

CHAPTER 1

CLAYS AND CLAY MINERALS

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1.1 WHAT'S IN A NAME

The term “clay” was used in everyday language long before being imbued with a well-defined scientific meaning. Therefore, it is not surprising that it carries different connotations to different communities. To the industrialist, it is a raw *material* available in large amounts at cheap prices, characterized by its macroscopic properties relative to various applications. To the geologist working in the field, it is a particular secondary *mineral* largely found in weathered deposits from sedimentary or volcanic origin. To the chemist and mineralogist, it refers to a particular type of mineral *structure* defined at the atomic level.

Recent recommendations of the JNC¹ advise to use the term “clay minerals” to refer to precisely determined crystallographic structures, and define “clays” in terms of macroscopic properties.² Therefore, a natural clay will consist of a/several clay minerals mixed with additional minerals as impurities. However, the distinction is not always clearly made and many papers that use well-defined clay minerals will refer to them as “clays” because the full denomination is somewhat cumbersome [1].

Here we will build on the crystallographic view, which is the most rigorous, and try to indicate how the atomic structure dictates the properties at other levels.

The most salient structural feature of clay minerals is that they are layered. That is to say they belong to a large class of inorganic compounds built by the stacking of

¹ Joint Nomenclature Committee of the AIPEA (Association Internationale pour l'Etude des Argiles) and the CMS (Clay Minerals Society).

² A clay is “a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired.”

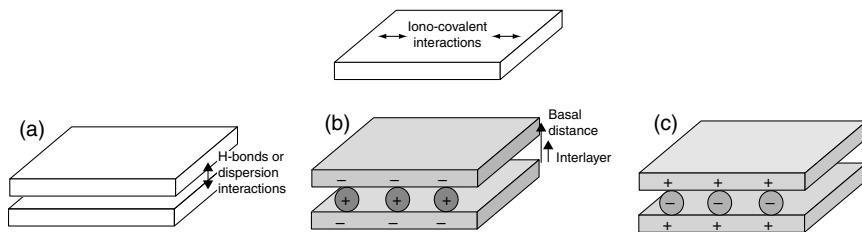


FIGURE 1.1 The basic architecture of a clay mineral at the nanometric scale: (a) neutral layers; (b) negatively charged layers with compensating cations (cationic clays); and (c) positively charged layers with compensating anions (anionic clays).

two-dimensional units, known as layers, whose internal coherence is due to strong iono-covalent bonds, while in the direction perpendicular to the stacking they are bound to each other through weaker forces. This means that the layers can be separated from each other relatively easily, and the volume included between two successive layers, whatever its content, is called the “interlayer space” (the term “gallery” or “intergallery space” was formerly used synonymously but has to be discarded). A macroscopic analogy would be a pile of paper sheets, or may be a deck of cards depending on the semirigidity assumed for the layers.

Clay minerals are a subset of the family of layered oxides (or oxyhydroxides), which can be classified in three different categories according to the electrical charge of the layer (Figure 1.1):

- (i) Neutral layers, as in pyrophyllite, talc, and kaolinite. The layers are held together by van der Waals interactions and/or hydrogen bonds.
- (ii) Negatively charged layers. Since the structure as a whole must be neutral, the negative layer charge must be compensated exactly by an equal amount of positive charges provided by cations located in the interlayer space (compensating cations). These minerals are most often listed as phyllosilicates, and the most widespread in nature (especially montmorillonite which is the major component of commercial bentonites) belong to this group, and are therefore called “cationic clays” when specification is needed.
- (iii) Positively charged layers with compensating anions in the interlayer space. The most common natural mineral in this group is hydrotalcite (HT), but this belongs to a broader family of “HT-like” materials most often synthesized in the laboratory and called layered double hydroxides or LDH. These are also called “anionic clays” [2–4].

It should be noted that we have characterized clay minerals as layered “oxides” or “oxyhydroxides” rather than layered silicates (or “phyllosilicates”). Indeed some of them do not contain any silicon in their formula (the LDH) and thus are certainly not silicates. Even in the case of cationic clays, an argument could be made that the term “silicate” obscures the real structure of the layers (as outlined in Section 1.3.1.3 and

corresponding inset) and is a leftover from a time when only the raw formula was known.

Let us come now to the clay as a macroscopic material. Historically, the criterion of particle size has been used a lot to define clays, although different disciplines and professions have fixed different size limits. The “clay fraction” has been defined as fine-grained materials with a maximum particle size (or, rather, an equivalent spherical diameter) $\leq 2 \mu\text{m}$.

However, the particle size limit used by different communities could vary from $1 \mu\text{m}$ (for colloid scientists) up to $4 \mu\text{m}$ (for engineers; see Ref. [5]). It is not considered as good practice any more to set a well-defined size limit to clay minerals [1], although the particles must be small enough to form colloidal dispersions in water. More than a definition, the size criterion is a practical recipe for separation since particles with different sizes will sediment at different rates in water, according to Stokes’s law [6] (which states that the settling velocity of a particle in a fluid is proportional to the square of the particle radius, all other things being equal) — the finest clay fraction can thus be obtained by centrifugation at the laboratory scale, even though industrialists use other methods to separate large quantities of clays for practical reasons (see Chapter 3).

Materials commercially available as clays may be (i) raw clays, containing several other associated minerals (carbonates, cristobalite, feldspars, quartz, etc.) and other associated X-ray amorphous phases (organic matter, iron hydroxides, etc.) as contaminants in addition to clay minerals proper or (ii) clay mineral fractions obtained by sedimentation, fragmentation, and/or several other treatments aimed, for example, at eliminating iron oxide impurities by selective dissolution. The recommended procedures to obtain pure clay mineral samples are reported in more details by Carrado et al. [7]. For some applications, *de novo* synthesis of clay minerals may be more attractive compared to the complexity of purification processes of the raw clays. Synthetic cationic clay minerals may indeed be prepared with high purity (cf. Section 1.5), but their cost will of course be higher than that of natural clays.

The JNC has kept among the clay-defining criteria some referring to specific properties that are relevant to their application as materials: plasticity in the presence of water, hardening on drying. In these properties, the behavior of clays in the presence of water plays an important role. We will therefore consider the behavior of clays in the presence of aqueous phases, first at a nanoscopic level, which includes mesoscopic level as shown in Figure 1.2, and later at a molecular level.

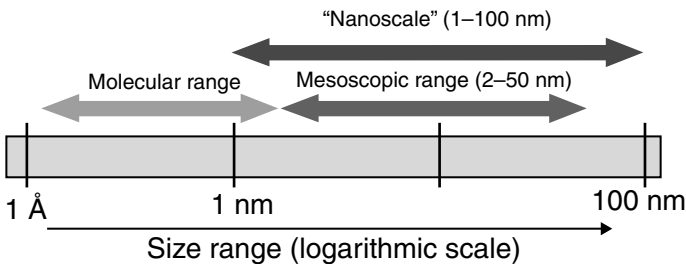


FIGURE 1.2 Mesoscale, nanoscale, and molecular scale.

1.2 MULTISCALE ORGANIZATION OF CLAY MINERALS

Clay minerals form pastes, then gels, when the amount of water is increased or other polar solvents are added to the dry solid, and that translates a specific organization of the dispersed solids in the presence of the solvent.

That organization is largely similar to the one that exists in native clays; in the simplest scheme, three successive levels of organization can be defined at different scales: in descending order of size, aggregates, particles, and layers [1,8].

1.2.1 Dispersion Versus Aggregation

At the upper level (macroscopic), the sample is made of millimetric-size aggregates. Upon closer inspection, the aggregates are seen to consist of a number of flat micrometer size particles (sometimes called *platelets*; the formerly used term of “tactoids” is rather ill-defined and should be avoided). Here “aggregation” is used in opposition to dispersion to mean the agglomeration of clay particles that results at the macroscopic level in the visual observation of flocculation (or coagulation; both terms are used indifferently); flocculation may be followed by sedimentation, or not. In water dispersion, particles and even single layers can be associated in different ways depending on solution conditions, especially on the pH value and ionic strength: face-to-face (FF, the most frequent arrangement), edge-to-edge (EE), or edge-to-face (EF). Extended EF agglomerates are sometimes called “*house-of-cards*” or cardhouse structures (Figure 1.3). This level of organization is important to understand the swelling (cf. Section 1.4.5) and rheological (cf. Section 1.4.6) properties of clays.

The *aspect ratio* is defined as the average ratio of the width to the thickness of the particles; values of 5–30 are typical, although for completely delaminated samples the aspect ratio might exceed 100.

Many factors can induce a strong tendency of clay particles to aggregate: high clay concentration, high ionic strength (concentration of ionized salts), presence of surfactants and organic polymers. The nature of the compensating cations plays a particularly important role in the aggregation/dispersion behavior: strongly hydrated cations, that is, cations with small radius such as Li^+ , induce the dispersion of the aggregates into small nanoparticles. Finer structural details such as the charge heterogeneity (cf. Section 1.4.2) of the clay surfaces, or the redox state of iron (Fe^{2+} or Fe^{3+}) also play an important role on dispersion/flocculation.

Sometimes it is desirable to increase the dispersion of a clay/water system. Vigorous mechanical agitation of a dispersion containing low clay concentration is needed. Several techniques are used involving industrial devices as extruders, internal mixers, ultrasonicators, and so on (see Chapter 3).

1.2.2 Delamination/Exfoliation Versus Stacking

At the lowest (molecular) level, the individual particles shown in Figure 1.3 are composed of the stacking of elementary layers, alternating with interlayer spaces

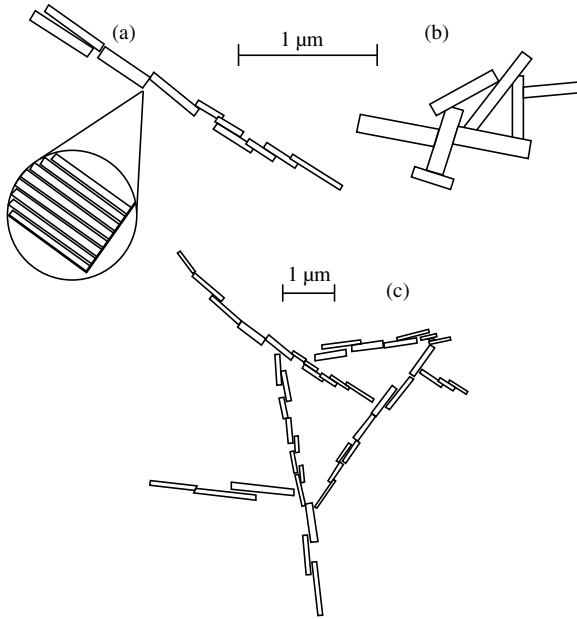


FIGURE 1.3 Top: aggregation of clay particles at the micrometer scale, mostly edge-to-edge (EE) (a) the inset shows the stacking of elementary layers within a particle; and mostly edge-to-face (EF) (b). Bottom: higher level organization of aggregates (c).

containing the compensating cations, and whatever other molecules may happen to be intercalated (cf. Section 1.4.4). The stacking exhibits crystallographic periodicity along the *c* axis, even though successive layers may be oriented differently according to the *a* and *b* directions.

