cations in *trioctahedral smectites* (*hectorite*, *saponite*, *sauconite*, *stevensite* and *saponite*) creates an excess of positive charge, and such events have implications on physical properties of smectites, such as swelling and rheological behaviour.

As aforesaid, the *montmorillonite* chemical formula can be expressed as follows: $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\ nH_2O$.

Montmorillonite was first described in 1847, and it is named after Montmorillon, a commune in the Vienne Department in the Nouvelle-Aquitaine region in western France, where the reference occurrence was found. Uddin (2017) provides an overview on *montmorillonite* structure, functional properties and applications.

In *beidellite*, Al^{3+} is the major octahedral cation; in *nontronite*, Fe^{3+} is the major octahedral cation; and in *volkonskoite*, Cr^{3+} is the major octahedral cation.

The interlayer space or thickness of *smectite* is variable depending upon the nature of the interlayer cation and of the humidity or moisture of the environment where it stays, reason why *smectites* are classified as *expansive* or *swelling clay minerals* (Fig. 6.11).

Emiel and Hensen (2002) discuss the mechanism that causes clay swelling. Swelling proceeds by the migration of counterions initially strongly bound to the clay mineral surface to positions in the clay mineral interlayer where these ions are fully hydrated. *Montmorillonite* swelling is dependent on charge locus (mostly on the octahedral sheet or mostly in the tetrahedral sheet), charge density and the type of counterion.

Most of *smectite* minerals applications are related to reactions that take place in the interlayer space. Na^+, K^+, Ca^{2+} and Mg^{2+} that balance the negative layer charge are commonly hydrated and exchangeable.

According to Emmerich (2013), the amount and location of layer charge, both in tetrahedral and octahedral sheets, together with the kind of interlayer cations, strongly influence both physical and chemical properties of smectites.

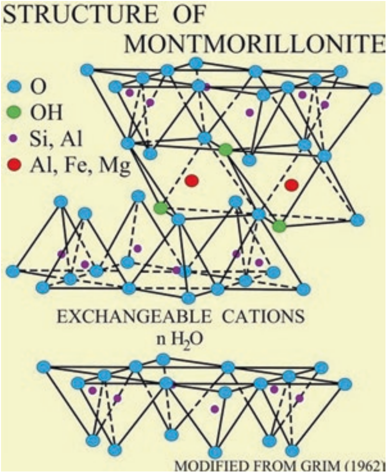


Fig. 6.11 Schematic representation of the crystalline structure of *montmorillonite*

Smectites contain water in several forms: structural, zeolitic and free water. *Smectite species* may be differentiated by the following criteria, particularly proposed by Emmerich (2009):

1. Overall chemical composition with particular attention to the content of elements other than Si, Al and Mg.
2. Dioctahedral or trioctahedral nature of the octahedral sheet.
3. Predominant octahedral cation.
4. Cation distribution within the octahedral sheet of dioctahedral smectites, that is, *cis* and *trans* positions.
5. Density and location of the layer charge.

Sodium montmorillonite, *calcium montmorillonite* and *hectorite* are the most industrially used *smectites* both in pharmacy and medicine. *Sodium montmorillonite* and *hectorite* have high base-exchange capacities, generally within the range of 80–130 meq/100 g.

Calcium montmorillonite, on the other hand, has a base-exchange capacity within the range of 40–70 meq/100 g.

In pharmacopoeias, the term *bentonite* is used to refer to a natural, colloidal, hydrated aluminium silicate (Viseras et al. 2006).

Gelwhite® N-NF, Bentolite® MB-NF, Mineral Colloid® BP and Mineral Colloid® MO are *bentonite* trade names. The clay mixtures of *montmorillonite* and *saponite* are known by the trade names Veegum®, Gelwhite® MAS, Gelsorb®, Carrisorb®, Pharmasorb Regular® and Bentopharm®. When the clay is only constituted by *montmorillonite*, it is known as purified bentonite, and its trade name is Veegum® HS (Viseras et al. 2007). To all the trade names referred to correspond a data sheet containing the product description, properties and applications.

Bentonite is a type of clay in which the clay mineral *montmorillonite* is the essential constituent and whose name goes back to the American geologist Knight. Around the year 1890, he explored in Wyoming (USA) near Fort Benton a clay deposit. After the place of discovery, this material was named *bentonite*.

Colloidal rheological and absorption properties justify the wide range of *bentonite* applications in the pharmaceutical industry (Carretero et al. 2013; Modabberi et al. 2015) and in *pelotherapy* and *medicine* (Karakaya et al. 2010; Carretero et al. 2010, 2013; Gomes et al. 2013a, b; Gomes 2018).

Especially in pharmaceutical and cosmetic formulations, *bentonite* must comply with restrictive chemical, physical, microbiological and toxicological requirements (Viseras et al. 2006; López-Galindo et al. 2007). *Smectite clays* have been used as support materials in drug slow-release systems.

The higher layer charge of *sodium montmorillonite* and *hectorite* makes possible the exchange of hydrated cations by polar organic molecules such as ethylene glycol, quaternary amine and polyalcohols. This important property is used in very useful products, the so-called organoclays.

Smectite clay mineral surfaces generally show selectivity for organic cations and protonated organic bases. Sorption of nonpolar or weakly polar organic molecules in the interlayer spaces can occur if the clay mineral is not highly hydrophilic. In the last two decades, the use of clay-organic interactions has rapidly expanding, with important technological applications, some in the human health field.

Because of the high specific surface, high layer charge and base-exchange capacity, *sodium montmorillonite* has a high swelling capacity of the order of 10–15 times when placed into water. *Calcium montmorillonite* has a much lower swelling index, 2–3.

Diosmectite is the trade name of a type of *calcium montmorillonite* valued in medicine for its antidiarrhoeal effects justified for its strong adsorbent properties, so it is used as an intestinal adsorbent in the treatment of several gastrointestinal diseases, including diarrhoea.

Montmorillonite clay mineral has proven to be effective against *Candida albicans*, a type of fungus which is a causal agent of opportunistic oral and genital infections known as *candidiasis*.

Very recently, Zhou et al. (2019) produced an interesting article entitled "Smectite Nanomaterials: Preparation, Properties and Functional Applications" that is Chap. 7 of a book of 13 chapters entitled *Nanomaterials from Clay Minerals: A New Approach to Green Functional Materials*, with Wang A and Wang W (editors), published by Elsevier. This article is an update overview on smectite clay minerals in what concerns their natural and modified properties, as well as the various functional applications. The authors enhance the applied interest of the modifications that can be promoted both on surfaces and interlayer spaces of montmorillonite crystals. For instance, the interlayer spaces of montmorillonite crystals can be intercalated with guest cations through an ion-exchange reaction or other physical and chemical interactions in order to yield organo-montmorillonite, and this can be exfoliated or delaminated into thin nanolayers for producing clay-polymer nanocomposites able to exhibit improved barrier, mechanical strength, thermal stability and fire retardant properties.

Hectorite is a rare natural white or near white clay mineral species belonging to the subgroup of trioctahedral smectites, and it is characterized by the chemical formula $Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH,F)_2$ and is well represented in an occurrence located near Hector, in San Bernardino County, California, USA, where it is associated with bentonite as an alteration product of the zeolite *clinoptilolite* in a deposit of volcanic ash and tuff with high glass content. *Hectorite* is important in the cosmetics industry, used as suspending agent and rheology modifier due to the specificities of its particle size, shape and charge. Hectatone™ is an organoclay based on *hectorite*.

Bentone® MA is a rheological additive based on purified *hectorite* clay that imparts thixotropy and good anti-settling to water-based cosmetic systems.

There is enough experience on the synthesis of certain clay minerals which applications require consistent properties that could not be provided by natural minerals (Zhang et al. 2010; Jaber et al. 2013).

Laponite is a synthetic trioctahedral smectite clay mineral with a hectorite-like composition, $Na_{0.7}Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4$. However, very recently, Christidis et al. (2018) have questioned if *laponite* is pure hectorite or a mixture of different trioctahedral phases.

Saponite is a trioctahedral smectite, a clay mineral of chemical composition $(Na,Ca)_{0.3}(Mg,Fe)_3(Si_{4-x},Al_x)_4O_{10}(OH)_2 4H_2O$, and was first described in 1840 in the occurrence type, in Lizard Point, Landewednack, Cornwall, England, UK. The name *saponite* is derived from the Greek word *sapo*, meaning soap.

The saponiferous clay with trade name Ghassoul or Rhassoul is produced in Morocco and commercialized by the Societé du Ghassoul et de ses derivés, SARL, Quartier Industriel de Sidi Brahim, Fes, Morocco. The name *ghassoul* signifies washing and cleaning, and *ghassoul clay* showing brown and beige colour and characterized by high water absorption power (15 g of *ghassoul* absorbs 25 g of water) and high cation exchange capacity (75 meq/100 g) is classified by the producer as a smectitic clay mainly constituted by lithium *stevensite*.

Stevensite is one Mg-rich (around 25% of MgO) trioctahedral smectite clay mineral.

6.3.4.1g Vermiculite Group of Clay Minerals

Vermiculite group of clay minerals comprises dioctahedral and trioctahedral species. As in *smectite* minerals, the 2:1 *vermiculite* structural layers are separated by hydrated cations occupying the interlayer space. However, the negative layer charge of *vermiculite* (>0.6 per formula unit), which arises mostly from substitution of Al^{3+} for Si^{4+} in tetrahedral sites, is larger than that of smectite.

Vermiculite group of clay minerals comprises dioctahedral and trioctahedral species. As in smectite minerals and in trioctahedral micas, the *vermiculite* 2:1 structural layers are separated by hydrated cations, as is the case of Mg^{2+}, occupying the interlayer space.

The water molecules solvating Mg^{2+} ions are structured in two planes. However, the negative layer charge of *vermiculite* (>0.6 per formula unit), which arises mostly from substitution of Al^{3+} for Si^{4+} in tetrahedral sites, is larger than the negative layer charge of smectite, reason why the expansion or swelling of *vermiculite* is more limited than the expansion of *smectite* that is characterized by lower electric charge (0.2–0.6).

The chemical composition of *vermiculite* can be expressed as $E^+(Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+})_6(Si,Al)_8O_{20}(OH)_4 nH_2O$, where E^+ represents the exchange cation, commonly Mg.

The *vermiculite* occurring in clays is characterized by a basal spacing d_{100} of ~14 Å that do not totally collapse to ~10 Å, as happens with smectites when heated to ~300 °C after saturation with K, and do not expand totally as *smectites* do.

