

Fundamentals of Clay Mineral Crystal Structure and Physicochemical Properties

Introduction

The word “clays” was assigned early to fine grained material in geological formations (Agricola 1546) or soils (de Serres 1600). Clays have been identified as mineral species in the beginning of the 19th century in the production of ceramic materials (Brongniart 1844). Then Ebelmen (1847) carefully analyzed the decomposition of rocks under chemical attack and the way that porcelain can be commonly made. Since this pionner works, the definition of clays has varied. Until recently, the definition of clay minerals was debated. Bailey (1980) restricted the definition of clay to fine-grained phyllosilicates. Guggenheim and Martin (1995) considered that clays are all the fine-grained mineral components that give plasticity after hydration to rocks or materials which harden after drying or burning. According to that definition, the fine-grained property is the dominating condition. That means that the mineral components involved can be any other mineral species than phyllosilicates.

What does fine-grained mean? Classically, fine-grained or clay size means size less than 2 μm which is approximately the level of spatial resolution of the optical microscopes. However, the value of the size limit considered to define clays varies according to the particular need of each discipline: 2 μm for, geologists; 1 μm for chemists; and 4 μm for sedimentologists. It is evident that such a definition based on the grain size alone is not convenient for the study of mineral species. Thus, we will use here the definition given by Bailey (1980) which restricted the term of clays to phyllosilicates (from the Greek “phyllon”: leaf, and from the Latin “silic”: flint). However, to be more complete, we shall include other aluminosilicate phases whose crystal structure derives from that of phyllosilicates: sepiolite, palygorskite, imogolite, allophane. Consequently, no size condition will be imposed. Indeed, the size of clay minerals can be much greater than 2 μm : for instance, 50 μm sized kaolinites or illites are frequently observed in diagenetic environments. However surface alteration usually produces new phases almost always of less than 2 μm diameter.

This chapter attempts to provide the basics for an understanding of the crystal structure of phyllosilicates from the most elemental level (sheets of atoms) to the most complicated structure involving layers of different composition (mixed-layers). More details can be found in specialized books (Brindley and Brown 1980; Meunier 2005 among others).

1.1 The Common Structure of Phyllosilicates

We consider here the low temperature minerals formed at the Earth's surface. Other clay minerals can be formed at higher temperatures and they have specific different

compositions and structures. However, in order to understand the structures and chemistry of surface alteration clay minerals it is often necessary to draw parallels from clay minerals of higher temperature origin. Such material is special, in that it can be found as a more or less mono-mineral deposit, a very uncommon occurrence for surface alteration clays. Hence many of the examples used as illustrations are not exactly the minerals which one encounters in weathering environments.

In general, all phyllosilicates, low and high temperature types, can be considered to be formed by superposed atomic planes parallel to the (001) face. Thus, a way to describe their crystal structure is to consider how each of these planes is occupied by cations and anions on the one hand and how they are linked together on the other hand. The first level of spatial organization of the atomic planes will be assigned here as “sheet” (a cation plane sandwiched between two anion planes), the second level of organization being an association of sheets called “layer”. Finally, the third level of organization to be presented is the way that layer stack and how they are bonded together to form “crystallites”.

1.1.1

From Atomic Sheets to Layers

Clay minerals, phyllosilicates, are composed of a combination of two types of layer structures which are coordinations of oxygen anions with various cations. Two types of sheets are known following the number of anions coordinated with the cations, one of six-fold coordinations (tetrahedra) and the other of eight-fold coordination (octahedral coordination).

The Tetrahedral Sheet

The tetrahedral sheets of phyllosilicates are composed of SiO_4^{4-} or AlO_4^{5-} tetrahedra which are linked together by sharing 3 of 4 vertices: the three basal oxygens, the fourth being the apical oxygen. Each of the basal O^{2-} anion bonds with a Si^{4+} - Si^{4+} or a Si^{4+} - Al^{3+} cation pair. The Al^{3+} - Al^{3+} cation pair sharing an oxygen is excluded (Löwenstein's rule). The basal oxygens form a two-dimensional lattice exhibiting hexagonal cavities (Fig. 1.1). The apical oxygens are located on the same side of the plane determined by the bonded oxygens. The tetrahedral sheet thus constituted can be represented by the Bravais' unit cell (C-centered) whose b and c dimensions are 9.15 Å and 2.12 Å respectively ($b = a\sqrt{3}$). Detailed calculations are given in Meunier (2005).

The Octahedral Sheet

According to their ionic radius, the Al^{3+} , Fe^{3+} , Fe^{2+} or Mg^{2+} cations exhibit a 6-fold coordination when bonded to O^{2-} or OH^- anions. Thus, the structure is formed by octahedra whose center is occupied by the cation. The octahedra are linked together by sharing their 6 vertices. This means that each anion is bonded to three cations in the trioctahedral type. It is bonded to two cations in the dioctahedral type so that the third site is vacant. These bonds constitute the framework of a continuous sheet in which octahedra form a lattice with a hexagonal symmetry. The dimensions of the unit cell (Fig. 1.2) depend on the cation: for Al^{3+} (dioctahedral) and Mg^{2+} (trioctahedral), the b - c values are 8.64 Å-2.74 Å and 9.43 Å-2.45 Å respectively. The b dimension of

Fig. 1.1. The structure of the tetrahedral sheet exhibits hexagonal cavities. The Bravais' unit cell (C centered) contains 10O^{2-} for 4Si^{4+}

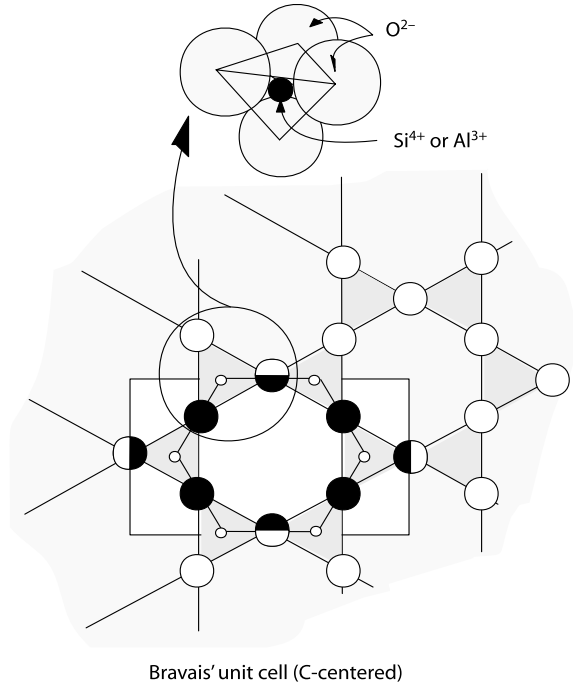
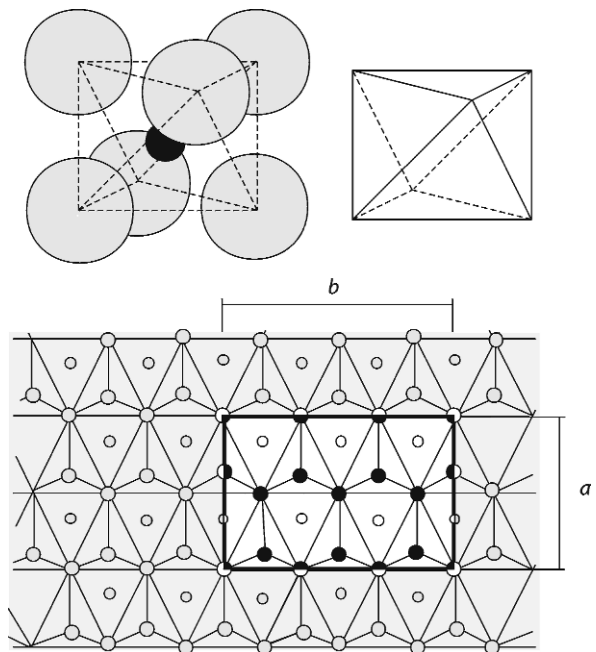


Fig. 1.2. Structure of the octahedral layer. The b dimensions of the trioctahedral (brucite) and dioctahedral (gibbsite) unit cells are 9.43 and 8.64 \AA respectively



phyllosilicates is measured using X-ray diffraction of randomly oriented powders. In absence of iron in the octahedral sheet, the position of the (060) diffraction peak at 1.49–1.50 Å or 1.52–1.53 Å is typical of dioctahedral and trioctahedral occupancies respectively. Typical values of d_{060} for the major species of clay minerals are given in Moore and Reynolds (1997, p. 245).

Linkage of the Tetrahedral and Octahedral Sheets

The a and b dimensions of the tetrahedral and octahedral sheets differ significantly. Thus, the linkage between them through the apical oxygens of the tetrahedra will not take place without deformations necessary to accommodate atomic dimensions of the cations. Both sheets are deformed to a certain extent:

- tetrahedral sheet: two types of tetrahedral rotation about axes perpendicular (rotation angle α) and parallel (thinning angle τ) to the basal plan deform the tetrahedral sheet which *slightly* loses its hexagonal symmetry.
- octahedral sheet: rotation about axes parallel to the plane (thinning angle ψ). Di- and trioctahedral sheets do not undergo identical deformations. The presence of vacant sites (vacancies) in the former alters the geometry of the octahedra (Fig. 1.3). Indeed, the absence of the cation reduces the attractive forces on anions and leads to the elongation of the edges of the vacant octahedron: from 2.7 Å to 3.2 Å. Therefore, the occupied octahedra become asymmetrical. Such distortions do not theoretically occur in trioctahedral sheets. In reality they are quite reduced (after Bailey 1980). Only the presence of bivalent cations with very different ionic diameter causes local changes in symmetry.

When linked together, the symmetry of the tetrahedral and octahedral sheets becomes ditrigonal. The internal energy of the crystal is increased by the bond deformations (angles and length) through the addition of the elastic energy.

The Two Layer Types (1:1 and 2:1)

General layer characteristics. The crystal structure of all phyllosilicates is based on two types of layers: 1:1 in which one tetrahedral sheet is bonded to one octahedral sheet (Fig. 1.4a); 2:1 in which one octahedral sheet is sandwiched and covalently coordinated between two tetrahedral sheets (Fig. 1.4b). Both types exhibit a ditrigonal symmetry, which means that the atomic positions form one layer of similar type to another is offset in space along the vertical, c axis. Deformations are significant in dioctahedral layers and only minor in trioctahedral ones. At this point it is important to define the unit cell: it is the smallest parallelepiped whose translation in the three crystallographic directions depicts the symmetry elements of the crystal. A unit cell has both the chemical composition (unit formula) and the symmetry elements of the crystal. Because of the difference of layer thickness, the presence of crystals formed of 1:1 and 2:1 types is easily detected using X-ray diffraction. The position of the (001) peak is at 7.1 and 9.2 to 14.2 Å respectively.

Fig. 1.3. Deformation of tetrahedral and octahedral sheets

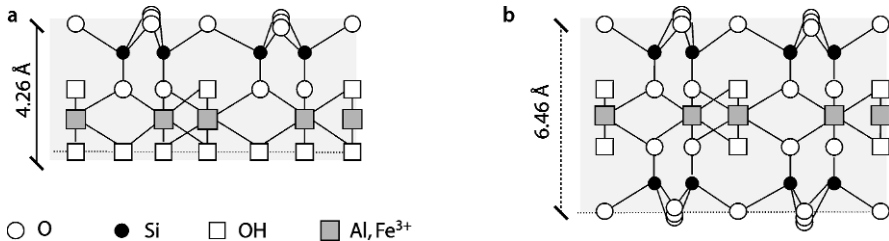
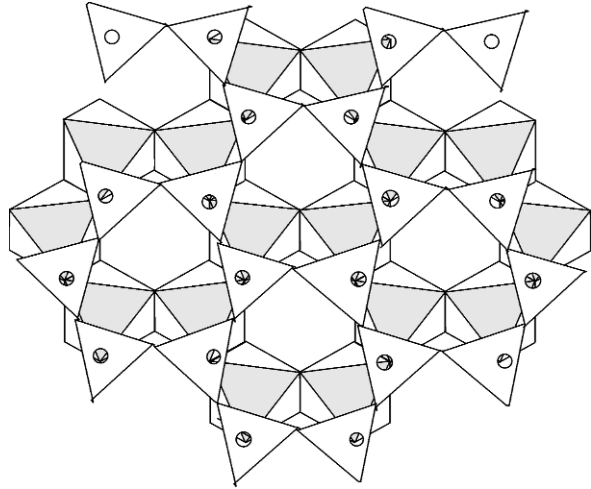


Fig. 1.4. The two crystal structure types of dioctahedral phyllosilicates; a 1:1 layer; b 2:1 layer

Two layer structures (1:1). The unit cell of a 1:1 dioctahedral phyllosilicate (kaolinite for instance) contains 4 octahedral sites which are occupied by Al³⁺ cations while two of the six possible sites are vacant. The unit formula of kaolinite is: Si₄O₁₀Al₄(OH)₈. In the trioctahedral sheet of the high temperature mineral lizardite all six sites are occupied by Mg²⁺ cations; the unit formula is: Si₄O₁₀Mg₆(OH)₈. The negative charge of the oxygen anion framework is balanced by the positive charge of the tetrahedral and octahedral cations.

Three layer structures (2:1). An example of the three cation layer, 2:1 structure can be seen in the high temperature mineral pyrophyllite. In this structure one finds two tetrahedral cation layers coordinated with an octahedral cation layer. The unit cell of a 2:1 dioctahedral phyllosilicate is [Si₈O₂₀Al₄(OH)₄]. The octahedral layer is characterized by the presence of two vacant cation sites of the six possible in the octahedral layer. As trioctahedral layers have fewer vacancies the deformations of the octahedral and tetrahedral sheets are limited and unit cell dimensions are close to the theoretical val-

ues of the 6-fold symmetry. The high temperature mineral talc is an example of this situation: unit formula $[\text{Si}_8\text{O}_{20}\text{Mg}_6(\text{OH})_4]$.

1.1.2

Negatively Charged Layers

The phyllosilicates of the 1:1 crystal structure type are constantly composed of 7 Å layers. There is no additional sheet of cations or anions. This is due to the fact that the positive charges of the cations in the tetrahedral and octahedral position are strictly compensated by the negative charges of the O^{2-} and OH^- anions forming the structure framework whatever the cation substitutions in the tetrahedral and octahedral sheets. On the contrary, most of the 2:1 phyllosilicates exhibit an additional cation sheet or a brucite-like sheet inducing a variation of the c dimension between 10 and 14 Å in the dehydrated state.

The Cation Interlayer Sheet (2:1 Phyllosilicates)

The interlayer cations compensate the negative charges in excess and insure the electrical neutrality of the 2:1 layer. They are not bonded to each other. According to the layer charge of the 2:1 unit, they are located at different places. The interlayer cations in high charge phyllosilicates (illite, micas) lose their loosely bonded water molecules and are housed in ditrigonal cavities among the oxygen anions of the facing tetrahedral sheets. In lower charge minerals the cations conserve a portion of the water molecules and are located in the interlayer space (between tetrahedral layers). The composition of the interlayer ionic occupation depends on the layer charge to be compensated. They are

- smectites, low charge (0.3 to 0.6) and vermiculites, high charge (0.6 to 0.75 per half unit cell $\text{O}_{10}(\text{OH})_2$): most of the interlayer cations are exchangeable (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , etc.). Consequently, the interlayer compositions vary with the cationic populations of the solutions in contact with the clays. The cations are normally hydrated under soil conditions.
- illites (0.75 to 0.9) and micas (1.0): the interlayer cations are strongly bonded to the facing layers. The dominating cation species are K^+ and NH_4^+ (Fig. 1.5a). These cations are not hydrated in the clay structure.

The Brucite-type Sheet (2:1:1 Phyllosilicates)

In some phyllosilicates the cation substitutions in the tetrahedral and octahedral sheets give the 2:1 layer a total negative charge of about -1 . In trioctahedral chlorites, this negative charge is compensated by a brucite-like sheet having an equivalent charge but of opposite sign. The main difference between a brucite-type layer and the interlayer cation sheet in other clay minerals is that the cations are coordinated to OH units which are linked to the tetrahedral units through electrostatic charge transfer instead of covalent bonding. The brucite-type layer is bonded to the 2:1 layer by a strong

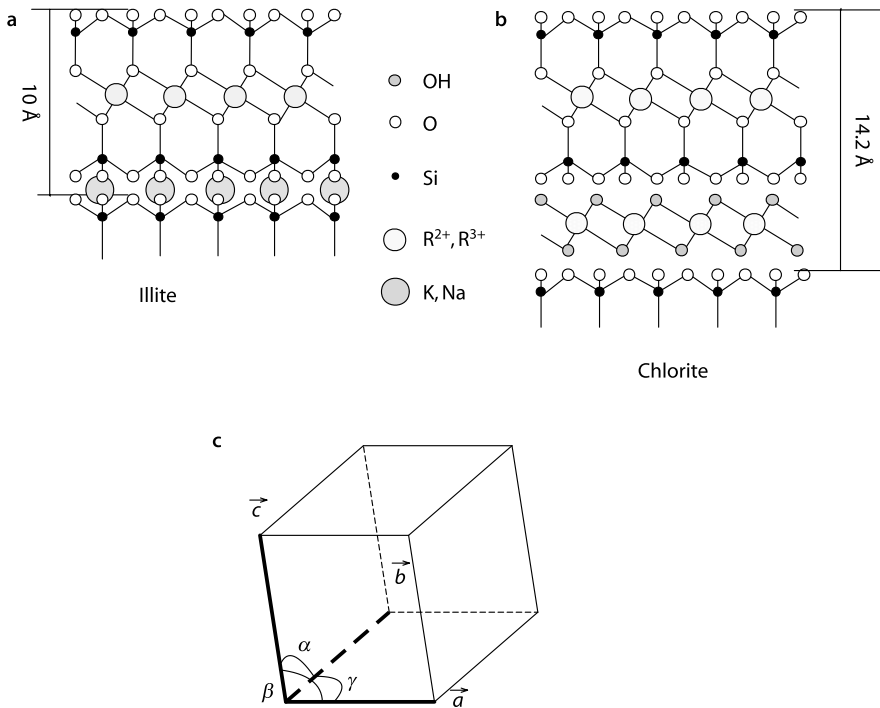


Fig. 1.5. Crystal structures of phyllosilicates derived from the 2:1 layer; **a** presence of an interlayer cation sheet (micas, vermiculites, smectites); **b** presence of a brucite-like sheet (chlorites); **c** schematic representation of the “layer unit cell” which is monoclinic or triclinic if the α angle is equal or lower to 90° respectively

Coulomb attraction. Therefore, the interlayer spacing remains at 14.2 Å; no expansion by adsorption of polar molecules is possible (Fig. 1.5b). The composition of the brucite-like sheet is poorly known because it escapes the usual means of investigation.

The two other varieties of 2:1:1 (high temperature) structures are:

- donbassite, dioctahedral variety whose structure is derived from a pyrophyllite-like layer with the addition of a gibbsite-like octahedral sheet;
- sudoite, di-trioctahedral variety, whose structure is derived from a of pyrophyllite-like layer with the addition of a brucite-like octahedral sheet.

Whatever their composition, chlorites are easily identified using X-ray diffraction by the harmonic series of ($00l$) diffraction peaks at 14.2, 7.1, 4.75 Å.

Thus, a “layer unit cell” can be defined as the smallest volume of the layer which is periodically repeated in the a^* and b^* crystallographical directions. The symmetry of this cell is necessarily monoclinic or triclinic (Fig. 1.5c).

1.1.3

The Different Layer-to-Layer Chemical Bonds

Some phyllosilicates are composed of layers which are electrically neutral because either there is no cation substitution in the tetrahedral and octahedral sheets (kaolinite, serpentine, pyrophyllite, talc) or because the negative charge in the tetrahedral sheet is compensated by a positive charge in the octahedral one (berthierine). Considering the most frequently encountered clay mineral of that type, i.e. kaolinite (Fig. 1.6a), we can observe that facing 1:1 layers (4.26 Å thick) are held together by weak chemical attractive forces. The hydrogen bond length is about 2.89 Å for a total thickness of 7.15 Å (Fig. 1.6b).

Most of the clay minerals which are commonly encountered in natural systems are of the 2:1 type, each layer being negatively charged. The electrical neutrality is respected by the addition of positively charged cations in the interlayer zone. These cations are isolated or linked to water molecules in illite (Fig. 1.7a), vermiculite and smectite minerals or they can be organized in a “pseudo-brucitic” sheet as it is the case for chlorite (Fig. 1.7b). The 2:1 layers being negatively charged, they repulse themselves and increase the thickness of the interlayer zone. When interlayer cations are present, the attractive forces they exert on the facing 2:1 layers decreases the thickness of the interlayer zone. The thickness of the interlayer zone depends on the equilibrium between attractive and repulsive forces (Norrish 1954; Van Olphen 1965; Kittrick 1969a,b; Laird 1996, 1999). We will see further that the interlayer cations may be hydrated and consequently introduce water molecules in the interlayer zone. Consequently, the thickness of the interlayer zone may vary according to the hydration state of the cations, i.e. the water partial pressure of the system.

It is obvious that the clay crystallites are composed of more than one layer. Thus, the way these layers are stacked is an important parameter for the identification of clay minerals. Whatever the way that layers are linked to their neighbors (hydrogen bonds, ionic bonds), they are stacked in the *c* direction. The stack may have different

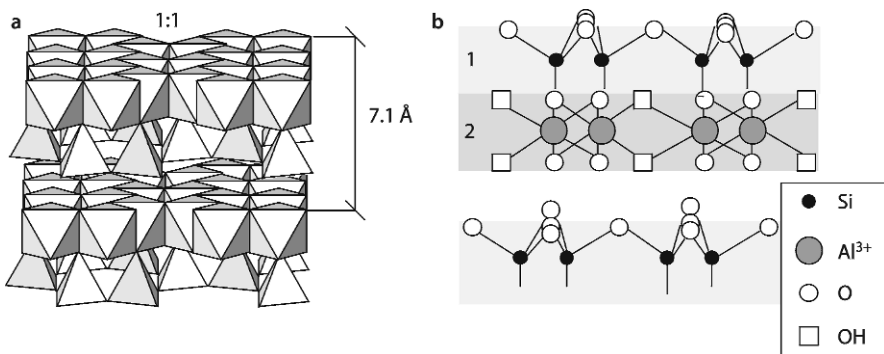


Fig. 1.6. The crystal structure of kaolinite; **a** the 1:1 layer is composed of a Al-bearing octahedral sheet linked to a Si-bearing tetrahedral one through the apical oxygens of each tetrahedron; **b** projection of the crystal structure on the (010) plane

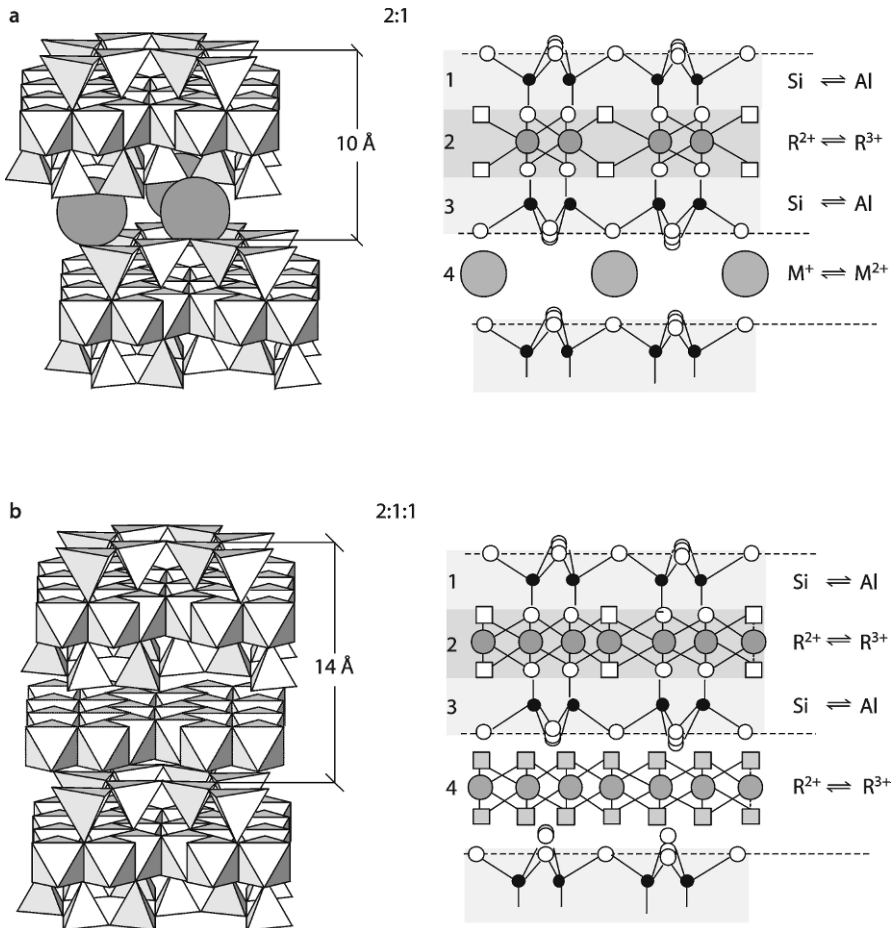


Fig. 1.7. The crystal structure of illite (a) and chlorite (b). The negative charge of the 2:1 layer is compensated by interlayer cations or a “pseudo-brucitic” sheet respectively

degrees of symmetry. The size (volume) and symmetry type of the “crystal unit cell” depend on the stacking mode.

1.2 Polytypes and Mixed Layer Minerals

1.2.1 Layers of Identical Composition: Polytypes

The different polytypes of clay or more specifically phyllosilicates are formed by specific positioning of the unit layers as they are found along the c crystallographic axis.