Depending on the environmental conditions, their size varies from a few stacked layers (2–5) to much greater numbers. Some conditions favor a separation of the individual layers (cf. Section 1.4.4), the term of *delamination* is used to designate the separation between the planar faces of two adjacent layers. The layers may eventually become completely independent from one another, with a loss of crystallographic orientation; each unit is then freely oriented in space, independently from the others. We propose to call this particular stage *exfoliation*, although no clear distinction is made between delamination and exfoliation in many papers. Exfoliation occurs when the delaminated units (including isolated layers or stackings of a few layers) are isotropically dispersed in the aqueous or solvent matrix. This is observed for instance in aqueous dilute Laponite dispersions. Figure 1.4 shows an electron micrograph of an exfoliated Laponite dispersion where the macroscopic heterogeneity of the sample is apparent (exfoliated layers coexist with stackings of a few layers).

The state of stacking/delamination depend not only on the considered clay mineral and on the dispersion medium but also on the thermodynamic conditions (pressure and temperature, pH, and ionic strength), just as was the case for the higher level of association, namely, aggregation (cf. Section 1.2.1).

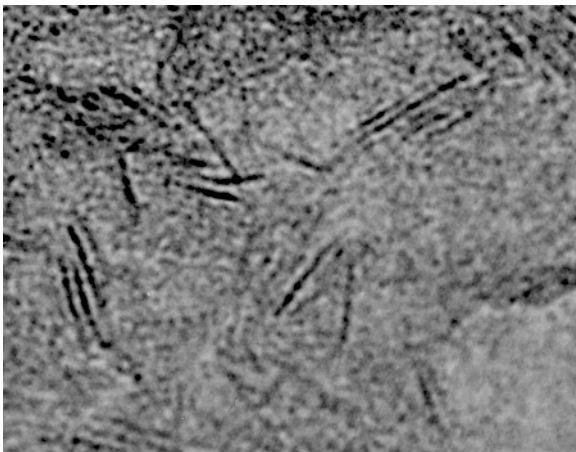


FIGURE 1.4 TEM micrograph of a dispersed Laponite.

In clay minerals of the smectite group, the more the layers are stacked, the thicker and more rigid the particles are. The thickest particles appear as “flakes” (e.g., for montmorillonite) or as “laths” (e.g., for hectorite), while completely exfoliated clay layers are flexible. The degree of stacking is, perhaps obviously, related to the specific surface area (SSA) of the clay mineral as measured by N_2 physisorption (the latter is of course applied to dry samples, and not to samples in aqueous dispersions), since the interlayer spaces are not accessible to N_2 sorption, which therefore takes place only on the external surface of the particles. For a typical montmorillonite, consisting of micrometric particles and stacking of a few tens of layers, one calculates that the developed surface area ranges between 10 and 20 m^2/g . This indeed corresponds to the low range of values observed experimentally (structural defects, cracks, etc., may lead to higher values).

1.3 INTIMATE ORGANIZATION OF THE LAYER

The broad definition of clay minerals presented above (Sections 1.1 and 1.2) does not provide information on the molecular structure of the units designated as layers, except that they must have a strong bidimensional cohesion. We will now consider in more detail some of the crystallographic structures that qualify as clay minerals.

1.3.1 Cationic and Neutral Clay Minerals

An important class of lamellar compounds of natural or synthetic origin involves the cationic clay minerals belonging to the phyllosilicate group [9,10].

1.3.1.1 General Organizational Principles The organization of phyllosilicates is particularly rich and well studied and we will briefly outline it here.

Each layer of the structure is in fact constituted by the assembly of two or three *sheets*, which are either tetrahedral or octahedral.

Tetrahedral sheets are abbreviated as “T,” and they are constituted of corner-sharing $[XO_4]$ units, where X is a small cation, which may be either Si^{4+} or Al^{3+} , although other substitutions are possible; oxide ions (formally O^{2-}) occupy the corners.

Octahedral sheets, abbreviated as “O,” consist of edge-sharing $[MO_4(OH)_2]$ units, where M can be either a trivalent (such as Al^{3+}), a divalent (such as Mg^{2+}), or a monovalent (Li^+) ion; the central site of the octahedron may also be vacant.

The structures of tetrahedral and octahedral sheets, showing the connectivity of the elementary units, are shown in Figure 1.5. The central feature explaining clay architecture is due to the fact that the repeat distances of the hexagonally symmetric tetrahedral and octahedral sheets are almost exactly coincident, which allows the outward-pointing oxygen of each tetrahedron in the tetrahedral sheet to be shared with the octahedral sheet.

A *first classification* can be proposed based on the layer type, that is, the particular succession of sheets building the layer:

- (i) In 1 : 1 or TO type clay minerals, the layer is formed by one tetrahedral sheet linked to one octahedral sheet.
- (ii) In 2 : 1 or TOT type clay minerals, two tetrahedral sheets are linked to both sides of a central octahedral sheet. This very frequent “sandwich” structure will be illustrated in Figure 1.6, which represents a montmorillonite (see below).

Note that some phyllosilicates such as chlorites have a main TOT layer with the same structure as above, which alternates with another octahedral sheet (brucite- or gibbsite-like) in the interlayer. They are also considered as TOT type [9,10]. The use of “TOTO” or “2:1:1” to designate this layer type, often found in the ancient literature, should be discarded.

The second criterion is the occupancy of the octahedral sheet leading to

- (i) clay minerals with “trioctahedral character”, where all the octahedral sites are occupied by a dication such as Mg^{2+} ;
- (ii) clay minerals with “dioctahedral character”, where 2/3 of octahedral sites are occupied by a trication such as Al^{3+} ion and the third octahedral site is empty.

Note that “trioctahedral” clay minerals contain dications, and conversely.

The third and last criterion is the charge per formula unit for each layer, which is due to isomorphic substitutions within the layers. Substitutions of high-charge cations by lower charge ones intrinsically generate a deficit of positive charges in the layers, which are therefore negatively charged. These negative charges must be counter-balanced for the structure as a whole to be electrically neutral. This is ensured by “compensating cations” in the interlayer.

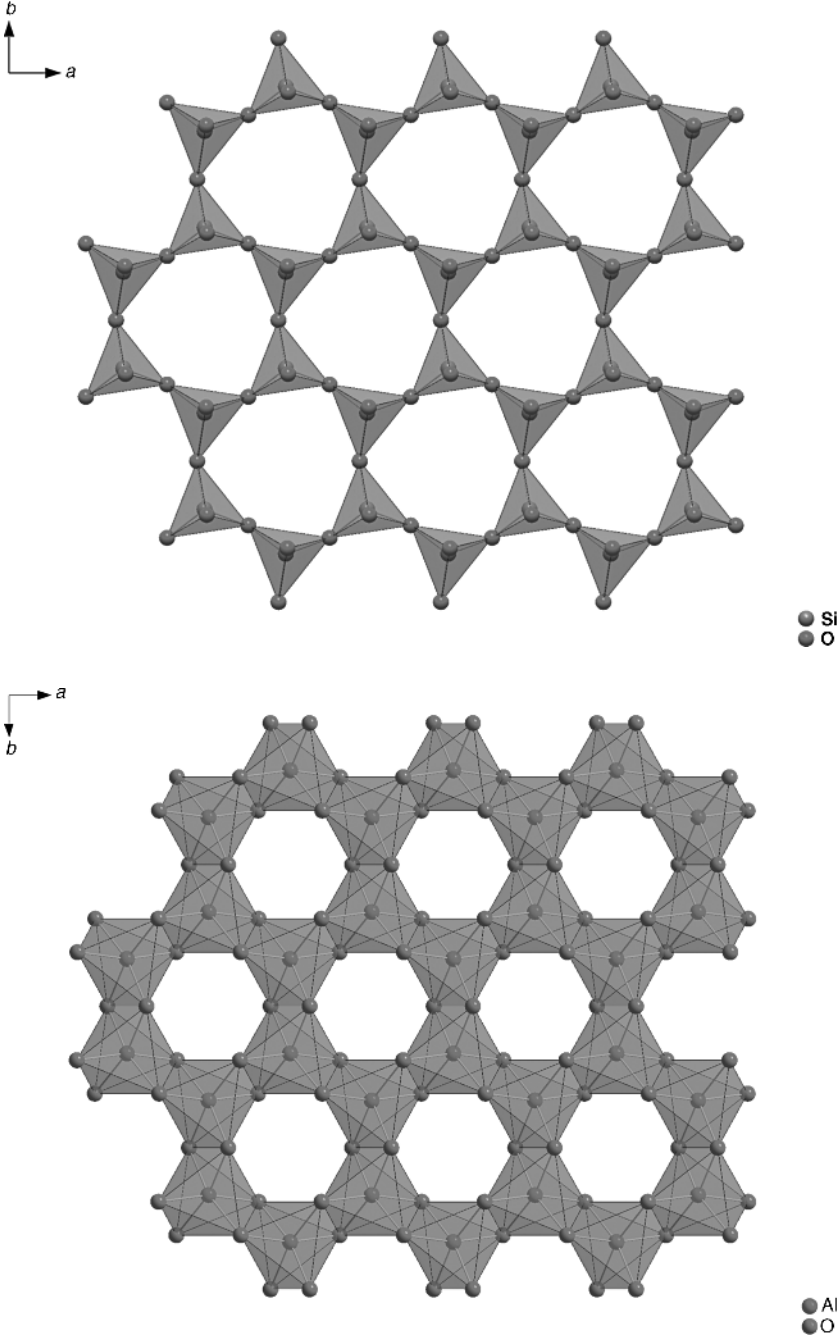


FIGURE 1.5 Showing the connectivity, in the tetrahedral sheet (a) of a clay layer and in the octahedral sheet (b) (for a dioctahedral mineral, where one of three octahedra is vacant).

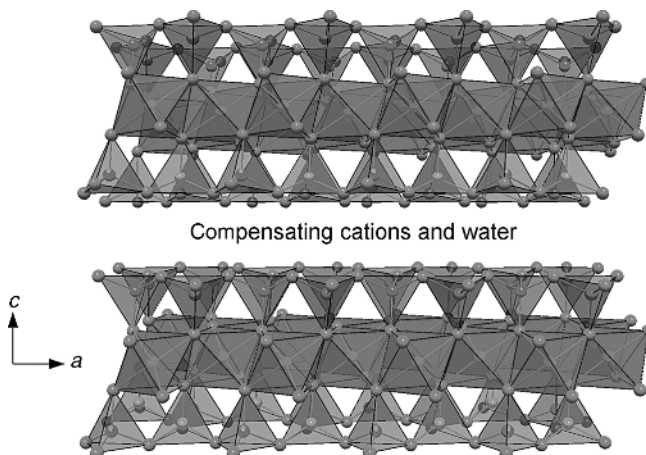


FIGURE 1.6 The structure of montmorillonite, showing two successive layers. The inter-layer space is occupied by compensating cations with varying degrees of hydration.

