
Bruce Velde · Alain Meunier

The Origin of Clay Minerals in Soils and Weathered Rocks

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With 195 Figures and 23 Tables

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Preface

Of course such a book as we propose here is not the product of just two people working together, although the experience has been a great pleasure for us. We would like to thank our many collaborators and students who have encouraged our effort by their, often, sharp criticism. We hope that we have used their comments to good effect. Especially we would like to thank Pierre Barré for his help, enthusiasm and consent for the use of much of his thesis material in formulating the last chapter of the book. Dominique Righi was instrumental in giving us ideas, useful comments and vigorous debate for a great number of our ideas and during the periods of formulation of our conclusions. Our approach is from mineral chemistry and hence has greatly benefited from discussions with people who know soils and plants. The project of this book was realized and encouraged with the help of Wolfgang Engel who, unfortunately is not with us to see its finalization. We greatly regret his passing.

This book is not in the general pattern of accepted knowledge and analysis of the phenomena which affect the occurrence of clays in the surface environment. We stress the role of plants at the bio-interface and the importance of microsystems at the water/rock interface. We believe that the literature at our and anyone's disposal shows that the system of clay formation and reaction is highly dynamic, especially at the surface. Clay alteration profiles are slow to form, thousands to hundreds of thousands of years, but they react quickly at the surface to chemical change, essentially engendered by plants. This is the message. Clays can react in short periods, years to tens of years, and hence should be considered as part of the active surface environment. Land use can be impacted by management for periods as short as those of elected officials in governments. Thus soil scientists and ecologists can forcefully argue for better management on a year to year basis and the results can be shown within the period of an appointed official's term. Therefore a clear understanding of plant and soil interactions and the fundamental alteration processes is vital to stewardship of one of the most precious parts of nature, the soil zone.

We hope that this book and some of the ideas presented will inspire young people to look more closely at the surface environment in a quest for a more rational and viable use of soils. Surface clay minerals appear to react very rapidly to changes in environments, specifically changes in plant regime in soils. The high reactivity of this kind makes clay minerals potential indicators of changes in the Earth's surface paleo-conditions and those engendered by the action of agricultural man.

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Introduction

As outlined in Chap. 1, clays are historically considered to be formed of $<2\ \mu\text{m}$ particles. The use of the optical microscope for petrographic observations at the end of the 19th century defined the limit of a recognizable crystal and mineral. Crystals whose size was lower than the resolution of the optical microscope, $2\ \mu\text{m}$, were unidentifiable and called clays. Because of this size-dependent definition, clays include different mineral species: silicates, oxides, carbonates. The largest part of the material of our investigation is called a phyllosilicate, i.e. silicate material which has a sheet like aspect, thinner than long and large. However such materials which are found in the small grain size fraction, though most often of small size, can at times reach several tens of micrometers in diameter. The same types of mineral can be found as high-temperature phyllosilicate equivalents, minerals such as micas and chlorites which can be found in centimetric sizes. Thus size is not a definite description of the silicate minerals found and formed at the Earth's surface. In a very general manner, one can say that phyllosilicates of high temperature origin, greater than $40\ ^\circ\text{C}$, are of diagenetic or metamorphic origin and are not stable under surface conditions. They tend to interact chemically at conditions where atmospheric water is present. It remains for us to show the differences between clay minerals whose origin is at the Earth's surface and those formed under other conditions. The first identification of a surface clay mineral is that it has a small grain size, generally $<2\ \mu\text{m}$.

Even if the reasons for small crystal size which are constantly observed are not fully understood at present, it is certainly the major characteristic of surface clay minerals. Because small size induces very great crystal surfaces, most of the remarkable chemical and physical properties of clay minerals are related to surface interactions. This was discovered very early during the first ages of human technical development: the plasticity of water-clay mixtures which was exploited during the Neolithic period for the production of pottery. Soils, and consequently clay minerals, are the support of the most fundamental activities of mankind: agriculture, ceramics and housing. Even today about 40% of the Earth's inhabitants live in dwellings composed in part by earth, i.e. clay assemblages with other materials. Therefore, the question of the origin of clay minerals is as important as that of the origin of humanity. Clay minerals are hydrated silicates. They contain hydrogen assigned to OH groups which contribute to the electronic stability of the framework of the crystal lattice (Grim 1953). However, they often contain molecular water associated with cations located between the basic structural layers of the minerals. It is clear that hydrogen and hence water is essential for clay mineral formation. Generally speaking, clay minerals form from aqueous solutions interacting with other, pre-existing, silicate species by dissolution-recrystalliza-