The name of the group is derived from the name *vermiculite* of the macroscopic species which crystals look like worms, vermiculus in Latin, crystal shape acquired after heating.

No pharmaceutical and medical applications are known for *vermiculite*. Vermiculites are commonly used in the form of expanded particles by rapid heating from 250 °C to 1500 °C followed by immediate cooling to 400 °C.

The evaporating water expands vermiculite particles in worm-like (vermiform) manner (Grim 1968; Bergaya et al. 2006) increasing its volume by up to 1500 times.

Expanded vermiculite is used in the building industry for heat insulation and sound dissipation (Harvey and Lagaly 2013).

6.3.4.1h: Chlorite Group of Clay Minerals

Chlorite group of clay minerals crystallochemically differ from the trioctahedral micas due to the existence of one octahedral sheet, a brucite-like sheet, positioned between the T:O:T mica layers. As a matter of fact, the *chlorite* layer structure can be expressed by T:O:T:O or 2:1:1 and is characterized by a basal spacing d_{100} of ~14 Å or 1.4 nm.

Chlorite ideal chemical composition is shown as $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2$. The brucite-like sheet occupying the interlayer position has the general composition $(Mg,Al)_3(OH)_6$. There is quite a range of cation substitution in *chlorites*, most commonly Mg^{2+}, Fe^{2+}, Al^{3+} and Fe^{3+}.

Bonding between adjacent *chlorite* structural layers is made by hydrated or solvated ions of Mg, Al, Fe or Li.

There are dioctahedral, trioctahedral (the most frequent with Mg^{2+}, Al^{3+}, Fe^{3+} and Fe^{2+} on octahedral sites), di-trioctahedral and tri-dioctahedral *chlorites* (Bailey 1980a, b). Tetrahedral cations are Si^{4+} and Al^{3+}. Occasionally, other cations different from those referred to can replace the normal ones.

Within trioctahedral chlorites, *clinochlore* (the Mg end member), *chamosite* (the Fe end member) and *pennantite* (the Mn end member) are the most common. *Donbassite* is an Al-rich dioctahedral chlorite; *sudoite* is a di-trioctahedral Al- and Mg-rich chlorite; *cookeite* is a di-trioctahedral Li- and Al-rich chlorite.

Di-trioctahedral chlorites, such as sudoite and *cookeite*, have a dioctahedral layer and a trioctahedral interlayer. There are no known tri-dioctahedral chlorite structures. The name chlorite is derived from the Greek name *chloros*, meaning pale green, a colour commonly exhibited by macroscopic *chlorite*. *Chlorite* is commonly found in shales and also in underclays associated with coal seams.

No pharmaceutical and medical applications are known so far for *chlorite*.

6.3.4.1i: Regular and Irregular Interstratified Planar Clay Minerals

In addition to the clay minerals or better to the clay mineral species referred to in subtopics 6.3.4.1a, 6.3.4.1b, 6.3.4.1c, 6.3.4.1d, 6.3.4.1e, 6.3.4.1f, 6.3.4.1g and 6.3.4.1h, there are still some clay minerals with a 2:1 planar structure which exhibit regular structures, called *regularly interstratified* or *mixed-layer clay minerals*. These minerals are characterized by series or stacks of structural layers in which A-type structural layers (e.g. *mica*/*illite*) occur interspersed with B-type structural layers (e.g. *smectite*).

The basal spacing of the resulting regular interlayer is expressed by $d_{AB} = d_A + d_B$. The regular interlayers of clay minerals from the crystallochemical point of view correspond to true mineral species. Regular interstratifications, such as chlorite-smectite, chlorite-vermiculite, talc-chlorite and biotite-vermiculite, are mentioned in the literature.

Table 6.2 shows the classification and representative species of regular interstratified clay minerals.

Table 6.2 Classification of clay minerals with regularly interstratified structures: interstratifications of alternating layers in 50/50 proportions (*In:* Guggenheim et al. 2006)

1:1	None	Octahedral layer	Mineral species
2:1	Pyrophyllite-smectite	Dioc-dioc	Brinrobertsite
	Talc-smectite	Trioc-trioc	Aliettite
	Talc-chlorite	Trioc-trioc	Kulkeite
	Mica-smectite	Dioc-dioc	Rectorite
	Biotite-vermiculite	Trioc-trioc	Hydrobiotite
	Chlorite-smectite	Trioc-trioc	Corrensite (low charge)
	Chlorite-smectite	Trioc-trioc	Corrensite (high charge)
	Chlorite-vermiculite	Dioc (on average)	Tosudite
1:1 and 2:1	Serpentine-chlorite	Trioc-trioc	Dozyite

Unlike the *regularly interstratified structures*, the *irregularly interstratified structures*, which are much more frequent, are not qualified with names, because they do not have crystalline periodicity, reason why they are not considered true mineral species. Regular and irregular mixed layers I-Sm (illite-smectite) and Sm-I (smectite-illite), i.e. mixed layers between expandable and non-expandable clay mineral species, have been the most studied, the transitions of both structures being used as geological markers in reconstructing the thermal and tectonic history of sedimentary basins.

XRD, TEM and HRTEM are the analytical techniques employed to find out the proportion and sequence of the mixed layering.

K-Sm (kaolinite-smectite) is another interesting mixed layer that has attracted the attention of many researchers.

AIPEA (Association Internationale Pour L'Étude des Argiles) had issued one interesting publication within the AIPEA Educational Series, Fiore S, Quadros J and Huertas FJ being the editors, with a 1st edition issued in 2009 and a 2nd edition issued in 2013. This publication entitled *Interstratified Clay Minerals: Origin, Characterization and Geochemical Significance* provides an overview of this type of clays and gathers contributions of the following researchers: Plançon (2013), Meunier (2013), Nieto and Arroyo (2013), Komadel and Madejová (2013a, b), Ferrell et al. (2013) and Srodon (2013).

6.3.4.2 Clay Minerals of Non-planar Structures

Table 6.4 shows the systematics of the clay minerals of non-planar structures, which are organized into two groups: (1) clay minerals with modulated structures (fibrous sepiolite and palygorskite) and (2) clay minerals with rolled, tubular and spheroidal structures and particle shape (rolled or tubular halloysite, antigorite, chrysotile and allophane-imogolite).

6.3.4.2a: Sepiolite-Palygorskite Group of Clay Minerals

Figure 6.12 shows the crystallochemical features that justify the fibrous crystal habit or shape of the clay mineral *sepiolite*, and Figure 6.13 shows the fibrous

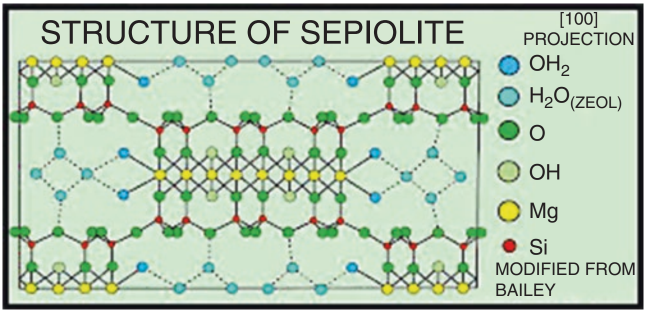
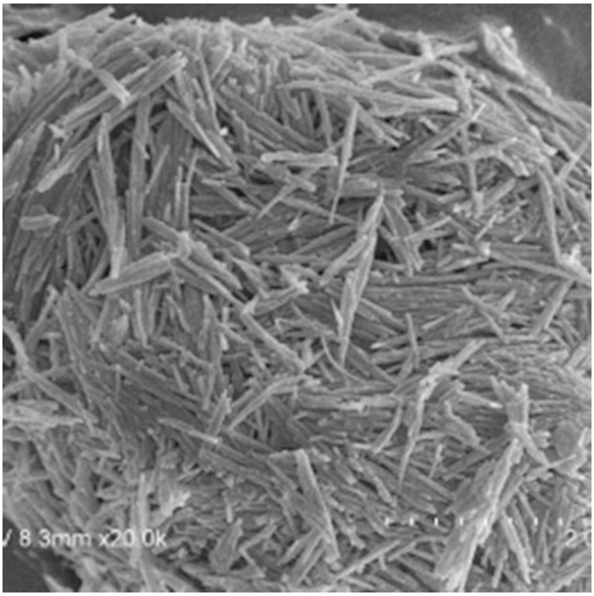


Fig. 6.12 Schematic representation of *sepiolite*'s structure (modified from Bailey 1980a, b)

Fig. 6.13 Fibrous morphology of *sepiolite*



particle shape of *sepiolite*. The first attempts to establish the sepiolite structure were carried out by Nagy and Bradley (1955), Brauner and Preissinger (1956), Brindley (1959) and Rautureau and Tchoubar (1976).

Figure 6.14 shows the crystallochemical features of *palygorskite*, and Figure 6.15 exhibits one specimen of *palygorskite* from an occurrence in the Kuzuu district, Japan. Despite the acicular crystal habit, *sepiolite* and *palygorskite* are phyllosilicates inasmuch as they exhibit continuous two-dimensional tetrahedral sheets. However, they just differ from other layer silicates in that they lack continuous octahedral sheets.

The crystal structures of *sepiolite-palygorskite* clay minerals show characteristics of both layer and chain silicates.

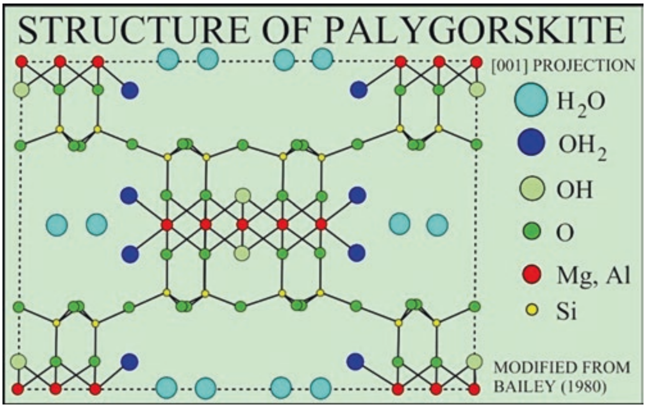


Fig. 6.14 Schematic representation of *palygorskite's structure*

Fig. 6.15 Fibrous morphology exhibited by a palygorskite specimen from an occurrence in the Kuzuu district, Japan

Tetrahedral sheets involve sixfold rings of tetrahedra and present a continuous basal oxygen atom plane; but unlike ideal phyllosilicates, these minerals show apical oxygen atoms pointing along opposing directions (Brigatti et al. 2006).