The positioning of the layers gives rise to more subtle symmetry arrangements of the atoms in their a-b crystallographic relations. Such relations are found in “well crystallized” crystallites, i.e. those where many unit layers form the crystal unit. Such material is not often found in surface alteration materials but the presence of mineral grains with such polytypes can be used as a diagnostic of provenance. We present a rapid explanation for this phenomenon in Annex 1. Several translation-rotation combinations are made possible first by the specific pseudo-hexagonal symmetry of the tetrahedral sheet and second by the position of the octahedra axes (see Annex 1). Consequently, the unit-cell symmetry depends on the polytype. The higher the symmetry degree, the more numerous the (hkl) peaks (Fig. 1.8).

The sub-species are assigned as polytypes. They should always be designed by addition of a symbol of the stacking to the family name: $1M$ mica, $2M_1$ mica, Ib chlorite, IIb chlorite, etc. The kaolin family is an exception since polytypes are assigned different mineral names: kaolinite, dickite, nacrite, halloysite. This was probably due to the big difference of crystal morphology: hexagonal plates, rhombs or tubes (Fig. 1.9).

Polytypes are determined using X-ray diffraction. For phyllosilicates, the mineral family and the polytypes are identified using the $(00l)$ and (hkl) diffraction peaks respectively (Moore and Reynolds 1997). Unfortunately, the polytype determination is made difficult because the (hkl) diffraction peaks are weak and interfere with each other and with quartz or feldspars. Disorder in the layer stacking broadens the peak pro-

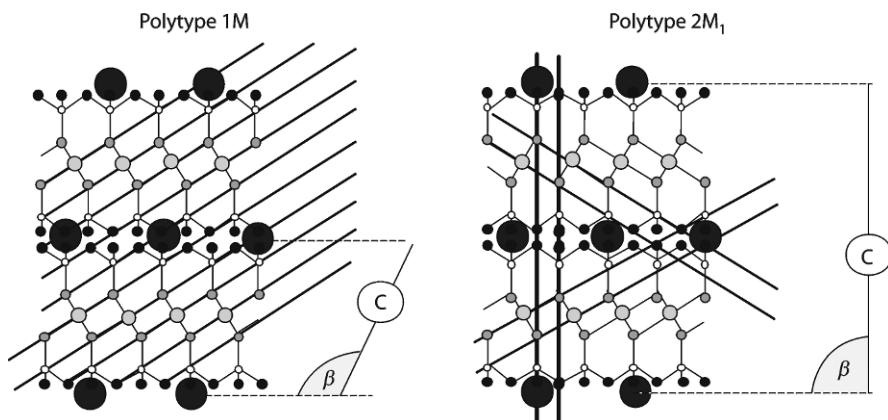
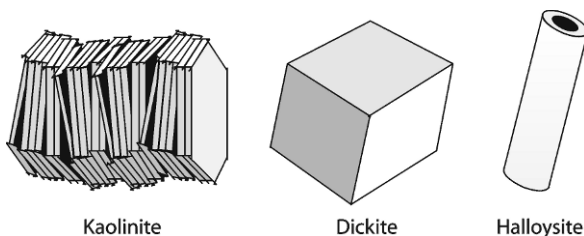


Fig. 1.8. Relation between the symmetry degree and the number of (hkl) planes in $1M$ and $2M_1$ micas

Fig. 1.9. Relation between polytype and crystal morphology for kaolin minerals



files and reduces the diffracted intensity. Disorder is due to the presence of rotational or stacking faults. Only (*hkl*) peaks with $k = 3n$ remain in totally disordered polytypes.

In spite of difficulties, the determination of polytypes should be included in any study of clay minerals in soils. It is one of the best criteria to separate the detrital inheritance from the neogenetic fraction. Indeed, in most cases, the neoformed clay minerals in soils are highly disordered. Oppositely, phyllosilicates from rocks formed in higher temperature conditions are more ordered.

1.2.2

Layers of Different Composition: Mixed Layer Minerals

Mixed layer minerals (MLMs) are crystallites composed of two or more types of basic structural layers, 2:1 or more rarely 2:1:1 and 1:1. These minerals are most frequently found in the soil or upper parts of an alteration sequence. Their importance as far as mineral stability and transformation is not well known at present. In some cases it appears that they are a transition between one structure and another, a sort of intermediate phase while in others their status is less evident. Their importance, though poorly understood, is most likely the key to understanding clay mineral stability in many soils. The most commonly described two-component mixed-layer minerals at Earth's surface are:

- *dioctahedral species*: illite/smectite (I/S) and kaolinite/smectite (K/S). These MLMs are randomly ordered. They are abundant in soils,
- *trioctahedral species*: biotite-vermiculite, chlorite-vermiculite or smectite (saponite). These MLMs are ordered and sometimes regular (presence of a sur-structure diffraction peak). They are formed in weathered rock microsystems.

The condition that apparently best explains the frequency of these MLMs is the slight difference between the *a* and *b* dimensions of the two types of layers. Mixed-layer minerals formed by the stacking of trioctahedral and dioctahedral layers are unquestionably rare. Recent studies show that, even though rarely described in the literature, naturally occurring three-component mixed-layer minerals may be more abundant than commonly thought (after Drits et al. 1997). The mixed-layer minerals exhibit specific rational or non-rational series of diffraction bands, depending on their crystal structure being regular or not, respectively. In both cases, XRD patterns are significantly different from those of pure species.

Basically two types of interlayering can be easily recognized, regular and disordered types. The first leads to a new mineral structure based upon two layers of different mineralogical characteristics. This gives in ideal cases a new diffraction pattern based upon a double unit cell, and hence a new cell dimension in the *c* sin beta direction. For example a regular interlayered illite (10 Å) and smectites (15.2 Å) mineral will give a first order reflection at 25.2 Å. Lower order reflections are divisions of this value. A disordered mixed layer mineral shows intermediate peak positions based upon the proportion of the layers present when the difference in interlayer distances is not too great (10 and 15.2 Å for instance). The (*ool*) peaks do not form a rational series because of interference between neighbouring peaks (Méring 1949). A very simple application of Méring's rule is shown in Fig. 1.10a and b for I/S and K/S respectively. Details of X-ray identification and ordering types are given in Annex 2.

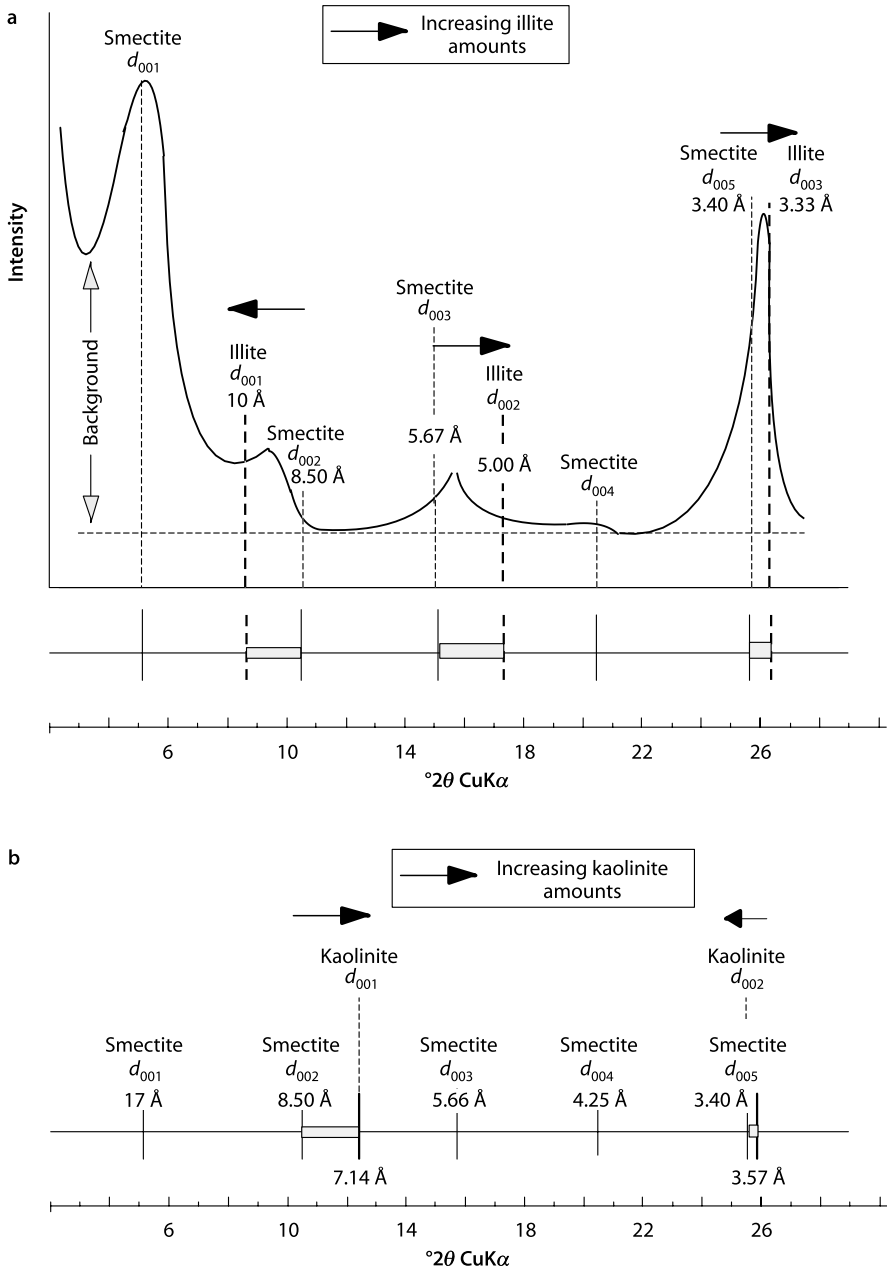


Fig. 1.10. Randomly ordered mixed layer minerals (peak interference rule, Méring 1949); **a** the diffraction peak interference for a illite-smectite MLM; **b** the diffraction peak interference for a kaolinite-smectite MLM

Summary

X-ray diffraction is the basic technique for the identification of clay minerals. The classical procedure needs two different preparations. Randomly oriented powders are used to determine the polytypes and the octahedral occupation according to the position of (*hkl*) and (*060*) peaks respectively. Oriented preparations are used to identify the layer type (1:1, 2:1 or 2:1:1) and their possible interstratification using the (*ool*) peaks. Details for the identification procedure are to be found in Brindley and Brown (1980) and Moore and Reynolds (1997).

1.3 Crystallites – Particles – Aggregates

1.3.1 Crystallites: The Limit of the Mineralogical Definition

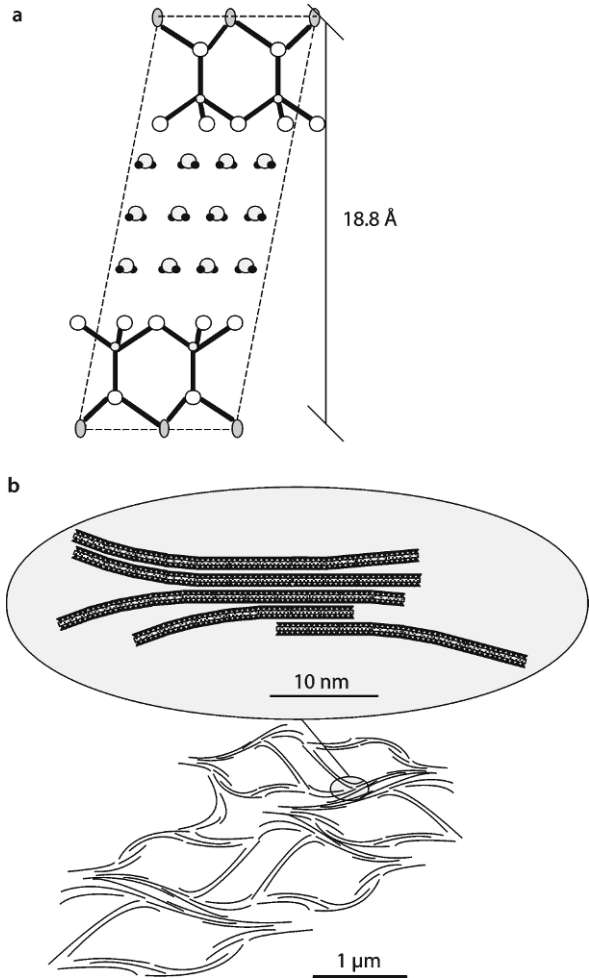
The term crystallite is used here for small dimension crystals. According to Putnis (1992), “a crystal is ideally made up of a repetition of identical building blocks, or unit cell, filling space, each unit cell in an identical orientation and related to the next by translation along of three crystallographic axes”. This definition can be properly applied to phyllosilicates which do not exhibit the swelling property, ie. different cell dimensions according to hydration state. Swelling is related to the incorporation of *cations surrounded* by polar molecules (water, ethylene glycol for example) in the interlayer space. If this incorporation leads to a constant number of molecules per unit cell, then the translation along the *c* axis is maintained. The crystallites conserve their shape (Fig. 1.11a). This is the case of vermiculite crystallites in which the layer charge of the 2:1 units is sufficiently high to interact at long distance. However, if the number of polar molecules is too high and/or the layer charge too weak, these interactions do not work, each 2:1 layer being independent. This is frequently observed with smectites. In that case, the crystal definition is not applicable: the swelling cancels the translation along the *c* axis. One must not use the term crystallite.

After swelling, most of the smectites exhibit a honeycomb texture in which pores are isolated by solid membranes. These membranes are formed by randomly ordered layer stacks (Fig. 1.11b). Because the periodicity along the *c* axis is destroyed, one cannot consider that they are formed by crystallites but rather by tactoids or quasi-crystals, the thickness and the size of which vary with the saturating cation.

The shape and size of crystals depend on the conditions of crystallization: temperature, chemical composition and pH of solutions, crystallization duration. The crystal habit for a given mineral species may change depending on these conditions. However, in spite of that variability, the principal clay mineral species exhibit typical shapes:

- crystallites: laths (beidellite, illite), hexagonal plates forming booklet (kaolinite)
- tactoids or quasi crystals: flakes (montmorillonite)

Fig. 1.11. Crystallite and tactoids; **a** expanded vermiculite (3 water sheets) conserving the periodicity along the *c* axis (crystallite); **b** honeycomb texture of smectite. The periodicity along the *c* axis is almost cancelled (tactoid)



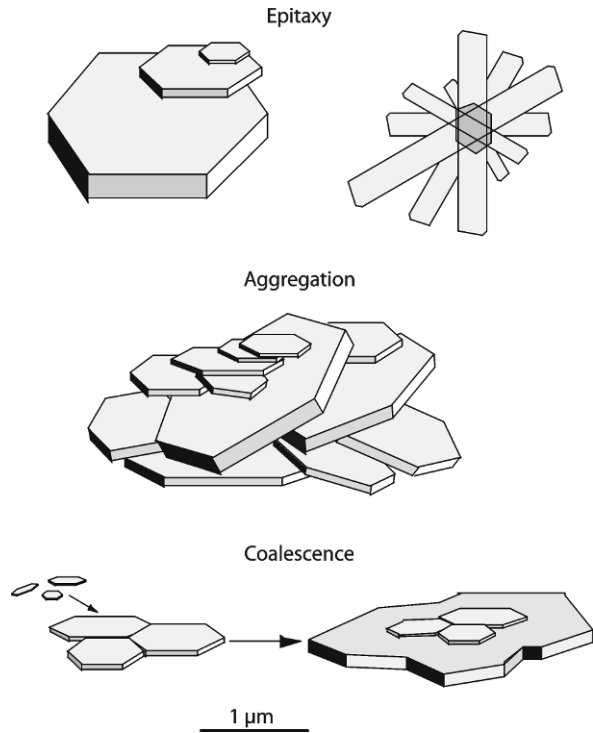
Generally, smectite crystals are small (crystallites below 1 μm) and very thin (a few nm, i.e. a few layers) while kaolinite and illite may reach higher dimensions (10 to 50 μm) and thickness (several tens of layers).

1.3.2

Particles and Aggregates

Because of their small size, clay mineral crystals are currently observed using transmission electron microscopes (TEM). Most often, clay minerals appear as complex bodies whose origin may be natural (particles, aggregates) or due to artefact (sedimentation during the grid preparation drying). Because of the difficulty to distinguish artefacts from natural bodies, definitions are needed for particles, aggregates and natural coalescence:

Fig. 1.12. The main types of particles and aggregates of clay minerals; **a** epitaxy, i.e. growth on a crystalline support; **b** aggregation of crystallites by Coulomb forces or by hydroxide or organic matter deposits; **c** coalescence: neighboring crystals are joined by the growth of common layers



- **Particles.** Such as twinned crystals, often exhibit reentrant angles allowing the boundaries of coalescing crystals to be recognized. These natural particles, contrary to artefacts, cannot be dispersed by chemical or ultrasonic treatment. They result from crystal growth processes on individual crystallites (epitaxy) or on an association of crystallites (coalescence),
- **Aggregates** are units of higher organization in which crystals and/or particles are bonded together by Coulomb forces or by hydroxide or organic matter deposits. They result from chemical and/or physical processes in soils.

Schematical representations of epitaxy, aggregation and coalescence are given in Fig. 1.12.

1.4 The Principal Clay Mineral Species

1.4.1 The Cation Substitutions

Ionic Substitutions and Solid Solutions

Pauling's empiric rules, stated in 1929, permit the determination of coordination domains from simple geometric relationships based on the ratio of the cation and anion

ionic radii (R_c) and (R_a), respectively. Thus, tetrahedra (4-fold coordination) exist if $0.225 \leq R_c/R_a \leq 0.414$ whereas octahedra exist if $0.414 \leq R_c/R_a \leq 0.732$. Since the ionic radii of the main ions taking part in the crystal structure of clays are known, determination of those ions capable of substituting for each other in the three main coordinations involved in phyllosilicates (4, 6 and 12) is easy. Two types of substitutions can be distinguished: $\text{Al}^{3+} \leftrightarrow \text{Fe}^{3+}$ or $\text{Mg}^{2+} \leftrightarrow \text{Fe}^{2+}$ (homovalent substitutions), $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ (heterovalent substitutions). Heterovalent substitutions induce a deficit of positive charge.

The chemical composition of the phyllosilicates varies with the amount of substitutions inducing the formation of solid solutions whose range depends on the physicochemical conditions. Three types of solid solutions can be distinguished:

- *Substitution solid solutions.* They are formed by the isomorphous replacement of ions or atoms in equivalent sites of the crystal structure. In the case of ions, valency must be identical. This is the case of Fe^{2+} replacing Mg^{2+} in the octahedral sheet of phyllosilicates (the difference in their ionic radii is only 7.5%). Geometrical distortions are slight and the local charge balance is maintained;
- *Addition solid solutions.* In the case of heterovalent substitutions, the electrical neutrality may impose the presence of additional ions that are located in particular sites. This is the case of the ions in the interlayer sheet of phyllosilicates.
- *Omission solid solutions.* As heterovalent substitutions change the charge balance, the latter is restored by the incomplete occupation of a crystallographic site (vacancies). This is the case of trioctahedral chlorites in which the substitution rate of R^{3+} for R^{2+} in the octahedral sheet imposes vacancies (symbolized by $\langle \rangle$).

Tetrahedral Substitutions

In most of the 2:1 phyllosilicates, Si^{4+} may be replaced by Al^{3+} in the tetrahedral sheets. The difference of valency between both ions produces a negative charge (positive charge deficiency) and changes the symmetry of the tetrahedral sheet. The maximum substitution ratio is 1 Si^{4+} in 4 replaced by Al^{3+} (recall that, according to the Lowenstein's rule, two Al tetrahedra cannot be direct neighbors). Consequently, the tetrahedral charge cannot be higher than 1 per $\text{O}_{10}(\text{OH})_2$, margarite being a rather exceptional mineral which does not form in the Earth's surface conditions. The charges varies from zero (pyrophyllite, talc) to 1 (micas).

Octahedral Substitutions

Some phyllosilicates do not have any heterovalent substitutions either in the octahedral or the tetrahedral sheets. This is the case of 1:1 minerals (kaolinite, serpentine) and 2:1 minerals (pyrophyllite, talc). Besides, in these minerals, the rate of homovalent substitutions ($\text{Al}^{3+} \leftrightarrow \text{Fe}^{3+}$ or $\text{Mg}^{2+} \leftrightarrow \text{Fe}^{2+}$) remains relatively low. However, heterovalent substitutions are very common in 2:1 and 2:1:1 minerals (chlorite) inducing a large composition variability. According to the distribution of heterovalent cations in the octahedral sheet, one can distinguish three types: random (true solid solutions); zoned (compositional clusters); additional cations occupying vacancies: the rate of octahedral occupancy varies between 2 and 3 (structural clusters).

Substitutions in the Interlayer Sheet

Cation substitutions in the interlayer sheet are much more varied than those in tetrahedral and octahedral sheets for three reasons:

1. the large-sized interlayer sites are able to house cations such as Sr^{2+} , Ba^{2+} , K^+ , Rb^+ or Cs^+ , whose ionic radius is between 1.75 and 2.02 Å.
2. for 2:1 layer charge lower than about -0.75 per Si_4O_{10} (smectites and vermiculites), the cations are adsorbed in the interlayer zone in their hydrated state (water molecules forming a shell). According to the water partial pressure, the cations are located either in the interlayer space (2 water sheets) or partially lodged in a hexagonal cavity (1 water sheet).
3. The interlayer cations may be exchanged with those of the solution in contact with the crystallites.

The water molecules fixed around the bivalent interlayer cations, whatever the type of smectite considered, are arranged in a configuration close to that of ice (Sposito 1989; Mercury et al. 2001). They form a non-planar hexagonal lattice whose vertices are alternately connected to the cavities of the tetrahedral sheets of the opposite layers. The hydration of the interlayer cations favors the disorder in the layer stacking (turbostratism) as was shown by Méring (1975).

Summary: The Use of Chemiographical Projections

Ionic substitutions are present in the tetrahedral, octahedral and interlayer sheets. This induces a high variability of the composition of phyllosilicates and especially of clay minerals. Nine major chemical elements are involved in the solid solutions. Such a complex chemical system is out of usual graphical representation procedures. Fortunately, some simplifications can be operated considering that:

- the interlayer composition can be ignored in a first step,
- some elements play the same role in the crystal structure.

In that case, most of the clay minerals can be represented in a four component system: $(\text{Si}-\text{Al})-\text{Fe}^{3+}-\text{Fe}^{2+}-\text{Mg}$ (Fig. 1.13a). This 3D representation divided into bi-dimensional diagrams which are more convenient for chemical projections. Two of them are represented in Fig. 1.13b,c.

1.4.2

The Principal Mineral Species of the 1:1 Phyllosilicate Group

In the unit cell of a kaolinite, 4 sites of the dioctahedral sheet are occupied by Al^{3+} cations and 2 are vacant. The unit formula of kaolinite is: $\text{Si}_4\text{O}_{10}\text{Al}_4(\text{OH})_8$. In the trioctahedral sheet of a lizardite all 6 sites are occupied by Mg^{2+} cations; the unit formula is: $\text{Si}_4\text{O}_{10}\text{Mg}_6(\text{OH})_8$. The negative charge of the oxygen anion framework is balanced by the positive charge of the tetrahedral and octahedral cations. The crystal structure of 1:1 phyllosilicates consists of 5 ionic planes. The actual a and b unit cell

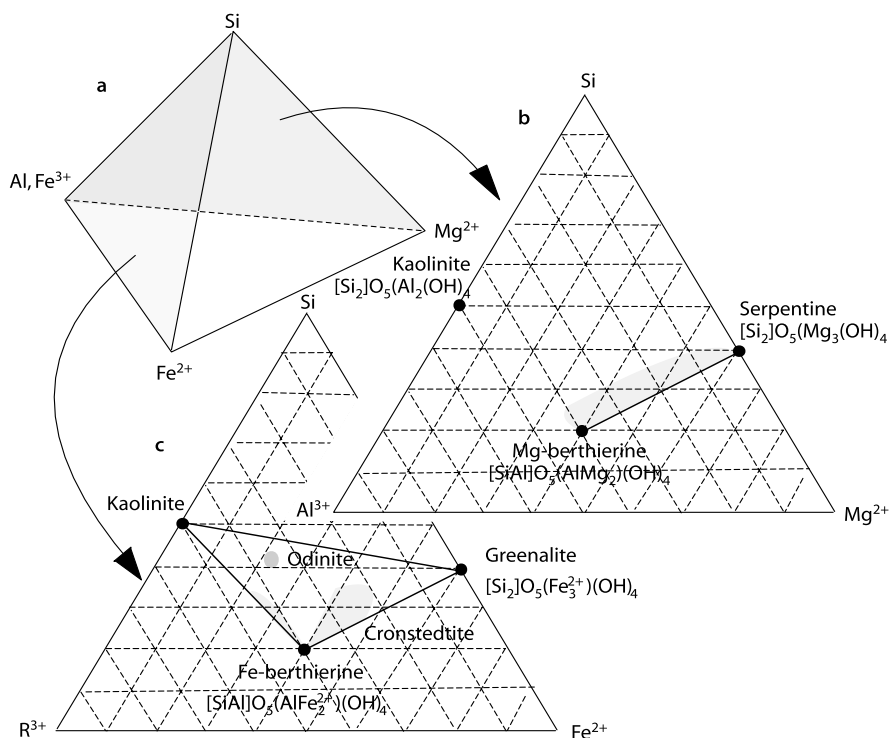


Fig. 1.13. Composition domains of 1:1 phyllosilicates in the Si–Al³⁺, Fe³⁺–Fe²⁺, Mg²⁺ system; **a** the four component system; **b** the Si–Al–Mg system; **c** the Si–R³⁺–Fe²⁺ system. The gray zones indicate the solid solutions

dimensions are respectively: $a = 5.15 \text{ \AA}$; $b = 8.95 \text{ \AA}$ for kaolinite and $a = 5.31 \text{ \AA}$; $b = 9.20 \text{ \AA}$ for lizardite.

