

Clays

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Crystal Structure – Species – Crystallisation

The guiding line of the first part of this book (Chaps. 1 to 5) is to understand some basic principles that repeatedly take place during geological processes. Since the clay scientist is concerned with phyllosilicates, he must first familiarize him- or herself with the fundamentals of the “layer” crystallography. The reconstruction of the silicon sheet and octahedral layer geometries is particularly important before the application of X-ray diffraction (XRD). This is the purpose of Sect. 1.1. Thereafter, this fundamental knowledge of crystallography will be used in Chap. 2 to understand how the chemical elements are distributed inside the layer structure.

The clay scientist’s task is not limited to XRD identification of clay species. Indeed, despite their small size, clay minerals are crystals, which means that their dimensions, shape, and number of defects result from specific, discoverable physico-chemical conditions. This is why it is important to understand how crystals were born (nucleation) and how they grow bigger and exhibit crystal faces (crystal growth). This is the purpose of Sect. 1.2.

1.1

The Crystal Structure of Clay Minerals

Clay minerals belong to the phyllosilicate group (from the Greek “phylon”: leaf, and from the Latin “silic”: flint). As a distinctive feature, they are very small (a few micrometers maximum) and their preferred formation occurs under surface (alterites, soils, sediments) or subsurface (diagenesis, hydrothermal alterations) conditions. Difficult to observe without using electron microscopy (scanning and transmission), they have been abundantly studied by X-ray diffraction, which is the basic tool for their identification. While the number of their species is relatively small, clay minerals exhibit a great diversity in their composition because of their large compositional ranges of solid solutions and their ability to form polyphased crystals by interstratification. Trying to list them would be gruelling and fruitless work. What is more important is to understand why their crystal structure affords them such a range compositional diversity.

This chapter is aimed at introducing the fundamentals of the crystal structure starting from the layer as the elementary unit and ending with the concepts of crystal, particle and aggregate. These basics are well complemented by re-

ferring to specialised resources in which crystal structures are described from X-ray diffraction: Brindley and Brown 1980; Moore and Reynolds 1989; Drits and Tchoubar 1990; Bouchet et al. 2000.

1.1.1

The Elementary Structure Level: the Layer

X-ray diffraction deals with distances between atomic planes. But how are these distances determined? The following sections will show how they are related to the length of the chemical bond that links the ions forming the clay mineral. The scale of investigation is one angström (0.1 nm).

1.1.1.1

Layer: Dimensions and Symmetry

Chemical Bonds and Coordination

As with any mineral species, phyllosilicates are characterized by a “unit cell”. In the first step, the unit cell will be considered at the scale of a single layer and its dimensions will be determined in 3D space (Fig. 1.1a). The *a* and *b* dimensions are in the x-y plane (the plane in which the largest faces are oriented). The *c* dimension along the z-axis corresponds to the “thickness” of the layer. A simple geometrical calculation provides approximate values for these three dimensions. One must study the structure of the elementary organisational level of the layers: the tetrahedral and octahedral “sheets” in order to make this calculation. The sheet’s framework is formed by cation-anion bonds (bonds intermediate between ionic and covalent bonds) whose

Table 1.1. Effective ionic radii of the main anions and cations contained in phyllosilicates (Shannon and Prewitt 1976)

Ions	Ionic radius (Å)		
	Coordinece 4	Coordinece 6	Coordinece 12
O ²⁻	1.24	1.26	
OH ⁻	1.21	1.23	
K ⁺	1.51	1.52	1.78
Ca ²⁺		1.14	1.48
Na ⁺	1.13	1.16	1.53
Mg ²⁺	0.71	0.86	
Fe ²⁺	0.77	0.92	
Fe ³⁺	0.63	0.79	
Al ³⁺	0.53	0.68	
Si ⁴⁺	0.4	0.54	
H ₂ O*		1.45	
NH ⁴⁺ *		1.61	