tion processes. Thus, the origin of clay minerals is related to water-rock interactions. In order to understand the mechanisms of fluid-rock interactions it is important to determine the driving force of these reactions typical of Earth surface conditions. Particularly, the role of chemical potential gradients must be considered in order to determine the stability domains of each species of clay mineral. One should keep in mind that clay minerals are first of all minerals, that is to say solids, able to react to changes in the conditions of their environment. Such changes are classically described in burial diagenesis where surface alteration clays are progressively transformed into illitic ones under increasing burial conditions, i.e. changes in temperature.

The most important geological occurrence where clay minerals are formed is that of rock weathering and soil formation. However, one must not forget that clay minerals are formed under the influence of hydrothermal action, i.e. the interaction of water and rock at conditions below the Earth's surface. Here one major clay resource is that of kaolinite, a mineral which has been used in many different industrial applications. Further, one finds significant alteration (weathering) of ocean bottom basalts creating proto-clay minerals which act as a sink for potassium in ocean water transfer, leaving sodium as the major alkali present in the greatest surface zone of the Earth. Diagenetic alteration of volcanic ash forms a near mono-mineralic material called bentonite (smectite) which has received recent attention in use for waste repositories for radio-active materials. Thus, atmospheric interaction with rocks is not the only source of clay minerals. However, the most likely interaction that humans are likely to have with clays is with those formed under conditions near those of the human environment, alteration of rocks to form soils.

We would like to attempt an explanation of the interactions of silicate and water at the surface of the Earth in systems generally described as weathering. This is the site of surface clay mineral formation. Water is the major motor of reaction, allowing and engendering chemical change. The minerals formed are stable at low temperatures, probably below 40–80 °C compared to those present in diagenetic series. However, the rapid change of mineralogy, on a geological scale at least, indicates subtle changes in the mineral structure as determined by X-ray diffraction, the major identification tool for clay minerals. Such change is the result of different chemical equilibria. Our objective is to clarify the factors which engender the change and persistence of surface clay minerals. In order to do this it is useful to understand the specificity of clay mineral structures and chemistry. The second step is to determine the chemical variables found under surface conditions which can produce and act upon surface clay minerals once formed. If one understands the origin of surface clays, and their stabilities, it will be possible to use them to better advantage in the coming era of environmental awareness.

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+}

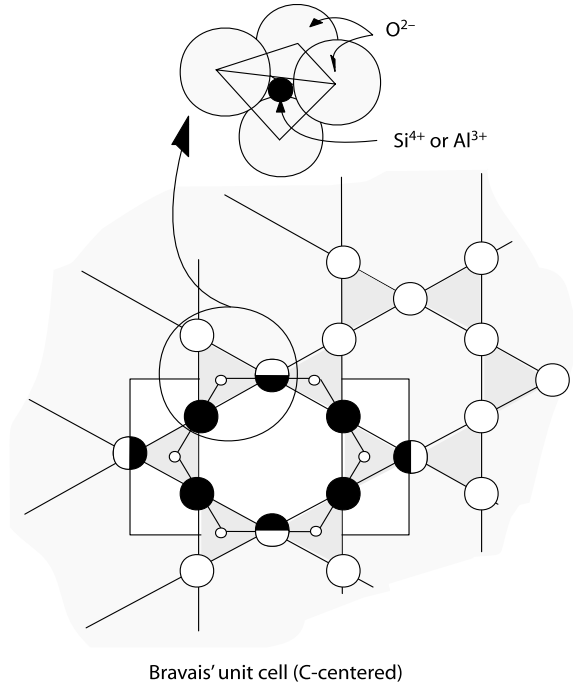
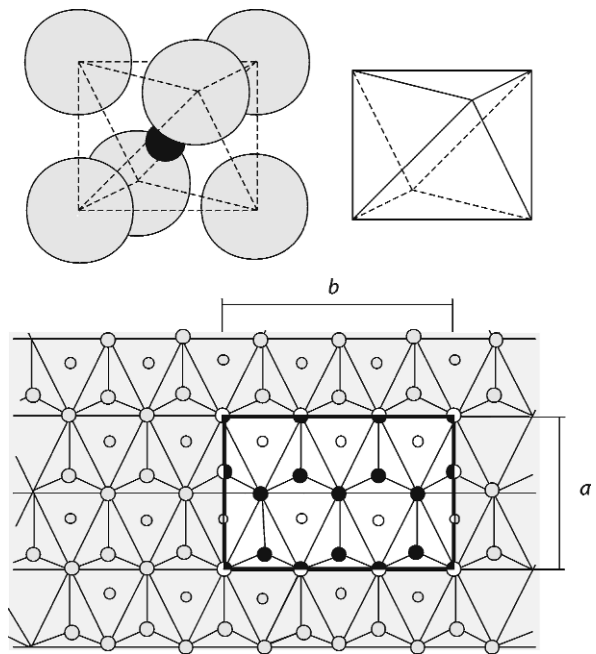