The substitutions may be chiefly present in the octahedral sheet (e.g., Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^+), or in the tetrahedral sheet (e.g., Si^{4+} replaced by Al^{3+}). This source of variability will be explored in more detail below, in the case of the smectite group. Tetrahedral substitutions generate localized layer charges, while the charges generated by octahedral substitutions are smeared out by the octahedral sheets on both sides and may be considered as delocalized on the layer surface.

1.3.1.2 The Main Clay Minerals Groups (TO and TOT) Taken together, the three criteria given above lead to nine clay minerals main groups (detailed below). It must be underlined that this classification is based on the molecular-level order and does not allow predicting the larger scale morphologies (plates, laths, fibers, rings, or nanotubes).

The raw formulas of some representative clay minerals are given in Table 1.1. Since they may be confusing for the nonspecialist, especially because different conventions may be used to write them, the question of clay formula interpretation is addressed in a separate inset (see p.16.)

- (I) The *kaolinite* and *serpentine* group, typical TO phyllosilicates, where the charge of the two-sheets layer is almost zero. The best-known species of the first subgroup are kaolinite (a planar phyllosilicate structure) and halloysite (a spheroidal phyllosilicate structure made of nanotubes). In the serpentine group, the best-known species is probably chrysotile (a rolled phyllosilicate structure). As indicated by the examples of halloysite and chrysotile, the two-dimensional connectivity of the layers does not guarantee that platelets will form at the upper organizational level; structural

TABLE 1.1 Layer Charge and Idealized Formula of Some Representative 1:1 and 2:1 Clay Minerals

Charge per Formula Unit (Half-Unit Cell)	Dioctahedral Species	Trioctahedral Species
I. Serpentine-kaolin group		
~0	Kaolinite ${}^{\text{IV}}(\text{Si}_2)^{\text{VI}}(\text{Al}_2)\text{O}_5(\text{OH})_4$	Serpentine ${}^{\text{IV}}(\text{Si}_2)^{\text{VI}}(\text{Mg}_3)\text{O}_5(\text{OH})_4$
II. Talc-pyrophyllite group		
~0	Pyrophyllite ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Al}_2)\text{O}_{10}(\text{OH})_2$	Talc ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Mg}_3)\text{O}_{10}(\text{OH})_2$
III. Smectite group		
~0.2–0.6	Montmorillonite ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Al}_{2-y}\text{Mg}_y)\text{O}_{10}(\text{OH})_{2+y}\text{M}^+ \cdot n\text{H}_2\text{O}$	Hectorite ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Mg}_{3-y}\text{Li}_y)\text{O}_{10}(\text{OH})_2, y\text{M}^+ \cdot n\text{H}_2\text{O}$
	Beidellite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Al}_2)\text{O}_{10}(\text{OH})_{2+x}\text{M}^+ \cdot n\text{H}_2\text{O}$	Saponite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Mg}_3)\text{O}_{10}(\text{OH})_2, x\text{M}^+ \cdot n\text{H}_2\text{O}$
IV. Vermiculite group		
~0.6–0.9	Vermiculite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Al}_{2-y}\text{Mg}_y)\text{O}_{10}(\text{OH})_2, (x+y)\text{K}^+$	Vermiculite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Mg}_{3-y}\text{Mg}_y^{\text{3+}})\text{O}_{10}(\text{OH})_2, (x-y)/2\text{M}^+$

V. True (flexible) and brittle mica group		
~0.9–1.0	Celadonite $IV(Si_{4-x}Al_x)^{VI}(Fe_{2-y}Mg_y)O_{10}(OH)_2, (x+y)K^+$	Lepidolite $IV(Si_{4-x}Al_x)^{VI}(Mg_{3-y}Li_y)O_{10}(OH)_2, (x+y)K^+$
	Muscovite $IV(Si_3Al)^{VI}(Al_2)^{VI}O_{10}(OH)_2, K^+$	Phlogopite $IV(Si_3Al)^{VI}(Mg_3)O_{10}(OH)_2, K^+$
~1.8–2.0	Margarite $IV(Si_2Al_2)^{VI}(Al_2)O_{10}(OH)_2, Ca^{2+}$	Clintonite $IV(SiAl_3)^{VI}(Mg_2Al)O_{10}(OH)_2, Ca^{2+}$
VI. Chlorites group		
Variable	Di–di (dioctahedral layer and dioctahedral interlayer sheet)	(Di–tri) and (tri–di)
VII. Palygorskite and sepiolite group		
Variable	Di (-tri) palygorskite $IV(Si_{4-x}Al_x)^{VI}AlMgO_{10}(OH)_2, 6H_2O$	Mg-palygorskite to Al sepiolite Sepiolite $IV(Si_6)^{VI}(Mg_{4-y}M_y^{2+})O_{15}(OH)_2, 6H_2O$
VIII. Allophane and imogolite group		
Variable	Allophane $IV(Si_2)^{VI}(Al_2)O_5(OH)_4$ Imogolite $IV(Si)^{VI}(Al_2)O_3(OH)_4$	

Left-hand superscripts refer to cation location in the tetrahedral (IV) or in the octahedral (VI) layer.

constraints in the layers may cause them to curl and adopt different morphologies.

- (II) The *pyrophyllite* and *talc* group are nonswelling TOT phyllosilicates without isomorphous substitutions; thus, the charge of the three-sheets layer is almost zero. The only species of this group are pyrophyllite (dioctahedral) and talc (trioctahedral), but the following groups can be understood as derived from them by increasing degrees of substitution.
- (III) The group of *smectites*³ is composed of TOT planar phyllosilicates; they are also known as swelling clay minerals. Their name comes from the Greek “σμηκτικός,” whose initial meaning is “cleaning earth.” The charge of the three-sheet layers varies from 0.2 to 0.6 per half unit cell. According to the importance of the smectite in the nanocomposites technology, only this group will be detailed further (Section 1.3.1.3). Figure 1.6 presents the structure of montmorillonite, a typical smectite.
- (IV) The *vermiculite* group, TOT phyllosilicates with a more limited swelling ability as compared to the smectites group and where the charge of the three-sheet layers varies from 0.6 to 0.9 per half unit cell. The most frequent vermiculite species are trioctahedral.
- (V) The *true (flexible) micas and brittle micas* groups, TOT phyllosilicates where the charge of the three-sheet layers varies from 0.9 to 2 per half unit cell. The most common mica, that is, *illite* is subject of controversy in the literature (see comment on p. 15 in Ref. [1] and pp. 39–40 in Ref. [10]). Illite is considered either as a species of the true mica group (lying at the borderline with vermiculite as regards the degree of substitution) or as a separate group [11,12]. Illite is thought to be a mineral derived from smectite dehydration, progressing from montmorillonite to beidellite to illite [13]. This probably explains the occurrence in nature of interstratified smectite–illite layers presented below.
- (VI) The *chlorites* group, currently considered as TOT phyllosilicates (see Section 1.3.1.1 above). Here, the TOT layer bearing a net negative charge alternates with a single octahedral sheet bearing a positive charge in the interlayer space. Trioctahedral chlorites are the most common, where both the TOT and the interlayer sheet are trioctahedral, but other combinations also exist [10].
- (VII) *Interstratified Clay Minerals Group*. The term of *interstratified* mineral is used to designate a lamellar material where different types of layers may be found in the stacking. It is a common phenomenon that may be considered as an intergrowth of different types of layers along the *c* axis (i.e., along the stacking direction). In fact, different combinations occur in nature between all the previous TO and/or TOT groups, in a regular or irregular manner, leading to different kinds of more complex layer types. For example,

³ Their morphology is two-dimensional, like that of “smectic” liquid crystals, whose name obviously comes from the same root.

irregular illite–smectite (I–S) are often encountered in mineralogy, where the particles contain variable proportions of swelling and nonswelling interlayers [14,15]; one also finds kaolinite–smectite (K–S) systems that consist of an alternating irregular layer sequence of kaolinite (TO) layers with smectite (TOT) layers. These combinations are called irregular interstratified clay minerals. However, when the succession of different layers occurs in a regular manner, a specific name is generally attributed to these interstratified stacked sequence [15] as, for example, rectorite that consists of a regular ordered succession of dioctahedral smectite and illite layers and may be symbolized as I–S–I–S [16].

It should be noticed that another kind of interstratification occurs when the simple smectite particles contain water interlayers of different thicknesses (cf. Section 1.4.4.2). This source of interstratification (filling interstratification) should not be confused with the above-mentioned structural interstratification of mixed layers systems.

(VIII) The *sepiolite* and *palygorskite* group with the TOT layer-fibrous structure. In opposition to the previously mentioned groups, this one presents only one continuous two-dimensional tetrahedral sheet but a discontinuous octahedral sheet. This structure contains in fact fragments of TOT structures that extend along the a axis (Figure 1.7). The two representative species are trioctahedral sepiolite and dioctahedral palygorskite, which differ by their unit cell dimension (larger in the case of sepiolite, with larger channels also than for palygorskite). However, a recent study has shown that intermediate compositions exist between these two species [17]. The term “attapulgitite” that was given by de Lapparent [18] to a clay mineral discovered in fullers’ earth from Attapulgis in the United States, has sometimes been used as synonymous with palygorskite and is still largely

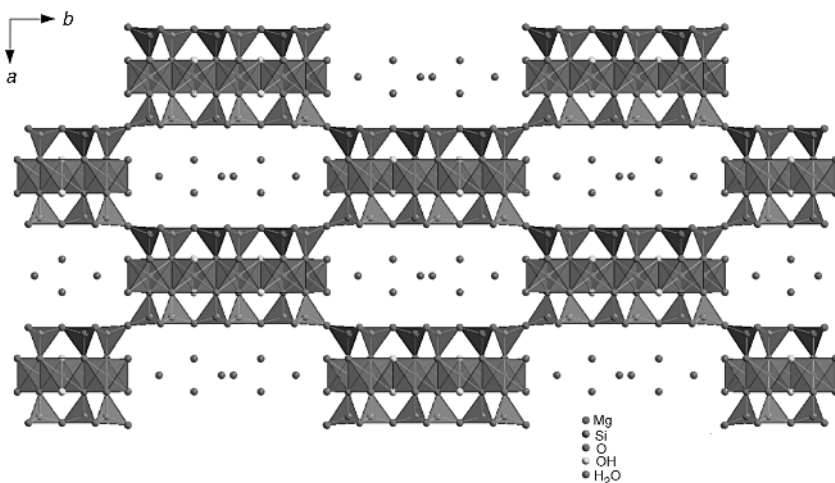


FIGURE 1.7 The structure of sepiolite. Note the channels perpendicular to the plane of representation, which are filled with water molecules under ambient conditions.