*The shape of H₂O and NH⁴⁺ here is compared with a sphere

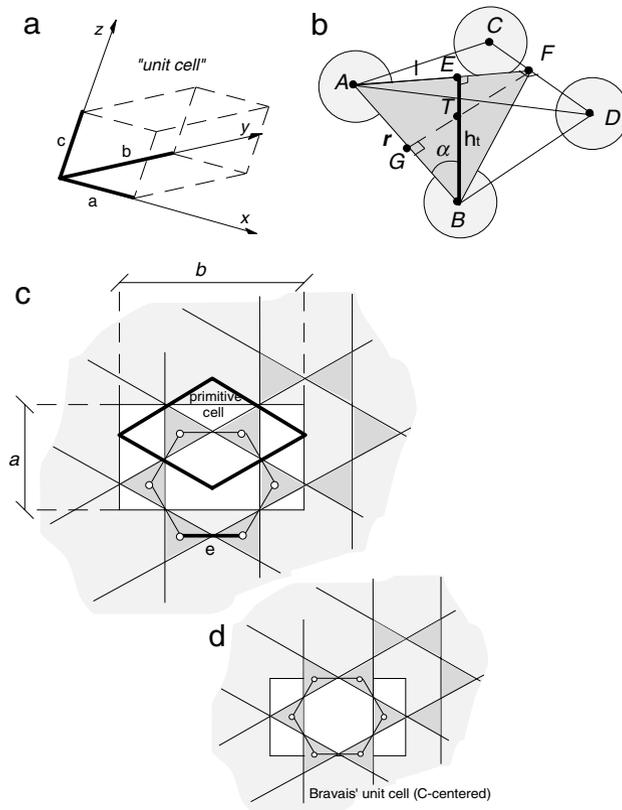


Fig. 1.1a-c. Structure of the tetrahedral sheet. **a)** The a, b and c dimensions of a “unit cell”. **b)** The thickness of tetrahedron h_t is 2.12 Å. **c)** The a and b dimensions are 5.36 and 9.27 Å respectively (the primitive unit cell is indicated). **d)** The Bravais' s unit cell is centred on the hexagonal cavity (Méring 1975)

length will be used as a reference in the calculation of the cell dimensions. Ionic diameters will be used for the determination of cation coordination.

Considering the difference in their ionic diameter (Table 1.1), three types of coordination determine the elementary polyhedra that make up the various sheets of the crystal structure:

- 4-fold coordination (SiO_4^{4-} or AlO_4^{5-} tetrahedron).
- 6-fold coordination (octahedron whose centre is occupied by a Al^{3+} , Fe^{3+} , Fe^{2+} or Mg^{2+} cation for the most part – the vertices being formed by O^{2-} or OH^- anions)
- 12-fold coordination (dodecahedron whose centre is occupied by a cation with a wide diameter: K^+ , Na^+ , Ca^{2+} , and vertices are formed by O^{2-} anions of two opposite tetrahedral sheets).

Size of Atoms and Ions

Because atoms and ions have fuzzy boundaries, the measurement of their radius is difficult. Nevertheless, it becomes easier when atoms or ions are bonded because the bond length can then be precisely measured in a given equilibrium state. Consequently, several radius values are available for a single element, depending on the nature of the chemical bond involved – i. e. ionic, covalent, or van der Waals. Bonds of the silicate crystal framework are typically intermediate between ionic and covalent. Consequently, each bond is polar and characterised by an electric dipole moment. This is of great importance for the electric charge distribution at the outer surfaces of each layer in a phyllosilicate structure. For details, refer to Sainz-Diaz et al. (2001).

The Tetrahedral Sheet

SiO_4^{4-} or AlO_4^{5-} tetrahedra (Fig. 1.1b) are linked together by sharing three of four vertices (three basal oxygens, the fourth being the apical oxygen). This means that one 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 is excluded (Löwenstein's rule). These bonds form a two-dimensional lattice (tetrahedral sheet) defining hexagonal cavities. All free oxygens (apical oxygens) are located on the same side of the plane determined by the bonded oxygens. The tetrahedral sheet so constituted can be “paved” by translation (without rotation) by either a 2-tetrahedron or a 4-tetrahedron unit. The first one is called *the primitive cell* (Fig. 1.1c), the second one is *the Bravais' unit cell* (Fig. 1.1d) whose a and b dimensions as well as thickness are easily calculable (C-centred).