Fig. 1.2. Structure of the octahedral layer. The b dimensions of the trioctahedral (brucite) and dioctahedral (gibbsite) unit cells are 9.43 and 8.64 \AA respectively



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

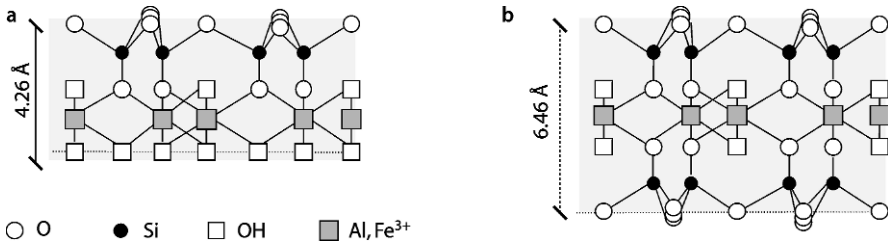
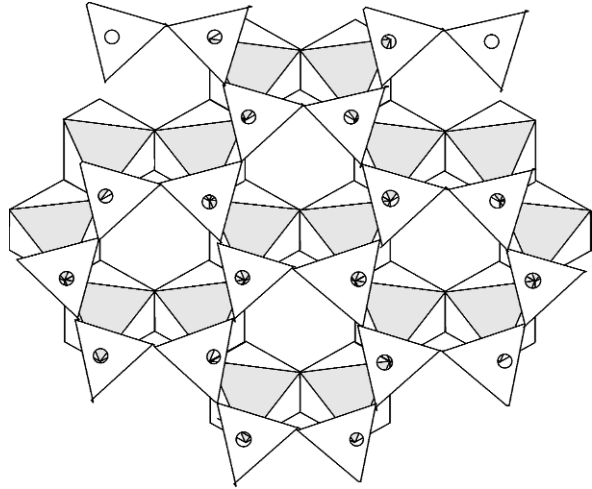


Fig. 1.4. The two crystal structure types of dioctahedral phyllosilicates; a 1:1 layer; b 2:1 layer