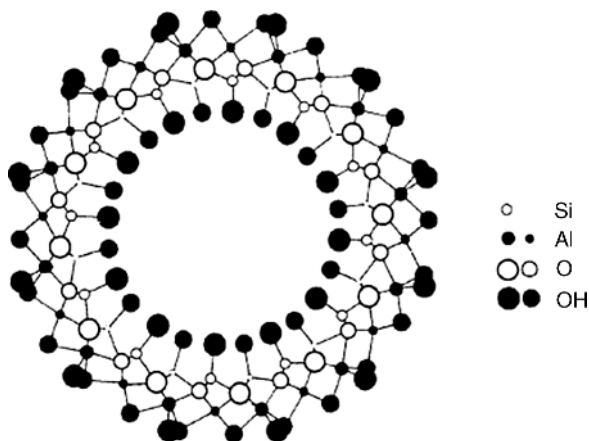


FIGURE 1.8 The structure of imogolite.

used in industry. Since connections in the direction perpendicular to the layers are assured in part by covalent bonds, minerals of this group cannot present the phenomenon of swelling that is defined in Section 1.4.5.

- (IX) *Allophane and Imogolite Group*. These aluminosilicates belong to the TO group (at least regarding short-range order) and are frequently found together in soils derived from volcanic ash. Both are very poorly crystalline minerals, being X-ray amorphous, and have an interesting fibrous morphology where the layers curl up to form 3–5 nm rings (allophane) or 2 nm tubes (for imogolite, the tubes being a few micrometers in length with an internal diameter of 1 nm). Allophane should actually be considered as a group since its composition is highly variable. The structure of imogolite is represented in Figure 1.8. It has been originally proposed by Cradwick et al. in 1972 [19].

Recently, this group of minerals has attracted renewed interest as it has been shown that imogolite-like materials (containing germanium instead of silicium) can be synthesized in large quantities [20], while double-walled Al–Ge imogolite-like nanotubes have been described; it is hoped that they could constitute a cheaper alternative to carbon nanotubes in some applications [21].

One can broadly distinguish all the previously described groups using their basal distances (d_{001}) as a criterion. The TO groups are characterized by a distance of about 0.7 nm as for kaolinite (however, halloysite that is a hydrated kaolinite includes one molecular layer water and thus has a d_{001} of 1.0 nm). Allophane and imogolite have rather broad X-ray diffraction (XRD) peaks since they are poorly crystalline materials. For example, allophane shows XRD peaks at about 0.3 nm.

The TOT groups exhibit basal distances of 1, 1.2, and 1.4 nm for mica, smectite, and chlorite groups, respectively. In the case of smectites, the observed value of 1.2 nm corresponds to an average distance, since it depends on the hydration state of the interlayer cations, which in turn may vary according to the treatment to

which the sample has been submitted (cf. Section 1.3.1.3). Thus, one has to be careful in interpreting X-ray diffractograms of a clay sample; a d_{001} peak at 1.0 nm does not necessarily indicate the presence of mica, but might correspond to a fully dehydrated smectite.

For the sepiolite and palygorskite group the basal distance is 1.2 nm.

For the interstratified groups the situation is more complex, except for regular interstratified layers where a high distance is observed depending on the constituent layers.

1.3.1.3 The Swelling Clays: Smectites–Montmorillonites–Bentonites

In view of the importance of smectites in the polymer nanocomposites technology, and their interesting swelling properties, this group will be studied in somewhat more detail. It includes the clay minerals most commonly used as rubber additives so far: montmorillonites, saponites, and hectorites.

The smectites group can be divided into dioctahedral and trioctahedral species as shown in Table 1.2.

TABLE 1.2 Dioctahedral and Trioctahedral Species Belonging to the Smectite Group with Their Idealized Formula^a

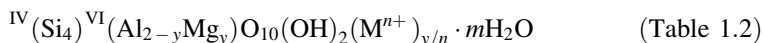
Dioctahedral Series	Trioctahedral Series
Montmorillonite ^a (Mt) ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Al}_{2-y}\text{Mg}_y)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{y/n}$	Hectorite ^a (Ht) ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Mg}_{3-y}\text{Li}_y)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{y/n}$
^a <i>Bentonite</i> : commercial name of a raw clay containing at least 50% of Mt (or other smectite)	^a <i>Laponite</i> and <i>Fluoro-Ht</i> are synthetic Ht (in <i>Fluoro-Ht</i> , the OH^- ions are replaced by F^-)
Beidellite (Bd) ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Al}_2)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{x/n}$	Saponite (Sap) ${}^{\text{V}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Mg}_3)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{x/n}$
Other species depending on the octahedral cation, which are different from Al or Mg	
Nontronite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Fe}_2)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{x/n}$	Stevensite ${}^{\text{IV}}(\text{Si}_4)^{\text{VI}}(\text{Mg}_{3-y}\square_y)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{y/n}$ (□ represents a vacancy)
Volkonskoite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Cr}_2)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{x/n}$	Sauconite ${}^{\text{IV}}(\text{Si}_{4-x}\text{Al}_x)^{\text{VI}}(\text{Zn}_3)\text{O}_{10}(\text{OH})_2(\text{M}^{n+})_{x/n}$

^a The given formulas are somewhat idealized because the (x) and (y) substitutions located in the octahedral and tetrahedral sheets, respectively, are not rigorously limited to a single type of site in reality. Thus, even for Mt that ideally has only octahedral substitution, a minor amount of tetrahedral substitution may exist as well, giving rise to further structural variability such as montmorillonite with more or less pronounced beidellitic character. This is discussed in Ref. [22] together with many finer points of smectite classification.

INTERPRETING THE CHEMICAL FORMULA OF A CLAY MINERAL

The chemical formulas of clay minerals are complex and may give the unpleasant impression that “anything goes,” especially since different conventions are used in the literature.

Let us take as an example the formula of a calcium montmorillonite:

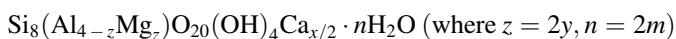


It must be understood that such a formula successively lists the following:

- The structural cations belonging to the layer, starting with those in the tetrahedral sheets (4Si^{4+}) followed by those in the octahedral sheet (two cations overall, mostly Al^{3+} ; the stoichiometric coefficient $(2 - y)$, means that there is an unspecified degree (y) of Al^{3+} substitution, in this case by Mg^{2+}). Note that cations belonging to the same sheet are associated by the use of brackets. In addition, we have used left-superscript roman numerals (VI and IV) to clearly identify the coordinance (number of neighbors) of the cations, VI in the octahedra and IV in the tetrahedra.
- The anions, most often O^{2-} and OH^- ; F^- may substitute for OH^- .
- The compensating cations, located in the interlayer region, which must be in the right amount to ensure electrostatic neutrality; sometimes, they are associated with interlayer water, written at the end of the formula as $m\text{H}_2\text{O}$.

Often the coordinance of the ions is not explicitly indicated and the different constituents may be listed in a different order, for example, with compensating cations at the beginning. It is then left for the reader to identify in which sheet each group of ions is located—this is easily done since Si, which is always present, is to be found exclusively in the tetrahedral sheet. Sometimes, right instead of left superscripts are used for the coordinance but this runs the risk of inducing unfortunate confusions with the accepted notation for the oxidation number; thus, one has to understand that Al^{VI} denotes six-coordinated aluminum, not the nonexistent Al^{6+} ion!

The above formula corresponds to the contents of half a unit cell, which is the most frequent choice. Sometimes the formula is represented per (full) unit cell, and the formula of our calcium montmorillonite could then be given as



Both conventions make sense crystallographically, and there is no point in seeking the stoichiometrically most simple formula since it would not be very enlightening for the understanding of the structure. At any rate, the structure as a whole must be electrically neutral and this is easily checked in many instances since most ions found in clay minerals have a single stable oxidation number under standard conditions—with some exceptions, the most conspicuous being iron that can be present as Fe^{2+} or Fe^{3+} .

Montmorillonite (Figure 1.9 and structure in Figure 1.6) is the most studied in literature and the most used in different applications. While one will often find it in the literature designated as Mtm, MMT, and so on, it is advised to abbreviate this mineral name as *Mt*.

The best-known montmorillonite-based material in the world is the mineral exploited in Wyoming (USA) at Fort Benton. The raw clay has been given the trade name of “bentonite” by Knight in 1898 [23]; it was marketed in 1920 by Baroid Corp., which later became NL Industries. The term of bentonite was introduced in Europe 10 years later [24] and has then been extended over the world to designate all the raw clays containing at least 50% of smectite and particularly of *Mt*. In fact, bentonites from Wyoming are somewhat atypical in that they contain Na^+ as compensating cations, while most other bentonites known in the world are saturated by Ca^{2+} , and this causes very peculiar rheological properties.

Usually, these Ca^{2+} bentonites are ion exchanged by sodium salts to convert them into their sodic form. This is called “sodium activated” bentonite.⁴ However, some properties such as viscosity remain different from the natural sodium Wyoming bentonite. For more information on Bentonites, see Refs [25] and [26].

It should also be mentioned that organobentonites (cf. Chapter 2) are called “bentones” in the industrial use. This term should not be confused with “bentonite” that refers to the raw clay.

In smectites, the layer thickness is around 1 nm, and the lateral dimensions of the layers may vary from 30 nm (Laponite) to several micrometers or larger, depending on the particular clay mineral. The cell parameters describing periodicity in the layers are $a = 0.5$ nm and $b = 0.9$ nm. This results in densities of about 2.6 g/cm^3 .

We have mentioned in Section 1.3.1.3 that the basal distance d_{001} of smectites has an average value of 1.2 nm. In fact, the basal distance corresponds to the sum of layer

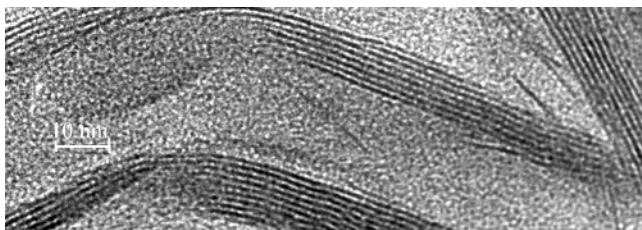


FIGURE 1.9 TEM micrograph of a montmorillonite.

⁴ “Activation” of clays has many meanings in literature; in different contexts, it refers to acid and/or to thermal treatments.

thickness + interlayer space and the thickness of the interlayer space is determined by the type of compensator cations located in the interlayer space and their degree of hydration. The value of 1.2 nm is observed for a Na^+ smectite under ambient conditions of temperature and water pressure and corresponds to the presence of only one water pseudolayer in the interlayer region; one would therefore expect the d_{001} value to be dependent on the water activity, that is, on the relative water pressure. Thus, a smectite calcined at high temperature (namely, above 110°C , the temperature chosen as a reference in mechanical studies) will have a d_{001} value equivalent to those of micas (about 1 nm) since the interlayer will be completely dehydrated; conversely, a fully hydrated smectite shows increasing values until a complete delamination of the clay layers is obtained. At this point, as the long-range order is lost (cf. Section 1.2.2), the d_{001} XRD peak does not appear any more.

The amount of adsorbed water in the interlayer space also depends on the location of the substitution in the layer, as shown by the difference in swelling behavior between beidellite and montmorillonite [27]. The amount of adsorbed interlayer water may be very high and has been underestimated till the 1980s. Moreover, the adsorbed water molecules are present as pillars forming a discontinuous layer more than a continuous layer.