The distance between two neighboring 1:1 layers corresponds to the thickness of the combined tetrahedral sheet + octahedral sheet (theoretically: $2.11 + 2.15 = 4.26 \text{ \AA}$) to which the thickness of the interlayer spacing is added. The latter depends on the length of the hydrogen bonds connecting the tetrahedral sheet in one layer to the octahedral sheet in the neighboring layer (about 3.0 \AA according to Bailey 1980). The interlayer spacing of kaolinite is 7.15 \AA , that of lizardite 7.25 \AA for the pure magnesian end member; it increases with the substitution rate of Mg²⁺ for Fe²⁺.

In spite of cation substitutions either in the tetrahedral or octahedral sheets, the “ 7 \AA phases” are all characterized by a neutral layer. If existing the deficit of positive charge in a given sheet is compensated by an excess in the other sheet (Table 1.1).

1.4.3

Principal Mineral Species of the 2:1 Phyllosilicates Group without Interlayer Sheet

The following examples are based upon model, or simple minerals. These minerals are for the most part formed under high temperature conditions and thus not surface alter-

ation phase. However they are of simple chemical composition and have been studied from a crystallographic viewpoint in the past and are hence useful as descriptive material.

The structure of dioctahedral 2:1 layers is formed by 7 ionic planes giving it a thickness of 6.46 Å (Fig. 1.4b). The octahedral sheet is formed by two kinds of octahedra: 2 *cis*-octahedra (M₂ sites) in which (OH)⁻ groups form one side of a triangular face on the right or on the left and 1 *trans*-octahedra (M₁ site) in which (OH)⁻ groups are located on the opposite vertices. Planes defined by the (OH)⁻ groups when they are in the *trans*-position become planes of symmetry of the octahedral sheet (Fig. 1.14a). This is not true for the *cis*-position (Fig. 1.14b).

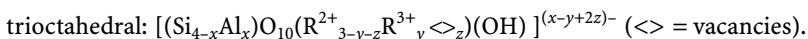
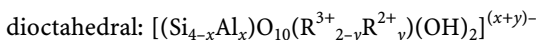
Pyrophyllite [Si₄O₁₀Al₂(OH)₂] is characterized by the presence of a vacancy in the *trans*-position. The actual unit cell dimensions are: $a = 5.160$ Å; $b = 8.966$ Å (angles α and γ are close to 90°: $\alpha = 91.03^\circ$ and $\gamma = 89.75^\circ$). Bonding between neighboring layers (from tetrahedral sheet to tetrahedral sheet) depend on van der Waals bonds. These bonds have a stable configuration when two neighboring layers show a shift of about $a/3$ spacing along one of the ditrigonal symmetry directions. The thickness of the 2:1 layer and interlayer spacing yields the following value of $c \sin \beta = 9.20$ Å ($c = 9.33$ Å; $\beta = 99.8^\circ$). The talc unit formula [Si₄O₁₀Mg₃(OH)₂] points out the absence of an octahedral vacancy. Deformations of the octahedral and tetrahedral sheets are limited and unit cell dimensions are close to the theoretical values of the 6-fold symmetry: $a = 5.29$ Å; $b = 9.173$ Å. The c dimension is 9.460 Å.

Because of the presence or absence of a vacant site, the structure of the octahedral sheet in pyrophyllite and talc implies different energetic states for OH radicals. In the dioctahedral structure, their negative charge is compensated for by 2 neighboring cations, each providing one-half of positive charge (Besson and Drits 1987). As the vacancy breaks the balance of the repulsive forces, the O-H bond is inclined to its direction (Fig. 1.15). In the tetrahedral structure, each OH is balanced by 3 bivalent cations, each providing one-third of positive charge. In the latter case, the H⁺ proton is systematically perpendicularly oriented in the center of the hexagonal cavity of the tetrahedral sheet (Fig. 1.15). This short discussion shows that crystal structure and energetic environments of OH radicals are related. These energies (or their wavelength equivalents) can be determined using infrared absorption spectrometry.

1.4.4

The 2:1 Phyllosilicates with an Interlayer Ion Sheet (Micas)

The crystal structure of dioctahedral and trioctahedral micas and clays is based on that of pyrophyllite and talc respectively through cation substitutions of Al³⁺ for Si⁴⁺ in the tetrahedral layer and of R²⁺ for R³⁺ in the octahedral layer (Méring 1975; Walker 1975). The general unit formulae per half-cell are the following:



The charge deficiency of the 2:1 unit is balanced by the addition of a cation interlayer sheet in the crystal structure (Fig. 1.7). The number of interlayer cations depends on their valency and on the negative charge of the 2:1 layer:

Table 1.1. Chemical composition of the half unit cell of the principal phyllosilicates. *x*: Si for R³⁺ substitution in the tetrahedral sheet; *y*: R²⁺ for R³⁺ substitutions in the octahedral sheet; *z*: number of octahedral vacancies (<>); *IC*: interlayer charge. Mineral types found in surface alteration are indicated in bold letters

1:1 phyllosilicates ("7 Å phases")		
Kaolinite	Si ₂ O ₅ Al ₂ (OH) ₄	<i>x</i> = 0; <i>y</i> = 0
Chrysotile	Si ₂ O ₅ Mg ₃ (OH) ₄	<i>x</i> = 0; <i>y</i> = 0
Antigorite	Si ₂ O ₅ (Mg,Fe) ₃ (OH) ₄	<i>x</i> = 0; <i>y</i> = 0
Nepouite	Si ₂ O ₅ Ni ₃ (OH) ₄	<i>x</i> = 0; <i>y</i> = 0
Fraipontite	[Si _{2-x} Al _x]O ₅ (Zn _{3-y} Al _y) ₃ (OH) ₄	<i>x</i> = <i>y</i>
Amesite	[Si Al]O ₅ (Mg ₂ Al)(OH) ₄	<i>x</i> = -1; <i>y</i> = +1
Berthierine	[Si _{2-x} Al _x]O ₅ [(Fe ²⁺ ,Mg) _{3-y-z} Fe ³⁺ _y <> _z](OH) ₄	<i>x</i> = 6 + <i>y</i> - 2 <i>z</i>
Cronstedtite	[SiFe ³⁺]O ₅ (Fe ²⁺ ₂ Fe ³⁺)(OH) ₄	<i>x</i> = <i>y</i> = 1
Greenalite	Si ₂ O ₅ (Fe ²⁺ _{3-y-z} Fe ³⁺ _y <> _z)(OH) ₄	<i>x</i> = 0; <i>y</i> = 1/2 <i>z</i>
2:1 phyllosilicates ("9 Å phases")		
Pyrophyllite	Si ₄ O ₁₀ Al ₂ (OH) ₂	<i>x</i> = 0; <i>y</i> = 0
Talc	Si ₄ O ₁₀ Mg ₃ (OH) ₂	<i>x</i> = 0; <i>y</i> = 0
Minnesotaite	Si ₄ O ₁₀ (Fe ²⁺ ,Mg) ₃ (OH) ₂	<i>X</i> = 0; <i>y</i> = 0
2:1 phyllosilicates ("10 Å phases")		
Muscovite	[Si ₃ Al]O ₁₀ Al ₂ (OH) ₂ K	<i>x</i> = -1; <i>y</i> = 0; <i>IC</i> = +1
Biotite	[Si ₃ Al]O ₁₀ (Fe ²⁺ ,Mg) ₃ (OH) ₂ K	<i>x</i> = 0; <i>y</i> = 0; <i>IC</i> = +1
Celadonite	Si ₄ O ₁₀ [(Al,Fe ³⁺)(Fe ²⁺ ,Mg)](OH) ₂ K	<i>x</i> + <i>y</i> = -1.0; <i>IC</i> = +1.0
Phengites	[Si _{4-x} Al _x]O ₁₀ [(Al _{2-y} (Fe ²⁺ ,Mg) _y](OH) ₂ K _{x+y}	<i>x</i> + <i>y</i> = -1.0; <i>IC</i> = +1.0
Glauconite	[Si _{4-x} Al _x]O ₁₀ [(Al,Fe ³⁺) _{2-y} (Fe ²⁺ ,Mg) _y](OH) ₂ K _{x+y}	<i>x</i> < -0.3; <i>y</i> < -0.6; <i>IC</i> ≅ +0.9
Illite	[Si _{4-x} Al _x]O ₁₀ [(Al _{2-y} (Fe ²⁺ ,Mg) _y](OH) ₂ K _{x+y}	-0.3 < <i>x</i> < -0.7; -0.2 < <i>y</i> < -0.6; <i>IC</i> ≅ +0.9
Vermiculite (Dioctahedral)	[Si _{4-x} Al _x]O ₁₀ [(Al,Fe ³⁺) _{2-y} Mg _y](OH) ₂ K _{x+y}	-0.3 < <i>x</i> < -0.7; -0.2 < <i>y</i> < -0.6; +0.6 < <i>IC</i> < +0.8
Beidellite	[Si _{4-x} Al _x]O ₁₀ (Al,Fe ³⁺) ₂ (OH) ₂ K _x	-0.3 < <i>x</i> < -0.6; <i>y</i> = 0; +0.3 < <i>IC</i> < +0.6
Montmorillonite	Si ₄ O ₁₀ [(Al,Fe ³⁺) _{2-y} Mg _y](OH) ₂ K _y	<i>x</i> = 0; -0.3 < <i>y</i> < -0.6; +0.3 < <i>IC</i> < +0.6
Vermiculite (Trioctahedral)	[Si _{4-x} Al _x]O ₁₀ [(Fe ²⁺ ,Mg) _{3-y-z} (Al,Fe ³⁺) _y <> _z](OH) ₂ K _{x+y-2z}	-0.3 < <i>x</i> < -0.7; -0.2 < <i>y</i> < -0.6; +0.6 < <i>IC</i> < +0.8
Saponite	[Si _{4-x} Al _x]O ₁₀ [(Fe ²⁺ ,Mg) _{3-y-z} (Al,Fe ³⁺) _y <> _z](OH) ₂ K _{x+y-2z}	-0.3 < <i>x</i> < -0.6; <i>y</i> + 2 <i>z</i> = 0; +0.3 < <i>IC</i> < +0.6
Stevensite	Si ₄ O ₁₀ [(Fe ²⁺ ,Mg) _{3-y-z} (Al,Fe ³⁺) _y <> _z](OH) ₂ K _{x+y-2z}	<i>x</i> = 0; 0.3 < <i>y</i> + 2 <i>z</i> < -0.6; +0.3 < <i>IC</i> < +0.6

Table 1.1. *Continued*

2:1:1 phyllosilicates ("14 Å phases")		
Chorite (Trioctahedral)	$[\text{Si}_{4-x}\text{Al}_x]_3\text{O}_{10}[(\text{Fe}^{2+}, \text{Mg})_{3-y-z}(\text{Al}, \text{Fe}^{3+})_y]_2(\text{OH})_2\text{AlMg}_2(\text{OH})_6$	$-0.3 < x < -1.0; 0 < y + 2z < -0.7;$ $/C \equiv +1.0$
Sudoite (Di-Trioctahedral)	$[\text{Si}_{4-x}\text{Al}_x]_3\text{O}_{10}[(\text{Al}, \text{Fe}^{3+})_{2-y'}(\text{Fe}^{2+}, \text{Mg})_{y'}]_1(\text{OH})_2\text{AlMg}_2(\text{OH})_6$	$-0.3 < x < -1.0; 0 < y < -0.7; /C \equiv +1.0$
Donbassite (Dioctahedral)	$[\text{Si}_3\text{Al}]_3\text{O}_{10}(\text{Al}, \text{Fe}^{3+})_2(\text{OH})_2\text{Al}_2(\text{OH})_6$	$x = -1.0; /C \equiv +1.0$

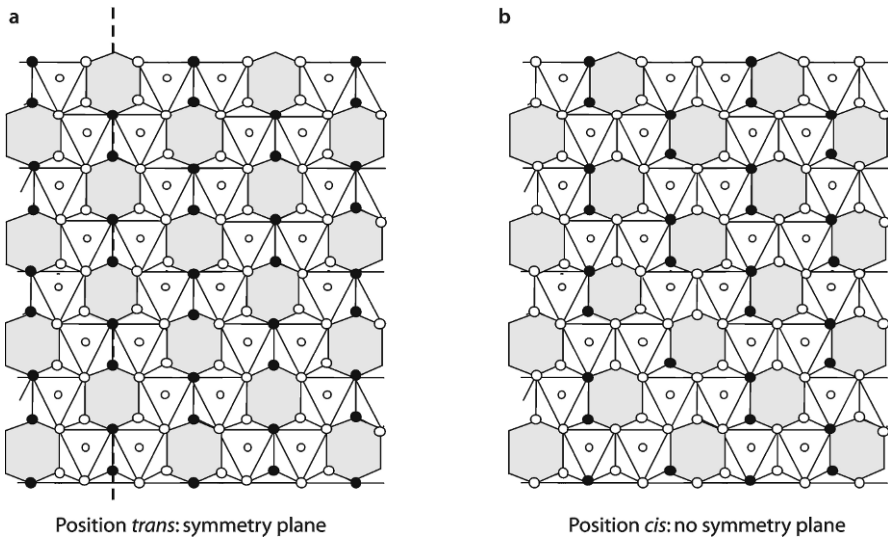


Fig. 1.14. Crystal structures of 2:1 dioctahedral phyllosilicates; **a** the octahedral vacant site is in the *trans* position inducing the presence of a symmetry plane in the octahedral sheet; **b** the octahedral vacant site is in the *cis* position, no symmetry plane

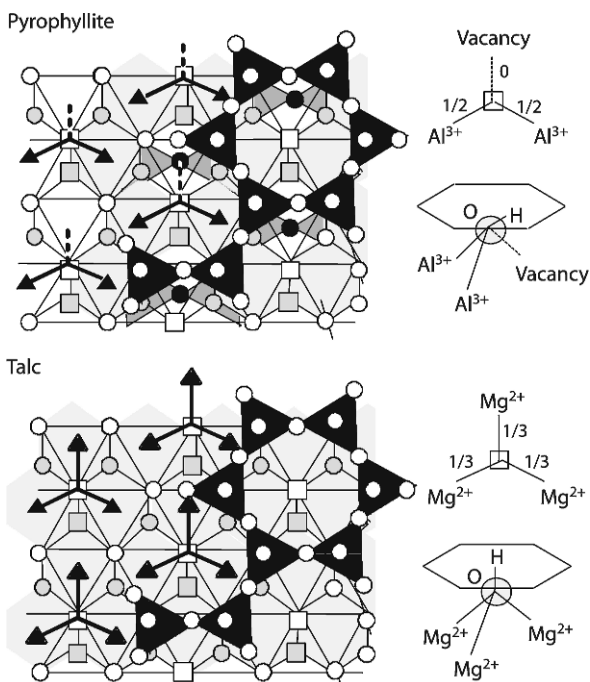
- dioctahedral minerals: brittle micas (margarite), $x + y = -2$, balanced by 1 Ca^{2+} ; micas (muscovite, phengite, celadonite), $x + y = -1$, balanced by 1 K^+ ; vermiculites or dioctahedral smectites whose respective charge $x + y = -(0.7-0.6)$ or $x + y = -(0.6-0.3)$ is balanced by K^+ , Ca^{2+} , Mg^{2+} or Na^+ ,
- trioctahedral minerals: micas (phlogopite, biotite), $x - y + 2z = -1$, balanced by 1 K^+ ; vermiculites and trioctahedral smectites whose respective charge $x - y + 2z = -(0.7-0.6)$ or $x - y + 2z = -(0.6-0.3)$ are balanced by K^+ , Ca^{2+} , Mg^{2+} or Na^+ .

1.4.5

Phyllosilicates with a Brucite-type Interlayer Sheet (2:1:1)

Trioctahedral chlorites are the most common representatives of this structure according to Bailey (1975). Their crystal structure derives from the combination of a talc-

Fig. 1.15. Position of cation-OH-cation bonds for pyrophyllite and talc



like 2:1 layer with a brucite-like octahedral sheet (Fig. 1.7b). Cation substitutions give the talc-like layer a negative charge of about -1 and the brucite-like sheet an equivalent charge but of opposite sign. Most of the negative charge in the 2:1 layer is the result of substitution of Al^{3+} for Si^{4+} in tetrahedral sites. The octahedral sheet usually has a low charge because the positive charge excess due to the replacement of bivalent cations ($\text{R}^{2+} = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}$) by trivalent cations ($\text{R}^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}$) is balanced by the positive charge deficiency related to the presence of vacancies (unoccupied sites): $x - y + 2z \cong 0$. The Coulomb attraction between the 2:1 unit and the brucite-like sheet is strong. Therefore, the interlayer spacing remains at 14.2 \AA ; no expansion by adsorption of polar molecules is possible.

The composition of the brucite-like sheet is poorly known because it escapes the usual investigation methods. Nevertheless, it most probably has no vacancy and has a positive charge excess due to the replacement of bivalent cations ($\text{R}^{2+} = \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Mn}^{2+}$) by trivalent cations ($\text{R}^{3+} = \text{Al}^{3+} + \text{Fe}^{3+}$). Two other varieties of chlorite are encountered in natural high temperature environments:

- donbassite, dioctahedral variety whose structure is derived from a pyrophyllite-like layer with the addition of a gibbsite-like octahedral sheet;
- sudoite, di-trioctahedral variety, whose structure is derived from a of pyrophyllite-like layer with the addition of a brucite-like octahedral sheet.

1.4.6

The Fibrous Clay Minerals: Sepiolite and Palygorskite

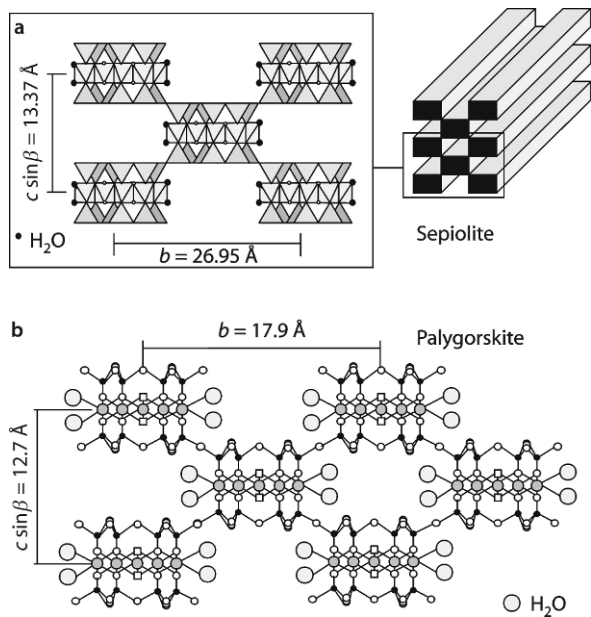
Sepiolite and palygorskite are considered to be clay minerals because they are always small sized crystals (most often less than 2 μm long) and because they form in soils or sediments in surface conditions. Their crystal shape is typically that of fibers because of two particularities of the crystal structure: (1) a discontinuous octahedral sheet; (2) the $[\text{SiO}_4]^{4-}$ tetrahedra are periodically inverted (Fig. 1.16a). The silicon tetrahedra form ribbons similar to amphibole which are elongated in the a direction. Because of the periodical interruptions of the octahedral sheet, the crystal structure exhibit “zeolitic” channels in which water molecules are fixed on the cation non satisfied valencies (Fig. 1.16b).

In palygorskite the octahedral sheet is nearly dioctahedral: the vacant site is in the middle of each ribbon with the Mg , Al , Fe^{2+} and Fe^{3+} cations around it. The negative charge due to $\text{Si} \leftrightarrow \text{Al}$ and $\text{R}^{2+} \leftrightarrow \text{R}^{3+}$ substitutions in the tetrahedral and octahedral sheets respectively is generally weak. It is compensated by exchangeable cations located inside the channels with the zeolitic water.

Summary

For most, the crystal framework of 2:1 or 2:1:1 clay minerals encountered in soils and weathered rocks is similar to that of phyllosilicates formed at higher temperature conditions. This is a great advantage since the same conceptual tools classically used for the study of diagenetic, hydrothermal, metamorphic or magmatic minerals can be also fruitfully applied to those formed at the Earth’s surface. This is the case for the identi-

Fig. 1.16. Crystal structures of fibrous clay minerals (periodical inversion of the silicon tetrahedra and discontinuous octahedral sheet forming channels in which are located the water molecules or zeolitic water and the exchangeable cations); **a** palygorskite; **b** sepiolite



fication procedure of the MLMs using X-ray diffraction. Only few surface mineral species occur in sedimentary formations (sepiolite or palygorskite). Two of them seem to be typical of soils: imogolite, allophane. These two species will be described further.

1.5 Typical Properties of Intermediate Charge Clay Minerals

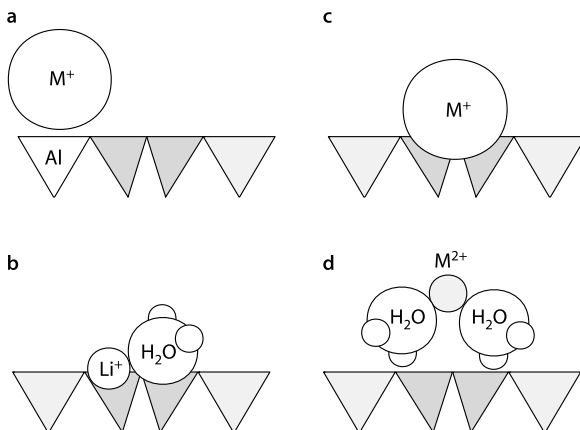
1.5.1 Hydration and Swelling

Cations in aqueous solutions are surrounded by water which form roughly spherical complexes of several water layers (outer sphere complexes). These complexes can be combined at least in part with basal oxygens on clay surfaces. When they are found between the tetrahedral layers of a clay mineral, they form inner-sphere complexes with only one water molecule layer (Sposito 1984). Two parameters control their complexing behavior: their size (ionic radius in octahedral coordination; Shannon 1976) and charge which determine their hydration energy (energy necessary to release the water molecules of the complex).

K^+ , Rb^+ and Cs^+ alkaline cations can readily lose their water molecule “shell”. They form anhydrous complexes with basal oxygens because their hydration enthalpy is low. Since their diameter is close to or greater than the size of the hexagonal cavity of tetrahedral sheets ($>1.4 \text{ \AA}$), they can occupy two positions according to the origin of the layer charge: either perpendicular to the basal oxygens of the tetrahedron in which Al^{3+} replaces Si^{4+} , or partially engaged in the hexagonal cavity when the charge is octahedral.

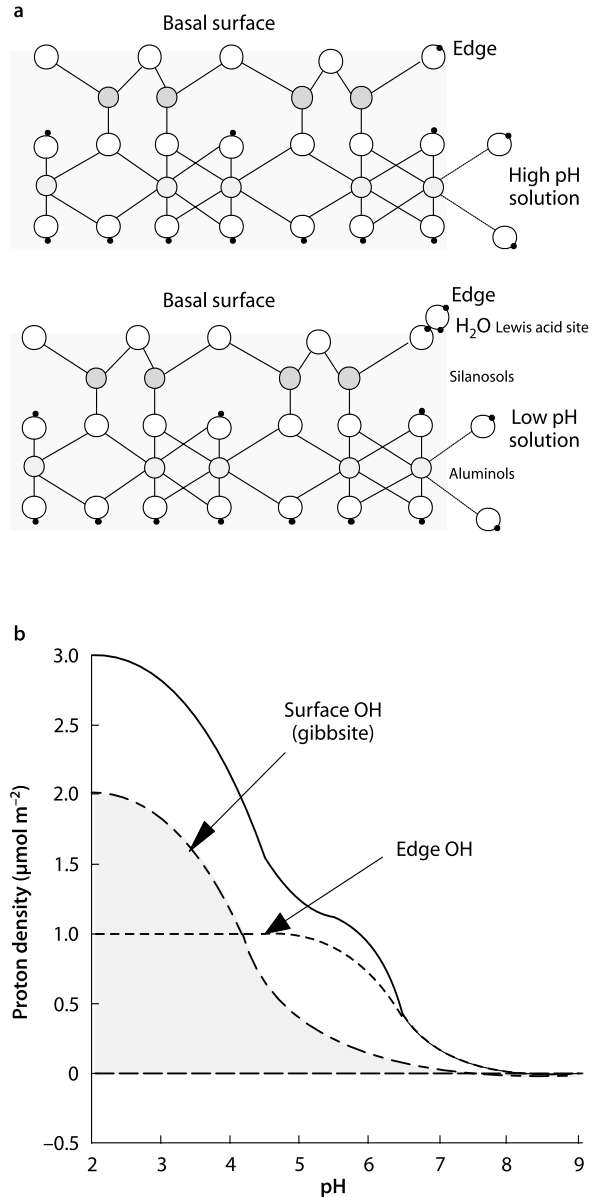
Molecular dynamics calculations show that the interlayer cations are located in different places according to their capacity to lose or conserve their water molecule “shell”. They are located near the negative charges when emerging at the surface of the 2:1 layer. If totally dehydrated, they are close to the Al^{3+} cations which replace Si^{4+} ones in the tetrahedral sheet (Fig. 1.17a) or inside the ditrigonal cavity (Fig. 1.17b).