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

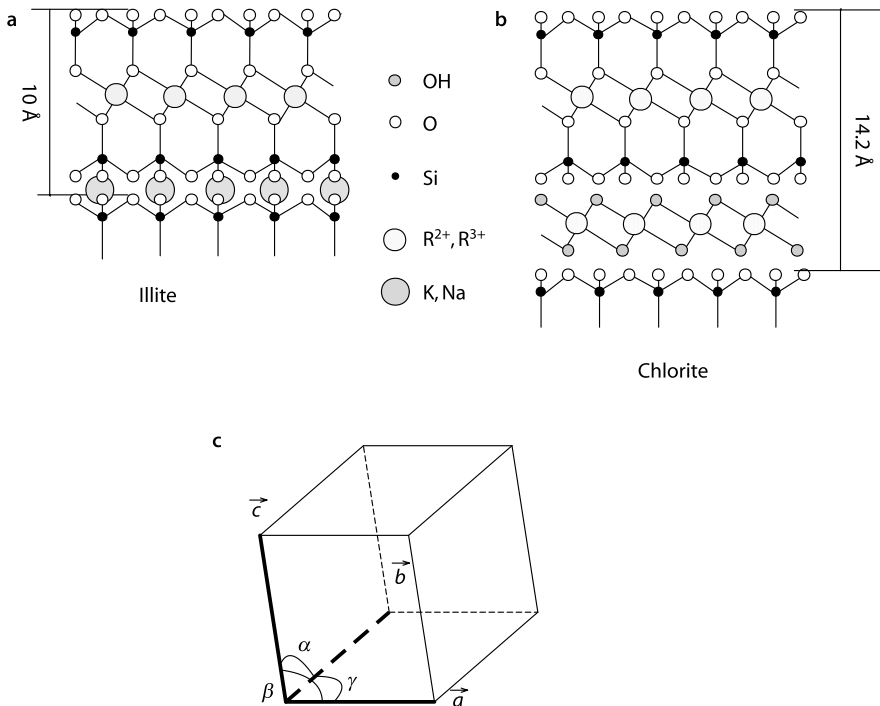


Fig. 1.5. Crystal structures of phyllosilicates derived from the 2:1 layer; **a** presence of an interlayer cation sheet (micas, vermiculites, smectites); **b** presence of a brucite-like sheet (chlorites); **c** schematic representation of the “layer unit cell” which is monoclinic or triclinic if the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

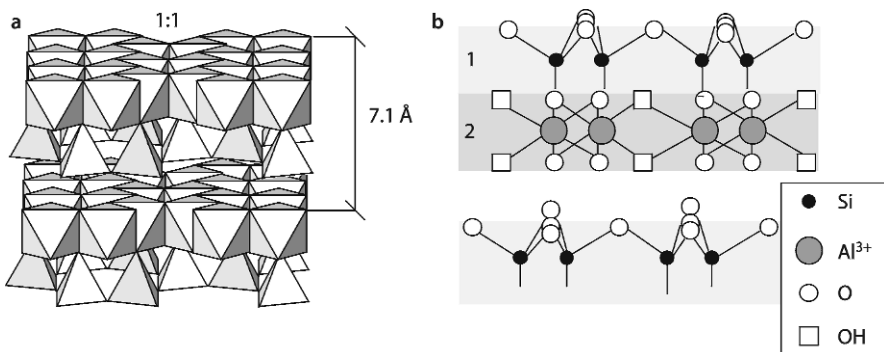


Fig. 1.6. The crystal structure of kaolinite; **a** the 1:1 layer is composed of a Al-bearing octahedral sheet linked to a Si-bearing tetrahedral one through the apical oxygens of each tetrahedron; **b** projection of the crystal structure on the (010) plane