When the hydrated cations are ion exchanged with organic cations, in the process of organoclay synthesis, this of course results in larger interlayer spacings (cf. Section 1.4.4.4 and Chapter 2). For clay–polymer nanocomposites (CPN), the d_{001} peak may disappear as in the case of fully swollen smectites, indicating delamination.

1.3.1.4 Clays, the Oldest Nanomaterials In view of the current fancy for everything “nano,” it is worth underlining that clay structures can rightly be viewed as nanomaterials, since one of the dimensions (namely the thickness of their most basic unit, the layer, along the c axis) is at the nanometer scale. Bidimensional clay minerals can also be considered as inorganic polymers by viewing the repeated half unit cells seen as monomers (Figure 1.10), as already stressed by Bergaya and Lagaly in 2007 [28].

The unmodified clay mineral is a natural nanopolymer of high regularity, which has existed for billions of years on our planet. In fact, the bidimensional phyllosilicates can have one dimension at the nanoscale (for montmorillonite), but also two or three dimensions at the nanoscale as in Laponite or in allophane, respectively. As for the intercalated clays and clay–polymer nanocomposites discussed in the present book, they constitute archetype examples of nanomaterials, but clay nanomaterials have actually been used long before their structure was understood, as witnessed by

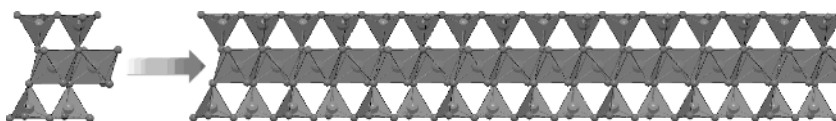


FIGURE 1.10 Clays as nanopolymers: a basic unit considered as monomer and repetition of this monomer leading to a structure of the layer.

the well-known example of “mayan blue” that is a nanocomposite of indigo pigments and clay minerals. This old nanotechnology was successful long before the structure of clay minerals was known.

1.3.1.5 Other Cationic Layered Silicates (T) In the realm of silicates, there also exist alkali silicates (with Na^+ as compensating cation) and silicic acids built only from tetrahedral (T) units, for example, the natural minerals magadiite and kenyaite [29,30], whose precise structure is still unknown, and a series of other structures both natural and synthetic [31].

Intercalation of organic compounds into these structures has been largely demonstrated. Studies on their interaction with polymers are few, and most have not been yet evaluated as rubber additives or fillers because of their high synthesis cost; however, magadiite has occasionally been used as a filler [32].

A particular mention must be made of CSH (calcium silicate hydrates) that are an essential constituent of cements. They contain two sheets of Si-containing tetrahedra with a very different organization from those found in clay minerals, surrounding a central sheet containing Ca^{2+} ions in octahedral coordination [33]. Since the bonding of the Ca^{2+} to the tetrahedral sheets is rather strong, they could be considered as a “TOT-like” structure. Yet there are important differences in behavior; in particular, CSH do not swell.

1.3.1.6 Nonphyllosilicate Cationic Layered Minerals (O or Mixed T–O)

The extended family of layered inorganic materials is not limited to silicates. There exist layers based on negatively charged octahedral sheets (O) with exchangeable hydrated cations between these sheets, for example, layered titanates $(\text{K}^+)_2(\text{Ti}_4\text{O}_9)^{2-}$, and so on [34] or titanoniobates $(\text{K}^+)(\text{TiNbO}_5)^-$, layered manganates, and so on. Zirconium phosphates and phosphonates have mixed sheets containing tetrahedral and octahedral units [35]; they have received considerable attention in the literature since the pioneering work of Alberti and his coworkers [36].

Also layered metal chalcogenides (LMC) involving a broad range of metals, including transition metals, have been the object of many academic and industrial studies due to their interesting intercalation properties [37].

Each of these families may represent a program of intercalation and organophilization in the waiting (initial reports may be found of the use of organophilized titanates as fillers [38]). So far however, the clay minerals family remains the most versatile and the most studied in industrial applications.

1.3.2 Anionic Clay Minerals (O)

One particular class of nonphyllosilicate compounds of high interest, is that of anionic clays of the hydrotalcite-like group. Hydrotalcite is probably the only example of a natural LDH. It has been used to synthesize elastomer nanocomposites [39,40]. Its formula unit is $\text{Al}_2\text{Mg}_6(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$. The hydrotalcite denomination probably stems from a perceived similarity with hydrated talc, although the two structures are in fact quite different.

The layers of hydrotalcite are constituted of a single octahedral sheet with all of the corners of the octahedra being occupied by hydroxide (OH^-) ions. While there exist other minerals such as brucite ($\text{Mg}_3(\text{OH})_6$) based on uncharged sheets of this type, hydrotalcite and other members of the LDH family contain isomorphous substitutions.

Isomorphous substitution in the octahedral sheet leads here to a positively charged sheet (as opposed to the negatively charged layer in cationic clays), and this positive charge is compensated by exchangeable anions in the interlayer. All the other studied anionic clay minerals called hydrotalcite-like compounds are synthetic LDH with the following general formula: $\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_3\text{X}_{x/q}^{q-} \cdot n\text{H}_2\text{O}$.

Their structures involve different types of cations leading to broad nonphyllosilicate families. The interlayer space is very reactive, allowing intercalation of different species, sometimes accompanied by swelling and interesting rheological properties.

1.4 MOST RELEVANT PHYSICOCHEMICAL PROPERTIES OF CLAY MINERAL

In the context of the present book, many of the relevant properties of clay minerals are determined by their surfaces and the interfaces they form with other phases. It is important to realize that clay surfaces are chemically very heterogeneous. We will successively consider properties that do not depend on the local chemical features of the surface (cf. Section 1.4.1), and those that do depend on them (cf. Section 1.4.2).

1.4.1 Surface Area and Porosity

One of the most common characterization techniques applied to solid materials is low-temperature nitrogen physisorption. Since physisorption is supposedly nonselective, it is generally considered that this technique can provide a quantitative measurement of the surface exposed by the sample, which is then transformed to a specific surface area (SSA or S_s , in m^2/g). The SSA is generally extracted from the physisorption data at relatively low pressure using the BET treatment.

The physisorption isotherm also gives access to the “porous volume,” and its distribution among micropores (pore diameter <2 nm), mesopores ($2 \text{ nm} \leq$ diameter ≤ 40 nm), and macropores (diameter ≥ 40 nm),⁵ using standard models such as the Barrett–Joyner–Halenda (BJH) method based on Kelvin’s equation of capillary condensation for mesopores; we refer to standard monographs on the subject for further discussion of the techniques [41,42].

In principle, the experimental value of the SSA should be equal to the geometric area developed by its elementary particles, which can be calculated if the shape and size of the latter is known. Thus, swelling clay minerals and particularly montmorillonite, should have a high total SSA of about $800 \text{ m}^2/\text{g}$ if all the layers are totally

⁵ These size limits are in agreement with the IUPAC recommended nomenclature.

exfoliated; on the other hand, we have mentioned in Section 1.2.2 that a SSA value of about $20 \text{ m}^2/\text{g}$ is expected based on the size of the secondary particles in a montmorillonite, and the values effectively measured by N_2 physisorption are closer to the second figure.

Thus, in general, for TOT clay minerals, two types of surface area (external and internal) must be clearly distinguished [43]. The specific external surface area is the geometric area of the particles (basal and lateral areas of the quasiparallelepipeds constituted by layers stackings) that is accessible to N_2 physisorption. The external surface varies from 30 to $130 \text{ m}^2/\text{g}$ depending on the granulometry and aspect ratio of the considered clay mineral, which are related to the number of stacked layers per particle, and therefore to such parameters as the nature of exchangeable cations.

The internal surface corresponds to the basal surface of the layers that are “stuck” together within a secondary particle. While it is not normally accessible to nitrogen, it can be revealed by other techniques such as the adsorption of ethylene glycol monoethyl ether (EGME) or glycerol. EGME adsorption [44] was one of the first classical methods used for internal surface area determination; it is based on the idea that EGME forms a bilayer in the interlayer space of clay minerals, as witnessed by the presence of an XRD peak at 1.77 nm. This is equivalent to a single dense layer of EGME molecules on each basal plane, and therefore a measurement of the adsorbed amount will give access to the total basal surface knowing that each molecule occupies a space of 0.44 nm^2 . However this view of EGME adsorption is somewhat idealized, and in fact its retention depends on the type of compensating cation and layer charge density [45]. In practice, this method only provides a semiquantitative comparison of a series of swelling clay samples [46].

The total surface area (internal + external) can also be measured by methylene blue (MB) adsorption that, like EGME adsorption, induces swelling. The “MB-spot” is a very rough method used in the field where the amount of swelling clays in the sample is evaluated from the intensity of a blue spot due to methylene blue adsorption. The “MB-titration” in laboratory is more accurate; however, both give similar results [47]. Interesting data on internal and external surface areas can also be garnered using other adsorbing molecules, for example, comparing water and N_2 adsorption [27].

The clay surfaces delimit pores with variable sizes (micropores, mesopores, and macropores) and shapes. The hierarchical porosity distribution that can be deduced from the hierarchical arrangement of the clay aggregates/particles/layers described in Section 1.2.1 is not simple to observe. A critical comparison of the numerous techniques of porosity characterization of different porous solids (including pillared clays and LDH) can be found in Ref [48] together with guidelines for the selection of the most appropriate method to follow.

For porous clay minerals, lenticular pores are often observed on TEM images. The pores can be accessible to adsorbates or not (open vs. closed pores) depending not only on parameters we have already encountered (chemistry of the clay mineral layer, type of exchangeable cation) but also on the experimental conditions such as air- or freeze-drying [49].

For macroporosity, the mercury intrusion method remains the main technique of quantitative measurement, even though it has been criticized because mercury is probably able to deform the geometry of the pores during invasion of smaller pores.

1.4.2 Chemical Landscape of the Clay Surfaces

The preceding discussion dealt with the geometric extension of the accessible clay surface. The reactivity at a clay interface obviously depends also on its chemical nature and it must be underlined that exposed clay surfaces are chemically heterogeneous. The very existence of a surface may be considered as a defect since it means the interruption of an ideally infinitely extended three-dimensional lattice. An interruption in the *c* direction results in the exposure of basal planes constituted of siloxane groups (bridging oxygens in Si–O–Si) that are chemically rather inert [50]. On the other hand, termination of the clay lattice in the *a* and *b* directions means cutting of partly covalent bonds, for example, Si–O–Si (in the tetrahedral sheets) or Al–O–Al (in the octahedral sheets). This results in “dangling bonds” that in ambient conditions are cured by the formation of, for example, Si–OH or Al–OH₂, very similar to those that are found on the surface of nonclay amphoteric oxides such as SiO₂ or γ -Al₂O₃. Therefore, the *edges* of clay particles should exhibit a different reactivity from that of basal planes, one that could be similar to that of amphoteric oxides [51].