The essential features of the palygorskite-sepiolite mineral group are apparently:

1. The continuous tetrahedral basal oxygen planes.
2. The inverted tetrahedral arrangement that forms ribbons of joined pyroxene-like chains generate channels visible using HRTEM (Rautureau et al. 1972; Rautureau 1974).
3. The discontinuous octahedral sheet (Guggenheim et al. 2006; Guggenheim and Krekeler 2011).

The name *palygorskite* was attributed by Savchenkov in 1862 and derived from the local name Palygorsk in Ural Mountains, Russia. In industrial and commercial nomenclature, the clay rich in this fibrous clay mineral is called *attapulgite*, a name that was attributed in 1935 by De Lapparent to a clay mineral he encountered in a fuller's earth occurrence in Attapulgus, Georgia, USA.

The name *sepiolite* was used for the first time by Ernst Friedrich Glocker in 1847 and derived from the Greek *sepion* due to its resemblance to the bone of the sepia or cuttlefish characterized by very low weight, whiteness and porosity. The white, soft and light *sepiolite* was originally named “meerschaum” by Abraham Gottlob Werner in 1788 and was initially used to make tobacco pipes known as “meerschaum pipes”. The German name “meerschaum” is equivalent to the English name “sea foam” and to the French name “écume de mer”.

S*epiolite* particles exhibit fibre shapes (Fig. 6.13). *Palygorskite particles or crystals* also exhibit fibre shape, needle-like, as a rule much thinner than sepiolite particles.

The internal arrangement of the tetrahedral and octahedral sheets in *palygorskite* as well as in *sepiolite* is unique within clay minerals in that there are channels or tunnels through the structure, channels that are filled with zeolitic water. When this water is driven off by heating the surface area and thus the sorptivity is increased, chemical compounds that are of the size that will fit into these channels could be absorbed (Fig. 6.14).

In *sepiolite*, the channels have the dimensions 3.7 × 10.6 Å, whereas in palygorskite, they measure 3.7 × 6.4 Å.

The first attempts to establish the structure of palygorskite were carried out by Bradley (1940), Preissinger (1963) and Drits and Alexandrova (1966).

Sokolova and Drits (1971) have proposed the following chemical composition for *palygorskite*: $(Mg_2,Al_2)Si_8O_{20}(OH)_2(OH_2)_44H_2O$. The thermogravimetric (TG) curves show three weight losses attributed to water. The water $4H_2O$ adsorbed on fibres external surfaces or occupying the channels existing in the structure (*zeolitic water*) is removed for temperatures below 200 °C without producing structural changes; the water $(OH_2)_4$ is weakly bonded in the structure (*crystallization water*) and its loss around 300 °C produces significant structural changes; finally the water $(OH)_2$, the *structural water*, being strongly bonded to the octahedral Mg cations is only removed for temperatures higher than 400 °C and produces irreversible structural changes.

As a rule, in *palygorskite*, some Mg is replaced by Fe. Also, some Si may be replaced by Al or Fe. Velde (1992) has proposed for *palygorskite* the following general chemical formula: $(R^{2+},R^{3+})_5(Si,R^{3+})_8O_{20}(OH)_2(OH_2)_4(H_2O)_4$, where R^{2+} may be Mg^{2+} or Fe^{2+}. According to Galán and Carretero (1999), *palygorskite* is intermediate between di- and trioctahedral.

Sepiolite is a related phyllosilicate being also a natural hydrated magnesium phyllosilicate that displays a crystal structure consisting of talc-like ribbons with $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4(H_2O)_8$ as the ideal chemical formula. It has negligible isomorphous substitutions of Al and Fe for Si. According to Galán and Carretero (1999) and Caillère et al. (1982, 1989), *sepiolite* is a true trioctahedral clay mineral with eight octahedral positions filled with Mg^{2+}.

Garcia-Romero and Suárez (2010) have provided complementary data on the chemical composition of both *sepiolite* and *palygorskite*, *sepiolite* occupying the most magnesic and trioctahedral extreme of the series and *palygorskite* occupying the most aluminic-magnesic and dioctahedral extreme.

In short, the main properties that *sepiolite* and *palygorskite*, the so-called fibrous clay minerals, have in common are as follows: fibre particle shape; fibre sizes vary in length from about 1 to 10 μm; high specific surface area 150–320 $m^2.g^{-1}$;

moderate base-exchange capacity 30–50 meq/100 g; melting point 1550 °C; high sorptivity; high water absorption up to 100% of the clay weight; and oil absorption up to 80% of the clay weight.

With regard to *sepiolite* and *palygorskite* applications quite a lot are known, some are herein being exemplified: pet or cat litter as absorbent; industrial floor absorbents; drilling fluids and paints as a dispersing, anti-settling, thickening and thixotropic additive; pesticides, insecticides and herbicides carriers; animal feed binders; catalyst carriers; cosmetics; pharmaceuticals; foundry sand binders; anti-caking agents. The microporous structure of these clay minerals is important for their applications in nanotechnology (Tang et al. 2012).

Pozo and Galán (2013) had edited an interesting publication that gathers interesting papers on the characterization, origin and applications of magnesium clays. *Sepiolite* in the form of "meerschaum" is utilized for pieces of jewellery and pipe bowls.

Ruiz-Hitzky et al. (2013a, b) within other applications emphasize the interest of *sepiolite* and *palygorskite* for bioplastics and membranes, uses in biomedicine as drug delivery systems and adjuvants of vaccines as well as in tissue engineering.

Very recent studies carried out by Ruiz-Hitzky et al. (2017) show how *sepiolite* and *palygorskite* fibrous clay minerals can be incorporated, as efficient fillers, into polymer matrices, not only to improve their mechanical properties, but also to provide functionality to the resulting polymer-clay nanocomposites.

The use of pharmaceutical-grade clay minerals as carriers of pharmaceuticals has particular advantages due to their biocompatibility, low toxicity and precise tailorability of surface properties. Also, clay minerals' rheological properties allow them to act as emulsifiers and stabilizers of pharmaceutical formulations and also as suspending agents for hydrophobic drugs.

Another important effect of some clay minerals is the retarded release of surface adsorbed pharmaceuticals, helping to modulate the drug release profile (Aguzzi et al. 2007). Controlled drug delivery is required to avoid overdosing or underdosing episodes during the therapeutic use.

The peculiar morphology and textural characteristics of *sepiolite* and *palygorskite* make these silicates appropriate as fillers in polymer matrices providing the reinforcement of these materials and improving their structural properties.

In the pharmaceutical industry, *sepiolite* is known as magnesium trisilicate and by the trade names Alenic Alka® and Recip®. In the pharmaceutical industry, *palygorskite* is known as *activate attapulgite* and magnesium and aluminium silicate and by the trade names Attaclay®, Attagel® and Attapulgite®.

Palygorskite and *sepiolite* are usually formed in shallow low-energy depositional environments such as estuaries and marine lagoons.

The largest commercial *sepiolite* deposit in the world is at Vicalvaro, Vallecas, near Madrid, in Spain, a country that is the largest producer of *sepiolite* clays in the world. In Vicalvaro's deposit, *sepiolite* occurs in layers with thickness ranging from 1 m to 5 m. In the world, most of sepiolite and *palygorskite* deposits are dated of Early Eocene. In Portugal, *palygorskite* characterized by long fibres occurs in some sites of the Lisbon Volcanic Complex.

Attapulgite is a commercial and industrial name that was attributed for the first time by De Lapparent in 1935 to the *fibrous clay* that occurs in Attapulgus, Georgia, USA. Also, in Portugal, very small occurrences of *sepiolite* are known. The variety of *sepiolite* called *xylotile* characterized by the partial substitution of Mg by Fe was identified in a gabbro quarry in Ribamar, Ericeira (Gomes 1992).

AIPEA (Association Internationale Pour L'Étude des Argiles) had issued in 2013 one interesting publication within the AIPEA Educational Series, Pozo M and Galán E being the editors. This publication entitled "Magnesium Clays: Characterization, Origin and Applications" provides an overview of this type of clays and includes contributions of the following authors: Guggenheim (2013), Calvo and Pozo (2013), Pozo and Galán (2013), Pozo and Calvo (2013), Tosca (2013) and Santarén (2013).

6.3.4.2b: Allophane-Imogolite: Group of Quasi-Amorphous Clay Minerals
Allophane-imogolite is the name of a group of clay-size poorly crystalline hydrous aluminosilicates characterized by short-range structural order, which are commonly found in soils formed from volcanic ash and weathered pumice. However, cases are known of *allophane* occurrences not associated to soils, for example, in precipitates from highly acidic silica-rich springs.

Occurrence, nature and properties of *allophane* and *imogolite* can be found in reviews such as those published by Parfitt (1990) and Harsh (2000). The association of *allophane* and *imogolite* with soils of volcanic origin arises from the fact that ash, tephra and other pyroclastic materials contain amorphous materials that can rapidly release Al and Si.

In *allophane*, the Al/Si ratio varies in the range of 1–2. *Allophane* and *imogolite* provide broad and diffuse diffraction maxima in their XRD patterns.

Allophane exhibits when observed in HRTEM (High Resolution Transmission Electron Microscopy) nanometric hollow spherules, whereas *imogolite* exhibits hollow tubules forming bundles of several micrometres in length. The internal diameters of *imogolite* nanotubes are around ~1 nm, significantly smaller than *halloysite* nanotubes' internal diameters (20–100 nm), but enough high to host most of the drug molecules.

In a recent scientific article entitled "Health and Medical Applications of Tubular Clay Minerals", Aguzzi et al. (2016) present an up-to-date and very interesting review of the effective and possible applications of *halloysite* and *imogolite* in nanopharmaceutics.

6.3.4.3 Systematics of Clay Minerals

Tables 6.3 and 6.4 show the systematics internationally adopted and established in 1966 by AIPEA ("Association Internationale pour L'Étude des Argiles") and in 1963 and by CMS ("Clay Minerals Society") for *clay minerals* exhibiting planar and non-planar structures, respectively:

1. The organizational model (layer type) of the fundamental structural unit (*unit cell*), and within layer type, by groups based on *electric charge p.f.u* (*electric*

charge per formula unit) expressed by the letter *x* and as a positive number, representing the net negative charge per unit layer.

2. The groups are divided by subgroups based on the occupation, *dioctahedral* or *trioctahedral*, of the structural octahedral sheet.
3. Each group and subgroup being represented by species based mainly on chemical composition.