Fig. 1.17. The possible positions of interlayer cations according to their hydration energy; **a** dehydrated cation close to the Al^{3+} cation replacing a Si^{4+} in a tetrahedral sheet; **b** dehydrated cation inside the ditrigonal cavity; **c** partially hydrated cation inside the ditrigonal cavity; **d** hydrated cation above the ditrigonal cavity



Ba^{2+} , Na^+ and Li^+ cations have a greater hydration energy than other cations. Some, due to their smaller ionic diameter, they can enter farther into the hexagonal cavity. The Li^+ ion is small enough to enter with water molecules (Fig. 1.18c). Mg^{2+} , Ca^{2+} and Sr^{2+} cations have very small hydration enthalpies and ionic radii even smaller. They remain strongly bonded to the water molecules forming the complex (hydration

Fig. 1.18. a Basal and edge surfaces of kaolinite crystals at basic and acidic pH, the interrupted bonds of the crystal lattice are neutralized by OH groups; **b** at near neutral pH, aluminol groups fix the H^+ protons thus yielding $\text{Al(III)-H}_2\text{O}$ groups that are Lewis acid sites (from Stumm 1992)



sphere). These water molecules are bonded to basal oxygens through weak bonds (hydrogen bonding). The interlayer spaces saturated by these bivalent cations exhibit 1 or 2 water layers depending on the partial water pressure, i.e. the relative humidity (Fig. 1.18d). Summarizing, if conserving totally or partly their water shell, cations are lodged inside or above the coordination polyhedra whose vertices are either water molecules or oxygens from the ditrigonal cavities.

The “swelling” property is determined by the ability of interlayer cations to retain their polar molecule “shell” (water, glycol, glycerol) within the interlayer environment (after Douglas et al. 1980). This property does not exist if the charge of the 2:1 layer is too high (micas, chlorites) or zero (pyrophyllite, talc). More simply, this property is characteristic of di- and trioctahedral smectites and vermiculites (Table 1.1). Polar molecules are organized into sheets whose number varies with the interlayer charge, the nature of the interlayer cations and the partial pressure of the polar molecules (Sato et al. 1992). In identical conditions, the higher the layer charge, the lower the number of water or ethylene glycol sheets (Table 1.2):

- a and 0.6 per $O_{10}(OH)_2$: 1 layer of polar molecules (di- or trioctahedral vermiculites and high-charge beidellites). High-charge saponites absorb 1 to 2 layers of polar molecules associated with the absorbed cations;
- b and 0.3 per $O_{10}(OH)_2$: 2 to 3 layers of polar molecules (beidellites, montmorillonites and saponites, stevensites).

Most often, the expandable clays appear to behave as mixed-layer minerals composed of layers having 0, 1 or 2 polar molecule interlayer sheets. This is due to segregated distribution of charge on the layers in a crystallite. Some layers lose their expandability when saturated with K^+ ions.

1.5.2

The Crystallite Outer Surfaces

The External Surfaces

The external surfaces of 2:1 layers are essentially formed by their tetrahedral sheets. The latter form “siloxane” surfaces. The SiO_4 tetrahedra are associated into a ditrigonal lattice in which the cavities are deformed hexagons of about 0.26 nm in diameter. The configuration of the electron orbitals of the 6 oxygens gives these cavities a character of Lewis bases. If no isomorphic substitution of ions occurs in the tetrahedral layer (Al^{3+} for Si^{4+}) or in the octahedral layer (R^{2+} for R^{3+}), the basic behavior, namely of electron donor, remains very low. It is merely sufficient to complex dipolar molecules such as H_2O for instance (the H^+ ion is located on a line orthogonal to the siloxane surface at the center of a ditrigonal cavity). These complexes are then of low stability and can be destroyed by low-energy processes.

The isomorphous substitutions of a bivalent cation for a trivalent one in the octahedral layer introduce a positive charge deficiency in the replaced octahedron. The resulting negative charge is distributed between the 10 oxygens of the 4 tetrahedra bonded to the deficient octahedron. Therefore, the Lewis base behavior of the ditrigonal cavity is reinforced and becomes sufficient to form complexes with dipolar molecules

Table 1.2. Relationship between the number of water or ethylene glycol layers and basal spacing (*c* dimension) in 2:1 clay minerals (revised from Suquet et al. 1975). *M*: montmorillonite; *B*: beidellite; *S*: saponite; *V*: vermiculite

Number of molecule layers	<i>c</i> dimension (Å)	Exchangeable cations				
		Li ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
Hydration state						
Infinite	–		MBSV	MB	M	
3 water layers	16.5 – 17				MB(S)	MBS
2 water layers	14 – 15	V	BSV	M	(B)SV	(S)V
1 water layer	12.3		BSV			
0 water layer	10		V			
Ethylene glycol saturation state						
2 glycol layers	16.9 – 17.1	M	M	M	MB	MB
	16.4 – 16.6	SB	S	S	S	S
	16.1	V	V		V	
1 glycol layer	14.3 – 15.2			B		V
0 glycol layer	10			V		

and cations with their hydration sphere. This occurs on the basal oxygen surfaces of tetrahedral units in the clay structure.

At the basal outer surfaces of the crystallites, cations are housed in the center of the coordination polyhedra whose vertices are either water molecules or oxygens from the ditrigonal cavities, or both. Surrounded by water, cations form outer-sphere complexes (OSC); combined at least in part with basal oxygens, they form inner-sphere complexes (Sposito 1984). Two parameters control their behavior: their size (ionic radius in octahedral coordination; Shannon 1976) and their hydration energy (energy necessary to release the water molecules of the complex; Burgess 1978).

The Crystal Edge Surfaces

The size of most clay mineral crystallites ranges between 10 nm and 10 μm. Such finely divided materials exhibit an enormous surface. However, the chemical properties of the outer surface of the clay crystallites are not homogeneous; they depend on their crystallographic orientation:

- basal surfaces (*001*) are not influenced by the pH conditions established by the solutions in contact with the clays;
- crystal edges (*hko*) are formed by interrupted Si-O or R²⁺-OH or R³⁺-OH bonds. As these interface sites are electrically charged, neutrality is obtained only by adsorption of ions from surrounding solutions. Negatively and positively charged sites can be found here.

Concerning the negatively charged sites, for example kaolinite exhibit two chemical functions (Fig. 1.18): silanol (Si-OH) and aluminol (Al-OH) groups which properties change according the pH of solutions (Stumm 1992):

- at low pH, aluminol groups fix H^+ protons thus yielding Al(III)- H_2O groups that are Lewis acid sites;
- at higher pH, the water molecule is replaced by an $(OH)^-$ group.

The edge of the tetrahedral layers is marked by O^{2-} ions whose available valency in a bond with Si^{4+} is compensated for by the bonding of a H^+ proton. Owing to the high valency of the Si^{4+} ion, the OH group thus formed is strongly bonded to the crystal structure and can only complex hydroxide anions; it cannot fix H^+ protons. The edge sites whose chemical properties depend on pH conditions are called “variable charges” by contrast with the “permanent charges” which depend on cation substitutions in the 2:1 layer. Both contribute to the cation exchange capacity (CEC) of the clay minerals. The relative importance of the variable charges in the overall CEC is negligible in smectites and important in kaolinite or illite.

The Electrical Field of the Outer Basal Surfaces

The (001) crystal faces, are considered to be uniformly negatively charged over their surface when ionic substitution occurs within the 2:1 layers. Thus, an electric field is locally developed. The bonding energy of the cations decreases with the distance to the electrically charged surface. If ions are considered as punctual charges (Gouy-Chapman model modified by Stern 1924), the number of cations (n^+) exponentially decreases with the distance to the charged surface (x), whereas the number of anions (n^-) increases inversely (Fig. 1.19a). If ion crowding is taken into account (accessibility to the charged surface), the Gouy-Chapman model must be modified. The distribution of ions (namely the electric potential) is no longer exponential in the area close to the surface up to a critical distance (r). The thickness of this fixed layer is the value of the ionic radius of the ion attracted by the surface charges; the critical potential (E_r) is called the “Stern potential” (Fig. 1.19b). Summarizing, from the outer clay crystallite surface, cations with their water molecule shell are numerous and organized roughly in planes (Stern layer), decreasing with distance and moving in a diffuse layer (Gouy-Chapman layer) with a progressive transition with the electrolyte (Fig. 1.19c).

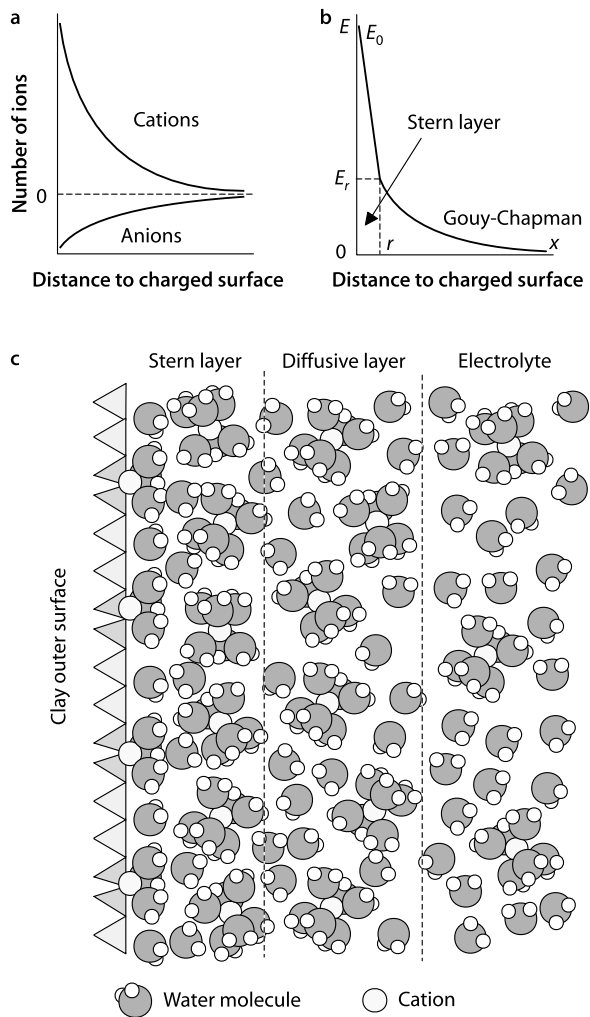
1.5.3

The Ion Exchange Capacity

The Cation Exchange Capacity (CEC)

Some clay minerals can reversibly adjust the composition of their interlayer zone as a function of that of the solution. This property is known as the cation exchange and the amount is the cation exchange capacity (CEC). It is measured by the number of positive charges held by exchanged cations expressed as milli-equivalents per 100 g (meq) or more recently in centimols per kg ($cmol\ kg^{-1}$). Cations can only be exchanged if they are weakly bonded to the external or internal surfaces (interlayer spaces) of

Fig. 1.19. The electric field at the surface of negatively charged clay particles; **a** bonding of cations and orientation of polar molecules (water). The shaded area is the equivalent of the Stern layer; **b** the number of ions decreases exponentially with the distance to the crystal surface. If ion crowding (volume) is not taken into account, their number can be considered to vary similarly (Gouy-Chapman model); **c** by contrast, if their size is taken into account, the law is no longer perfectly exponential; it becomes linear in the area close to the surface (Stern-Graham triple layer model)



crystals. The CEC reflects the charge deficiency of 2:1 layers in the case of vermiculites and smectites. Consequently, the CEC depends in a large part on the *permanent charges* of clay species. One might think that the higher the structural charges, the greater the CEC. This would mean that the CEC of micas should be greater than that of smectites or vermiculites. In reality, it is the opposite because when structural charges are too high, cations are irreversibly fixed in the interlayer space. Because of the competition between H^+ and other cations for adsorption on the exchangeable sites, the CEC is measured at pH = 7 at room temperature.

The CEC is increased by the contribution of negatively charged sites at the edges (interrupted bonds of the hko faces) of the crystallites or at the crystal defects emerging on the (001) faces (Fig. 1.20). This "external" CEC measured on kaolinite represents

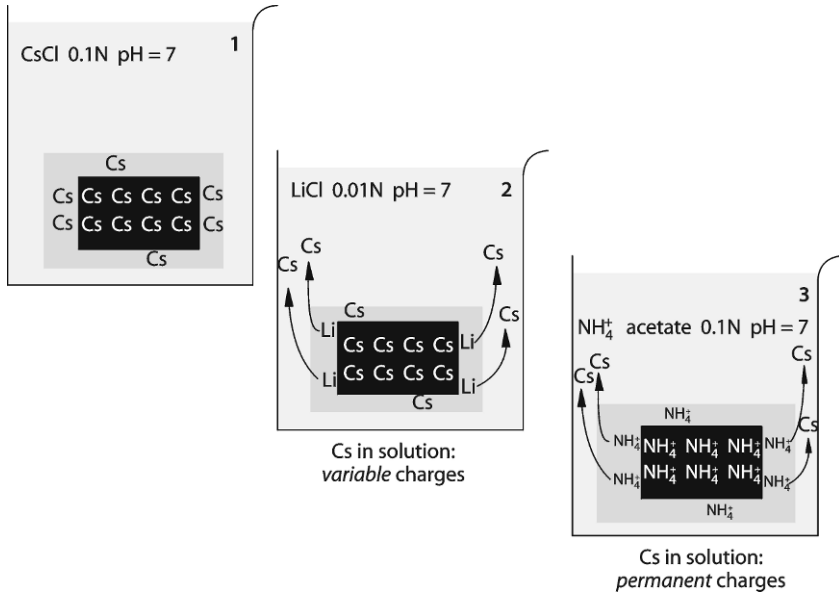
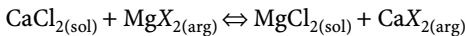


Fig. 1.20. Cation exchange controlled by variable and permanent charges

5 to 10 cmol kg⁻¹. It is a direct function of the crystal size: for a given volume or mass, the bigger the external surfaces, the smaller the crystal size. The pH dependence of the “external” CEC is greater than that of the CEC linked to the permanent charges. For that reason, these edge charges are assigned as the *variable charges* of the clay material. Representative CEC values are given for the main clay species in Table 1.3.

How does cation exchange proceed in a solution containing different cations? Theoretically, if a clay, whose negatively charged exchangeable sites (X_2) are saturated by Mg^{2+} , is dispersed in a $CaCl_2$ solution, the Ca^{2+} ions replace the Mg^{2+} ones according to the following mass law reaction (McBride 1994):



Due to non-ideal behavior of cations activity in solution and on the clay surfaces, clays show a preference or selectivity for certain ions compared to others. The selectivity relation can be expressed as:

$$K_S = \frac{f_{Ca}}{f_{Mg}}$$

The factors affecting the selectivity between cations can be a function of temperature, solution concentration, charge on the clays, site of charge on the clays and probably other factors. Hence, clay mineralogists when treating natural clay assemblages

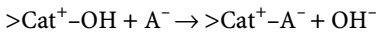
Table 1.3. Representative CEC values of the main clay species as measured at pH = 7 and 25 °C

Mineral	CEC (cmol kg ⁻¹)
Kaolinite	5 – 15
Illite	25 – 40
Vermiculite	100 – 150
Montmorillonite	80 – 120
Chlorite	5 – 15

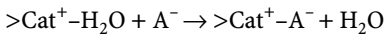
tend to use standard methods of determination, fixed solution concentrations and room temperature to determine the exchange phenomena of soil clays. Further information on the way cation selectivity operates is given in Annex 3.

The Anion Exchange Capacity (AEC)

The anion exchange capacity of clays involves the edge sites where OH groups cannot totally compensate for their valency (interrupted bonds between the structural cations and the oxygens or OH groups of the tetrahedral and octahedral sheets). At low pH conditions, the bonding of a proton to the OH groups forms a water molecule which is easily removed because weakly bonded to the structural cation. The reactions leading to the adsorption of anions in phyllosilicates can be written as follows:



or



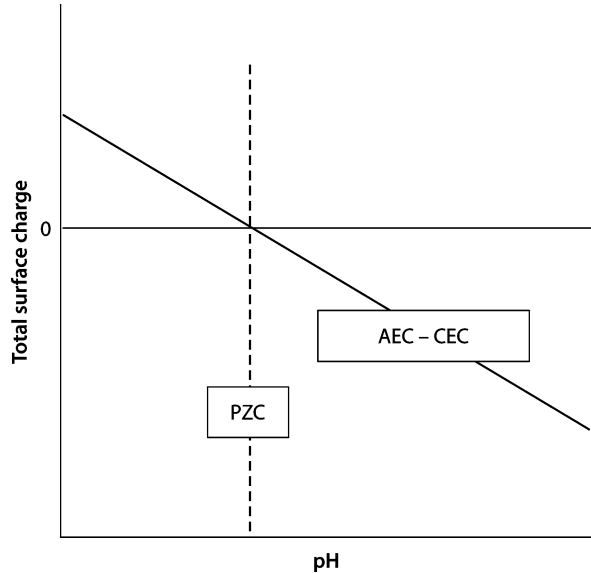
The AEC is obviously greater for minerals having a great number of interrupted bonds (allophanes and hydroxides).

Clay minerals behave similarly to amphoteric compounds. Thus, the sum AEC + CEC is zero for a specific pH, i.e. point of zero charge (PZC). At this point, the exchange capacity of the phyllosilicate internal and external surfaces is minimized. This implies that the electrostatic repulsive forces are minimized too (Fig. 1.21.). Under such conditions, clay particles get closer and flocculate.

The Variable Charges

The size of most clay mineral crystallites ranges between 10 nm and 10 μm. These very small dimensions greatly increase the contribution of edges to the overall surface. That is where the specificity of clays lies compared to the other families of minerals. In other words, per volume unit, the number of Si-O or R²⁺-OH or R³⁺-OH bonds interrupted by edges is very high (Fig. 1.18a). These interface sites are electrically charged. Neutrality is obtained only by adsorption of ions from surrounding solutions (Fig. 1.18b). Thus, in the case of kaolinites, two chemical functions appear: silanol (Si-OH) and

Fig. 1.21. Variation of anion and cation exchange capacities (*AEC* and *CEC*) versus pH. The point of zero charge (*PZC*) corresponds to the equality $AEC = CEC$



aluminol (Al-OH) groups. The properties of these groups change according to the pH of solutions (Stumm 1992):

- at low pH, aluminol groups fix H^+ protons thus yielding Al(III)- H_2O groups that are Lewis acid sites;
- at higher pH, the water molecule is replaced by a $(OH)^-$ group.

The edge of the tetrahedral layers is marked by O^{2-} ions whose available valency in a bond with Si^{4+} is compensated for by the bonding of a H^+ proton. Owing to the high valency of the Si^{4+} ion, the OH group thus formed is strongly bonded to the crystal structure and can only complex hydroxide anions; it cannot fix H^+ protons.

1.6

Particularities of Clay Minerals: Size and Continuity

1.6.1

Clay Minerals Are always Small

The Ordinary Size and Shape of Clay Minerals

It is remarkable that the silicate phases stable at the Earth's surface conditions, i.e. continents or oceanic floor, are clay minerals. Of course, they are not the unique abundant mineral species and they are largely associated with zeolites, oxides, hydroxides or carbonates. Nevertheless, if clays are found everywhere on the planet, they are specially concentrated at the interface with the atmosphere or the oceanic water. This means that they must adjust their crystal structure and their chemical composition

to very different types of environments including soils, weathered rocks, geothermal systems, diagenetic series, etc. In spite of this large crystallochemical variability, all the clay minerals have one common point: they are small! So small crystals are called “crystallites”, “tactoids” or “quasi-crystals” according to their species or to the dominating cation in the interlayer zone. For simplification here we will use uniquely the term “crystallite” for single crystal bodies and “particles” for composite ones (see definitions in Meunier et al. 2000). Most of their particular physical and chemical properties are due to their small size.

Why are they so small while in other conditions such as that typical of metamorphic or magmatic rocks, the phyllosilicates form much bigger crystals? In other words, why is the growth of clay minerals limited to few micrometers and nanometers in surface and thickness respectively?

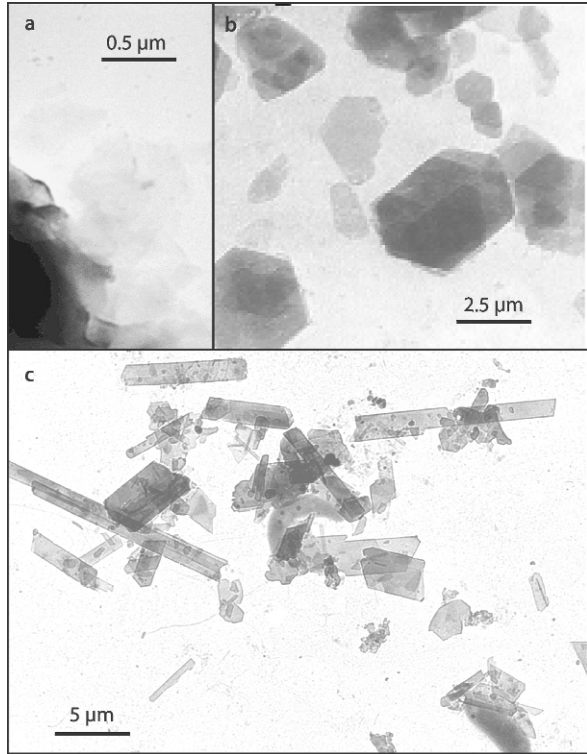
In order to attempt to answer this question we will often consider high temperature clay minerals, of diagenetic or hydrothermal origins in the discussion which follows. We assume that there is a strong parallel between these phases and those formed under conditions of lower temperature at the surface of the Earth, i.e. under conditions of weathering.

TEM Observations: The Shape of the Crystallites

Could we imagine what is, physically speaking, a montmorillonite crystallite of 1 000 nm size having 10 layers coherently stacked? It could be schematically represented by a flat cylinder which diameter is 1 000 nm and the thickness 10 to 15 nm according to the hydration state. This crystallite is incredibly thin in one direction considering its physical coherence (spatial continuity of the crystal lattice) in the two others. The cylinder outer surface area is $785 \times 10^3 \text{ nm}^2$ and 31 400 to 47 100 nm^2 for the basal and edge surface areas respectively. The edge area is 17 to 25 times lower than each outer surface. Such a particle is so thin that it is practically transparent to an electron beam. The size and shape of clay mineral crystallites vary with the clay mineral species. Montmorillonite are shapeless, small and thin (Fig. 1.22a) while kaolinite and illite crystallites are frequently euhedral (Fig. 1.22b,c) and the maximum length of their crystallites may reach 10 to 50 μm . Most often, they are thicker than the montmorillonite crystallites: 15 to several tens of layers coherently stacked. However, the thickness of phyllosilicates (size in the *c* direction) is not easy to measure because, as they are flat, the axis of observation is the *c* direction.

The mechanical resistance of the layer lattice structure has been demonstrated by Nadeau et al. (1984) who experimentally delaminated the smectite crystallites. Delamination was shown to not alter the structure of the isolated smectite layers (1 nm thick; about 1 μm in diameter) since they are able to diffract X-rays when stacked in new particles. This phenomenon was assigned to interparticle diffraction. This is why the fundamental particle concept has been proposed. In spite of the fact that the effects of the interparticle diffraction have been strongly reduced to some particular cases (Kasama et al. 2001), it remains that the smectite structure is highly resistant even if reduced to a single layer. This is confirmed by the high flexibility of a single layer. Using molecular dynamics, Sato et al. (2001) showed that the layer fractures under a stress over 0.8 GPa because, below this value, any pressure deforms the crystal lattice by modification of the Si-O-Si angle in the tetrahedral sheets. Thus, smectite crystallites

Fig. 1.22. Particle shape and size; **a** montmorillonite particles (from MX80 bentonite); **b** kaolinite crystals from diagenetic sandstones; **c** illite crystals from diagenetic sandstones



are most often less than 10 layers thick. They appear as shapeless particles which edges are frequently rolled (Fig. 1.22a).

The Surface and Thickness of Clay Crystallites through SFM and AFM Observations

If the surface, i.e. area of the (001) face, is quite easy to measure using transmission electronic microscopy (TEM), it was not possible to measure the volume of the crystallites. Indeed, the surface area and the thickness of the clay crystallites are now measurable using the atomic (AFM) or the scanning (SFM) force microscopes (see Nagy and Blum 1994 for a review of these techniques). However, most studies published recently concern clay species exhibiting frequently euhedral rather thick (several nanometers) crystallites such as illite or kaolinite (Nagy 1994; Zbik and Smart 1998). It seems that the observation of thin shapeless smectite crystallites remains difficult.

Theoretically, the surface area measurement can be performed using these microscopy techniques. A recent attempt by Bickmore et al. (2002) showed that measurements of the specific surface area (SSA) for three kaolinite standards using AFM agree to within 4% with those obtained using the adsorption of nitrogen (BET method). The measured areas vary from 10 to 90 m² g⁻¹. The AFM technique provides a very useful information which is not given by the BET method: the statistical distribution of SSA values. The distributions obtained are coherent with a log-normal law and the modes

vary from 20 to 30 m² g⁻¹ for the three specimens. Such data are fundamental for crystal growth studies.

Because of their variable hydration state, the number of layers involved in smectite crystallites varies. Using AFM, the thickness of smectite crystallites in aqueous suspensions was shown to be reduced to 1 or 2 layers while it is near 20 layers in the dehydrated state (Tournassat et al. 2003). However, whatever the crystallite thickness, the lateral surface area remains constant at 8 m² g⁻¹. The good correlation between AFM measurement and low-pressure gas adsorption results allows one to use a simple morphological parameter to calculate the particle edge-site density:

$$n_{Al} = \frac{N_{oc} \times R_{p/A}}{\rho}; \quad n_{Si} = \frac{N_T \times R_{p/A}}{\rho}$$

n_{Al} and n_{Si} : site density of aluminol and silanol edge sites respectively (mol kg⁻¹),
 $R_{p/A}$: mean perimeter vs. area ratio (m⁻¹),
 N_{oc} and N_T : site densities (mol m⁻²)
 ρ : clay density (g cm⁻³).