As indicated by the term “amphoteric,” a surface group such as Si–OH may react both with a proton (thus giving rise to Si–OH₂⁺ in acidic conditions) or with a hydroxide (thus giving rise to Si–O[−] in basic conditions). This group may have other chemical properties that are not found on basal planes such as H-bonding or the capacity to act as a ligand; in summary, the edges of clay particles will be able to react in very different ways from the basal planes at solid–liquid or solid–gas interfaces. The amphoteric behavior means that clay minerals have intrinsic acid–base properties; aqueous smectite dispersions have pH values from 7.5 for Mt to 10 for Laponite.

The heterogeneity of clay surfaces is also manifested in adsorption from the gas phase. Even for Ar or N₂ physisorption that is supposed to be nonspecific, a precise examination of adsorption isotherms at low pressure indicates that the atoms first adsorb on specific sites such as ditrigonal cavities next to Al substitution [52] or more generally sites with high acidity, only later covering the rest of the surface.

1.4.3 Cation (and Anion) Exchange Capacity

1.4.3.1 Definition The notion of cation exchange capacity (CEC) comes from soil science, where it designates the capacity of the soil to hold cations. The soil cations are mostly held by the negatively charged clay minerals (and organic matter particles) through electrostatic forces. As mentioned before, compensating cations must be present in the clay interlayers because the layers bear a negative charge due to isomorphous substitution, and they are easily exchangeable by other cations. For example, a very important mechanism for organoclay preparation is based on the exchange of pristine alkali cations (sodium or calcium) by alkylammonium cations, as will be seen in Chapter 2.

TABLE 1.3 CEC or AEC Ranges (in meq/100 g) of Some 2:1 Cationic and Anionic Clay Minerals

Clay Mineral Species	CEC
Montmorillonite	80–120
Hectorite	120
Saponite	85
Vermiculite	150
Kaolinite	3–15
Sepiolite–palygorskite	20–30
Allophane	25 or (10–40) at pH 7
Imogolite	17–40
	AEC
LDH	200–400

The CEC represents the total amount of cations available for exchange at a given pH. It is commonly expressed as meq/100 g of calcined clay (meq = “milliequivalent,” i.e., amount in millimole divided by the ionic charge) and can be evaluated by different methods [53]. Typical CEC values of 2:1 phyllosilicates are listed in Table 1.3. Similarly to the CEC of phyllosilicates, LDH present an anionic exchange capacity (AEC).

1.4.3.2 CEC Measurement and Evaluation The CEC is of course directly linked to the charge density of the layers (which itself corresponds to the density of isomorphous substitutions). In first approximation, the CEC is equal to the charge density of the layer (except that it is expressed per unit of mass, rather than per formula unit) if all the compensating cations are susceptible to exchange.

The layer charge of smectites and vermiculite groups can be deduced from the chemical structural formula if the sample is very pure and has a known mineralogical composition, or it can be determined by the “alkylammonium method” based on XRD of the organomodified clay mineral, as described by Lagaly [54]. This author has noticed that for smectites the alkylammonium method leads to values 10–20% smaller than the actual CEC. As organic cations are preferentially exchanged over inorganic cations, they have been widely used for semiquantitative CEC determination (and thus for a rough estimate of the amount of swelling clays in pure sample). Particularly, the MB method was used for this purpose as well as for specific surface area determinations.

Another method has been applied for dioctahedral smectites with a pronounced beidellitic character, where the tetrahedral substitution that induces the CEC has been estimated through an exchange of the pristine cations by NH_4^+ cations, followed by the IR observation of these ammonium-saturated clay minerals [55]. As one can guess from the large number of proposed methods, CEC is difficult to determine very accurately, but in any case, its determination requires the complete replacement of all initial exchangeable cations by added “index” cations that should not be present in the

studied clay. To the best of our knowledge, the most versatile method of CEC determination for several type of clays and clay minerals uses copper complexes with ethylene di- or triamine (e.g., $[\text{Cu}(\text{en})_3]^{2+}$) as index cations [56].

1.4.3.3 Cation Exchange Selectivities and Other Chemical Features of Ion Exchange Cation exchange equilibria may be described as simple chemical reactions; however, if one attempts a thermodynamic description, care must be taken to use activities rather than simply concentrations since the participating species are in different phases (solid and solution). Thermodynamic modelization can help to predict the ions exchange, but it should be based on accurate data obtained under fixed experimental conditions.

Cation exchange reactions exhibit definite preferences for some cations over others (exchange selectivity). Many data for clay minerals exchange selectivities are available in the literature and they exhibit some regularity. Usually for smectites, there is a preference for larger inorganic cations over the smaller ones, and for cations with higher valence. However, the selectivity of a particular clay mineral for a particular cation is not a simple matter and depends in fact on several physico-chemical properties of the cations: their hydration state, their interaction with the clay surface, their polarizability (hard and soft acid base character), and so on, as well as properties of the clay matrix pertaining to their mineralogical structure and including the heterogeneous distribution of charge, the heterogeneity of energy surface sites, site inaccessibility due to aggregation, and so on.

As regards the cations, they may be classified in three separate groups:

- (i) the two monovalent cations Li^+ and Na^+ ,
- (ii) other monovalent cations with higher radius such as K^+ , and
- (iii) the bivalent cations. When the exchange reaction on clay minerals is carried out between two cations of different groups, it generally shows a hysteresis effect, which is not yet completely understood.

As regards the clay matrix, in some cases, the cations are not easily exchangeable; for instance potassium ions may be trapped in the “ditrigonal” cavities that exist in the tetrahedral layers at the surface of illite and micas, because the radius of K^+ exactly fits the cavity size, in a phenomenon of molecular recognition similar to the selectivity for specific alkali cations of crown ethers. This type of strong selectivity indicates that the macroscopic phenomenon of ion exchange is not entirely explainable in terms of electrostatic interactions between the matrix and the ions; other interaction may be superimposed to it and play a role in determining the energetics of exchange.

Although we have approximated the CEC as corresponding to the amount of substitutional layer charges in the above discussion, it is in fact the sum of two kinds of charges:

- (i) “permanent” charges arising from isomorphous substitutions or site vacancies in the octahedral and/or tetrahedral sheets of the layer, and

- (ii) variable edge charges, induced by the amphoteric behavior of edge groups (cf. Section 1.4.2), which depend on the pH and ion strength of the solution. Their contribution to the total CEC depends of course on the particles morphology and arrangement. The ratio of the edge/permanent surface charge is estimated to lie between 10 and 20% [57] in smectites. In kaolinite particles, on the other hand, there is little to no isomorphic substitution giving rise to permanent charge, and in addition the stacking of layers is more extensive so that the area of edge surfaces exceeds that of planar surfaces. In this case, the CEC is mainly attributed to edge contribution.

Finally, it is little known that cationic clay minerals can also adsorb anions in some conditions. The adsorption mechanisms are different from the simple electrostatic compensation of layer substitutional charge; they include the substitution by the anion of variable hydroxyl groups (sometimes called “ligand exchange” because the substituted anion then plays the role of a ligand to the underlying cation). This occurs at the edges of TOT clay minerals, and also on basal surfaces in the case of kaolinites.

It is possible to modify the CEC values of a clay mineral by applying what is called the Hofmann–Klemen (HK) effect [58]. Clay minerals are first partially exchanged with small cations (generally Li^+) and heated at about 200–300°C, followed by glycerol adsorption. The thermal treatment leads to an irreversible migration of the small cations inside the layer. This apparently irreversible ion fixation decreases the layer charge and thus the CEC. While the HK effect has a respectable history, its mechanism was recently revisited and there is some controversy concerning the location of the migrated cation after heating and the reversibility of this effect.

1.4.4 Intercalation and Confinement in the Interlayer Space

1.4.4.1 General Definition Most of the technological applications of clays are related to reactions that occur in the interlayer spaces. The properties of “intercalated” species (i.e., species present in the clay mineral interlayer) are often different from those of the same species in solution; the interlayer may be considered as a nanoreactor that imposes on the intercalated species several modifications collectively known as confinement effects, which may be due to local chemical environment, size restrictions, specific orientation, mobility limitations, and so on. Confinement is not limited to clay minerals, it may also be observed in zeolites, mesoporous silicas, in the cavities of protein enzymes, and so on, but clay minerals are specific in providing tunable cavity size because of the variable interlayer distance.

1.4.4.2 Intercalation of Small Polar Molecules (e.g., Water) Intercalated water, naturally present in clays, has a very high acidity compared to aqueous medium. In the interlayer space, polar molecules such as water or alcohols interact with compensating cations through cation–dipole interactions, which no doubt have some amount of covalent character and could therefore be called coordinative bonds; this results in a weakening of the O–H bond and thus increased acidity.

This type of intercalation mechanism may also be called “inner-sphere adsorption” because the water molecules are in the coordination (i.e., inner) sphere of the cations. Further water molecules are not directly bound to the cation but form H-bonds with the first sphere, in “outer-sphere adsorption.” By using the desorption of a small polar molecule, namely methanol that contains a single hydroxyl group as opposed to the two O–H of water, it was shown [59] that in addition to the well-defined coordinative interaction with different compensating cations, the adsorbed molecules also form hydrogen bonds between themselves in the interlayer space and perhaps even to the siloxanes of the basal clay surface. Similar phenomena may occur with other polar solvents.

In some cases, a single clay particle may contain solvent-filled interlayers of different thicknesses. This leads to interstratified phases [60–63] that have been mentioned before: alternance of zero, one, two, or three water pseudolayers (or water pseudosheets) between the TOT layers (strata).

1.4.4.3 Intercalation of Bulky Inorganic Oligomers Some bulky cationic species such as the $[Al_3O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions with anti-Keggin structure, called “ Al_3 ” ions for short, may lead to intercalated clay minerals by ion exchange of the initial compensating cations. After heating, these oligomers become irreversibly fixed between two adjacent layers and act as “pillars” leading to microporous clay minerals with constantly accessible interlayer porosity called pillared clays or PILC [64,65]. This permanent pore opening could favor the intercalation of other species in the empty microporosity. Although these materials have been extensively studied in literature, and despite many hypotheses proposed to explain the fixation of these pillars in the interlayer space after heating, the pillaring process is not well understood and there is probably no universal mechanism for this irreversible polycation fixation.

1.4.4.4 Intercalation of Organic Species There are several routes to the intercalation of organics corresponding to different intercalation mechanisms. Neutral organic ligands can form complexes with the interlayer cations, and more generally polar organic solvents can displace water. Alternatively, the pristine cations can be exchanged by organic cationic species. The most studied, and most relevant example is the exchange by alkylammonium cations (most often quaternary ammonium). This will be developed in more detail in Chapter 2 since it is the starting point of the modified bentonites called bentones.

Intercalation by grafting reactions is also often seen in literature. Here covalent bonds established by condensation of some reactive groups on the organic chain with the clay silanol surface groups or with the hydroxyl groups of octahedral layer of kaolinite allows the expansion of the interlayer space. Consequently, the surface becomes hydrophobic. This route will also be treated in more detail in Chapter 2.

1.4.4.5 The Particular Case of Intercalation into Kaolin It is quite frequent to use preswelled kaolin in CPN application, since this clay is the

least expensive on the market. Three main categories of molecules can give intercalates in kaolin:

- Compounds like hydrazine and formamide that are both H-bond acceptors and donors and can swell the interlayers by forming H-bond networks.
- Compounds like dimethyl sulfoxide (DMSO) with high dipole moments.
- Compounds like salts of short-chain fatty acids.