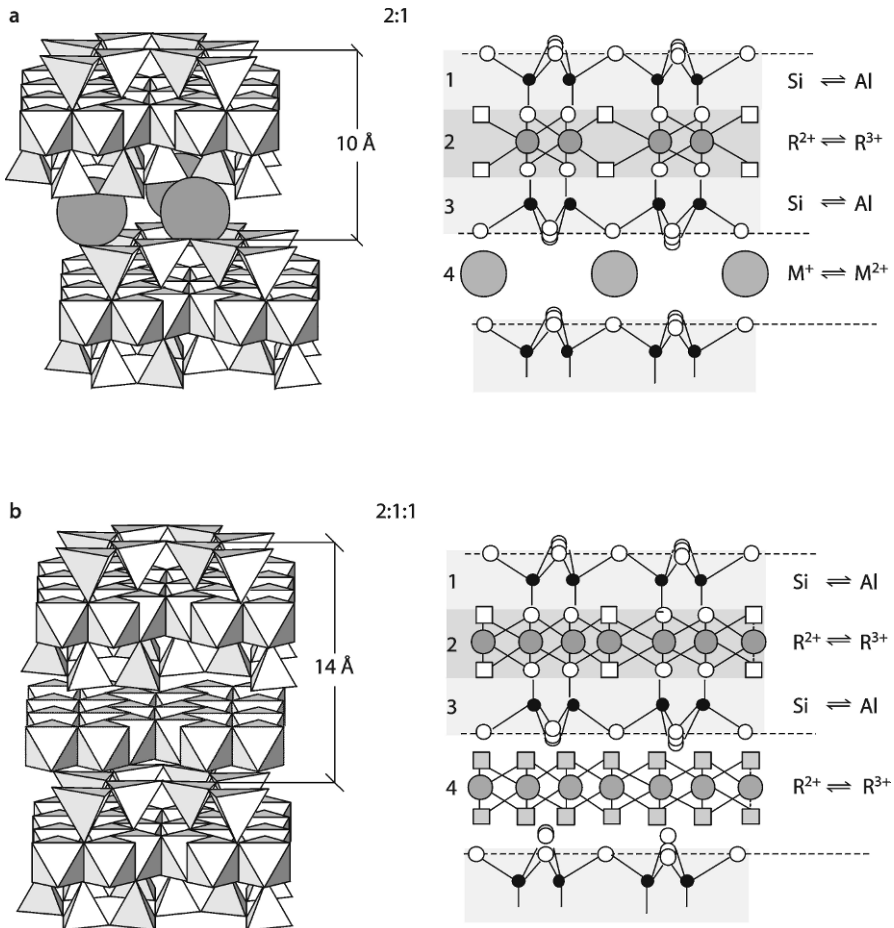


Fig. 1.7. The crystal structure of illite (a) and chlorite (b). The negative charge of the 2:1 layer is compensated by interlayer cations or a “pseudo-brucitic” sheet respectively

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, 2M₁ 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-

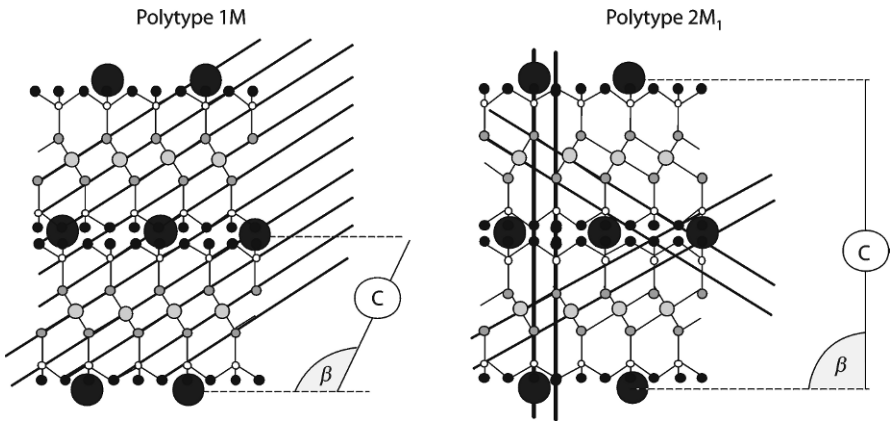
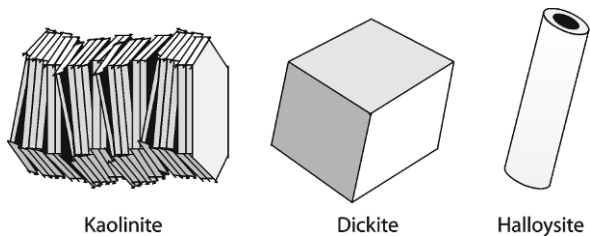


Fig. 1.8. Relation between the symmetry degree and the number of (hkl) planes in 1M and 2M₁ micas

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.