1.6.2

The Reduced Number of Layers in the Stacks Typical of Clay Minerals

The crystal structure of clay minerals is composed of two elements:

- layers which are stacked in the *c* direction. Each layer is formed by strong ionic-covalent bonds retaining the cations in the framework of O²⁻ and OH⁻ anions,
- an interlayer zone which can contain or not other cations.

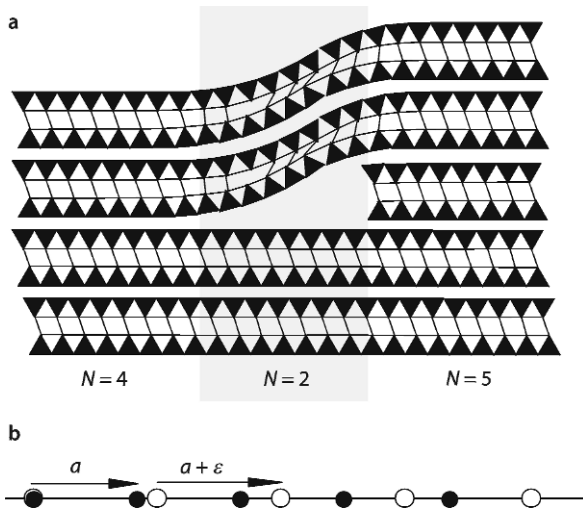
In any phyllosilicate, a layer can be described by a unit cell having a chemical composition summarized in a unit formula. The unit cell of the layer stack depends on the periodicity degree (1, 2, 3 layers or more). Thus the structural formula is a multiple of the unit formula.

Crystal defects are theoretically disruptions of the 3D periodicity. The dimension scale of the defects is that of the unit cell. Because of their specific layer organization, the crystal defects for phyllosilicates have to be considered in the *a-b* plane (1:1 or 2:1 layers) and in the *c* direction.

We have seen above that the theoretical number of layers in a crystallite of a given thickness can be calculated. This calculation ignores the crystal defects which may destroy the periodicity of the stack. The defects cannot be ignored because they contribute to chemical exchange properties and to growth processes. Thus, it is important to measure the quantity of defects in the three directions, i.e. along the *c* direction and in the *a-b* plane. This is made possible using X-ray diffraction because the higher the number of defects in a given direction, the weaker the diffracted intensity. The corresponding diffraction peaks are less intense and broader than the equivalent in a defect free lattice. The size of the coherent scattering domains is reduced.

The presence of defects in the *c* direction decreases the number of layers in the coherent scattering domains. An example is depicted in Fig. 1.23a: the layers in the left

Fig. 1.23. The crystal defects in clay minerals (from Ferrage 2004); **a** in the c direction; **b** in the a - b plane



and right parts are regularly stacked while they are deformed and not perfectly stacked in the middle one. In that case, the presence of a crystal defect reduces the size of the coherent scattering domain from 4 to 2. It is theoretically possible to calculate the number of crystal defects in the c direction by dividing the crystallite thickness (AFM) by the size of the coherent scattering domains (XRD).

Crystal defects in the a - b plane are due to non-periodic positions of atoms. Indeed, in a perfect crystal, the position of a given component is given by a translation vector \vec{a} (Fig. 1.23b). If the module is slightly modified ($a + \epsilon$), the position of atoms shifts and produces a defect after a given number of translations (Guinier 1964). This kind of defect modifies the diffraction profiles. Using a gaussian distribution of these defects, Drits and Tchoubar (1990) calculated the effects of the phase displacement on the profile of diffraction peaks. Crystal defects in the a - b plane are related to anomalies during the crystal growth or to post-growth deformation events such as irradiation by α particles (Allard et al. 1994).

1.6.3

From Order-Disorder to Crystal Defects

The clay mineral structures have been long recognized to be partially or totally disordered at the different scales. According to Brindley and Brown (1980), the order-disorder can be classified as follows:

- disorder in the cation distribution in tetrahedral, octahedral or interlayer sheets,
- disorder in the layer stacking,
- disorder in mixed-layered structures,
- lattice disorder due to finite crystal size.

Plançon (2001) reviewed the recent progress in the analysis of long- and short-range order-disorder by modelling X-ray patterns and various spectroscopy methods such as infrared, Mössbauer or EXAFS. We will focus the followings on the 2:1 type phyllosilicates in which the unit layer may have a negative charge. This charge is compensated by cations or a “brucite”-type sheet in the interlayer zone.

Layer Stacking Disorder in Polytypes

According to the periodicity along the c direction, different polytypes have been determined for each mineral species: 1M or 2M for high temperature micas, IIa, IIb for high temperature chlorites, kaolinite to dickite (Brindley et al. 1986), etc. However, screw dislocations emerge on the (001) faces indicating the presence of crystal defects in the c direction (Fig. 1.25a). Whatever the polytype, the periodicity may be interrupted by stacking faults (Nespolo 2001 and references therein). The most commonly encountered defect in clay minerals is the non-rational rotation between facing layers (stacking fault). The periodicity in the c direction which is nearly perfect for most of the high-temperature phyllosilicates while defects in the c direction are extremely frequent for the low-temperature clay minerals such as smectites. When the periodicity in the c direction is totally erased by non rational rotations between adjacent layers in a stack, the crystallites are considered to be turbostratic, a totally disordered polytype. Turbostratism is easily detected using X-ray or electron diffraction (Fig. 1.24b):

- X-ray diffraction of randomly oriented powders because it lowers the intensity of the hk bands which form broad peaks asymmetrical peaks: for example the (13; 20) peak (Reynolds 1992),
- electron diffraction on single crystallites which give circles or parts of circles instead of dots as seen in 2D methods of observation. In fact the diffraction of a crystallographic plane is a line which is deformed into a cone of diffraction as the atomic diffraction becomes less well ordered.

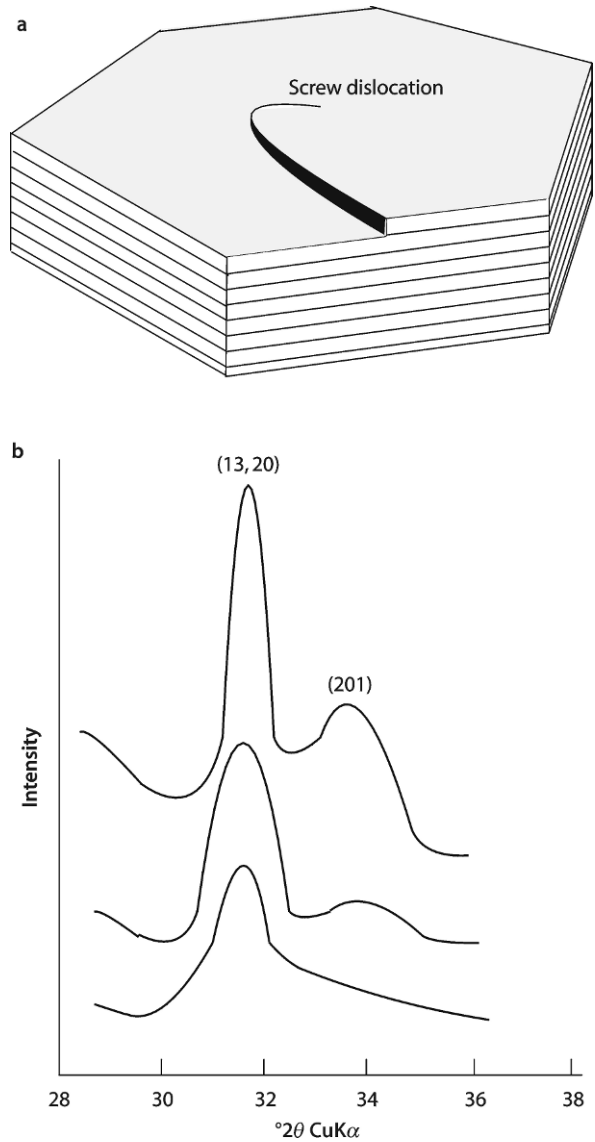
Crystal Defects in Mixed Layer Minerals

Interstratification is very common in clay minerals. The mixed-layer minerals (MLMs) are easily identified using XRD. They exhibit specific rational or non-rational series of diffraction bands, depending on their crystal structure being regular or not, respectively. In both cases, XRD patterns are significantly different from those of pure species (Brindley and Brown 1980). The most commonly encountered MLMs are illite-smectite and chlorite-smectite (I/S or C/S). MLMs exhibit frequently specific crystal defects due to partial expandability of some layers as depicted in Fig. 1.26.

Layers of Variable Thickness (Deformed Layers)

The variation of the layer thickness (d_{001}) is related to the number and the spatial organization of water molecules in the interlayer zone. Thus, this kind of crystal defect is typical of smectites. The presence of these defects is detected by the modification

Fig. 1.24. Crystal defects and disorder in phyllosilicates; **a** screw dislocation emerging on the (001) face; **b** progressive demodulation of the $(13; 20)$ diffraction bands with decreasing degree of turbostratism



of the $(00l)$ peak profiles of XRD patterns of oriented preparations. Ferrage et al. (2005, 2007) using XRD profile modelling showed the co-existence of smectite layers having contrasted hydration states: homogeneous 2 water layers (Fig. 1.26a) and variable number of water layers (Fig. 1.26b). The hydration heterogeneity is not adequately described by a random interstratification of $0W$, $1W$ and $2W$ layers but rather by domains.

Fig. 1.25. Crystal defect in an illite-smectite mixed layer mineral

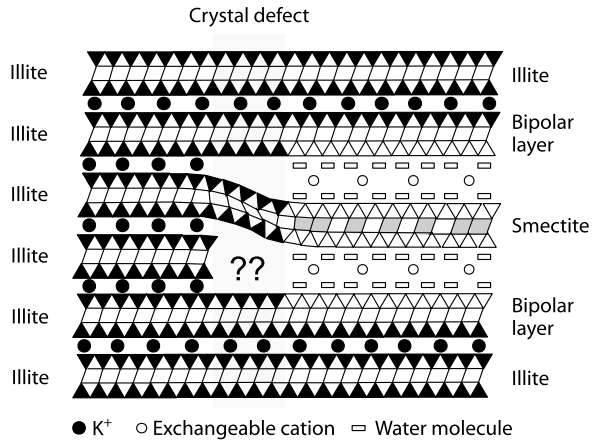
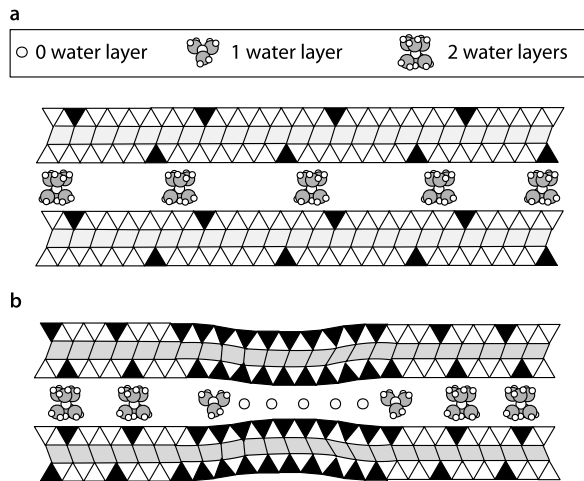


Fig. 1.26. Variation of the d_{001} thickness of smectite due to different hydration states for a given relative humidity (RH); **a** homogeneous distribution of the layer charge; **b** heterogeneous distribution (from Ferrage 2004)



1.6.4 Composition Heterogeneity at the Scale of a Single Layer

Mineralogists are ordinarily satisfied when the structural formula of the mineral under study has been established. Unfortunately, although it is a useful information for many problems, a structural formula is not more than an average composition of millions of unit cells (a smectite layer of 1 μm diameter is composed of about 1.7×10^6 unit cells). Thus, it is not adapted to describe the composition heterogeneity of the 2:1 and 1:1 layers in clays which are due to the cation distribution inside the tetrahedral, octahedral and interlayer sheets. The way to investigate the degree of order of the cation distribution is to compare the data provided by different spectroscopic analyses with theoretical simulations based on Monte Carlo simulations.

Order-Disorder in the Tetrahedral Sheet

The tetrahedral sheets in clay minerals can exhibit a variety of compositions depending on the mineral. For instance, the number of Al^{3+} for Si substitutions in the 2:1 phyllosilicate group may vary from 0 to 1 per $\text{O}_{10}(\text{OH})_2$. How are the Al^{3+} cations distributed in the tetrahedral sheets? The phenomenon of aluminum avoidance (Löwenstein's rule) is considered to control the Al-Si ordering: the Al-O-Al linkages are excluded. Such an exclusion is favored by low Al/Si ratio that is to say there is no need of long-range ordering since there is enough room in the sheet to avoid the nearest neighboring of Al tetrahedra. If, however, a long-range ordering exists, then the driving force must be found from interactions between tetrahedral sites that are not the nearest neighbors (Dove et al. 1996). Until now, the systematic study of order-disorder degree in phyllosilicates has been presented in recent papers focused on dioctahedral micas (Palin et al. 2001, 2003; Palin and Dove 2004). Of course, if the conclusions of these papers cannot be directly applied to surface clay minerals such as smectites or illite, some points are potentially interesting for these minerals:

- even in muscovite (tetrahedral sheet: Al/Si = 1/3), the probability of the existence of the unit cells with no Al for Si substitution is not equal to zero. It is clear that it should increase in illite and smectite which have lower Al for Si substitution ratios;
- in phengites (dioctahedral potassic micas in which the layer charge originates both in the tetrahedral and octahedral sheets), there are interactions between the cation distributions in tetrahedral and octahedral positions;
- simulations of a dilute Al for Si substitution system such as phengitic micas show that Al-O-Al linkages are avoided because Al^{3+} cations are dispersed. There is no requirement for long-range order.

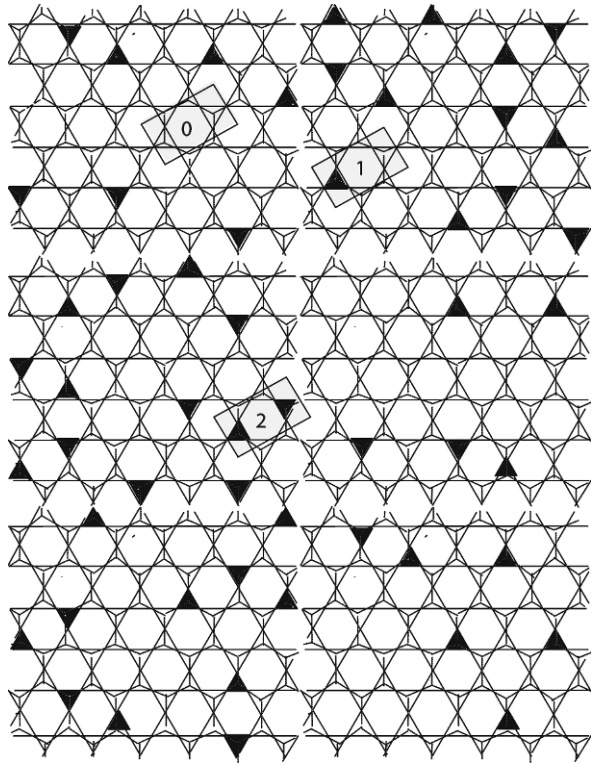
A typical Al^{3+} cation distribution in the tetrahedral sheet of phengite is given in Fig. 1.27. It theoretically allows three different sites having a unit-cell charge of 0, -1 or -2 respectively. The probability for the existence of -2 charged sites is weak.

From the above, one can extrapolate some consequences for clay minerals such as illite and smectites. Indeed, their tetrahedral structure can be similar to that of phengites (no long-range order) with less Al-substituted sites (Fig. 1.28). However, these extrapolations do not take into account the fact that higher temperature illite as well as beidellites exhibit euhedral shapes and consequently have conserved some of the mica PBCs (PCB: periodic chain bond). As the number of uncharged hexagonal cavities increases with decreasing layer charge, it is probable that the charged sites are organized along some crystallographic directions and contribute to the corresponding PBCs. This is made possible if the tetrahedral-octahedral interactions suggested for phengite exist also for illite and beidellite.

Order-Disorder in Dioctahedral Sheets

The main octahedral cations are Al^{3+} , Fe^{3+} , Mg^{2+} , Fe^{2+} , Mn^{2+} which are present only in specific occurrences. The distribution of Fe^{3+} cations in dioctahedral smectites varies from random to ordered and from ordered to segregated of two or more octahedral sites (Fig. 1.29). Such distributions have been simulated using inverse Monte Carlo

Fig. 1.27. Theoretical Al^{3+} cation distribution in the tetrahedral sheet of phengite



calculations (Cuadros et al. 1999; Sainz Diaz et al. 2001; Vantelon et al. 2001, 2003). Order is linked to the limitation of neighboring possibilities for two cations of the same element. The presence of a divalent cation in place of a trivalent one induces locally a negative charge in the octahedral sheet. Consequently, the distribution of these divalent cations controls that of the compensating cations in the interlayer zone.

Order-Disorder in the Layer Charge Distribution

The distribution of the negative electrical charges on the layer surfaces of phyllosilicates results from the combination of the tetrahedral and octahedral ones. In phengites, it is admitted that each hexagonal cavity is charged and that the charge is -1 . Thus, tetrahedral and octahedral negative charges alternate in the structure. Illites have a lower charge than mica: 0.9 instead of 1 per $\text{O}_{10}(\text{OH})_2$. Consequently, some hexagonal cavities (more or less 1 upon 10) are not charged (Meunier and Velde 2004). However, it seems that tetrahedral and octahedral charges alternate as they do in phengites. In other words, the greatest frequency is for two hexagonal sites in illite in which the charge is 0 or -1 .

In most smectites and vermiculites (specifically those formed in soil or altered rocks), the presence of different charged sites is shown by alkylammonium saturation (Lagaly and Weiss 1969). Of course, this treatment gives an average statistical

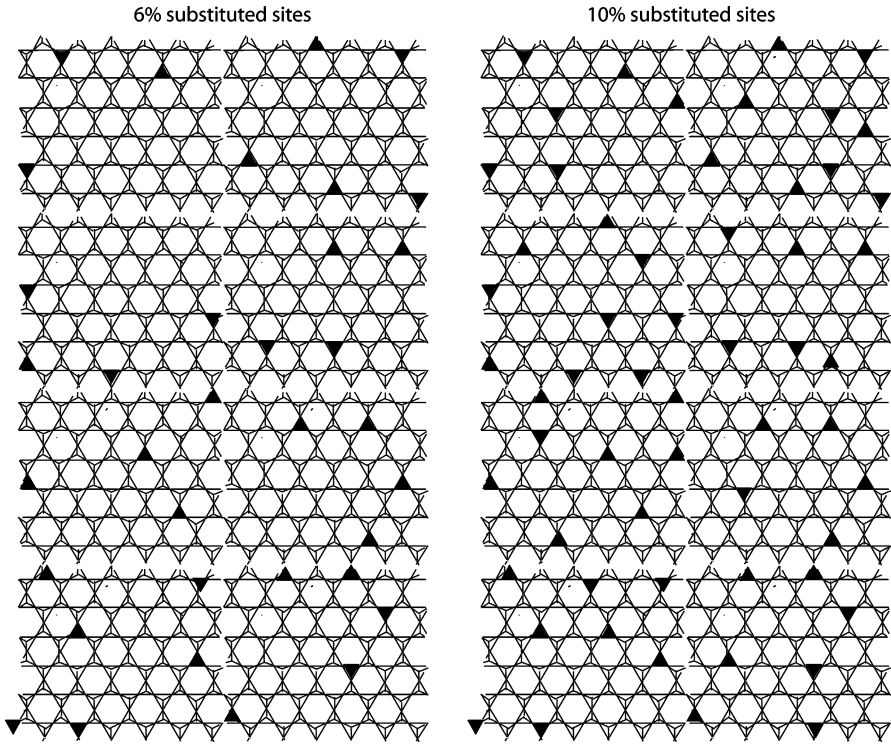
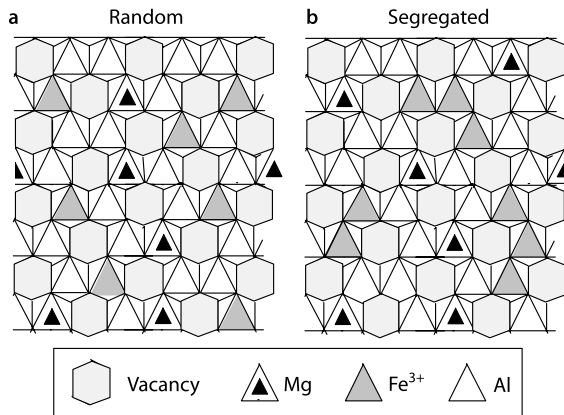


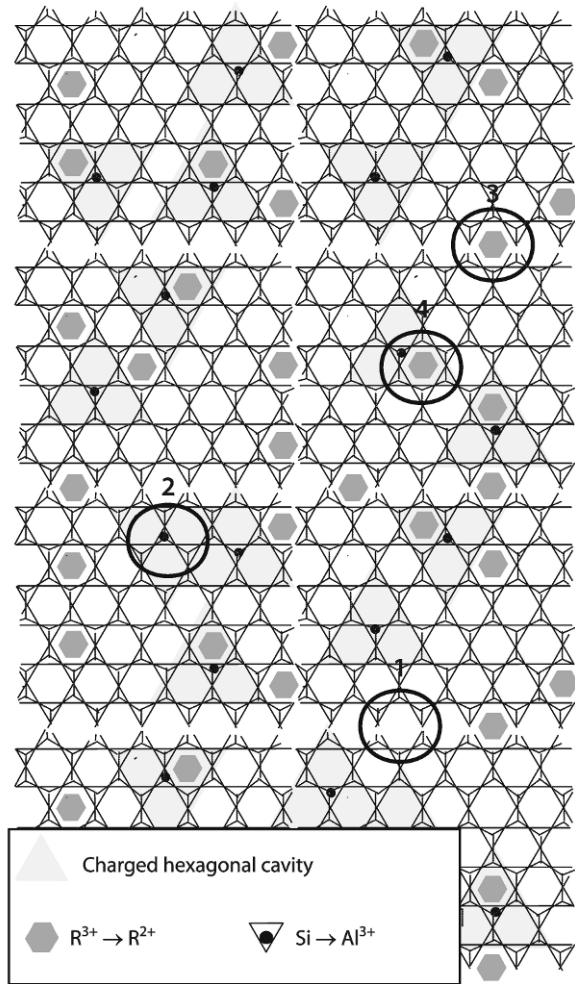
Fig. 1.28. Possible structures of the tetrahedral sheet according to different Al/Si ratios without long-range order

Fig. 1.29. Variable order-disorder degree in dioctahedral sheets of smectites (from Vantelon et al. 2003); **a** random distribution; **b** segregated distribution



analyses of charged sites in a population of particles and not at the scale of a single layer. However, we have to explain the origin of these different charges.

Fig. 1.30. Theoretical existence of four different charged sites in a dioctahedral 2:1 layer



Theoretically, according to the relative distribution of tetrahedral and octahedral ionic substitutions in a single layer, four different charged sites may exist as shown in Fig. 1.30 for a dioctahedral layer:

- 0 charge: no tetrahedral and octahedral charges,
- -1 charge originating in a R^{3+} for R^{2+} ionic substitution in the octahedral sheet,
- -1 charge originating in the R^{2+} for R^{3+} ionic substitution in the tetrahedral sheet,
- -2 addition of both ionic substitutions.

The distribution of these four sites in a single layer may vary according to a great number of patterns. Today, we are just able now to identify the presence of high and

low charge layers using X-ray diffraction of the same sample from the difference of expansion observed after several ionic saturations (Ca, K and K-Ca for example, Calarge et al. 2003).

Order–Disorder in the Interlayer Zone

Homogeneous distribution of electrical charges. Considering dioctahedral phyllosilicates, the 2:1 layers are negatively charged by heterovalent cation substitutions in the tetrahedral sheets (Al^{3+} for Si^{4+}) or in the octahedral one (R^{2+} for R^{3+}). In the mica family (muscovite, phengite), the negative charge is -1 per $\text{O}_{10}(\text{OH})_2$. These negative charges are considered to be homogeneously distributed on the surface of the 2:1 layers, i.e. -1 for each hexagonal cavity. Thus, the interlayer cations (K^+ , Na^+ , NH_4^+) are periodically distributed. Heterogeneity appears for phyllosilicates whose layer charge is lower.

Heterogeneous distribution of electrical charges. The location of the negative charge at the surface of the 2:1 layer depends on the location of the cation substitutions. Tetrahedral substitutions induce under-saturated negative valencies for the oxygen cations neighboring the Al^{3+} one. On the contrary, octahedral substitutions induce a more diffuse undersaturation of a large number of basal oxygens. Therefore, the attractive force on the interlayer cations is more intense for tetrahedral substitutions and reduces the expandability of hydrated layers (Laird 1996, 1999).

If, for simplification, one considers the negatively charged hexagonal cavities whatever the location of the negative charge in the 2:1 layer, several distribution types are theoretically possible for phyllosilicates whose layer charge is lower than that of micas: random, order, cluster (Fig. 1.31). In spite of technical difficulties to obtain a statistical representation of the distribution of the interlayer cations, it seems clear that the lower the layer charge, the higher the disorder. However, for a given layer charge, several distribution types are possible as shown in Fig. 1.31. Indeed, one can assume that the crystallite morphology is related to the order-disorder degree of interlayer cations: the low-charge smectites exhibit allomorph or lath shapes for montmorillonite and beidellite respectively.

1.7

How Do Clay Minerals Grow?

(This chapter is inspired from the following paper: Meunier (2006) Why are clay minerals small? *Clay Minerals* 41:551–566.)