1.4.4.6 Intercalation of Polymers Of particular concern for the present book is polymer intercalation in swelling clay minerals. Many polymers are able to directly intercalate with pristine clay minerals, but they are mostly restricted to hydrophilic polymers bearing, for example, ether or alcohol groups: PEO (polyethylene oxides) [66,67], PVA (polyvinyl alcohol) [68], PEDOT (poly(3,4-ethylenedioxythiophene)) [69], polypeptides or proteins such as gelatin [70], polylysine, and polyglutamic acid [71], and so on. For a recent update, see Ref. [72] (especially Section 3.9 in this reference). Hydrophilic polymers/clay nanocomposites can be used instead of more classical organoclays as rubber fillers.

In practice, in many reported syntheses, polymers are probably adsorbed on the external surface of the particles rather than intercalated. However, if the starting clay mineral is delaminated and well dispersed, nonionic polymers can definitely be intercalated from aqueous solutions. The basal distance observed is usually not very large and corresponds to a thickness of one or two linear macromolecule chains at maximum. The picture of clay–polymer interaction is certainly complex, showing simultaneous loops of polymer chain that remain amorphous in the interaggregates porosity and part of polymer tails intercalated in the interlayer space [71] and leading to more crystalline domains due to the nanoconfinement of the intercalated part of polymer.

The existence of cationic groups on the polymer, such as in polylysine, is a particularly favorable factor for intercalation into smectites since the electrostatic interaction with negatively charged layers will provide a driving force for intercalation. For neutral polymers and/or neutral layers (e.g., in kaolinite), the formation of intercalated layer does not occur by ion exchange but by other interactions such as H bonds, ion–dipole interaction, charge transfer, and van der Waals forces. All of these interactions contribute to the enthalpic part of the driving force for polymer intercalation. As regards the entropic part, it is more difficult to evaluate; the intercalation of a single polymer molecule is expected to displace many interlayer solvent molecules, which should be favorable, but the effects on the configuration entropy of the polymer are not so clear.

Polymers intercalation into pristine clay minerals is usually carried out from solutions, although there are a few successful examples of intercalation from polymer melts [73,74]. This procedure will be discussed later in the present book in the frame of organoclay–polymer nanocomposites; in spite of its industrial importance, it has probably not received enough attention in academic studies so far. It should be noted, however, that even authors reporting direct polymer intercalation in unmodified clays state that apolar hydrocarbon polymers cannot be intercalated in this way.

A completely different procedure to obtain clay/intercalated polymer nanocomposites is the *in situ* polymerization of previously intercalated monomers such as acrylonitrile [75] leading to intercalated polyacrylonitrile (PAN). This often occurs through enhancement by an initiator molecule or UV radiation or temperature.

In summary, intercalation of inorganic and organic species in clay minerals is a vast research domain. Intercalation can occur from vapor, from solutions, from pure melt, and in the solid state. The latter two procedures that are the most interesting for industrial use (avoiding the use of polluting solvent) are very scarce in academic studies.

1.4.5 Swelling

The ability to swell in water (or in any polar solvent) is a defining property of the smectite group of cationic clay minerals. Swelling is easily observable at the macroscopic level, by the formation of gel-like phases when water is added to clay minerals, with a large increase in volume as compared to the dry solid. A swelling index may be defined as the gel volume (in mL) obtained per 10 g of clay mineral, and it may reach values of 25–30 mL/10 g [76].

There is some ambiguity here because “swelling” is used to denote a macroscopic phenomenon as well as its molecular counterpart. Swelling as noticed at the macroscopic level, with gel formation, betrays some kind of microscopic scale structuration of the solvent–clay system. In principle, this could simply be a consequence of the formation of associations between the clay particles and aggregates (cf. Section 1.2.1). However, when used at the molecular scale, this term most often refers to the intercalation of large amounts of water in the interlayer space between the layers resulting in increasing interlayer distances.

Swelling is therefore a process whose end result may be high delamination of the clay layers and even exfoliation, if the distance between the layers is large enough.

The first steps of swelling are discrete, as they consist in the intercalation of crystallographically ordered water layers; discontinuous jumps in the d_{001} spacing are then observed with increasing water content [77]. When additional water is intercalated, at a given point, intercalated water molecules are not rigorously ordered any more, and therefore swelling is better described as a continuous phenomenon; osmotic swelling, that is, migration of water from the bulk solution into the interlayer region, driven by the lower water activity there. This osmotic transition (OT) is manifested by the transition from a hydrated powder to a paste. If more water is added, the clay dispersion remains in the form of a gel that can persist down to low overall clay contents: about 10% for Mt in water or as low as 3% for Laponite in water (a beaker containing a 3% Laponite dispersion can be turned upside down without spilling its content). Upon further dilution, the sol–gel transition occurs at the “SGT” threshold, where isolated aggregates are formed. In even more dilute dispersions, isolated particles are formed after a “local osmotic transition” (LOT) that is found at about 3% for Mt in water [78].

Whether swelling proceeds to delamination or not hinges on a delicate balance between the osmotic forces and the electrostatic interactions, which depend on the

compensating cations charges, and the layers charge density; for instance, Na^+ -montmorillonites can swell extensively.

It would seem that at an intermediate degree of swelling, the morphology of layers stackings goes from “columnar” to “zigzag,” for example, in the case of kaolinite, where the kaolinite layers become free to slide alongside each other.

Recent research reveals additional phenomena, thus, in the gel region, smectite dispersions can organize as nematic liquid crystals and exhibit a nematic-to-isotropic transition occurring before the sol–gel transition [79,80].

The swelling behavior of clay minerals is important to consider in the frame of CPN because clay interaction with surfactants or with water-soluble polymer occurs in aqueous media.

1.4.6 Rheology

Smectites display a complex rheological behavior when dispersed in an aqueous medium. When present in low concentrations they form dispersions with almost Newtonian properties. In other words, the consistency curve of such dispersions (shear stress τ , in Pa, vs. shear rate $\dot{\gamma}$, in s^{-1}) is linear, the slope of the straight line giving access to the dispersion viscosity. At higher clay concentrations, a Bingham plastic behavior is observed, that is, the consistency curve becomes linear only after a threshold shear stress is exceeded, the so-called yield stress, τ_e [81]. The rheology of clay dispersions is a testing ground for competing models of interaction in colloid science, and we will only offer some basic developments here.

The viscosity of inorganic dispersions is classically explained by the fact that the particles hinder each other’s motions, and distort flow patterns in their vicinity, leading to increased friction. Einstein proposed that the viscosity of a dispersion containing a size fraction ϕ of dispersed particles is given by $(\eta/\eta^0) = 1 + (5\phi/2)$ [82,83], where η is the viscosity of the dispersion and η^0 is the viscosity of the pure liquid.

Actually, in a dispersion of charged particles, the effective size is not that of the particle itself, but of the particle surrounded by its “diffuse layer,” and electroviscous effects are at work. This needs some explanation. Since electric charge cannot accumulate macroscopically, a charged particle in an electrolyte solution will induce the formation in its vicinity of a swarm of ions of the opposite charge; for instance, the basal planes of a smectite clay particle that bear a net negative charge will be surrounded by a region of the solution where the positive ions (Na^+ , Ca^{2+} , etc., as the case may be) outnumber the negative ions. The thickness of this diffuse swarm or diffuse layer extends to a few nanometers (high ion strengths cause diffuse layer contraction), and the properties of the “double layer” are extensively studied in colloid chemistry (e.g., Chapters 3 and 5 of Ref. [84]), as well as their effects of interparticle interactions (the positive diffuse layer of any clay particle will repel that of its neighbors). The “DLVO” theory (Derjaguin–Landau–Verwey–Overbeek, see, e.g., Chapter 8 of Ref. [84]) explains the stability of colloidal dispersions by the interplay between double-layer repulsions and van der Waals attraction.

When the dispersion is submitted to shear flow, the diffuse layers will tend to oppose the ensuing deformation, causing further friction upon the liquid, this is called the “first electroviscous effect,” while the “second electroviscous effect” refers to the viscosity increase due to the electrostatic repulsion between colloidal particles during flow-induced encounters.

These considerations can explain the variations of viscosity in the Newtonian regime. As regards the existence of a threshold stress (yield stress), it is correlated with a long-range organization of the dispersion that we have already mentioned when discussing the stability of clay gels (Section 1.4.5).

The effect on yield stress of varying liquid phase parameters such as pH and ion strength has been studied and it is not straightforward; for example, at high clay concentrations an increase in the ion strength causes an initial decrease of the yield stress, followed by a slow increase. As another example, for a Na^+ -montmorillonite, there is a maximum in shear stress (at constant shear rate) at pH 7, but it disappears when the compensating cation is Ca^{2+} ; and the behavior of the dispersion can change from Newtonian to Bingham plastic as the pH is varied ([85], pp. 204–205).

This is because the structure of the dispersion will be the result of different types of interparticle association: face-to-face, face-to-edge, edge-to-edge (cf. Section 1.2), each one reacting independently to changes in those parameters, and each one able to give rise to clay particles aggregation. The chemical heterogeneity (or patchwise heterogeneity) of the clay surface underlined in Section 1.4.2 is particularly important here. Recall that basal planes of smectites bear a permanent, pH-independent negative charge; in contrast, the edge groups of clay minerals (and the exposed OH-bearing octahedral sheets of kaolin) can be positively or negatively ionized by pH-dependent reactions. As a result, the latter regions of the clay surface will have a net positive charge at low pH (where, e.g., Si-OH_2^+ groups predominate), and a net negative charge at high pH (where Si-O^- groups predominate). Thus, in some conditions the edges can have a charge of opposite sign to the basal faces, and it is not hard to understand that this will influence the preferred type of particle association. Further interesting developments may be found in the work of Tombacz and Szekeres for montmorillonite [86] and for kaolinite [87].

For these amphoteric surfaces, there must be a pH value at which positively charged groups will be present in exactly the same number as negatively charged ones. This is called the point of zero (net protonic) charge or PZC (PZNPC). The PZC is important to understand the colloidal properties of a dispersion and can be measured simply by protonic titration; for example, a PZC of 6.5 was measured for montmorillonite edge surfaces [86]. The PZC must not be confused with the isoelectric point (IEP) obtained from electrophoretic mobility measurement. The IEP is the pH for which a particle will not migrate in an electric field, and it is determined by the overall charge of the particle (basal planes + edges, which may be of opposite sign), and in addition the particle usually moves in a solidary way with a few water layers that will contain part of the compensating cations in the diffuse layer. It may thus happen that a well-defined PZC may be measured, although the system as a whole does not have an IEP. More generally, it has been proposed to relate the zeta potential (calculated from electrophoretic mobility data measured as a function

of pH) to clay dispersibility. Although qualitative, and in some cases, semiquantitative agreement between the zeta potential of clay dispersions and their dispersibility has been reported, the usefulness of zeta potential measurements as an indicator of the dispersibility of colloidal systems has been strongly contested [88,89].