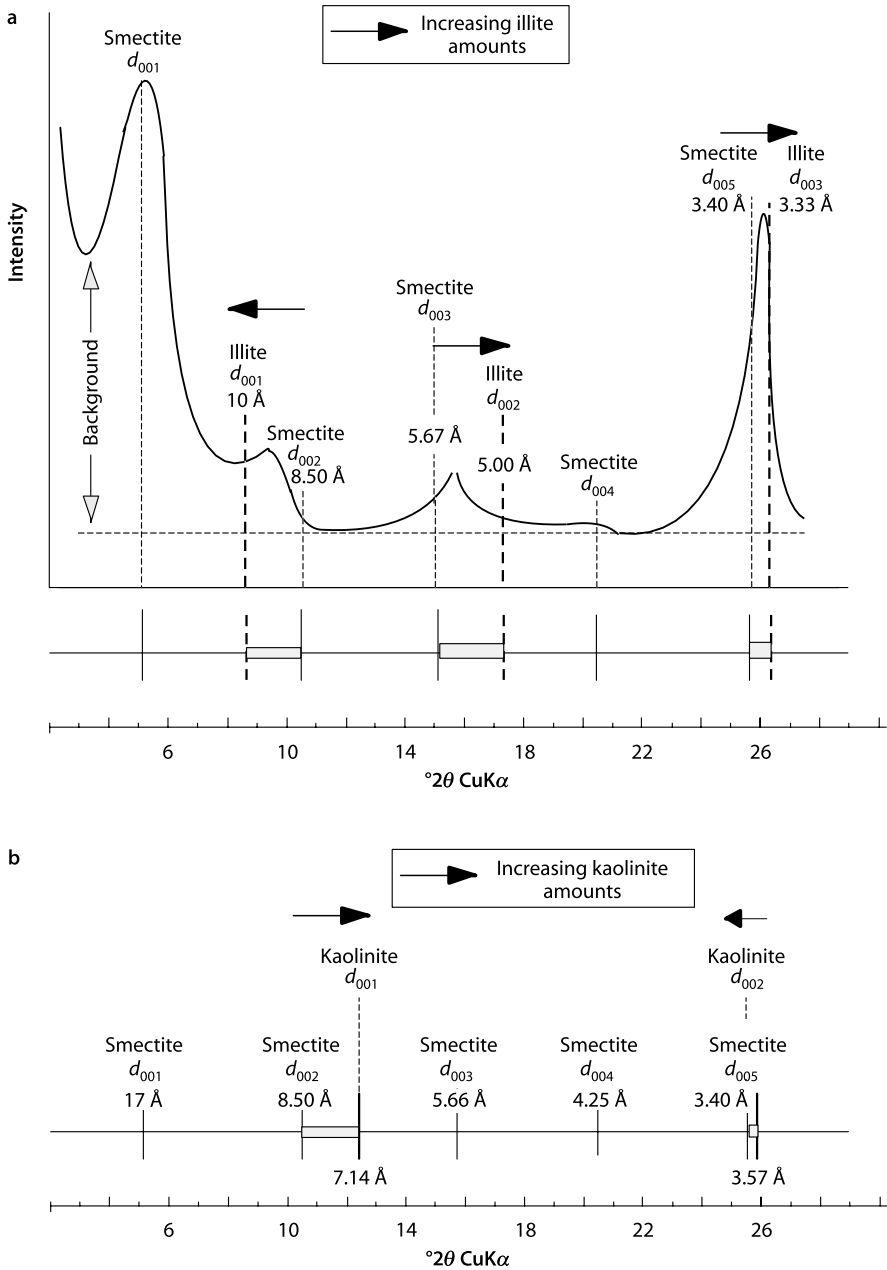


Fig. 1.10. Randomly ordered mixed layer minerals (peak interference rule, Méring 1949); **a** the diffraction peak interference for a illite-smectite MLM; **b** the diffraction peak interference for a kaolinite-smectite MLM

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

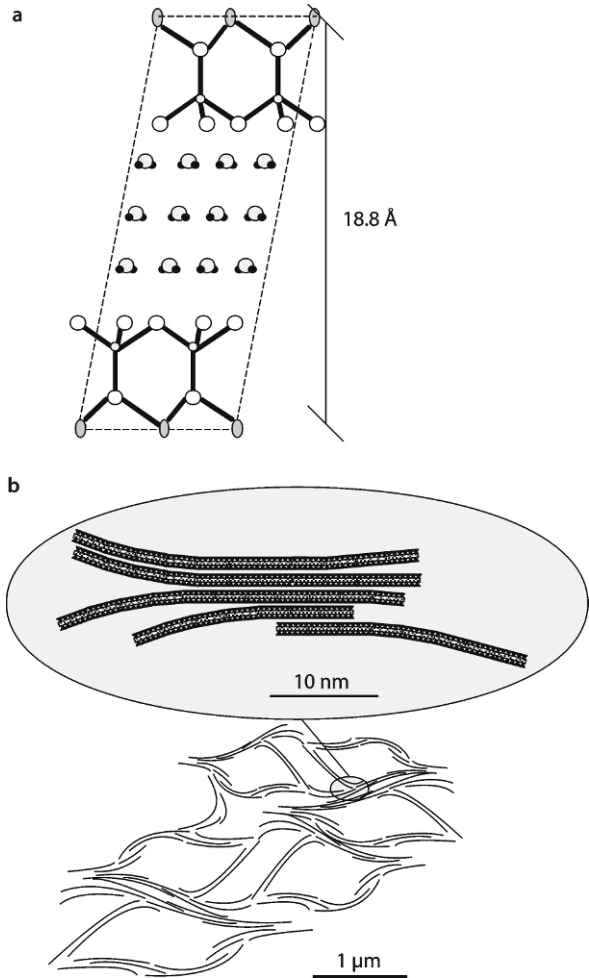
The term crystallite is used here for small dimension crystals. According to Putnis (1992), “a crystal is ideally made up of a repetition of identical building blocks, or unit cell, filling space, each unit cell in an identical orientation and related to the next by translation along of three crystallographic 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)