1.7.1

Phyllosilicate Growth Principles

The observations above lead to the following questions: why are clay minerals always small? Why are some of them allomorph? This is obviously a matter of crystal growth processes.

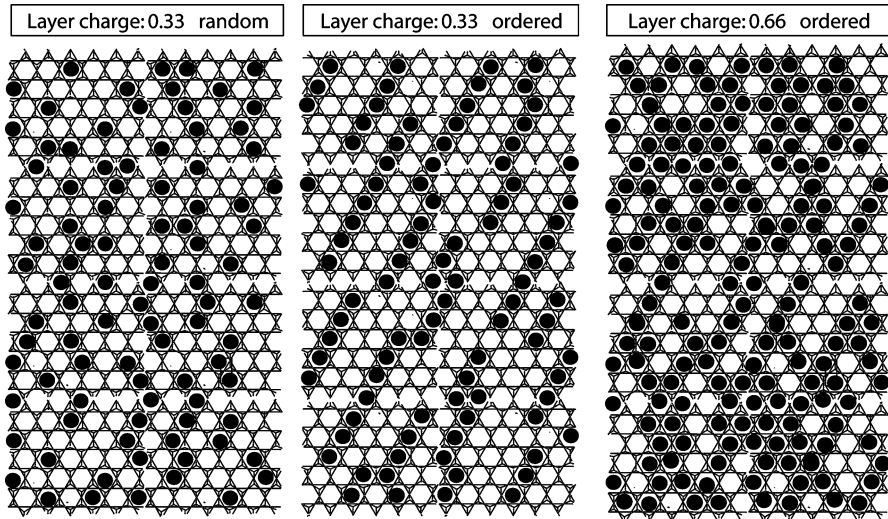


Fig. 1.31. Some possible interlayer cation distributions for different layer charges per $O_{10}(OH)_2$; a $LC = 0.33$, random distribution; b $LC = 0.33$, ordered distribution; c $LC = 0.66$, ordered distribution

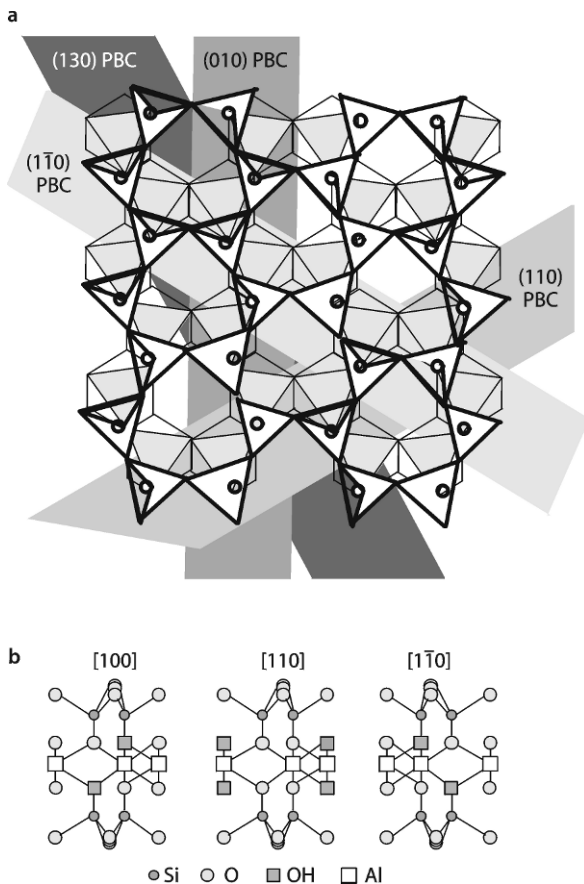
Crystal growth is approximated as the formation of strong bonds within the crystal structure (Periodic Bond Chains or PBCs). These chains must have the following characteristics:

- they must divide the crystal into stoichiometric units
- they must not have common bonds with neighboring chains
- they must not be a multiple of other chains.

The growth faces of the crystal are observed to lie parallel to one or more continuous chains of strong bonds: flat faces F (2 PBCs) stepped faces S (1 PBC); kinked faces K (0 PBC). The phyllosilicates are characterized by huge F faces in the (001) planes. The (010) , (110) and $(\bar{1}\bar{1}0)$ faces are stepped faces. According to the dissolution experiments of Bickmore et al. (2001), the (100) and (130) faces which are parallel to zigzag PBCs behave chemically as intermediate between S and K faces (Fig. 1.32a). The growth processes govern the crystal habit of the forming phyllosilicates. When euhedral, all exhibit a more or less regular pseudo-hexagonal shape from thin elongated fibres to large plates. Therefore, analysing the crystal shape may indicate how the mineral grows. Two parameters have to be taken into account: the aspect ratio (length/width) and the thickness in the c direction.

A question is evident: how are chemical elements incorporated into a growing PBC? This point is still speculative. However, the concept of “building blocks” (Fig. 1.32b) seems to be coherent with the structure of the different PBCs (White and Zelazny 1988). How these “building blocks” are formed is ignored. Assuming that they really exist, their incorporation in the PBCs of clay minerals such as illite, vermiculite or smectite

Fig. 1.32. The periodic bond chains (PBCs) in phyllosilicates (from Bickmore et al. 2001); **a** the different PBCs; **b** the “building blocks” which are assumed to be incorporated in the PBCs (modified from White and Zelazny 1988)



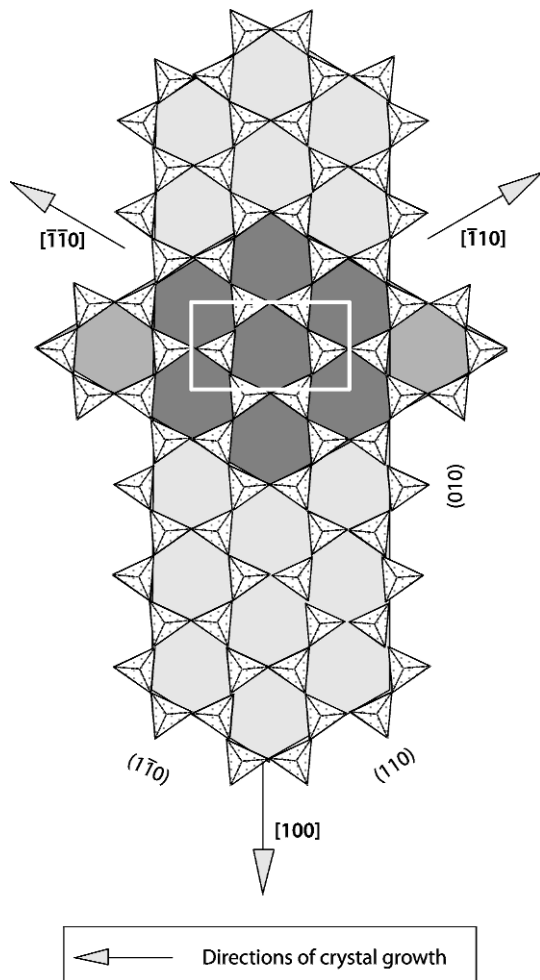
should be associated with that of the interlayer cations. Re-examining the distribution models of interlayer cations depicted in Fig. 1.31 shows that the random one cannot allow any PBC to develop. This could explain why the montmorillonite crystallites are always small and shapeless. On the contrary, interlayer cations being ordered in beidellite, vermiculite and illite, their crystallites can be euhedral. As interlayer occupancy is more dense in illite than in vermiculite or beidellite, the three types of PBCs may develop giving hexagonal shaped crystallites. When euhedral, beidellite crystallites always form elongated laths, indicating that only 1 PBC has grown.

If the physical existence of a PBC has not been proved by a direct imaging of a growing crystal using AFM for instance, it is indirectly supported by the in situ real-time dissolution experiments observations made on hectorite platelets (Bosbach et al. 2000). The authors showed that dissolution takes place exclusively at the edge surfaces while the basal ones remain unaltered. They also showed that the short edges of the hectorite laths react more quickly than the long edges. This means that the chemical attack depends on the crystal lattice directions, i.e. the orientation of the PBCs.

Considering first the aspect ratio parameter, Güven (2001) suggested that the shape of the crystallites depends on the growth rates in the $[100]$, $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$ PBC directions (Fig. 1.33). The growth rate depends on different factors: (1) ion transport to the crystal surface, (2) surface processes, (3) removal of non-incorporated elements from the crystal surface. The surface processes are complex and still under investigation. They include theoretically the following phenomena: adsorption, surface nucleation, surface diffusion, ion dehydration, cation exchange. White and Zelazny (1988) proposed a model for the growth of dioctahedral phyllosilicates considering the incorporation of “building blocks” which associate tetrahedra and octahedra in different chains along the three directions.

Two processes may control the crystal growth in the c direction: nucleation on the (001) face of the phyllosilicate, continuous incorporation of atoms or “building blocks”

Fig. 1.33. Relation between the direction of crystal growth for illite from Güven (2001)



on a spiral step originating from a screw dislocation emerging on the (001) face (see Fig. 1.5a). The first necessitates a higher degree of oversaturation in order to overcome the nucleation energy barrier. The spiral step growth is more “economic” on an energetic point of view. It has been showed first on biotite crystals (Amelinckx 1952) and related to polytype formation for phlogopites (Baronnet 1972). Later it was described in clay minerals using decoration techniques: kaolin group minerals (Sunagawa et al. 1975; Sunagawa and Koshino 1975) and illite (Inoue and Kitagawa 1994). Spiral growth steps have been observed even on high temperature elongated illite laths (Fig. 1.34).

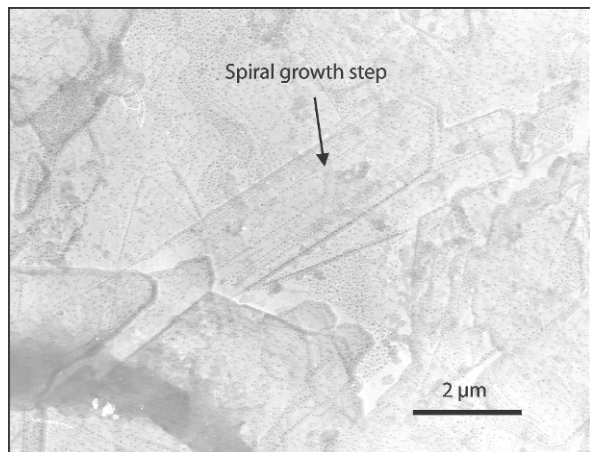
1.7.2

Speculative Interpretation of Growth Processes – Crystal Morphology Relations

The clay minerals which commonly exhibit a euhedral morphology belong typically to the kaolin and illite groups. Smectites are rarely euhedral except beidellite or nontronite in certain circumstances. On the contrary, montmorillonite is always allo-morphic. Considering these observations, we must look for the common phenomenon which may control the morphology of either 1:1 or 2:1 phyllosilicates. Obviously, we first should consider the way that layers stack in euhedral crystals and particularly, how the structure of the interlayer zone controls the stacking.

The minerals from the kaolin group do not have interlayer cations; the interlayer zone is structured by the hydrogen bonds between two adjacent 1:1 layers. The layer stacking is controlled by these electrical interactions which link the tetrahedral sheet oxygens of layer 1 to the octahedral sheet OH groups of the layer 2. Stacking disorder is due to rational rotations of $\pm 60^\circ$ between adjacent layers. Such rotations conserve the pseudo-hexagonal crystal lattice orientations, then the pseudo-hexagonal morphology (Fig. 1.35). This typical shape of kaolinite platelets is lost when formed in soils, particularly oxisols, because some of the Al^{3+} cations are substituted by Fe^{3+} ions in the octahedral sheets (Muller et al. 1995; Balan et al. 1999). The presence of Fe^{3+} cations in place of Al^{3+} enlarges the b parameter. When multiplied by a great number of

Fig. 1.34. Spiral growth steps on elongated hydrothermal illite laths (microphotograph from Inoue and Kitagawa 1994)

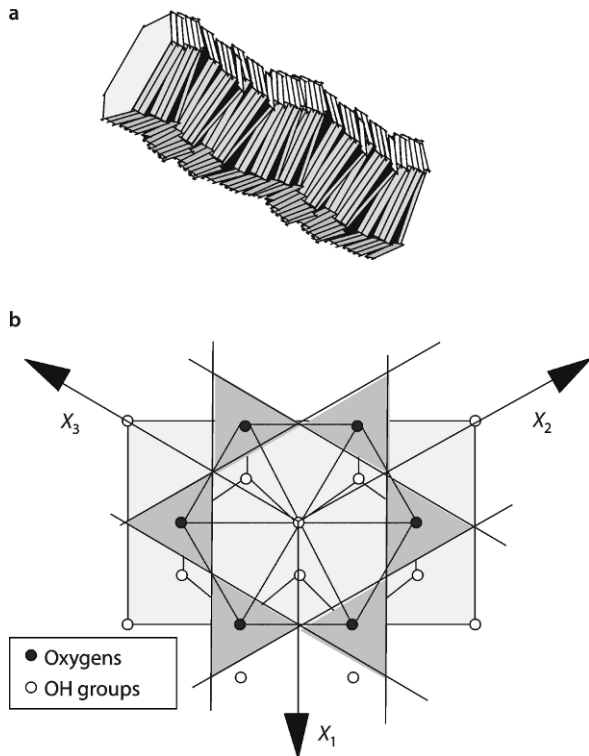


unit cells, the size difference induces the formation of crystal defects (Brindley et al. 1986) and the crystallites become shapeless (Petit and Decarreau 1990).

Illite crystals are always smaller and their morphology more variable than that of micas. Indeed, illite may be as well formed of either thin elongated laths (hairy illite) or hexagonal platelets in diagenetic conditions. What are the reasons for such differences between illite and mica in spite of the fact that their compositions are almost identical? The lattice structure of the 2:1 units in illite or mica being very similar, the cause of the contrasted morphologies should be related to the structure of the interlayer ion zone (Louks 1991; Meunier and Velde 2004). Indeed, in micas, each hexagonal cavity of the tetrahedral sheets is occupied by a monovalent cation (K^+ or Na^+). Thus, the PBCs along the three axis of symmetry $[100]$, $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$ are identical (Fig. 1.36a). Isometric shapes are favored. On the contrary, in illite and beidellite crystallites, some of the hexagonal cavities are vacant. The facing PBCs of two adjacent 2:1 layers are not linked by the monovalent cation. This could be considered as a crystal defect. Thus, the elongated lath shaped crystallite could result from the “poisoning” of certain PBCs by the accumulation of crystal defects in their direction. Indeed, “poisoning” is not only due to incorporation of impurities in a chemical meaning; it can also be due to misaligned building bodies (self-poisoning, Schilling and Frenkel 2004).

According to Güven (2001), the growth direction is along the $[100]$ direction for lath shaped illites (Fig. 1.36b). It is supposed that beidellites grow in a similar way, but

Fig. 1.35. The pseudo-hexagonal morphology of kaolinite crystallites is conserved in spite of disorder in the layer stacking; **a** typical kaolinite crystallite in diagenetic environment (“booklet” morphology); **b** the rational rotations



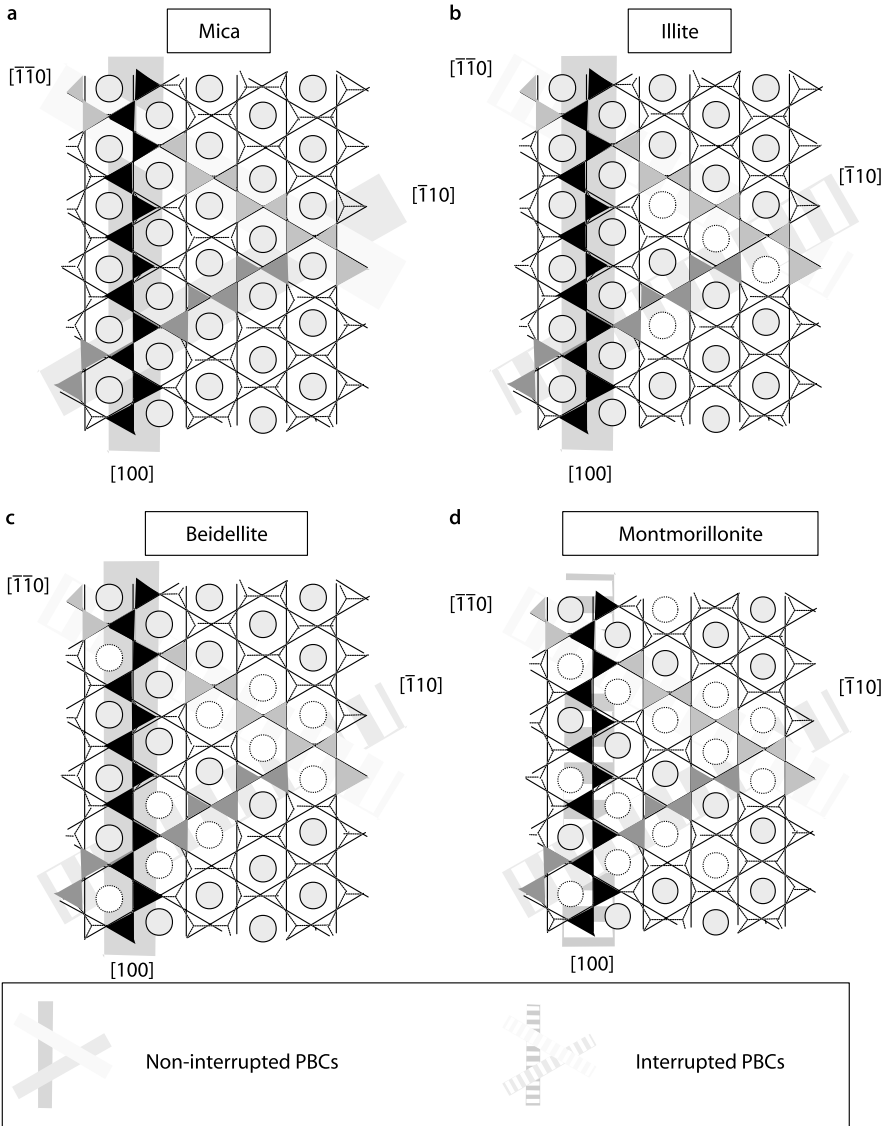


Fig. 1.36. Possible relation between the crystal morphology and the structure of the interlayer zone; **a** mica; **b** illite; **c** beidellite; **d** montmorillonite

the vacancies being more numerous, the poisoning effect is higher and crystallites smaller (Fig. 1.36c). If these vacancies are randomly distributed, the poisoning effect should be identical whatever the direction. Consequently, the crystallites must be shapeless (Fig. 1.36d).

1.7.3 Nucleation Processes in Clay-Bearing Rocks

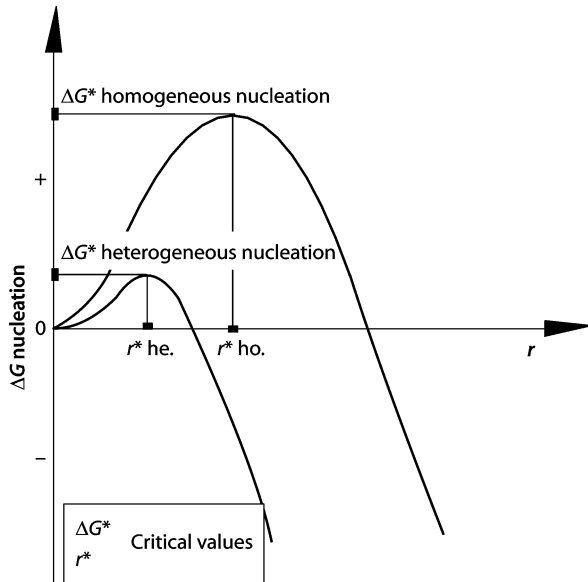
The Energy Barrier for Nucleation

The environments where clays form typically produce fine-grained rocks. In other words, the clay-rich zones, even monomineralic are composed of a great number of crystallites instead of a few big crystals. This simple observation leads one to suspect that nucleation is favored over growth. Indeed, while crystal growth is limited by the presence of crystal defects, nucleation is accelerated by the catalytic effects of the surfaces of the pre-existing solids. Two ways are offered according to the degree of solution oversaturation: homogeneous or heterogeneous nucleation. Homogeneous nucleation happens when the oversaturation degree necessary to overcome the energy barrier is abruptly reached. Then, nuclei form directly in the solution. On the contrary, if the solution oversaturates slowly, then the nuclei form on the surfaces of pre-existing solids. They form first on the emerging crystal defects which furnish locally an excess of energy. This process is less energy consuming since the energy barrier is lower than that of the homogeneous nucleation (Fig. 1.37).

The heterogeneous nucleation is particularly obvious in clay-free rocks when submitted to alteration or diagenesis. For example, illite fibres are commonly observed growing on quartz or detrital mica surfaces in reservoir sandstones formed under diagenetic conditions. Sometimes they grow on pre-existing diagenetic clay minerals such as kaolinite or dickite (Lanson et al. 2002).

The heterogeneous nucleation of metal-bearing phyllosilicates has been experimentally reproduced on different pre-existing solids: trioctahedral Co-clay on quartz

Fig. 1.37. The energy barrier for homogeneous and heterogeneous nucleation



(Manceau et al. 1999), Zn-phyllsilicate on the edges of hectorite (Schlegel et al. 2001), Ni-phyllsilicate on the outer (001) faces of montmorillonite (Rainer et al. 2002). It is deduced from these experiments that

- nucleation begins by the formation of a hydroxide on which silica is adsorbed.
- the outer surfaces of non-phyllsilicate minerals (quartz) may catalyse the nucleation of phyllsilicates,
- the edges as well as the (001) layer surfaces of pre-existing phyllsilicates may catalyse the nucleation.

A similar process has been observed in the formation of the clay minerals from altered pyroxene or amphibole. Using HRTEM, Eggleton and Boland (1982) showed how silicate layers are formed from chain silicates (Fig. 1.38). The structural continuity between the lattices of the host and neofomed crystals suggests that the dissolving silica chains catalyse the formation of the 2:1 layers. Such an autocatalytic process has been shown in mineral pseudomorphosis (Putnis 2002).

Basics of Nucleation-Growth Processes

In any nucleation-growth process occurring in a closed system, the oversaturation ratio of the solution decreases with increasing amounts of crystals (Baronnet 2003). Several steps can be distinguished from the germination to the spiral growth stage (Fig. 1.39). For phyllsilicates (including clay minerals), two growth processes have to be considered:

- the largest crystal faces being oriented parallel to the (001) planes, i.e. so-called basal faces, they are laterally developed by incorporation of “building blocks” along the PBCs emerging on the (hko) faces,
- the formation of a layer stack is related to “island growth” or “spiral growth” processes according to the oversaturation degree of the solution.

Clay mineral crystals are small (basal face dimensions lower than $1\ \mu\text{m}$) and have a reduced thickness (number of layers in the stack). That classical observations have a double consequence: (1) the incorporation of “building blocks” in the PBCs is limited; (2) the “island growth” or the “spiral growth” processes are stopped quickly after the germination stage. The causes could be of three origins: quick decrease of the oversaturation ratio, poisoning of growth sites, prohibitive energetic cost.

Solution Oversaturation Ratio in Natural Environments

In weathering processes meteoric water is introduced in soils or rocks through fracture networks whose aperture is large enough to allow gravity flowing. Then, capillary forces push water in smaller pores. Water diffuses inside all the voids until the rock or soil matrices are totally impregnated. It is obvious that the ion concentration in solutions flowing in the large fractures is weak because the solutions are continuously diluted by rainwater. Consequently, they cannot satisfy the conditions for nucleation and crystal growth of clay minerals but rather for their dissolution. We will see

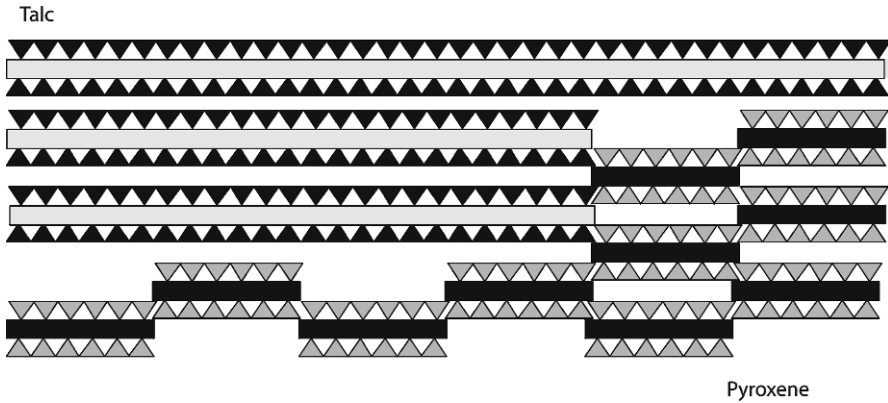
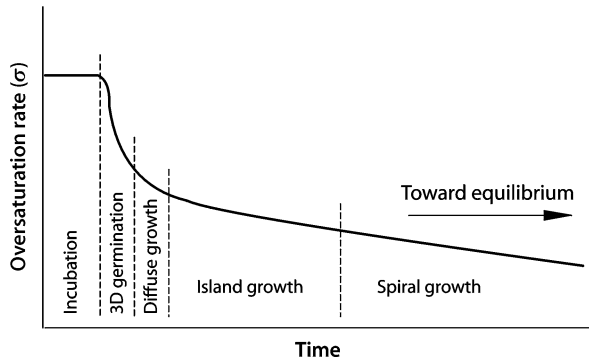


Fig. 1.38. Growth of talc or smectite in the altered zones of an enstatite (after Eggleton and Boland 1982). This type of transformation is said topotactic because the crystal lattice of pyroxene is in structural continuity with those of its alteration products

Fig. 1.39. Evolution of the oversaturation ratio of the solution in a closed system with associated growth processes (Baronnet 2003)



further (Chap. 4) that these particular conditions explain the monophase composition of the fracture wall coatings (cutans). Because their residence time is much longer in capillary pores than in large fractures, the solutions are more concentrated. They approach the chemical equilibrium with the more soluble pre-existing mineral phases they are in contact with. They can be locally oversaturated with respect to some secondary mineral phases.