The net negative layer charge is balanced by the positively charged interlayer material.

6.4 General Notes on Clay Typologies and Main Properties

Clays and *clay minerals* most probably started being formed on Earth immediately after planetesimal formation (Hazen et al. 2013). Indeed, the necessary conditions for clay minerals formation, the existence of water, sources of acids and alumino-silicate rocks, would have prevailed on the early Hadean Earth.

There are several clay types based on geological, technological and commercial arguments, such as primary or residual clay, and secondary or sedimentary clay; expansive clay; plastic clay; absorbent clay; refractory clay; nanoclay; special clay (ball clay, bentonite, kaolin, fuller's earth, fibrous clay, fire clay and flint clay); and common clay (pottery clay and heavy clay):

1. Primary or residual clay
2. Secondary or sedimentary clay
3. Special clay: ball clay, bentonite, kaolin, fuller's earth, fibrous clay (sepiolite and palygorskite), and "flint" or "hard" clay, and refractory clay
4. Common clay: pottery clay, structural construction clay and heavy clay (the last two clay types being used for the manufacture of brick and of roof and floor tiles)

The nomenclature referred to encompasses geological and commercial names and typologies attributed to natural clays used as they occur or after being submitted to some kind of simple industrial processing comprising refining (involving physical processes) plus beneficiation (involving chemical processes).

The largest and highest-quality primary or *residual kaolin* deposits in the world are located in Cornwall and Devon in south-western England, *kaolinite* being derived from late-stage magmatic or hydrothermal alteration or decomposition of feldspar in the granite, and the *kaolinite* content in the altered granite ranges between 10 and 20%. The largest and highest-quality secondary or sedimentary *kaolin* deposits occur in the Amazon region in northern Brazil and in Georgia, USA. The clayey products of the weathering of source or mother crystalline rock were transported by several streams.

The main natural deposits of *kaolin* composed by *tubular halloysite* are from Dragon Mine and Matauri Bay in Utah (USA) and Northland (New Zealand), respectively. Tubular halloysites are being used for the development of innovative nanomaterials useful for biotechnological applications, such as controlled release of drugs (Shutava et al. 2014; Wei et al. 2014; Lvov et al. 2016; Cavallaro et al. 2015), tissue engineering (Fakhrullin and Lvov 2016), oil recovery and eco-compatible packages.

The name *kaolin* is derived from Kauling or Gaoling, in Jiangxi province of China, where Chinese geologists discover that the local kaolin deposit is derived from the alteration of a granite stock of Middle Jurassic age (Chen et al. 1997).

Kaolin is a basic raw material for the manufacture of traditional white ceramics (porcelain stoneware, earthenware), paper filler and coating and of many modern materials such as nanocomposites, although the most well-known product, the sophisticated porcelain from Jingdezhen, Jiangxi, China, is manufactured from 2000 years ago up to the actuality. Gaoling Shan, translated literally as “high ridge”, is located at about 40 km to northeast of the city of Jingdezhen, and there was the first mining site of *kaolin* clay.

Special clays relative to *common clays* are characterized, as a rule, by the following specificities:

1. Less number and smaller dimension of clay deposits.
2. Simple composition although requiring more complex and expensive processing.
3. Higher commercial unit value of the respective manufactured products.

With regard to the so-called industrial clays, Harvey and Lagaly (2013) have proposed four categories:

Category 1: High-quality, high-technology clays requiring major investment for large tonnage production to supply both local and international markets.

Examples of industrial clays classified into category 1: the sedimentary kaolin deposits with large occurrences in the south coast of Georgia, USA; the hydrothermal kaolin deposits of Cornwall, UK; and the sedimentary kaolin deposits of the Amazon basin, Brazil.

Category 2: Unique specialty clays requiring advanced mining and processing technologies for small tonnage niche markets, locally and internationally.

Examples of industrial clays classified into category 2: the low-temperature hydrothermal alteration of volcanic ash halloysite deposits of Northland, New Zealand; the hectorite Li- and Mg-rich smectite deposits (bentonite) with occurrences in the USA, derived from hydrothermal alteration of basaltic ash; and the white bentonite deposits occurring in some countries.

Category 3: Relatively low-technology clay of moderate quality that mainly supplies local markets.

Examples of industrial clays classified into category 3 are worldwide frequent, characterized by not rigid specifications and moderate-grade processing; all known deposits of category 1 clays contain associated category 3 clays, as are the cases of kaolins from Georgia, USA, and Cornwall, UK; kaolin deposits from the Czech Republic, Ukraine, Germany, France and Spain, as well as the filler-grade kaolins of Indonesia, and the bentonite deposits of Wyoming, USA, could be classified into category 3.

Category 4: Comprises industrial clays of variable but low quality, the applications requiring low-technology; the low-quality materials may justify little or no processing, nevertheless suitable for large-tonnage local markets; some clays of category 4 may be of moderate to high quality but for one or more reasons considered non-economic; these reasons may include isolation from markets, politically or economically unstable locations and unfavourable legislative environment.

Examples of industrial clays included in category 4 are the numerous small-size deposits of kaolin, bentonite, ball clay, fibrous clay and heavy clay with occurrences in most countries of the world, mined and particularly used in ceramics.

It matters to say that on the industrial applications of clays, Robertson (1960) was a real pioneer.

Kaolin is a naturally occurring clay-rich material that geologically corresponds to a rock dominated by *kaolin group minerals*, a group that comprises four mineral species: *kaolinite*, *halloysite*, *dickite* and *nacrite*, expressed by a basic T:O or 1:1 layered structure and the chemical formula $Al_2Si_2O_5(OH)_4$.

In terms of volume of geological deposits and applications importance, *kaolinite* and *halloysite* are really important species of the *kaolin group minerals*. *Kaolinite* and *halloysite* are secondary minerals frequently formed by the action of weathering processes upon aluminous felsic igneous and metamorphic rocks. *Dickite* and *nacrite* geological occurrences are extremely small and rare, being related to hydrothermal alteration processes of primary rock-forming minerals, such as potassium feldspars and micas.

The geological, geomorphological and geochemical environment favourable to primary or residual kaolinization (origin meteoric, hydrothermal, hydrothermal/meteoric) should satisfy the following criteria referred to by Gomes (2002):

1. Removal of Ca^{2+}, Mg^{2+}, Na^+ and K^+ from the precursor mineral silicates, particularly tectosilicates exemplified by feldspars (mainly microcline and orthoclase) and phyllosilicates exemplified by micas (muscovite and biotite), which requires (a) precipitation exceeding evaporation; (b) drainage systems facilitating the leaching and removal of alkaline and calc-alkaline cations; (c) mother rock (mainly granite, granodiorite and gneiss) showing fracturation and fissuration; (d) water easy percolation; (e) oxidation of Fe^{2+} to Fe^{3+}; and (f) climate alternation, dry season alternating with moist season
2. Acidic environment, which requires (a) aqueous fluids, as is the case of meteoric water, containing CO_2 in solution and with origin in the air and organic acids derived from organic matter decomposition and (b) hydrothermal liquids and gaseous fluids containing SO_2, N_2, HF, CH_4, NaCl, KCl, etc.
3. High Al/Si ratio, which requires (a) Si mobilization and removal in acidic environment and (b) Al immobilization and concentration in acidic environment and formation of Al-OH or Al-Si-OH polymers

Bentonite is a rock term defined by Ross and Shannon (1926) as a clay material resulting from the alteration of glassy igneous rocks, usually volcanic ash. According to Christidis and Huff (2009), bentonite deposits could be formed by the following three mechanisms:

1. Diagenetic alteration of volcanic glass in an aqueous environment.
2. Hydrothermal alteration of volcanic glass.
3. Formation of smectite-rich sediments in salt lakes and in salt-rich environments.

The geological, geomorphological and geochemical environment favourable to primary or residual smectization or montmorillonization (origin meteoric, hydrothermal, hydrothermal/meteoric) should satisfy the following criteria referred to by Gomes (2002):

1. Retention of Mg^{2+}, Ca^{2+}, Fe^{2+} and Na^+ derived from precursor minerals dissolution, which requires (a) evaporation exceeding precipitation, (b) mother rock showing little or moderate permeability, (c) prevailing alkaline environment and (d) no or little oxidation of Fe^{2+} to Fe^{3+}.
2. Precursor minerals characterized by high specific surface area and high susceptibility to hydrolysis, which requires (a) easily alterable glassy rocks, such as ash and volcanic tuff.
3. Low Al/Si ratio, which requires (a) Al less mobile than Si and (b) Si fixation under the form of cryptocrystalline silica (cristobalite).

Bentonite is mainly composed of clay minerals of the *smectite group* minerals, *montmorillonite* being the most frequent species.

Grim and Guven (1978) had used the term *bentonite* for any clay which was dominantly composed of clay minerals of the smectite group without regard to its origin. Bentonite is named after Fort Benton, Wyoming, USA, where its largest sources are found. The name of its principal clay mineral, *montmorillonite*, comes from Montmorillon, France, where it was first found. Greece, the USA and Turkey are the countries' major producers of *bentonite*.

Bentonite has a variety of properties provided by its major clay mineral: high adsorption and absorption capacities, high pore volume, high specific surface area, high intra-crystalline swelling capacity and high water retention capacity. The thixotropic behaviour is an important property of bentonite; when products containing bentonite as additives are shaken and stirred, they can change from gelatinous to liquid state; and at rest again gel is formed.

The originally hydrophilic bentonite surface can be made hydrophobic. This will allow the complete dispersion of silicate platelets in organic solvents.

For the production of organophilic bentonites, quaternary alkyl ammonium compounds are used. The exchange of interlayer cations results in products which are used to modify the rheology (e.g. the thixotropy) of organic solvents, oils, fats, ointments and plastics.

Bentonite is widely used as an essential thickener and extender for paints. Also, it is used in drilling muds; the drilling fluid acts as a lubricant to reduce the friction between the drilling string and the hole walls. Also, the circulation of the drilling fluid can cool the bit, can bring the drill cuttings from beneath the bit up to the ground surface and can produce an impermeable filter cake on the hole walls.

In civil engineering construction, bentonite dispersions by injection can be used to grout cracks and fissures in rocks and can be added to waterproof concrete walls and floors or added to mortar to increase its plasticity (Harvey and Lagaly 2013).

Bentonite natural properties can be changed (for instance, the rheological properties) by a process called activation. It is the case of alkali or soda activation that uses sodium carbonate (Na_2CO_3) to transform the calcium/magnesium bentonite into the sodium form. To achieve such modification, bentonite with water contents of 35–40% (m/m) is usually kneaded or milled with 1–5% (m/m) sodium carbonate and homogenized.