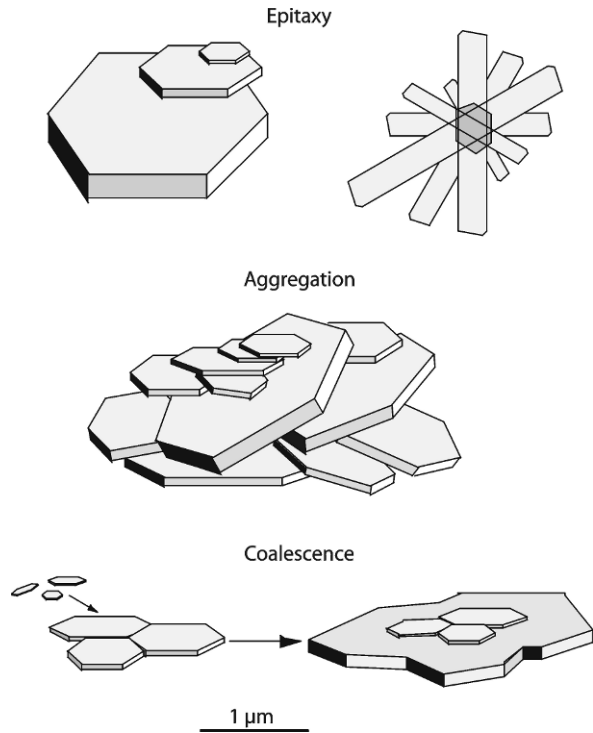
Generally, smectite crystals are small (crystallites below 1 μm) and very thin (a few nm, i.e. a few layers) while kaolinite and illite may reach higher dimensions (10 to 50 μm) and thickness (several tens of layers).

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

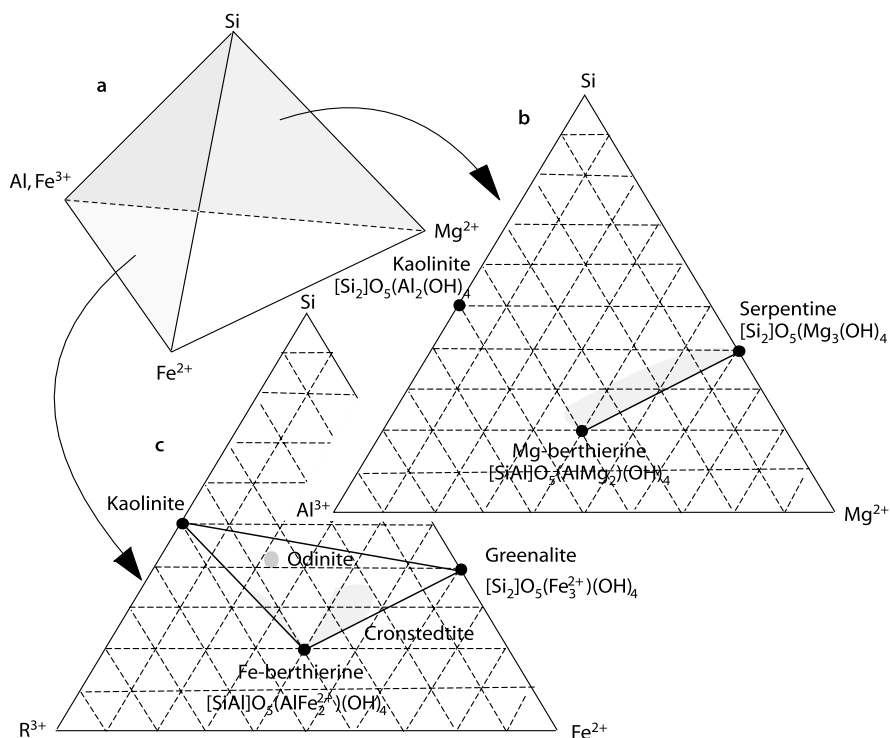


Fig. 1.13. Composition domains of 1:1 phyllosilicates in the Si–Al³⁺, Fe³⁺–Fe²⁺, Mg²⁺ system; **a** the four component system; **b** the Si–Al–Mg system; **c** the Si–R³⁺–Fe²⁺ system. The gray zones indicate the solid solutions

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 Å 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-