Because chemical alteration weakens the mechanical resistance, the structure of the weathered rocks changes with time. Gravity movements modify the structure: new fractures are opened, and minerals previously in contact are separated. The porosity and permeability are severely modified. These physical modifications change the local composition of the solutions and interrupt the mineral reactions. These processes are accelerated in soils where the biological processes are active. Compared to other geological processes, weathering and pedogenesis do not offer thermodynamical conditions stable during periods of time long enough to produce large sized secondary minerals.

Growth Site Poisoning

The growth of a crystal can be inhibited by two different poisoning effects: (1) adsorption on growth sites of foreign ions or molecules which cannot be incorporated in the crystal lattice; (2) increase of the density of crystal defects which breaks the 3D periodicity (self-poisoning). The growth of clay minerals, particularly in natural environments, is affected by these two effects. Soils solutions contain many different dissolved species and organics which can be adsorbed on the clay crystal surfaces. The (*hko*) faces are specifically concerned because of the presence of unsatisfied chemical bonds (Tournassat et al. 2003).

Energetic Cost of Crystal Defects

The question then is why are numerous small size clay crystals formed in soils or weathered rocks instead of a few big ones? Logically, the answer should be: because nucleation, particularly heterogeneous nucleation, consumes less energy than does crystal growth. In this field of speculation, a possible reason could be that the growth of clay minerals is made difficult because of the presence of crystal defects. The energy necessary for the growth of defectuous crystals is too high especially in low temperature conditions. The energy barrier may be overcome in high temperature-pressure conditions. Nakasawa et al. (1992) synthesized giant montmorillonite crystals in high energy experiments where coesite and kyanite have been formed.

The question is: does a ripening process similar to that described in diagenetic series (Eberl et al. 2002) can contribute to crystal size increase in soils and weathered rocks? As far as we know, this point has not been documented until now probably because of two reasons: (1) most of soil clay fractions are polyphased; (2) it is very difficult to separate authigenic from inherited crystals. However, a ripening process of clay minerals, if existing, has certainly very reduced effects at low temperature conditions. The biggest particles observed using TEM are frequently polycrystalline. They result from a coalescence process.

1.8

Summary: Clay Minerals in Soils and Weathered Rocks

1.8.1

The 2:1 Clay Structure and Its Importance in Soils

Our considerations here are focused upon phyllosilicates (silica, alumina-containing minerals) with a 2:1 structure. There are several reasons for this choice. First, phyllosilicates represent the great majority of minerals in most clay size fractions (<2 μm in diameter). However, in some soils they are in a minority or not present at all. In fact roughly two cases exist when 2:1 clay minerals are not present: those where the soils are dominated by sand (quartz) materials and hence largely infertile and those where the soil fine fraction minerals are only oxyhydroxides and kaolinite (1:1 Al-Si phyllosilicate). This last case represents the last stages of intense weathering and one where soils are also largely infertile. The kaolinite-hydroxyl oxide stage with kaolinite, gibbsite (aluminum hydroxide) and iron oxide and hydroxides are found in cli-

mates of intense rainfall which have drained all of the fertile elements from the surface horizon. Plants can subsist under such circumstances but they form a sort of closed system living upon itself at the surface of the alteration profile, such as in the tropical rain forests.

The major part of our interest here is then focused upon the 2:1 minerals because they form fertile soils. They are the matrix of plant-soil interaction. They respond to changes in vegetation and create the necessary qualities for soil fertility. Soil structure (aggregation and capillary retention of water) are largely dominated by 2:1 clay mineral interaction with organic matter. Cation exchange and retention (concerning essential elements for plant growth) are dominated by these clay minerals and the organic matter present in the soils. These scientific facts have been understood with the implantation of agricultural communities on soils containing 2:1 minerals for the last 6 000 years, at least in the European experience. Agricultural man has developed and selected the soil properties best suited to the growing and reaping of crops necessary for his subsistence and development. In the great civilizations of the temperate climates it has been possible to use gramine-derived plants to give sustenance and growth to human activity. This has been largely due to the capacity of the clay minerals in soils to respond to the needs of these plant regimes. The key to soil fertility in the context of grain crops is found in the behavior of 2:1 clay minerals.

We will give a short summary of clay mineral species or types using a non-conventional approach, up until now, but one designed to, we hope, be functional. Clay can be classified as being of fixed crystallographic dimension under surface conditions or of variable dimensions. The possibility to change the dimension of a clay particle is normally called expandability, referring to the change in dimension in one direction, along the *c* axis. Fixed dimension 2:1 clays are illite, or chlorite – soil vermiculite hydroxy-interlayered type.

1.8.2

The Illitic Minerals in Soils and Weathered Rocks

It is important to note initially that no Na or Ca micas are known to form below 250 °C. Low temperature micas and mica-like minerals (illite) are potassic. Mica and illite are 2:1 structures where ionic substitutions create a charge imbalance of near one negative charge for a unit cell, usually near 0.9 charges for illite. The charge is compensated by potassium or perhaps in soil clays to a certain extent by ammonium, NH_4^+ ions. The unit cell thickness perpendicular to the sheet (*c* dimension) is very near 10 Å, 10.0 Å for potassium ions and 10.2 Å for ammonium ions. Glycol saturation does not change the basal spacing of the mineral. The potassium present is an anhydrous cation held between the 10 Å structural units due to a relatively high charge on the structure.

Ordinarily one can assume that mica can be distinguished from illite by considering the 10 Å peak profile: mica shows a very sharp, symmetric peak (peak width of less than $0.3^\circ 2\theta \text{ CuK}\alpha$) which is more narrow than the asymmetric illite peak. However, such a qualitative criterion is not sufficient to compare or differentiate between high temperature and soil illite since more accurate tools are available to interpret XRD patterns. The decomposition procedure (Lanson 1997) is particularly efficient when used to compare series of samples or series of cation saturation states for a given

sample. Each elementary band is characterized by three parameters: position, intensity and full width at half intensity (*FWHM*). This procedure was used to show that three “phases” are easily distinguishable in what is usually attributed to an “illite peak” (see the review in Meunier and Velde 2004).

If we consider the illite that forms at temperatures above those of the surface (weathering), in diagenetic or high temperature (compared to soils) materials, the major components of “illitic” minerals are:

- ordered illite/smectite mixed layer minerals (I/S MLMs) of high illite content (usually more than 80%): partly expandable where the position of the peak changes to higher *d* spacings after ethylene glycol solvation and forms a strong peak at slightly less than 10 Å.
- poorly crystallized illite (PCI): the slightly broad peak ($<1^\circ 2\theta$) at about 10.2–10.4 Å does not change position after glycol treatment. The X-ray scattering domains size (CSDS) which can be deduced from the peak width is low (less than 8 layers: $FWHM > 0.4^\circ 2\theta \text{ CuK}\alpha$),
- well crystallized illite (WCI): the 10 Å peak is sharp indicating that the CSDS is high (more than 10 layers: $0.2 < FWHM < 0.4^\circ 2\theta \text{ CuK}\alpha$).

Differing proportions of these peaks, especially the PCI and WCI change the shape of the illite overall peak to a large extent. These definitions of phases are based upon data for higher temperature materials than found in soils and surface alteration processes.

Using these designations, it is possible to establish the criteria which can be used to separate the different contributions to the intensity of the classical “illite” peak. In most cases a soil illite peak is composed of the two illite “phases” or diffraction peaks: PCI and WCI (Fig. 1.40a). Soil and alteration clay illite minerals appear to have a great similarity in their X-ray diffraction characteristics compared to their higher temperature counter part illite.

It is generally assumed, and probably true that the 10 Å material is concentrated in the more coarser fractions of the clay mineral assemblages. Figure 1.41 indicates an example of clay assemblage by size fraction, coarse (2–0.2 μm) and whole clay.

In this example one sees that illite is very abundant as is kaolinite in the coarse clay fraction. This illustrates a typically held idea of illite. It is assumed to be a fine grained muscovite or diagenetic illite compared to the finer, more smectite-rich clay minerals.

However, it has also been observed in a number of soil clay assemblages (Velde 2001) that the relative intensity of the PCI and WCI band can increase compared to the MLMs after low concentration K-saturation (0.01 M KCl solutions) of clay fractions (Fig. 1.42). The width of the WCI peak after KCl treatment is slightly above that of large crystal material ($0.3^\circ 2\theta \text{ CuK}\alpha$) which would indicate a smaller CSDS. This implies that the relative quantity of the illitic phase increased but the CSDS remains lower than that which could be attributed to a detrital mica. The formation of a phase with illite behavior using XRD methods seems to be possible on material after treatment with a relatively low concentration potassium solution. This is important in that current fertilizer treatment in most agricultural areas will tend to favor the formation of such

Fig. 1.40. Definition of the illitic components using the decomposition procedure (Lanson 1997). *WCI*: well crystallized illite; *PCI*: poorly crystallized illite; *I/S*: illite-rich ordered illite-smectite mixed layers; *S/I*: smectite-rich randomly ordered illite-smectite mixed layer

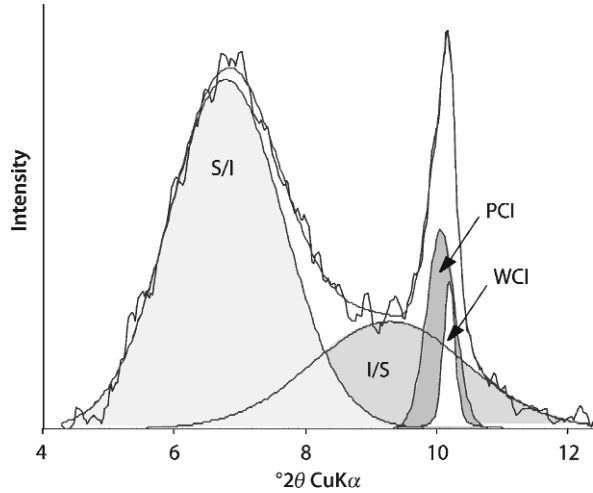


Fig. 1.41. Iowa size sequence (data courtesy of D Laird, NSTL Ames Ia); **a** coarse clay fraction; **b** whole clay

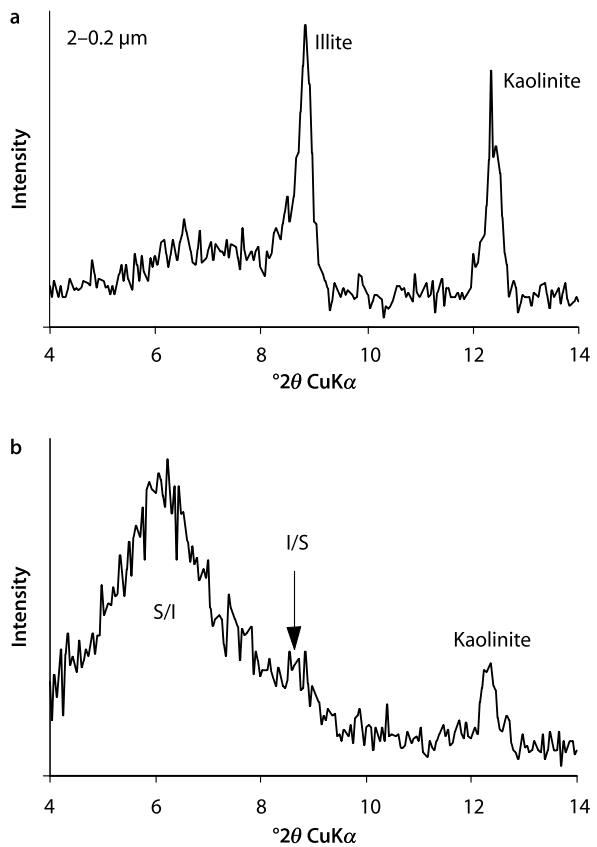
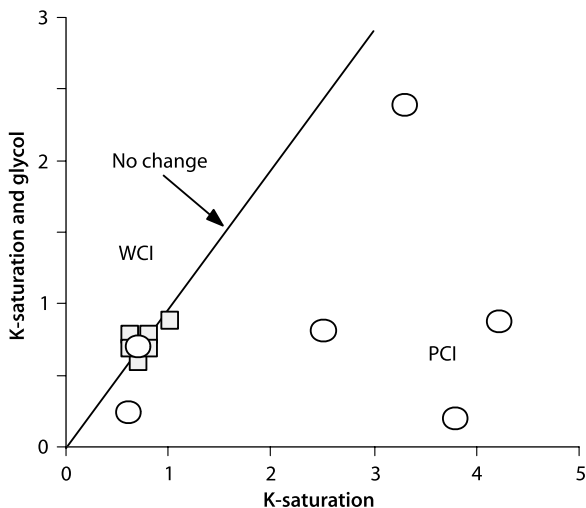


Fig. 1.42. Proportion of PCI and WCI compared to kaolinite for KCl treated samples before and after glycol treatment



illite particles, i.e. minerals with anhydrous potassium ions between the 10 Å layers. Thus the phase which has a 10 Å interlayer spacing can be increased in a soil clay assemblage, and probably decreased under soil conditions of plant growth or alteration. If in fact one extracts the exchanged potassium, the illite then becomes a smectite.

Thus in soils, some of the 10 Å layers can contain hydrated ions such as Ca, Mg, Na or anhydrous potassium. Using X-ray diffraction identification methods and classical mineral definitions, one can follow the “transformation” of smectite into illite by low intensity potassium treatment. However, in many instances a portion of the new “illite”, essentially the PCI component, is affected by glycol saturation, i.e. it expands whereas it is anhydrous under normal atmospheric conditions. This suggests that a portion of soil illite, especially PCI has exchangeable or at least more loosely bound potassium present. These relations are shown for six prairie agricultural soils reported by Velde (2001). In Fig. 1.42, peak intensities of PCI at near 10.3–10.5 Å and WCI at 10 Å, were ratioed to kaolinite which is unaffected by glycol treatment. Here peaks not changed by glycol treatment will have a constant ratio. Points on the diagonal line in the figure show no effect upon glycol treatment, which is the case for WCI. However, many PCI peaks lose intensity relative to kaolinite suggesting that some expand upon glycol treatment. As some of the WCI peak intensity was enhanced upon potassium treatment, some of this new “illite” becomes stable 10 Å material, while in a portion of the PCI material the anhydrous potassium layer can be opened to glycol, a stronger polar molecule.

This demonstration indicates that the material in soils which might be called illite using standard operating procedures, Sr-saturation and glycol treatment for example, does not totally characterize what is normally called illite formed at higher temperatures. However, strong extraction of interlayer ions with concentrated solutions of exchange ions will not resolve the problem either. What one is interested, in fact, is the state of the clay mineral in the soil or alteration zone where it occurs and functions. If a clay mineral can behave at times as a closed layer illite, and at others as an

open layer smectite, this is a problem of nomenclature. We will discuss this problem, of illite identification, as well as that of the identification of other common clay minerals found in alteration zones, throughout the book and hope to conclude (Chap. 8) summing up the observations and comments made throughout the literature.

1.8.3

Expandable Minerals (Smectites – Vermiculites)

In natural soil and alteration materials one finds minerals which initially contain hydrated cations, such as Ca, Na, Mg and K. It is assumed that these minerals can have a range in charge from near 0.2 to 0.8. The high charge range (0.6–0.75) is called vermiculite. These high charge minerals tend to form a non-hydrated cation layer when high concentrations of potassium are present, for the most part in the laboratory. Thus vermiculites form a type of illite (anhydrous potassium, non-expandable behavior), under laboratory treatments. Cations in lower charge smectites, on the other hand, remain hydrated under room temperature conditions and a large range of humidity conditions. The potassium and especially sodium cations will lose one water hydration layer under conditions of low humidity and higher temperature. The normal peak position for smectites is 15.2 Å. In X-ray patterns of soil smectites which are most often mixed layered to a certain extent, peaks are normally rather large, greater than $1^\circ 2\theta$ and frequently near $2^\circ 2\theta$ $\text{CuK}\alpha$. The water molecules structured around the interlayer cations can be removed either by heating or reducing the partial pressure of water in the atmosphere. The normal state for divalent hydrated cations is two water layers and hence the 15.2 Å state. These minerals expand further upon their exposition to polar organic ions such as glycerol or ethylene glycol. However, heterogeneous hydration states can occur (Ferrage et al. 2005).

One finds expandable minerals of both di- and trioctahedral occupancy in soils but the dioctahedral type is by far the more predominant. Trioctahedral smectites are almost exclusively magnesian which means a very special chemical environment in a soil. For the most part soils and alteration profiles are dominated by aluminum which produces dioctahedral minerals.

A very typical case for smectites is to form an interlayered (MLM) mineral with non expanding layers, or structures with a basal spacing less than 15.2 Å in the air dried state. In a great number of smectite-bearing soils, the smectite is in fact interlayered. Further, it is typical to find two types of MLM phases present, one smectite-rich (S/I) and another illite-rich (I/S). These minerals co-exist and can be distinguished under Sr-treated (0.01 M SrCl solutions) and air-dried conditions by X-ray diffraction. Both minerals are disordered in stacking type (see Righi et al. 1995) which means that they both expand to near 17 Å with glycol treatment. Thus it is necessary to observe soil clay minerals under air-dried hydration conditions in order to distinguish the two MLM types. Wetting-drying cycles due to season alternation modify the expansion properties of smectites in soils. The stacking order for a montmorillonite increases after saturation with K^+ ions and several wetting-drying cycles (Mamy and Gautier 1976; Eberl et al. 1986). Besides, clay particles experience rearrangements during the drying period. The extraction of water tends to reorganize the crystallites according to face-face contacts rather than edge-face contacts (Tessier 1984). The pore walls become thicker.

Since the two MLMs have wide peaks, near $1.5\text{--}2^\circ 2\theta$ $\text{CuK}\alpha$, it is necessary to decompose the spectra in order to distinguish the peak position of each component, especially the I/S mineral which is almost always overlooked in visual identification of clay minerals. The problem is illustrated in Fig. 1.40. Overlooking the I/S mineral means that a significant portion of the clay assemblage is lost to observation.

1.8.4

Hydroxy Interlayered Minerals (HIMs)

Pedogenic HI-Chlorite, HIV and HIS: Different Minerals or Different Compositions for the Same Mineral Species?

Hydroxy-interlayered minerals are described by Barnishel and Bertsch (1989) along with aluminous chlorites. They are considered to be a transitory step in the chlorite to smectite transition. These authors designate HIS and HIV types based upon apparent layer charge. Most authors since these definitions were established follow the nomenclature and genetic approach to the stability of HI minerals. HIS and HIV minerals do not change spacing upon K-saturation at 25°C (Barnishel and Bertsch 1989, p. 748), but they do change basal spacing upon heating above 300°C . Vermiculites (Douglas 1989) are high charge smectites which expand in the Mg-saturated state under glycol saturation and which close to 10 \AA upon potassium treatment at 25°C . Peak positions in the hydrated divalent cation state are above 14.5 \AA (Ildefonse et al. 1979). Dioctahedral soil chlorites would be aluminous 2:1 minerals which do not close their interlayer spacing upon heating to 300°C whereas other hydroxyl interlayer minerals do (April et al. 1986). In order for the mineral to be considered a chlorite, the 14 \AA peak should be of equal or lower intensity than the 7 \AA peak according to the XRD calculation criteria of the NEWMOD program of Reynolds (1985). These descriptions and interpretation follow, more or less, those proposed by Jackson (1964a, p. 259) except for the genetic relations. In fact Jackson proposes some reversibility in the evolution of HI minerals, called pedogenic intergrade minerals. As we will see in further chapters this view seems to be more fully substantiated than the unique transitional concept of more recent authors. However, data presented by authors in more recent papers indicate that a significant amount of 14.2 \AA non-expanding minerals (Mg and glycol saturation) collapses to 10 \AA at 25°C . This suggests a vermiculitic behavior for some HI minerals.

Therefore, there are four mineral behavior groups which have the following characteristics, as summarized from published X-ray diffraction data:

1. 14.2 \AA narrow peak, stable under exchange treatments and glycol saturation. Stable under heating to 300°C . This is a *soil chlorite*.
2. 14.5 \AA or greater peak, near $1^\circ 2\theta$ $\text{CuK}\alpha$ FWHM, expanding upon Mg and glycol saturation with collapse to 10 \AA upon K treatment at 25°C . This is a *vermiculite*, high charge smectite.
3. 14.2 \AA peak, $1^\circ 2\theta$ $\text{CuK}\alpha$ FWHM, no expansion upon Mg and glycol treatment, collapse to 10 \AA on K-saturation at 25°C . This is a *HI exchangeable mineral*.
4. 14.2 \AA peak near $1^\circ 2\theta$ $\text{CuK}\alpha$ FWHM, no expansion or collapse with CEC treatments at 25°C but collapse toward 10 \AA upon heating to 300°C . This is a *HI non-exchangeable mineral*.

Table 1.4. Typical d_{001} values (in Å) for HI minerals in different saturation and temperature states

	Air dried (Sr, Ca, Mg)	Glycol	K-saturation	Heated (300 °C)
Al-chlorite	14.2	14.2	14.2	14.2
Vermiculite	>14.5	16	10	10
Smectite	15.2	17	10	10
HI exchangeable (HIS)	14.2	15	12	10 – 11
HI non-exchangeable (HIV)	14.2	14.2	14.2	12 – 13

The identification criteria for the different HI minerals are presented in Table 1.4.

The difference between these different 2:1 minerals is the interlayer ion occupancy and its stability under conditions of CEC treatment and heating. Basically the different behaviors under laboratory testing are due to the occupancy of interlayer positions by different types of aluminum ion complexes. If no or few Al ions are present the minerals behave as smectites, either low or high charge. If Al ions are present in an exchangeable form we have HI exchangeable. If Al ions are present with a high proportion of Al-OH polymer we have HI non-exchangeable. If Al is present in a completely structured Al-OH polymer we have a dioctahedral aluminous soil chlorite.

HI minerals and vermiculite then have peaks near 14.2 Å or slightly more and are relatively narrow (about 1° 2θ CuK α). Smectites (lower charge minerals) have a peak at 15.2 Å air dried state and are wide, $>1.5^\circ$ 2θ CuK α . HI minerals as well as smectites (vermiculite and lower charge expanding minerals) have high intensity 001 and 003 peaks and very low intensity peaks for the other orders (see Annex 4). Thus peak position, peak width and peak intensity can be used to identify the different mineral types. Potassium treatment distinguishes the vermiculitic behavior with exchangeable Al-hydroxyl ions of the HIS minerals. The progressive but incomplete collapse of the HIV crystal structure toward 10 Å after K-saturation and progressive heating has been shown by Barnishel and Bertsch (1989, p. 7.47; Fig. 1.43a). The presence of the interlayer polymers causes a partial to total reduction in the CEC of these minerals, as they are themselves large, though immobile, cations (Fig. 1.43b). Additionally, they cause a loss of the expansible nature of the original clays. The resistance either to swelling or to collapse is attributed to the presence of “gibbsite” islands in the interlayer zone (see Annex 4).

These distinctions are not just of use for mineralogists but they also indicate the behavior of the clays in soil systems with respect to exchange ion types and potentials. These aspects are especially important for plant growth in a soil context.

Aluminous and Dioctahedral Soil Chlorites (2:1:1 Minerals)

Soil chlorites are HI minerals with a well ordered, more than 60% interlayer of gibbsite present. They have significant $00l$ peaks in diffractograms. The intensity of the peaks near 7 Å is greater than those at 14 Å.

The classical scheme for Al-chlorites to be formed is that the positively charged Al-polymer replaces progressively the exchangeable cations in the interlayer zone.

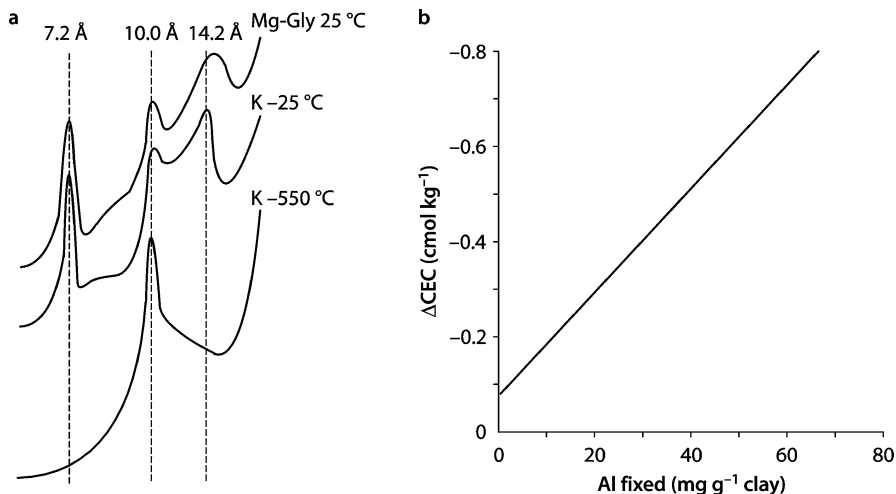


Fig. 1.43. HI mineral characteristics; **a** XRD patterns: HIV does not expand or collapse at room temperature even after Mg- or K-saturation respectively. These minerals partially collapse toward 10 Å after K-saturation and heating to 550 °C (from Barnishel and Bertsch 1989); **b** lowering of the CEC with increasing amounts of Al cations (from Dixon and Jackson 1962)

Thus, the remaining CEC decreases from HIS to HIV and finally to Al chlorites in which the polymers may form an incomplete “gibbsitic” layer. Although structurally these minerals are rather like chlorites, the main difference is that the interlayer space is not completely filled by the interlayer hydroxide polymer. The presence of these interlayer polymers causes a partial to total reduction in the CEC of these minerals, as they are themselves large, though immobile, cations (Fig. 1.43b). Additionally, they cause a loss of the expandable nature of the original clays (Table 1.4). The resistance either to swelling or to collapse is attributed to the presence of “gibbsite” islands in the interlayer zone.