Calculating the dimensions of a tetrahedron when ion diameters are known is easy (Jaboyedoff 1999). The edge r of the tetrahedron is equal to the ionic diameter of the O^{2-} anion. The first interesting dimension is h_t , the height of a tetrahedron. Figure 1.1b shows the procedure in triangle AFB where AF and BF are the medians of the equilateral triangles ACD and BCD respectively:

$$\text{AE} = 2/3\text{AF} = l \quad (1.1)$$

$$\text{AF}^2 + \text{FD}^2 = \text{AD}^2 \Rightarrow l = \frac{r}{\sqrt{3}}. \quad (1.2)$$

In triangle AEB, $\text{EB} = h_t$ can be calculated as follows:

$$h_t = \sqrt{r^2 - l^2} \quad \text{or} \quad h_t = r\sqrt{\frac{2}{3}}. \quad (1.3)$$

In the case of a SiO_4^{4-} tetrahedron, $r = 2.60 \text{ \AA}$ so $h_t = 2.12 \text{ \AA}$.

The relationship between the a and b unit cell dimensions in the tetrahedral sheet is simple. The distance between one vertex and the centre of the tetrahedron (Si–O bond) determined by the intersection T between EB and FG is given by the relationship:

$$\text{TB} = \frac{r}{2 \cos \alpha} \quad \text{or} \quad \cos \alpha = \frac{h_t}{r} \quad \text{so,} \quad \text{TB} = r\sqrt{\frac{3}{8}} \quad (1.4)$$

The a dimension (Fig. 1.1c) is determined as follows: $a = 2r = \frac{4}{3}\sqrt{6} \cdot \text{TB}$

Figure 1.1b shows that the b dimension is three times the hexagon side e : $b = 3e$.

And $e = 2l$ hence $e = 2\frac{r}{\sqrt{3}} = \frac{a}{\sqrt{3}}$. Accordingly:

$$b = 3e = a\sqrt{3} = 4\sqrt{2}. \text{ TB} \quad (1.5)$$

The Si–O bond length can be calculated according to the values given in Table 1.1: 1.64 Å. Consequently the theoretical value of the b dimension is 9.27 Å. In reality, the Si–O bond length is 1.618 ± 0.01 Å, so $b = 9.15 \pm 0.6$ Å. The ionic diameter of the 4-fold coordination Al^{3+} cation is greater than that of Si^{4+} ; accordingly the theoretical value of the Al–O bond length will be greater than that of the Si–O bond length: 1.77 Å (Table 1.1). In reality, it is 1.748 ± 0.01 Å. Therefore, the b dimension will increase with the substitution rate of Al^{3+} for Si^{4+} . Suppose that this increase is directly proportional to the Al^{3+} content, this leads to the following relation:

$$b_{(\text{Si}_{4-x}\text{Al}_x)} = 9.15 + 0.74 \times x \quad (1.6)$$

The representation of the distribution of atoms is easier in crystallography (for X-ray diffraction notably) for a four-half-tetrahedron unit cell centred on the hexagonal cavity (Méring 1975).

The Octahedral Sheet

Octahedra are laid on a triangular face (Fig. 1.2a). They are linked together by sharing their six 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 hexagonal symmetry. The di- and trioctahedral layers are “paved” by a 6-octahedron unit cell (Fig. 1.2b) whose a and b dimensions as well as thickness can be easily calculated.