Many bentonite applications require hydrophobization which is currently achieved using the reaction of bentonite with quaternary ammonium salts such as dialkyl dimethylammonium, dialkyl benzyl-methylammonium and alkyl benzyldimethylammonium salts.

Bentonite can be used in environmental applications, such as filtering, decolourizing, clarifying, and pelletizing animal feed, and can be used too as pet litter adsorbent and pesticide carrier. Bentonite also plays an important role in the development of health products, such as cosmetics and pharmaceuticals (Viseras et al. 2010).

Fuller's earth is a sedimentary clay assumed as being the alteration product of volcanic ash deposits in seawater that shows characteristics close to those of bentonite, Ca-montmorillonite being its main constituent clay mineral; its name is derived from its earlier use as fulling or cleaning of the grease from wool clothes; the name *fuller* derives from the Latin name fullon attributed to the person whose job was the degreasing of dirt clothes. Within the Romans the *fullon* used to first steep into urine (alkaline liquid rich in ammonia) the pieces of cloth, some time after the pieces were placed into a basin containing a slurry of *fuller's earth* (*creta fullonia* in Latin), and finally they were washed with fresh water (Robertson 1986).

Fuller's earth is a low plastic clay characterized by its bleaching capacity used to filter animal, mineral and vegetable oils. It is used too as a bonding agent for foundry sands and in the manufacture of carbonless copy paper.

In the UK, *fuller's earth* deposits occur in the Redhill-Nutfield area in Surrey and in Bedfordshire. In the USA, there are extensive deposits in Georgia.

Fuller's earth is used to treat dye solutions used for colouring clothes from the textile industries (Khan et al. 2018).

Bleaching earth is a type of modified clay behaving similarly to *natural fuller's earth* that is used in certain industrial applications. It is usually produced from the treatment of Ca-bentonite with hydrochloric acid or with sulphuric acid, the calcium ions being replaced by hydrogen ions. Acid-activated bentonite comparatively to non-activated bentonite is characterized by an increase of specific surface area, porosity and surface acidity. It has been a traditional product for several decades used in bleaching or decolourizing applications, for instance, as adsorbents for oil and wine clarification, and as catalysts too particularly in the case of pillared smectites (Kendall 1996; Bovey et al. 1996; Falaras et al. 1999; Pagano et al. 2001; Komadel 2003; Onal and Sarikaya 2007).

Ball clay, a term of English origin in the eighteenth century, by definition is a kaolinitic sedimentary clay that commonly consists of 20–80% kaolinite, 10–25% mica/illite and 6–65% quartz. As a rule, kaolinite is structurally disordered, reason why it is called kaolinite D.

Ball clay, as a rule, occurs as clay seams, and in the same deposit, variations in clay composition also occur, including the quantity of the major minerals, accessory minerals and carbonaceous materials such as lignite. *Ball clay* is formed from the weathering of granite and granitoid rocks, the weathering products being washed and transported by ancient rivers and streams from upland grounds to sedimentary basins located in nearby low-lying grounds where they settle down and form various overlaying clay seams showing both vertical and lateral variation in composition and granularity.

Ball clay is an extremely rare mineral resource found in very few places around the world. Its name dates back to the early methods of mining when specialized hand tools were used to extract the clay in rough cube shapes of about 30 cm. As the corners were knocked through handling and storage, these cubes became rounded and "ball" shaped. *Ball clay*, a fundamental raw material of great importance in white ceramics (fine tableware porcelain, electric porcelain, stoneware, earthenware, sanitary ware, floor tiles and wall tiles of white or nearly white ceramic bodies), is sometimes referred to as highly plastic clay of grey, light brown or black colour that changes to almost white colour after firing. High plasticity, high refractoriness, excellent workability, controlled organic content and controlled rheology are *characteristic* properties of ball clay.

Ball clay content in the ceramic formulations, e.g. in fine porcelain, as a rule is 2–4%, whereas in sanitary ware and in earthenware the contents could attain 40%. Mitchell and Vincent classified worldwide ball clay deposits, mainly formed during Lower Tertiary, into four categories, based on reserves and quality (Worrall 1982; Gomes 2002).

Internationally, deposits of ball clay of high quality are much rarer than those of kaolin. The principal traditional ball clay deposits occur in the southwest of England, in the Bovey and Petrockstow basins in Devon and in the Purbeck and Wareham in Dorset. There are also important deposits of *ball clay* in Westerwald in Germany; in Skalna and Cheb in the Czech Republic; in the Mississippi basin with occurrences both in Western Tennessee and in Jackson/Purchase, Kentucky, USA; and in the Charentes and Provins basins in France.

Fire clay, a term of English origin and related to the clay high refractoriness and to its geological occurrence, is defined as sedimentary clay of refractoriness not lower than 1,500 °C, and that after firing shows light brown, light grey and ivory colours. The traditional fire clay from the Yorkshire in England occurs immediately under the "coal seams" or "coal measures" dated of the Carboniferous, reason why the fire clay is also called *underclay*. *Fire clay* is essentially composed of disordered kaolinite or kaolinite D, mica/illite, quartz, illite-montmorillonite mixed layers and organic matter, sometimes with dickite associated (Gomes 2002; Worrall 1975, 1982). *Fire clays* are utilized to manufacture tableware, stoneware and ornamental ceramics.

Refractory clay is a type of clay still more refractory than the fire clay, however distinct in matter of geological occurrence. Refractory clays comprise the so-called flint clay or hard clay, and the *semi-flint clay* or *semi-hard clay*. These clays are kaolinite-rich, the kaolinite content could reach values higher than 95%, and sometimes show associate free aluminium hydroxides, *gibbsite* and *boehmite*, and iron oxides/hydroxides, *goethite* and *hematite*.

Interesting examples of flint and semi-flint clays are the deposits of karst bauxite reported by Gomes (1966a, b, 1968), Valeton (1983), Bardossy (1982), Combes and Bardossy (1995) and Putzoulu et al. (2018).

Synthetic clay minerals with well-designed chemical composition, structure and morphology under controllable synthetic conditions possess much improved properties in comparison with their natural counterparts and have practical applications. *Synthetic clay minerals* provide new choices of layered solids and can be tailored to promote specific properties. They provide better understanding of the various processes involved in the formation of natural mineral counterparts.

Carrado et al. (2006) and Zhang et al. (2010) summarize and discuss the recent advances on synthetic clay minerals such as *kaolinite*, *pyrophyllite*, *mica*, *smectite*, *chlorite* and *sepiolite*. The first group of authors present and discuss the variables of clay minerals synthesis, with an emphasis on starting materials and hydrothermal conditions.

The first attempts to synthesize clay minerals go back to the 1950s of the twentieth century, well represented by the works of Caillère et al. (1953, 1954, 1955). In fact, kaolinite and several species of smectite have been synthesized during the last 70 years from diverse starting materials, mostly other aluminosilicates, glasses and gels. Regarding *smectites* synthesis, Kloprogge et al. (1999) summarize, evaluate and criticize the various approaches to smectites synthesis being adopted and the long-term stability of the obtained products. Clay minerals synthesis is generally performed either at low temperature or at a higher temperature by hydrothermal technology. New high-tech products derived from these synthetic clay minerals are being developed in China.

Examples of *synthetic clay minerals* commercially produced in China are referred to by Zhou et al. (2016): *synthetic hectorite* (the ideal chemical composition $\mathrm{Na_{0.50–1.20}[(Mg_{5.50–4.80}Li_{0.50–1.20})(Si_{8.00})O_{20}(OH)_4]}$) (Zhou et al. 2005; Zhang et al. 2010), *synthetic saponite* ($\mathrm{Na_{0.50–1.20}[(Mg_{6.00})(Si_{7.50–6.80}Al_{0.50–1.20})O_{20}(OH)_4]}$) (Zhang et al. 2010) and *synthetic mica* (Chen and Peng 1990).

It is worth pointing out that *synthetic hectorite* comparatively to natural *montmorillonite* offers the general benefits of higher rheological efficacy (viscosity and yield value), lower iron content and lighter colour.

Hectorite clay and *hectorite organoclay* have less antiperspirant potential than montmorillonite-based products. The *hectorite* particle platelets are much smaller and elongated compared to the more equidimensional montmorillonite platelets. Therefore, *hectorite clay* has more platelets per gram providing greater swelling capacity and improved rheological efficiency compared to *montmorillonite clay*.

Hydrotalcite, also called *anionic clay*, is not a real clay mineral but has a layered structure and properties similar to those that characterize clay minerals. Hydrotalcite

Mg_{1-x} …… Al_x ….. $(OH)_2$

…..H_2O….CO_3….H_2O

Mg_{1-x} …… Al_x ….. $(OH)_2$

Fig. 6.16 Schematic structure of *hydrotalcite*. The symbol $_x$ indicates the possibility of isomorphous substitution of Mg for Fe^{2+}, Zn^{2+}, Cu^{2+}…, and Al for Fe^{3+}, Cr^{3+}…

is a layered double hydroxide (LDH) whose name is derived from its resemblance with the clay mineral talc and is characterized by its anion-exchange properties and high water content. *Hydrotalcite* is a magnesium-aluminium hydroxycarbonate with the formula $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ and constituted of positively charged brucite-like $Mg(OH)_2$ layers intercalating mobile anions, as a rule CO_3^{2-} (Fig. 6.16). The natural form of *hydrotalcite* was identified in a serpentine-magnesite deposit associated to serpentine, dolomite and hematite in the Snarum area of Norway and exhibits white or pearl-like colours. The synthetic form of *hydrotalcite*, a high-temperature chemical sorbent, started being produced since 1966, and is used in pharmacy as antacid, and in industry as sorbent, as sunscreen for UV absorber, as catalyst support, and as intercalator of polymeric chains, and in environment protection.

Various scientific articles show the main properties and applications of hydrotalcite and of the class of lamellar inorganic solids with structure similar to hydrotalcite structure, called "layered double hydroxides (LDHs)": Leroux and Besse (2001), Wang and O'Hare (2012), Mishra et al. (2018) and Revuri and Lee (2019).

6.5 General Applications of Clay and Clay Minerals

Clays and clay minerals most probably started being formed on Earth immediately after planetesimal formation (Hazen *et al*. 2013). Indeed, the necessary conditions for clay minerals formation, the existence of water, sources of acids and aluminosilicate rocks, would have prevailed on the early Hadean Earth.