The Problems in the Classical Explanation of HI Mineral Formation in Soils

The presence of HI minerals is critical to an understanding of the genesis and stability of 2:1:1 minerals. The following is a rather new departure in the interpretation of the origin and significance of these minerals. Hydroxy-interlayered minerals have been identified in soils, predominantly in alfisols and ultisols (see the pioneer works of Jackson 1964a,b). These minerals are considered to adsorb Al hydroxy polymers in the interlayer region. Due to the difficulties in identification these minerals present, many of the reported occurrences are in question. There is little doubt, however, that these minerals exist in some soils, and that they form through the polymerization of Al-hydroxides in the interlayer. Further it is well known that acid soil clays have high Al exchange ion occupancies (Black 1968, p. 284 for example)

However, in spite of the fact that HI minerals are frequently encountered in moderately acidic soils, their crystallochemical characteristics are still poorly known. Indeed, the detailed description given by Barnishel and Bertsch (1989) in their review paper does not respect the fundamentals of any crystal structure, i.e. the electrical

neutrality and the distribution of chemical elements in a 3D space coherent with X-ray diffraction data. The problem of electrical neutrality is detailed in Annex 4. To be consistent with chemical composition data (variation of the OH/Al ratio between 2.5 and 2.9), water molecules should replace OH groups in the Al-polymers. The CEC versus fixed Al curve should be reconsidered in the light of the polymerization degree.

Whatever the unit cell formula is, it clearly indicates that a continuous gibbsite-like layer cannot be formed in HIV or HIS because its positive charge become negligible when the polymer covers hundreds of unit cells. This confirms the presence of “Al islands” linked to water molecules in the interlayer zone (see Annex 4). However, in the present case, the unit cell formula is no more than an average composition including different layer types. Indeed, the shift of the d_{001} value from 17 to 14.2 Å militates for a mixed layer model rather than for a solid-solution one.

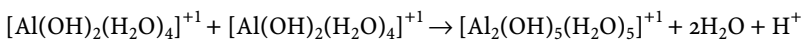
Al Ion Adsorption and Polymerization Processes

Any coherent model aiming to explain the structure and the formation of the interlayer zone of HIV and HIS must take into account two parameters: (1) the aluminum polymers in the interlayer zone must compensate the negative charge of the 2:1 layer; (2) whatever the aluminum speciation in the solution, each Al ion in the interlayer zone prefers to be in a hexacoordination state (octahedron). Indeed, even if the dominant aluminum speciation in solution is a complex structure of 13 Al ions (Al_{13}), it is not adsorbed in that state because of size incompatibility with the measured 14.2 Å for the HIV d_{001} . Besides, there is no evidence of the presence of tetrahedrally coordinated Al inside the interlayer zone. Consequently, when adsorbed, Al cations must be in the following state: $[Al_n(OH)_x(H_2O)_y]^{(3n-x)+}$. Whatever the value taken by n, the size of the polymer must not exceed that of the “gibbsite” layer thickness: 4.7 Å.

Two phenomena have to be considered in the formation of HIV or HIS minerals:

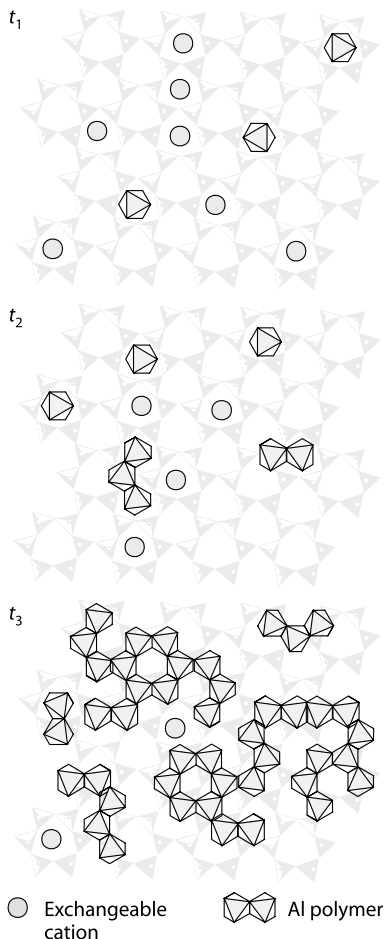
- *the incorporation of Al ions in the interlayer zone*: whatever the polymer state in solution, the incorporation is controlled by a cation exchange mechanism,
- *the polymerization of the adsorbed Al ions in the interlayer sheet of HIV or HIS minerals*: because the 2:1 layer has a given negative charge, the polymerization occurs at a constant positive interlayer charge

Considering for simplification that aluminum ions are adsorbed as: $[Al(OH)_2(H_2O)_4]^{+1}$ monomers, the first step is their exchange of alkali cations in the interlayer (t_1 in Fig. 1.44). The exchange ratio depends on the activity of Al ions in the solution and the selectivity of the vermiculite or smectite layer inner surfaces for Al versus alkali ions. In a second step (t_2 in Fig. 1.44), the adsorption of additional Al ions from the solution depends on the state of polymerization inside the interlayer. Indeed, the polymer having to compensate the local negative charge, this means that compensation required several Al ions. The polymerization reaction should be:



How polymerization physically proceeds inside the interlayer zone remains unknown until now. It is probably controlled by processes similar to that of the crystal

Fig. 1.44. Schematic representation of the Al ion adsorption and polymerization in the interlayer zone of vermiculite or smectite. For simplification, Al ions are considered to be adsorbed in a monomer state. t_1 : the amount of adsorbed Al ions is controlled by the cation exchange capacity. t_2 : additional Al ions can be adsorbed proportionally to the polymerization degree. t_3 : almost all the alkali exchangeable cations are replaced by Al polymers which form chains or rings in the interlayer zone



growth on (001) faces (migration of ions on the surface, formation of strong chemical bonds, rejection of impurities). At the end of the process (step 3), almost all the exchangeable alkali cations are replaced by Al-polymers which form rings or chains in the interlayer zone (t_3 in Fig. 1.44). By coalescence, these rings and chains build a discontinuous gibbsite-like structure (dioctahedral layer). At the end of the process, whatever the degree of polymerization is, the gibbsite-like structure must conserve a positive charge which compensates the negative charge of the 2:1 layer.

New Interpretations of the Interlayer Structure of HIV and HIS

HIMs can be considered as randomly ordered HI-chlorite/smectite mixed layered minerals (see Fig. A4.6 in Annex 4). Their expandability depends on the proportions of “chlorite-like” layers in the stacking. This explains why the d_{001} values of HIMs vary from 17 to 14.2 Å and 14.2 to 10 Å in the ethylene glycol solvated and heated to 300 °C

states respectively. From that point of view, HIV and HIS should no more be considered as different mineral species but only as different compositions of the HI-chlorite/smectite mixed layered minerals. Details are given in Annex 4.

1.8.5

Mixed Layer Minerals in Soils

Specificity of Soil MLMs

One of the most striking characteristics of clays found in alteration sequences and soils is their frequent “intermediate” behavior. Neither a pure 14.2 Å nor a pure 15.2 Å type and not a 10 Å type for example. This is called a mixed layer behavior, one where it appears that different proportions of one of two, or perhaps more, responses to laboratory treatments is revealed by X-ray diffraction techniques. This type of behavior is most common in 2:1 minerals, except in some rare cases between 1:1 (kaolinite) and 2:1 expanding minerals (see Sect. 1.8.6). Mixed layering has been interpreted as a form of phase change between illite and smectites in diagenetic sequences (Hower and Mowatt 1966 for example). In these circumstances smectites transform under the influence of temperature and at times chemical influence to form illite. Mixed layering has been interpreted in this sense, i.e. phase change, in soils as well, especially when mica is seen to be unstable forming clay minerals in soils (see Jackson 1964a,b or Millot 1964 for example). However, in alteration and soil profiles one can find a reaction sequence and its reverse in going from bottom of the alterite material to soils. Hence it is not all that clear whether the mineral change is sequential and irreversible due to mineral instability such as the transformation of a high temperature mineral into one stable at Earth surface conditions or one due to more transient changes in surface chemistry.

The interlayering behavior indicates that the different 2:1 layers in a given structure are not all of the same charge or charge site (tetrahedral or octahedral). In rare cases, notably the alteration of biotite, the high temperature ferrous mica, a regular alternance of behavior is observed. This gives rise to a combined structural unit (super structure) which can be seen in X-ray diffraction spectra. For example in the air-dried state one finds a 25 Å peak, which is the combination of a mica (biotite)/smectite alternance. Most mixed layer 2:1 minerals show a peak at an intermediate position from the end members under hydrated cation, air dried conditions. Identification of these phases can be done using the methods described by Moore and Reynolds (1997) and in Sect. 1.2.2 in many cases.

If we consider the definitions given above (smectites, illite, HIM), it is clear that the mixed layer mineral identified will depend upon the relative attraction of the different types of layers in a crystallite for ambient cations, hydrated, non-hydrated (K) and hydroxyl (Al). It is to be expected that laboratory treatment, chemical extraction and saturation with other cations, will change the initial state of the clay minerals. Their X-ray diffraction characteristics will then depend upon the chemical treatments that they have undergone and as a result the mineral name given will depend upon laboratory treatments. For example, an expandable, high charge clay mineral, vermiculite, in a soil will become an illite upon potassium saturation which could occur during the agricultural cycle or normal growing cycle of prairie plants under temperate climates. In order to better understand the function of clays in soils we feel that it is wise

to use minimum treatments in observing and determining the clays mineral species present. The extraction of ions by chemical treatment with bivalent cation exchange should be the basis of identification. Air dried states under Ca- or Sr-saturation are highly stable in the two water layer hydration state. A peak at 15.2 Å is adequate to identify an expandable mineral (smectitic behavior).

A New Interpretation of Soil and Alteration 2:1 Clay Minerals

As seen above, a certain portion of the different phases called smectites, illite or HIM (hydroxy-interlayered or “soil vermiculite”) can be changed, as far as their X-ray diffraction characteristics are concerned into another mineral type. Smectites treated with low concentration ionic solutions of KCl can form some illite, either PCI or WCI types. The same treatment on HI minerals forms some illite, and so forth. Further, most smectites are inter layered types, MLMs, with another type of layer element, usually of fixed dimension (non-exchangeable ions present). This strongly suggests, upon reflection, that the behavior of 2:1 minerals is variable and that the material present is heterogeneous. Not only is there a mixture of mineral types but one of types with variable behaviors. The controlling factor for such behavior giving characteristic X-ray diffraction responses is layer charge. Bauer et al. (2006) indicate that there is a variation in layer charge in bentonite materials, and that this layer charge can be changed under chemical influence (concentrated KOH solution at 80 °C) by internal ionic migration creating new charge sites in the structure without re-crystallization. We believe that such a model can be used to explain the variations in clay mineralogy in surface alteration deposits. If a given crystallite is subject to chemical forces which induce internal ionic migration, it could be expected to be internally heterogeneous and would behave as a composite material, mixed layered mineral. Variable and changing layer charge will give equivocal responses to laboratory treatments. Surface clay minerals should be considered as a grouping of different crystallites with variable charges on different layers. The ambient chemistry of aqueous solutions will determine whether Al ions enter into a structure forming HI mineral behavior, or in the case of potassium availability forming illite type minerals. The high charge layers will tend to attract either Al ions or K ions, while the lower charge layers will select divalent ions such as Ca and Mg. If one keeps this concept in mind, one can more easily explain some of the more difficult results reported in the literature and above all those to come to light as one works more and more with decomposition methods on surface clay minerals.

It should be kept in mind that such mineral structures and chemical types are probably not stable under conditions of higher temperature and hence these mineral treatments and nomenclature are not valid for diagenetic or hydrothermal clay mineral species.

1.8.6

Kaolinite and Kaolinite/Smectite Mixed Layer Minerals (K/S)

Kaolinite Crystals

Kaolinite is the most common non 2:1 mineral in soils. This mineral has a 1:1 structure, with one silica tetrahedral layer with an aluminum-hydroxyl layer coordinated

to it. Kaolinite is not chemically reactive and tends to be found in high proportion in very evolved soils. In such situations it is accompanied by iron oxides and oxy-hydroxides. However, kaolinite can also be found in the very early stages of clay mineral formation where high temperature minerals are transformed under hydration.

When formed in Earth surface conditions, kaolinite is frequently slightly Fe substituted. (Delineau et al. 1994; Gaite et al. 1997 among others). A complete solid solution domain has been observed between the $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ and $\text{Si}_2\text{Al}_{1.4}\text{Fe}_{0.6}\text{O}_5(\text{OH})_4$ end-members (Iriarte et al. 2005). The presence of Fe^{3+} in the octahedral sheet increases the b parameter. This is a source of crystal defects due to the misfit between the Al-Al and Al-Fe unite cells. That explains why, most often, the substituted crystals are small and shapeless in soils or weathered rocks.

Kaolinite/Smectite Mixed Layered Minerals (K/S MLMs)

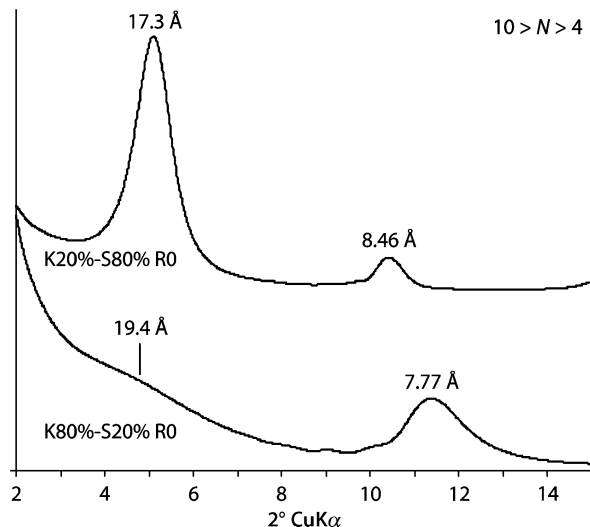
These minerals have been described in different sedimentary or pedogenetic environments (Hughes et al. 1993). Their chemical composition is highly variable since the smectite component can be beidellite or montmorillonite (see review in Meunier 2005). These minerals are certainly more common in soils or weathered rocks than thought. Indeed, they can be easily confused with smectites/illite MLMs. An easier way to detect them is to check the d_{002} position: if it is lower than 8.50 Å, K/S MLMs are likely to be present (Fig. 1.45). This is probably the case for vertisols in which unusual high smectite d_{001} have been measured (up to 18 to 20 Å after ethylene glycol saturation).

1.8.7

Allophane and Imogolite

Allophane and imogolite are minerals whose crystal structure is ordered over short distances (small size of X-ray diffraction coherent domains). Their characteristics are

Fig. 1.45. Typical XRD patterns of kaolinite/smectite mixed layer minerals calculated using NEWMOD software (Reynolds 1985); **a** randomly ordered K/S MLM 80% smectite-20% kaolinite; **b** randomly ordered K/S MLM 20% smectite-80% kaolinite

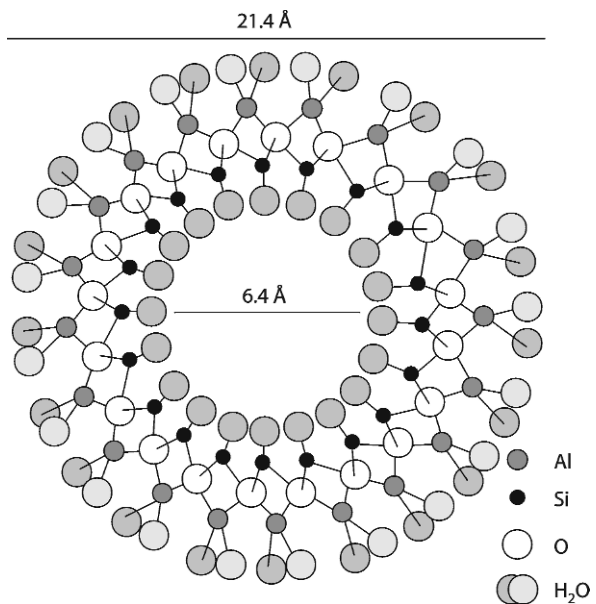


summarized in Table 1.5. Allophane is practically undeterminable using X-ray diffraction. On the contrary imogolite presents some broad diffraction peaks. Both minerals are currently detected in soils using a combination of infrared spectroscopy, thermal and chemical analyses. Even if still debated, the short range “crystalline” structures of these minerals have been approximated (Cradwick et al. 1992; Wada 1989). Figure 1.46 schematically represents the section of an imogolite tube.

Table 1.5. Some characteristics of allophane and imogolite which are short range order crystalline substances typical of soils formed on glassy rocks

	Allophane	Imogolite
Discovery	1816 STROMEYER	1962 YOSHINAGA and AOMINE
Particle morphology in soils	Rounded, 10–30 nm	Smooth and curved threadlike (μm)
Origin	Andisols	Andisols spodic horizons
“Crystalline” morphology	Spheres, diameter 35–50 Å	Tubes, diameter 6.4 Å and 21.4 Å
Chemical composition	$\text{Al}_2\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	$\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$
CEC (pH 7)	10–135 cmol kg^{-1}	17 cmol kg^{-1}
AEC (pH 4.0)	5–30 cmol kg^{-1}	40 cmol kg^{-1}
Surface area	700–900 $\text{m}^2 \text{g}^{-1}$	900–1 100 $\text{m}^2 \text{g}^{-1}$

Fig. 1.46. Crystal structure of imogolite (after Cradwick et al. 1972)



Imogolite and allophane are typical of soils formed on glassy rocks in various types of climates (andisols). The nearly constant moisture content of andisols maintains the stability of these minerals. Under drying conditions these minerals become unstable and rapidly transform into halloysite. They form complex associations with organic matter in the humic horizons of these soils. The preferential complexation of Al by humic compounds may inhibit the formation of allophane. Imogolite has been identified in spodosols where its formation is related to the degradation of the Al-organic matter complexes.

The ion exchange capacity of imogolite and allophane is not constant because the surface electric charges are controlled by the pH and ion concentration of solutions. The CEC (cations) increases whereas the AEC (anions) decreases when pH varies from 4 to 8:

- pH = 4: the CEC is almost zero, the AEC is close to 20 cmol kg⁻¹;
- pH = 8: the CEC is close to 30 cmol kg⁻¹, the AEC tends towards zero.

1.8.8

The Non-Phyllosilicate Minerals in Soils and Weathered Rocks

Recall that the <2 μm fraction of soils is formed of fine debris of pre-existing minerals (quartz, micas, feldspars, ...), clays and neoformed or inherited oxides, sulfides, sulfates, zeolites, etc. All these mineral phases have been extensively described in the SSSA Book Series in 1989 and 2002. We shall present here only two groups of minerals:

- the most widespread one is Fe-oxides and hydroxides, which are currently associated with clay minerals in soils or weathered rocks. Aluminum hydroxides are commonly encountered in deeply weathered rocks in tropical countries;
- zeolites which are equivalent to clays in some environments.

Oxides and Hydroxides

Oxy-hydroxides, mostly of iron, are very common but rarely form a significant portion of the soil fraction except in cases of very intense weathering. They tend to be associated with heavy metals and transition metals and are hence very important in considering problems of pollution by these materials. For instance, the high capacity of heavy metal retention has been extensively studied for Mn-hydroxides.

Fe-oxy-hydroxides. Different species of Fe-oxides and hydroxides are formed in weathering or soils reflecting the moisture, pH, Eh and microbial activity conditions. The Fe³⁺ cation is framed in different oxide or hydroxide crystal structures:

- the most important oxides are hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃) or magnetite (Fe₃O₄),
- the hydroxides are goethite (α -FeOOH), lepidocrocite (γ -FeOOH) and ferrihydrite (Fe₂O₃·2FeOOH·2.6H₂O).

These minerals become the dominating phases in the weathering ultimate step because of their low solubility in the Earth's surface conditions. They form thick indurated horizons in the intertropical zone (laterite). However, they are present in all the weathering process including the initial steps where they are associated with different types of clay minerals. They have a great importance in the distribution of iron since after oxidation, Fe^{3+} ions expelled from the silicate structures spontaneously form oxides or hydroxides. Scheinost and Schwertmann (1999) shown that the color of oxides, hydroxides and hydroxy sulfates is determinative for that of soils (Table 1.6).

Al-oxy-hydroxides. In soils and weathered rocks, aluminum may form different hydroxides, the most abundant being gibbsite (α -alumina trihydrate: $\text{Al}(\text{OH})_3$) while its polymorphs bayerite and nordstrandite are much rarer. Boehmite (α - AlOOH) is common in bauxite deposits but less common in soils. The aluminum oxides and hydroxides have a non-distinctive grayish-white color, which is easily masked in soils except when large concentrations occur. These minerals form platelets in which the (001) faces are considerably more developed than the (hko) ones. This is due to the fact that the Al-OH-Al bonds in the *a-b* plane (layer) are much stronger than the hydrogen ones between layers in the *c* direction. Consequently, the gibbsite morphology looks like that of clay minerals. For this reason, it was called "hydrargillite". Aluminum hydroxides may accumulate in the most weathered rock levels in tropical countries forming bauxite deposits. As do Fe-hydroxides, gibbsite may form also in the earliest steps of the weathering process. thus, this phase is competing with clay minerals for aluminum ions. We will not consider these minerals in detail in this work. For detailed descriptions see the review papers of Schwertmann and Taylor (1989) and Hsu (1989) for Fe and Al oxyhydroxides respectively.

Mn-oxy-hydroxides. Manganese oxide minerals have a black color. They show even a greater tendency than iron oxides to occur in concretions. Manganese-rich micromorphological zones in peds that are black, often also contain large amounts of iron oxides. The main mineral species are pyrolusite (MnO_2), birnessite ($\text{Na,Ca,K,Mg,Mn}^{2+}$) $\text{Mn}_6^{4+}\text{O}_{14} \cdot \text{H}_2\text{O}$, lithiophorite ($\text{LiAl}_2\text{Mn}^{2+}\text{Mn}_2^{4+}\text{O}_9 \cdot 3\text{H}_2\text{O}$), and hollandite ($\text{BaMn}_8\text{O}_{16}$).

Table 1.6. Color of Fe oxides and hydrosulfates (simplified from Scheinost and Schwertmann 1999)

Fe oxide	Most frequent color	Formula
Hematite	Moderate reddish brown	$\alpha\text{-Fe}_2\text{O}_3$
Goethite	Strong yellowish brown	$\alpha\text{-FeOOH}$
Lepidocrocite	Moderate orange	$\gamma\text{-FeOOH}$
Ferrihydrite	Brownish orange	$\text{Fe}_3\text{HO}_8 \cdot 4\text{H}_2\text{O}$
Akaganeite	Strong brown	$\beta\text{-FeOOH}$
Schwertmannite	Dark orange yellow	$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$
Feroxyhite	Strong brown	$\delta\text{-FeOOH}$
Maghermite	Dark yellowish brown	$\gamma\text{-Fe}_2\text{O}_3$
Jarosite	Grayish yellow	$\text{MFe}_3(\text{OH})_6(\text{SO}_4)_2$

Zeolites

Zeolites are tectosilicates (similar in structure to feldspars, hydrated by OH ions) which present a high cation exchange capacity. Their presence in soils was first suspected by their unusually high CEC (Schultz et al. 1964). It is not always easy to know if zeolites in soils have been neofomed or inherited from altered volcanics or aeolian inputs. It is now established that in soils where high pH conditions are durably established, these minerals can form. Whatever the silica and alumina sources, i. e; volcanic glass or smectites, zeolites form in sodic salted soils (Franckart and Herbillon 1970; Gibson et al. 1983). For this reason we will not discuss their properties. However, when present they can play a very important role in soil chemical properties.

1.8.9

Stability of Clay Minerals Formed under Weathering Conditions

The physical conditions of weathering are limited in pressure and temperature compared to the overall range found in the geological experience. When clays are displaced from their regions of origin, sedimentation and eventual burial, they begin to experience different physical and to a certain extent chemical constraints. Initially, as sediments are buried, the ratio of water to solids changes, approaching that of rocks. Concomitantly, temperature rises as burial is more important. Instead of the 0 to 30 or 40 °C range one finds temperatures above these values at one kilometer depth in post sedimentary basins. It is striking to find that few of the clay minerals or alteration minerals resist this change in physical and chemical conditions. The poorly ordered materials, imogolite and allophane appear to be lost from the clay assemblages. HI minerals also are rarely if ever reported in shallow basin sediments. Mixed layer kaolinite/smectites seem to disappear as well. In fact one finds the illite/smectites minerals along with illite. However, in diagenesis it seems that the soil clay mixed layered minerals re-crystallize at near 50–80 °C burial temperatures in shales (Velde, personal observation.) One finds that at these burial temperatures the scattered compositions of MLM phases becomes very smectite-rich and one begins the smectite to illite transformation (see Claret et al. 2004) via an almost pure smectite phase.

These observations suggest that soil clays and those formed by water/rock interaction are minerals of the surface and not those of burial diagenesis. This is an important point to consider when thinking of the origin of clays under conditions of alteration.

Suggested Reading

- Brindley GW, Brown G (1980) Crystal structures of clay minerals and their X-ray identification. Mineralogical Society (Monograph 5, 485 pp)
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