Finally, rheological properties may change upon mixing, and also simply upon aging, often in a reversible manner (thixotropy) [90]. There is continued interest in their evaluation due to the relevance for such phenomena as mud flows, or applications to drilling fluids.

The relationship between bentonite dispersion/flocculation and the rheological behavior of the corresponding dispersions, their dependency on aqueous phase parameters, and the various theoretical attempts to explain this dependency have been the object of a review by Luckham and Rossi [91].

1.5 AVAILABILITY OF NATURAL CLAYS AND SYNTHETIC CLAY MINERALS

Natural clays are very abundant, even though clays and clay minerals form under a fairly limited range of thermodynamic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. Most clay minerals form where rocks are in contact with water, air, or steam. Examples of these situations include weathering boulders on a hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water, and rocks in contact with water heated by magma (molten rock). All of these environments may cause the formation of clay minerals from preexisting minerals by dissolution–reprecipitation. The soil solution concentration of Si and Al from the weathering of volcanic rock is one of the most important factors determining the type of clay minerals that will be formed. For instance, the Al:Si ratio of allophane ranges from 1 to 2 according to the conditions of formation. They have been identified as being of three types: (1) Al-rich allophane (proto-imogolite), (2) Si-rich allophane, and (3) an hydrous allophane (feldspathoid allophane) [92].

Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits that are of economic interest (e.g., bentonites used for drilling muds and clays used in ceramics). In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed at places as residual deposits in soil, but thick deposits usually are formed as the result of a secondary sedimentary deposition processes after they have been eroded and transported from their original location of formation. Primary clays, mostly kaolins, are located at the site of formation.

The already mentioned bentonites form mainly from alteration of pyroclastic and/or volcanoclastic rocks. Extensive deposits, linked to large eruptions, have formed repeatedly in the past. Bentonites generally form by diagenetic or hydrothermal alteration, favored by fluids that leach alkali elements and by high Mg content. Smectite composition is partly controlled by parent rock chemistry. Recent studies

TABLE 1.4 Some Examples of Procedures for the Obtention of Synthetic Clays in Moderate Conditions

References	Starting Materials	Conditions	Obtained Phases
[94]	Silicic acid, MgCl ₂ , Na-, K-, Ca-hydroxide	Boiling, 20h	Amorphous hectorite, small amount of poorly crystalline Ht
[95–99]	SiO ₂ , FeCl ₂ , Mg-, Al-salts	Boiling at 100°C, in very dilute solutions 300–350°C <100°C	Hectorite, Fe-saponite, nontronite Saponite Hectorite, saponite, stevensite, phases depend on starting composition
[100,101]	SiO ₂ , Al(OH) ₃ , Mg(OH) ₂ , NH ₄ OH (or NH ₄ F)	Boiling 45 days in Mg acetate	Saponite
[102]	Na ₂ SiO ₃ , metal salts, acid	75°C, 15 day, 1 month; 100°C, 1 month; 150°C, 12 days Reflux, 12h	Nontronite, trace-Fe(OH) ₂ ; Fe-smectite under oxidizing conditions (“defect” nontronite) Cu-, Mg-fluorhectorite possible total replacement of Mg by Cu
[103,104]	Gel from Na ₂ SiO ₃ , NaAlO ₂ in HCl	<100°C, ≤8 weeks	Saponite, nontronite formed phases depend on starting composition
[105,106]	Gel SiO ₂ , Fe(SO ₄) ₂	100°C, reflux, 2 days	Organo-hectorite, direct uniform intercalation, but crystallinity varied with ion
[107]	TEOS, MgCl ₂ , CuCl ₂ , NaOH, LiF, NaF	400°C, 1 month	Saponite
[105,108,109]	TEOS, AlCl ₃ , FeCl ₂ , Ca(OH) ₂ , hydrazine	90°C, <2 days, homogeneous solution 100°C, ≤3days	Badly crystallized saponite
[110,111]	Mg(OH) ₂ , organic cations, LiF	95°C, 15 days, redox cycles, 10–13 weeks	Hectorite, crystallinity and stacking increase with TEA
[112,113]	TEOS, Mg(NO ₃) ₂ , Al(NO ₃) ₃ , Na ₂ CO ₃ , Li ₂ CO ₃	220°C, 72h 220°C, 48h	Hydroxy-interlayered, Fe-beidellite, poorly crystalline Montmorillonite
[114]	SiO ₂ /Al ₂ O ₃ gel, divalent metal nitrates, urea	Boiling, 20h	Saponite
[115]	Silica sol (Ludox), Mg(OH) ₂ , TEA, LiF		Amorphous hectorite, small amount of poorly crystalline Ht
[116–121]	TEOS, AlCl ₃ , FeCl ₂ , Ca(OH) ₂ , hydrazine	Boiling 100°C, in very dilute solutions 300–350°C	Hectorite, Fe-saponite, nontronite Saponite
[122]	SiO ₂ -Al ₂ O ₃ -MgO (ZnO) -Na ₂ O H ₂ O		
[123]	SiO ₂ , Al ₂ O ₃ , MgO, HF, H ₂ O		
[124]	Silicic acid, MgCl ₂ , Na-, K-, Ca-hydroxide		
[125]	SiO ₂ , FeCl ₂ , Mg-, Al-salts		
[126]	SiO ₂ , Al(OH) ₃ , Mg(OH) ₂ , NH ₄ OH (or NH ₄ F)		

have shown that bentonite deposits may display cryptic variations in layer charge—that is, the variations are not visible at the macroscopic scale—and these correlate with physical properties. As an unfortunate consequence, the properties of clay minerals obtained from the same deposit may show some variability as the resource is used up and different parts of the deposit are dug and collected.

Geographically, clays are not a scarce resource as clay deposits are spread all over the world (Algeria, Morocco, Tunisia, Spain, Sardinia, Greece, Russia, China, USA, etc.). They differ by their composition and the nature of the impurities. They are available in big quantities and most deposits are commercialized.

Two major problems encountered in clays exploitation and industrial use are the depletion of the deposits, at least those with easy exploitation access, and their occurrence as a mixture of several phases, instead of a pure clay mineral phase. To overcome these inconvenients, laboratory syntheses of clay minerals have been developed [93]. A lot of effort has been deployed to obtain well-crystallized clay minerals with controlled composition and properties, starting from initial oxides. Usually, synthetic clay minerals are crystallized from gels under hydrothermal conditions. Several methods have been reported in the literature where a great number of parameters have been changed such as the nature of the starting gel, the temperature, the pressure, and the duration. Some relevant results are reported in Table 1.4.

All these syntheses were performed at temperatures ranging from 150 to 450°C and pressures ranging from the autogenous water pressure to 1500 bar. The syntheses were performed in alkaline or fluoride medium. Trioctahedral clay minerals such as hectorite and saponite that are based on Mg oxides as starting materials are the easiest to synthesize. Laponite, first commercialized by Laporte and more recently by Tolsa,⁶ is a synthetic trioctahedral hectorite with very small size (its particles are discs with a diameter of about 30 nm). Dioctahedral species as montmorillonite are more difficult to obtain in laboratory and are usually very ill-crystallized. Until now, the conditions required for clay minerals synthesis make their commercialization very expensive and thus limited to high-added value applications. Therefore, so far, most commercial applications are based on natural clays after the application of several purification steps to eliminate the major impurities, even though synthetic clays can technically be used as filler materials for CPN [127].

1.6 CLAYS AND (MODIFIED) CLAY MINERALS AS FILLERS

Clay minerals are a key material in a great number of agricultural and industrial applications [128]. Particularly, they are used as fillers in the formulation of various products based on polymers matrices as, for example, in drilling fluids, in the paper industry, and/or in rubber. One of their advantages is that clays are attractive in our time of ecology-conscious chemistry; most probably, unforeseen adverse health effects (such as became painfully obvious for asbestos) need not be feared in the case of clay minerals that have accompanied mankind for millennia—for instance, natural

⁶ Laponite (Laporte, Rockwood) and Fluorohectorite (Somasis ME 100).

montmorillonite is used as an oral drug, sold in pharmacy under the trade name of “Smecta™.”

The first reason for industrialists to add nanoclay fillers to polymers was simply to reduce costs as compared to previously used fillers such as calcium carbonates or glass fibers. But it later turned out (actually it was not realized until the last two decades) that a small amount of clay added as a filler could bring additional benefits, as exemplified the synthesis of nylon 6–clay hybrid [129] that has been commercialized by Toyota in Japan. In fact, in other domains it was already known that their small size (typically $<1\ \mu\text{m}$, see Section 1.1) and large aspect ratio allow clay minerals to strongly influence the physical properties of soils and sediments. The paramount importance of clays in determining the CEC of soils has been mentioned before; they are also used as pond liners and for the isolation of hazardous wastes.

Just as in soil science and in geomechanics, small amounts of clay mineral can dramatically influence the final properties of CPN in nanotechnology. A few percent of clay minerals are incorporated in various CPN to improve the initial properties of the major (polymer) component or to gain new properties not seen in the net polymer alone. Several important books, reviews, and book chapters have been dedicated to these CPN [130–135]. The superiority of clays over other nanofillers has been reported many times in the literature and particularly the high performance of elastomers using clays as nanofillers.

Among the vast family of layered silicates, Mt is particularly attractive as reinforcement for CPN because it is environmentally friendly, readily available in large quantities with a relatively low cost. Moreover, its intercalation chemistry is more or less well understood.

Na^+ -Mt is hydrophilic and swells readily when immersed in water. Via cation exchange of Na^+ with alkylammonium ions under proper conditions, the clay mineral surface can be converted from hydrophilic to organophilic. The space between the silicate layers depends greatly on the length of the alkyl chain and the ratio of cross-sectional area to available area per cation. The conversion of hydrophilic inorganic clay to a hydrophobic organoclay also improves the interfacial adhesion properties between the organic and inorganic phases when a hydrophobic polymer matrix is involved.

Nowadays, several pristine clays and organoclays are available commercially at relatively low cost, and are used in different CPN applications.

In conclusion, clays, clay minerals, and organoclays are actually attracting exponential research interest and seem to be promising CPN fillers for applications in the future. Their properties, although intensively studied, are not yet completely understood, particularly concerning the interaction with guest species (water, surfactants, polymer, etc.) at the clay interfaces. Fundamental clay research in all disciplines still leads to open questions. For example, and particularly relevant for the subject of this book, it is difficult to rationalize and even more to foresee the interaction mechanisms of a given clay with a given polymer, and the behavior of the partially intercalated polymer in the confined interlayer space is not very clear. Nevertheless, clays are an abundant resource with a high potential for the preparation of a wide range of high-performance nanocomposites.

The huge potential applications of organoclays as effective reinforcement for polymers have prompted many researchers to investigate their structural behavior. The next chapter will concern the different modifications of clay minerals by organotreatments and other procedures in order to use them as fillers in polymers to obtain CPN.

ACKNOWLEDGMENT

The authors are particularly grateful to Dr. Fabrice Gaslain for preparing the structural figures.

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