Both main fields of interest and applications of clays are schematically shown in Fig. 6.17.

Clay and naturally stone have been used by humans since the Stone Age due primarily to the fact that clay and stone are quite common at the Earth's surface and are utilized for agriculture (clay is a fundamental component of soil), ceramics and building materials.

Ceramics is the main and conventional field of clay application worldwide. Any clay could be used in ceramics. Dondi et al. (2014) propose a simple technological classification of clay raw materials used in ceramics based on chemical (Fe_2O_3 content) and mineralogical parameters (content of phyllosilicates and carbonates) together with particle size (fractions <2 μm and >63 μm) and plasticity (methylene blue index and Atterberg plastic index). The chemical argument could firstly

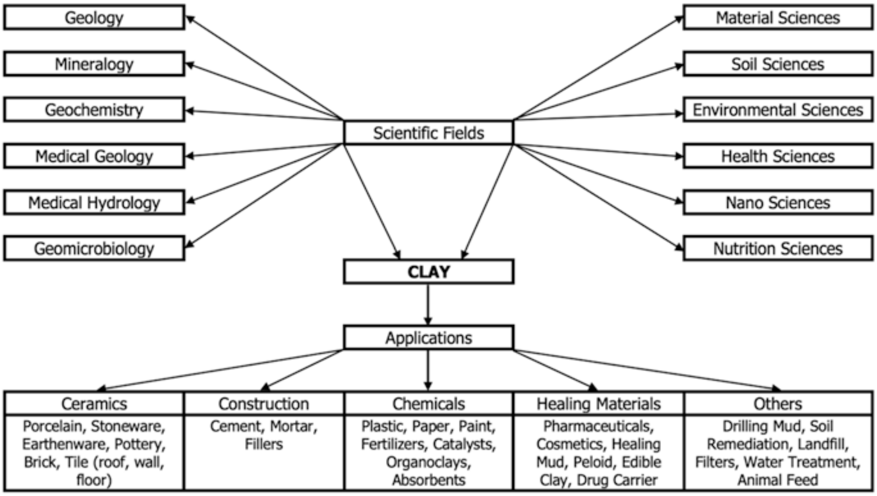


Fig. 6.17 Scientific fields and traditional areas of clay application

discriminate light-firing and dark-firing clays just using a total iron oxide threshold of 3%.

Light-firing clays are distinguished by the amount of kaolinite group minerals and plasticity in “kaolins” (high-grade, low-grade, raw kaolins and kaolinitic clays) and in “plastic clays” (ball clays, pyrophyllitic clays, white bentonites).

Dark-firing clays are classified according to grain size and carbonate contents in carbonate-rich types (marls), red loams and red clays. These clays could be further differentiated by the relative abundance of clay minerals.

Clays are differentiated on the basis of the so-called clay general properties, such as colour; granularity assessed by particle size distribution; specific surface area assessed in $m^2.g^{-1}$ that can change from types to types, from 10 $m^2.g^{-1}$ (in the case of kaolin) up to 300 $m^2.g^{-1}$ (in the case of *fibrous clays*) and even up to 800 $m^2.g^{-1}$ (in the case of total exfoliated or delaminated *smectite clays*); ionic exchange capacity (cation and anion exchange); viscosity; and plasticity. All these clay properties, which are which are commanded by clay minerals crystallochemistry, condition all clay applications.

Within all geological resources, clay is the one that has the most diverse applications, and with the new developments in geology and materials science new insights into the field of clay applications are getting through.

Clay mineralogy and geochemistry and the new developments in analytical methods and procedures can provide useful information for reconstructing and interpreting paleoclimates and even the processes involved in the evolution of extraterrestrial environments (Pearson 2002; Zhou and Keeling 2013).

The interest for clay minerals is particularly due to their biocompatibility and ecocompatibility, low toxicity for oral administration, low cost and natural availability. There is increasing interest and research in the use of clay minerals as agents able to carry specific and functional drugs adsorbed or absorbed to be delivered to target sites in the human body and released in controlled manner. A recent article by Massaro et al. (2018) is a good review of the use of some clay minerals, halloysite in particular among the plethora (about 70 species) of clay minerals, as natural resources for drug carrier applications.

As aforesaid, Fig. 6.17 shows the main and traditional areas of clay interest and application, both scientific and technological. Two scientific areas mainly deal with both positive and negative interactions of *clay* and *clay minerals* on human health. One is *Medical Geology* whose definitions, targets, methods and applications have been referred to and commented in previous topics dealt with in this book. The other is *Medical Hydrology*, a scientific field that studies the impact of mineral water, particularly natural mineral water from thermal spas on human health, and studies too the so-called healing muds and peloids which formation is highly dependent from water, clay being an important constituent of them. Most of the goals, methods and applications of *medical hydrology* will be dealt with in Chaps. 7 and 14 of this book.

Schoonheydt (2016) states that the production of clay minerals for industrial and environmental uses continues to grow annually, and new possible applications for clay minerals are continuously being explored, the author enhancing three areas of application:

1. Clay-polymer nanocomposites, including clay-biopolymer nanocomposites
2. Hybrid clay mineral films with special optical and electrochemical properties
3. Heterogeneous clay mineral catalysts, including bioreactive clay minerals

Schoonheydt (2016) states too that for such purposes the natural clay minerals comparatively to the corresponding synthetic clay minerals suffer from several disadvantages, such as presence of impurities and inhomogeneities in particle size and shape as well as in electric charge distribution.

Clays are important industrial rocks, and as a rule, before their commercialization, they have to undergo industrial processing in order to improve the essential physical and chemical properties required for specific applications, such as:

1. *Purity* (appraised on the basis of mineralogical and chemical data improved by the removal of impurities in order to increase the clay mineral content)
2. *Texture* (particle size and shape); *colour*; *cation and anion exchange*
3. *Hydration and swelling*; *plasticity* (controlled by the clay mineral nature, the amount of water, the particle size distribution and particle shape)
4. *Rheology* (viscosity and thixotropy)
5. *Organic reactions* (via ion exchange, via replacement of interlayer water molecules by polar organic molecules, and via grafting reactions too)

Clay processing may involve various physical or chemical treatments such as wet grinding and gritting, magnetic separation, selective flocculation, froth flotation and activation with inorganic or organic compounds.

Christidis (2011, 2013) reports the relevant properties and the laboratorial or industrial procedures currently used to assess industrial clays and to improve clay quality and grade. Some other reports on clay properties and applications have been provided by the following authors: Robertson (1960), Grim and Guven (1978), Jepson (1984), Odom (1984), Scott (1990), Galán (1996), Psyrillos et al. (1999), Pruett and Pickering (2006), Laird (2006), Murray (2007), Bergaya and Lagaly (2007), Bergaya et al. (2011), and Bergaya et al. (2013).

For instance, with regard to kaolin as basic raw material for ceramics, paper and many other industrial applications, the following properties are essential: whiteness, brightness, refractoriness, chemical inertness, softness, hydrophobicity, fine particle size, easy dispersion in water, water slurries with low viscosity and high solids content, low abrasiveness, low electrical conductivity and low shrinkage.

Clay minerals can play important roles in the environment protection. They have been used in the disposal and storage of hazardous chemicals as well as in the remediation of polluted water. The use of clay minerals as adsorbents for the adsorption of various hazardous substances from aqueous systems, such as heavy metals, dyes, antibiotics, biocide compounds and other organic chemicals (Dal Bosco et al. 2006; Mukherjee 2013; Bhattacharyya et al. 2014; Ismadji et al. 2015; Uddin 2017). The last author referred to has produced an interesting review about the progress in one decade (2006–2016) of the adsorption of heavy metals by clay minerals and confirmed that both natural and modified forms of clay minerals have excellent feasibility in removing different toxic aquatic metal pollutants.

Concerning the application of clays and clay minerals in pharmacy and in therapeutics, there is much more ancient and recent scientific information.

The benefits of clays to human health are well documented in several recently published articles: Robertson (1986, 1996), Novelli (1996, 1998, 2000), Reinbacher (1999, 2003), Viseras and Lopez-Galindo (1999), Veniale (1996, 1998, 1999), Carrtero (2002), Veniale et al. (2004, 2007), Gomes and Silva (2007), Tateo et al. (2006, 2009), Carretero and Pozo (2007), Viseras et al. (2007), Gomes et al. (2009, 2013a, b), Rautureau et al. (2010), Kikouama and Baldé (2010), Fioravanti et al. (2011), De Vos (2010), López-Galindo et al. (2011), Peiró and Tejero (2014), Williams and Hillier (2014), Gomes (2015) and Awad et al. (2017).

Regarding the books, all of a general character, the authors of some of them are herein mentioned: Selinus et al. (2005), Gomes and Silva (2007), Carretero and Pozo (2007) and Rautureau et al. (2010, 2017).

Within all clay typologies, *kaolin*, *bentonite* and *fibrous clays* (*sepiolite* and *palygorskite*) are the clays most interesting in terms of applications in *geopharmacy* and *geotherapeutics*.

Kaolin and bentonite are special types of clay having unique properties of widespread technological importance and traditional applications such as ceramics (porcelain, earthenware, tableware and sanitary ware), paper coating, plastics, pharmaceuticals, paints and cosmetics.

New kaolin applications include nano-sized materials for use in the inks of modern printers, nontoxic pesticides in organic farming and polymer composites used in the packaging industry; in the future, expectations are great in the field of nanocomposites derived from *kaolins* to improve the rheological, thermal and organic complexation capabilities of products used in engineering and medicine, in the last case to carry and deliver pharmaceuticals by using nanotubes of *halloysite* as a Trojan horse (Schroeder and Erickson 2014).

With regard to kaolin and kaolin minerals, Awad et al. (2017) in an excellent article entitled "Kaolinite in Pharmaceutics and Biomedicine" comprehensively and exhaustively report their applications in health-care uses, especially in the pharmaceutical, cosmetic and biomedicine industries.

In the pharmaceutical industry, *kaolin* and *kaolin minerals* in particular are used as active ingredients or as excipients. In the case of *kaolinite*, both as active ingredient and excipient, the action of this clay mineral is attributed to its adequate physical, chemical and surface physicochemical properties. The most important functionalities of *kaolin* or *kaolinite* as excipients in pharmaceutical formulations are as follows: diluent, binder, disintegrant, pelletizing and granulating, amorphizing, particle film coating, emulsifying and suspending agent. Also, the most important functionalities of *kaolin* and *kaolinite* as active ingredients are due to their safe bioactivity, enabling their use in topical applications as haemostatic agent, as dermatological protector and anti-inflammatory agent, and in oral applications as gastrointestinal protector, antibacterial, antiviral, detoxification and antidiarrhoeal agent.

Kaolinite is the most commonly used geophagic clay mineral, especially in tropical areas (Wilson 2003). In other parts of the world, geophagists consume clay or clayey soil rich in *smectite* and *mixed clay mineral assemblages*.

Awad et al. (2017) report that in pharmacopoeias (USA Pharmacopeia 32, British Pharmacopeia BP 2009 and 2012, and European Pharmacopeia PhEur 6.3 monograph 0503 and 7.0 volume 2), kaolin is described as a native hydrated aluminium silicate, powdered and freed from gritty particles by elutriation. The British Pharmacopeia (BP) 2009 considers three kaolin grades: light, light natural and heavy.

With regard to bentonite, numerous research articles exist disclosing the use in many cultures of this type of clay, both externally and internally, for maintaining body health or treating some diseases. Published in PubMed about 100 articles have been produced on the effects of bentonite on human body function.

Detoxification is one of the bentonite effects on body function. This property is referred to its polycationic nature which leads to absorption of negative charge toxins (Williams et al. 2009).

Bentonite is being used in humans as a dietary supplement to prevent and cure *aflatoxin* toxicity. Aflatoxins are poisonous and cancer-causing chemicals that are produced by certain moulds which primarily affect the liver. Bentonite has been recognized as a reliable treatment for pesticides and metal toxicity or poisoning if the clay mineral *montmorillonite* is supplemented in diet. Bentonite has been used in the treatment of diarrhoea and other affections of the gastrointestinal tract that, for instance, can produce borborygmi – the stomach rumblings caused by gas moving through the intestines, the driving force of the treatment with bentonite being the attractive power of clay-particle surfaces (Carretero et al. 2006).

Experience has shown yet that bentonite can decrease the bleeding and clotting time and therefore is suggested as a haemostatic agent. Also, pastes of *healing muds* and of *peloids* made of *bentonite* and spring thermal water or seawater are commonly used in *pelotherapy*.

All the articles referred to disclose important information about properties, applications and functions of clay, clay minerals and clay-based products in human health. However, most of the industrial applications require an industrial processing involving in particular the chemical beneficiation of the natural clay. It is the case of the so-called designed and engineered clay, such as *acid-activated clay* and *organo-clay*, materials actually in progressive and continuous demand. The term "acid-activated clay" has generally been reserved in the industrial literature for partially dissolved bentonites.

Acid-activated bentonite through treatment with both sulphuric and hydrochloric acids has been a standard product for many decades, with a significant market in the decolourizing of vegetable, animal and mineral oils. Usually Ca^{2+}-bentonite is treated with inorganic acids such as sulphuric and hydrochloric acids that remove the Ca cations from particle surfaces and edges, replacing them by monovalent hydrogen ions and leaching out Fe^{3+}, Fe^{2+}, Al^{3+} and Mg^{2+} cations, and as a consequence particle overall negative electric charge, specific surface area and porosity increase (Christidis et al. 1997; Falaras et al. 1999; Jozefacink and Bowanko 2002; Onal and Sarikaya 2007; Carrado and Komadel 2009; Hussini et al. 2011; Komadel and Madejová 2013a, b; Komadel 2016; Dutta 2018).

According to Komadel and Madejová (2013a, b), acid activation is a common chemical modification of clays, usually bentonites, with a hot solution of a mineral acid (typically HCl or H_2SO_4), and it is used for both scientific and industrial purposes. The aim is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity. The product consists partly of the remains of the starting mineral and partly of an amorphous, porous, protonated and hydrated silica phase with a three-dimensional cross-linked framework. Acid activation modifies principal clay properties and thus also their industrial applications.

Onal and Sarikaya (2007) have used acidic aqueous bentonite suspensions heated at 97°C for 6 hours, the acid content being changed from zero to 70% by mass based on the dry bentonite-acid mixture.

Alkali-activated bentonite, more precisely Na-activated bentonite, is the result of the following reaction:

$$\mathrm{Ca\quad bentonite} + \mathrm{Na_2CO_3} \rightarrow \mathrm{CaCO_3} + \mathrm{Na\quad bentonite}$$

In nature Na-bentonite is less abundant than Ca-bentonite, and Na-bentonite having more and interesting industrial applications than Ca-bentonite justifies the technological processes of alkaline or alkali activation of Ca-bentonite. One important application of Na-bentonite is in slurry walls, also known as *diaphragm walls*, used in modern construction to prevent the seepage of groundwater, the slurry wall being a trench filled with a thick colloidal mixture of Na-bentonite and water. Na-bentonite, in small amounts of 2–4%, has also an important practical application in ceramics, in particular in the processing of wall tiles and floor tiles which use high-pressing methods of dry powders of kaolin/feldspar mixtures, taking advantage of the clay plastifying and bonding capacity.

Organoclays are organically modified clays or clay minerals by exchanging the original interlayer cations of 2:1 clay minerals, particularly *montmorillonite*, for organic cations, typically quaternary alkylammonium ions, generating organophilic surfaces (Betega de Paiva et al. 2008; He et al. 2014; Guégan 2019). The final characteristics of *organoclays* mainly depend on the type of inorganic layered materials used and the chemical nature of the surfactant for the surface modification.

Organic treatment of some clay types, particularly of smectitic clays, has sparked an explosive interest on a class of materials called polymer-clay nanocomposites (PCNs) utilized for structural reinforcement and mechanical strength, as flame retardants in thermoplastics and bionanocomposites.

Organoclays are also appropriate for the adsorption of organic contaminants such as pesticides, herbicides and pharmaceuticals that are more and more found in the water resource despite wastewater treatments. Claytone APA V and Claytone MPZ V are the trade names of organoclays based on montmorillonite. The corresponding data sheets contain the technical description of products, properties and applications. Claytone APA V, for instance, is an organoclay used in cosmetics, in which it acts as thickening and suspending agent for medium to high polar oil and solvent phases.

Montmorillonite, the most widely known clay mineral of the *smectite group minerals*, and the main constituent of *bentonite* is the most commonly used clay mineral in PCNs (Carrado and Bergaya 2007; Darder and Ruiz-Hitzky 2007; Carrado and Komadel 2009).

As said before, *cationic clay minerals* can be both natural and synthetic, the last having the advantage relative to the first, of homogeneous structural and compositional properties, as well as lower rates of chemical and microbial contamination.

Clay minerals used in pharmaceutical formulations should be highly consistent in terms of particle size, chemistry, water content and free from chemical (heavy metals) and microbial (pathogens) contaminations.

Based on the application, for instance, synthetic cationic-smectite could be modified in order to become enriched in specific metals, Fe, Zn, Co, Cu and Ni. The additives could be organic compounds such as surfactants and polymers that become fixed on the surface, edges or interlayer spaces of clay particles.

The modified clay minerals could be divided in subgroups: clay-drug hybrids, clay-polymer hybrids and organoclays.

Figure 6.18 shows the different types of cationic clay minerals and their applications in various biological systems (Ghadiri et al. 2015).

Clay of the *nanoclay* typology besides important general applications in fields, such as *catalysis* (Garrido-Ramirez et al. 2010; Nagendrappa 2011), food packaging (Azeredo 2009; Majeed et al. 2013); *textile industry* (Floody et al. 2009; Shahidi and Ghoranneviss 2014); *high strength materials with thermal and gas barrier properties* (Liu et al. 2011; Wu et al. 2014; Gamelas and Ferraz 2015); has specific and other rather important applications in fields such as *medicine* (Ambre et al. 2010; Suresh et al. 2010), *cosmetics* (Patel et al. 2006; Carretero and Pozo 2009, 2010) and *pharmacy* (Carretero and Pozo 2009, 2010).

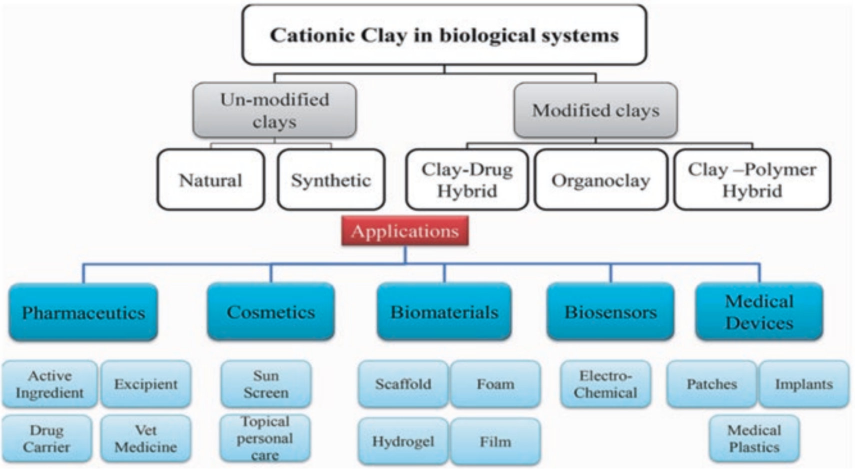


Fig. 6.18 Different types of cationic clay minerals and their applications in various biological systems (*In*: Ghadiri et al. 2015)

Biocomposites are materials composed of biomolecules and inorganic solids, such as clay minerals. The term “biocomposite” was initially introduced by Toyota Central Research Laboratory by the end of 1985, while they secured success in fabrication of *nylon-montmorillonite* clay-based nanocomposites in order to produce a belt cover for car (Kojima et al. 1993a, b).

Very recently, Oliveira et al. (2018) produced an interesting article on “Immobilization of Biomolecules on Natural Clay Minerals for Medical Applications”. Indeed, clay minerals combining nanometric particle size with adsorptive capacity, lack of toxicity and biocompatibility are really promising materials to be used as biocomposites able to immobilize biomolecules on their electrically charged surfaces, which are characterized for having positive and negative sites, and as so, high surface reactivity (Ruiz-Hitsky et al. 2015).

Clay minerals can reversibly fix and protect the biomolecules, organic entities of biological origin, such as polysaccharides, lipids, enzymes, amino acids, peptides and nucleic acids. Clay minerals need to undergo modification and functionalization of their particle surfaces before incorporation into polymer matrices to develop polymer-clay nanocomposites.

Nanoclays are clay minerals which particles have a high form or aspect ratio with at least one dimension of the particle in the nanometre range. The purity, electric charge, cation exchange capacity and specific surface area are critical characteristics.

Montmorillonite, *halloysite*, *hectorite* and *saponite* are the most commonly used nanoclays. Montmorillonite after being Na^+-activated to improve its swelling is able to insert organic cations. These cations reduce the surface energy of the clay mineral, making it more organophilic, thus facilitating access between the layers of monomers and polymers with different polarities.

As a consequence of clay minerals' electric charge, in general, they show hydrophilic character turning them incompatible with a wide range of polymer types. However, organophilic clay minerals can be produced by ion exchange with an organic cation. For instance, in *Na^+-montmorillonite*, sodium ions can be exchanged for an amino acid such as 12-aminododecanoic acid (ADA) to turn the clay mineral hydrophobic and therefore more compatible with polymers.

Nanoclay specific surface area is an important factor, since higher surface areas facilitate the interaction clay-polymer. Refining, i.e. going down from micro- to nanoscale, as well as delamination or exfoliation of the platy particles of clay minerals such as *kaolinite* and *montmorillonite* could significantly increase their specific surface areas and consequently the exposure to the polymer matrix. In all applications, nanoclay improves the product quality, costs economy and environment safety (Nazir et al. 2016).

Nanoparticles of other materials are currently available, such as aluminium oxide, copper oxide, iron oxide, titanium dioxide, zinc oxide and calcium carbonate.

Clay minerals are naturally hydrophilic and most polymers are hydrophobic. Hence to render miscible one clay mineral with a hydrophobic polymer, the clay mineral has to be treated with certain organic substances becoming an organoclay that could be employed in biological applications, for instance, for drug delivery or tissue engineering (Lee and Fu 2003; Vasilakos and Tarantili 2012).

Clay is the main constituent of the so-called healing clays and edible clays, and within the *healing clays*, it is the main constituent of most natural peloids and *peloids s.s. (strictu sensu)* particularly of the essentially inorganic peloids used for therapeutic and cosmetic purposes, either applied outdoors in the natural environment, or applied indoors in specialized spas. *Edible clays* and *healing clays* are described in subchapters 7.2 and 7.3 of Chap. 7, respectively.

A particular reference is due yet to the so-called antibacterial clay or killer clay or bactericide clay, a natural clay whose name is grounded on scientific arguments (see subchapter 7.5 of Chap. 7 in this book).

Kaolin and bentonite are special types of clay having unique properties of widespread technological importance and traditional applications such as ceramics (porcelain, earthenware, tableware and sanitary ware), paper coating, plastics, pharmaceuticals, paints and cosmetics. New *kaolin* applications include nano-sized materials for use in the inks of modern printers, nontoxic pesticides in organic farming and polymer composites used in the packaging industry.

In the future, expectations are great in the field of nanocomposites derived from kaolins to improve the rheological, thermal and organic complexation capabilities of products used in engineering and medicine, in the last case to carry and deliver pharmaceuticals by using nanotubes of *halloysite* as a Trojan horse (Schroeder and Erickson 2014).

6.6 Specific Properties of Clay Minerals That Justify Their Interest in Pharmacy, Therapeutics and Cosmetics

Kaolinite, *halloysite*, *montmorillonite*, *beidellite*, *talc*, *sepiolite* and *palygorskite* are the most commonly used clay minerals for medical, pharmaceutical and cosmetic applications, either as active substances or as excipients.

With respect to the clay/human body interaction, clay particles can adsorb and make accessible for incorporation, by ingestion or dermal absorption, either bio-essential elements or toxic elements (e.g. heavy metals). The clay particles may also adsorb and make available for disposal or excretion any potentially toxic elements or toxins that have been ingested or produced by metabolism.

Much of what is discussed in this subchapter is a replica of the information provided in the article entitled "Healing and Edible Clays: A Review of Basic Concepts, Benefits and Risks" recently published by Gomes (2018) in the journal *Environmental Geochemistry and Health*.

The clay and clay mineral properties that justify their use in human health care are the following:

1. Ubiquitary of clay deposits, located on or near the Earth's surface, making its access and extraction simple.
2. Extraordinarily small size of clay minerals (usually less than 2 μm, but down to the nanometre size) and anisometric particle shape diversity (lamellar in most clay minerals, but fibrous, tubular or spherical in others) – both these characteristics are essential conditions to provide the clay with a high specific surface area value (commonly between 10 and 300 $m^2.g^{-1}$), a property that is a determining factor when the clay is used, for example, or in the lining of the stomach and small intestine to alleviating nausea and indigestion, or topical coating and adhesion to the skin, or for localized and controlled delivery and delivery of medicament; however, these characteristics may not be good if the clay, taking into account the small size and shape of its particles, provides toxicity associated with continued inhalation.
3. Clay minerals have a generally negative electric charge, due mainly to structural defects (isomorphous atomic substitutions, atomic omissions, and broken bonds at the edges of the particles); the clay minerals of the *kaolinite group* have a low net electric charge (0.1–0.2), corresponding to a half unit cell; the clay minerals of the *smectite group* have an intermediate liquid electric charge (0.2–0.6), also corresponding to a half unit cell, which is responsible for the expansion of the structure (the degree of expansion depends on the nature and hydration capacity of the intercalation cations, this is positioned in the spaces between structural layers and the degree of humidity of the environment in which the minerals occur) and also responsible for the collapse of the structure in dry environment; the clay minerals of the *illite group* have high net electric charge (0.6–0.9), corresponding to a half cell unit, reason why they do not expand when hydrated; the overall negative charge of the clay minerals being

dependent on the pH of the occurrence environment can be modified (even compensated and neutralized) by the effect of surface coatings, for example, quasi-amorphous or amorphous iron hydroxides of positive electric charge; such modifications will have consequences on relevant clay properties, such as ion exchange, plasticity and rheology.

4. Low hardness and abrasiveness, properties that provide pleasant sensation when a paste of clay comes in contact with the skin and is spread on it.
5. High affinity for water, facilitating the formation of both plastic pastes with adequate fluidity, suitable scattering and adhesion to the skin and stable dispersions/suspensions.
6. High adsorption/absorption capacities, properties that allow the adsorption/absorption of toxins, bacteria and viruses, and their elimination from the skin, making efficient the use of certain types of curative mud/peloid in the treatment of skin conditions such as acne, seborrhoea, eczema and psoriasis, and allowing the use of certain nanotubular clays as is the case of halloysite in the process of controlled release of medicaments at the desired site.
7. Alkaline pH clays can neutralize the gastrointestinal acidity, while clays of acid pH, if similar to the pH of the skin, avoid skin irritations.
8. High cation and anion exchange capacities, properties that promote reversible attachment and exchange of chemical elements/compounds (polar, in particular), for example, or between clay and skin-based facial masks, or incorporation of elements/compounds of medicinal interest.
9. Reduced species of exchangeable elements, such as Fe^{2+} and their oxidation, are responsible for the bactericidal action of certain clays, for example, those known as “French green clays”, which become toxic to microorganisms that are pathogenic to humans.
10. High heat retention capacity and low heat diffusivity, important characteristics for curative mud/peloid coatings, packs and poultices that are applied, either hot (not above 45 °C), or cold, depending on the nature of the affections to deal with; the cooling rate of curative mud/peloid (typically 15–20 min from 45 °C to 37 °C) is conditioned by factors such as global composition and clay texture, nature and quantity of clay minerals, nature and amount of the associated organic substances and the nature of the liquid phase (natural mineral water, spring water, seawater, salt lake water, etc.), the amount of which is also very influential, as a rule, between 40 and 80%.
11. Great diversity of natural colours and possibility of artificial pigmentation, in case the clay presents white colour.

Due to these and other properties, such as dispersibility, hygroscopicity, greasiness, plasticity, thixotropy, chemical inertia and none or negligible toxicity, clay and clay minerals are widely used in the pharmaceutical industry as a lubricant, desiccant, disintegrant, diluent, stabilizer, binder, opacifier and pigment, as well as emulsifier, thickener and as an isotonic and anticaking agent, they can still be used as a flavouring agent and active ingredient carrier.

Clay mineral surface properties are also of paramount importance in medical applications. In the last few decades, some clay minerals, particularly *halloysite*, *montmorillonite*, *sepiolite* and *palygorskite*, based on basic and clinical research, have been considered efficient carriers of active drug molecules providing important applications in the medical industry.

Clay minerals have important roles in drug encapsulation (Delcea et al. 2011;), in drug delivery systems, in the formation of antimicrobial surfaces (Babu et al. 2018), in the release of active substances (da Silva et al. 2016) and in drug efficiency (Ambrogi et al. 2014). Some clay minerals, such as *montmorillonite*, are efficient sorbents of various types of drugs, such as antibiotics, photosensitizers (Donauerová et al. 2015) or disinfectants. *Organoclays* such as *montmorillonite* treated with quaternary ammonium salts have been tested as antimicrobial and disinfection agents (Hong and Rhim 2008; Bragg et al. 2014; Yuen et al. 2015).

Among the main healing properties of clay and clay minerals are the following: antacid, gastrointestinal protector, antidiarrhoeal, laxative, homeostatic, emetic and antianaemic. Besides the bibliographic references mentioned in the chapter's body, some others have provided relevant information used in the preparation of this chapter, such as: Abad et al. (2001), Al-Ani & Sarapaa (2008), Bailey (1977), Bailey (1981), Bergaya & Lagaly (2001), Bergaya & Lagaly (2006), Brigatti et al. (2011), Bujdáková et al. (2018), Cervini-Silva et al. (2015), Chang et al. (2009), Choy & Park (2004), Churchman & Lowe (2012), Clauer & Chaudhuri (1995), Cuadros et al. (2013), Cuadros (2013), Direcção-Geral de Geologia e Minas, Ministério da Indústria e Energia (1985), Drits & Zviagina (2009), Fiore et al. (2009), Galán (2003), Galán & Ferrell (2006), Galán & Aparício (2013), Gomes & Rautureau (2013), Gomes et al. (2015), Guggenheim (2011), Heller-Kalai (2013), Hu & Yang (2013), Keller (1970), Keller (1976), Keller (2000), Låg (1990), Limpitlaw (2004), Merriman (2005), Merriman (2006), Mitchell & Vincent (1997), Moore & Reynolds (1997), Murray et al. (1993), Murray (2000), Nagasawa & Moro (1987), Ponto & Berg (1918), Pozo & Calvo (2018), Savechenkov (1862), Savic et al. (2014), Suárez & Garcia-Romero (2006), Tateo & Summa (2007), Thompson (1914), Weiss & Range (1970), and Wesley (2014).

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