The edge of the octahedron corresponds to the ionic diameter of the O^{2-} or OH^- anions considered equivalent here. In triangle OMO' , the cation-anion distance MO (or MO') is then given by:

$$\text{MO} = \frac{s}{\sqrt{2}} \quad (1.7)$$

The thickness of the sheet is given by the value of RV in rhomb QRTU whose sides equal $s\frac{\sqrt{3}}{2}$. In rectangle triangle QMU , angle α can be determined by its \sin : $\sin \alpha = \frac{\frac{s}{2}}{\frac{s\sqrt{3}}{2}} = \frac{1}{\sqrt{3}}$ thus $\alpha = 35.26^\circ$. In triangle RVU , RV is given by:
 $\text{RV} = s \cos \alpha$.

Bond lengths are not always accurately known; as an approximation, they can be considered as the sum of the ionic radii of the cation (Mg^{2+} , Fe^{2+} , Al^{3+} , Fe^{3+} ...) and of the 6-fold coordination O^{2-} anion (Shannon and Prewitt 1976). The values for Mg–O and Al–O bonds are $0.86 + 1.26$ Å and $0.68 + 1.26$ Å

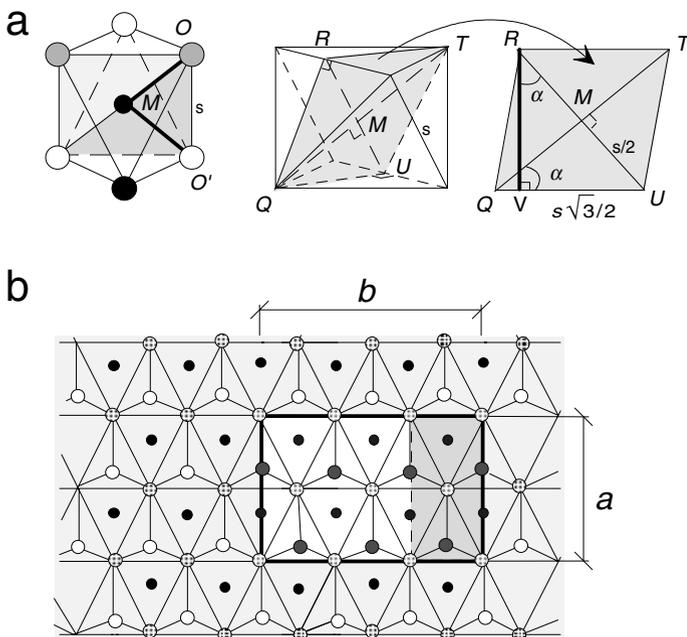


Fig. 1.2a,b. Structure of the octahedral sheet. **a)** Thickness is given by $RV = s \cos \alpha$ (with $\alpha = 35.26^\circ$). **b)** The b dimensions of the trioctahedral (brucite) and dioctahedral (gibbsite) unit cells are 9.43 and 8.64 Å respectively ($a = \frac{b}{\sqrt{3}}$)

respectively. Therefore, the value of the edge of a “Mg octahedron” will be 3.00 Å and that of an “Al octahedron” will be 2.74 Å while their respective thickness will be 2.45 and 2.24 Å.

Figure 1.2b shows that $b = 3s$, so $b = 3\sqrt{2} \cdot MO$. Using the values in Table 1, the theoretical values of this dimension can be calculated for a brucite-like trioctahedral sheet $[Mg_3(OH)_6]$ and for a gibbsite-like dioctahedral sheet $[Al_2(OH)_6]$. The value of MO is 2.12 and 1.94 Å respectively, hence $b_{\text{brucite}} = 8.99$ Å and $b_{\text{gibbsite}} = 8.23$ Å. These theoretical values differ from the real values 9.43 and 8.64 Å respectively.

Adjustment of the Tetrahedral and Octahedral Sheets

The theoretical b dimensions calculated for the tetrahedral sheet (9.27 Å) and for the tri- and dioctahedral sheets (8.99 and 8.19 Å respectively) differ significantly. It is the same for the a dimension, which depends on the b value. This indicates that the linkage between tetrahedral and octahedral sheets through the free oxygens of the tetrahedra will not take place without deformations. The tetrahedral sheets lose their hexagonal symmetry by rotation of the tetrahedra about axes perpendicular to the basal plan (Fig. 1.3a). The symmetry

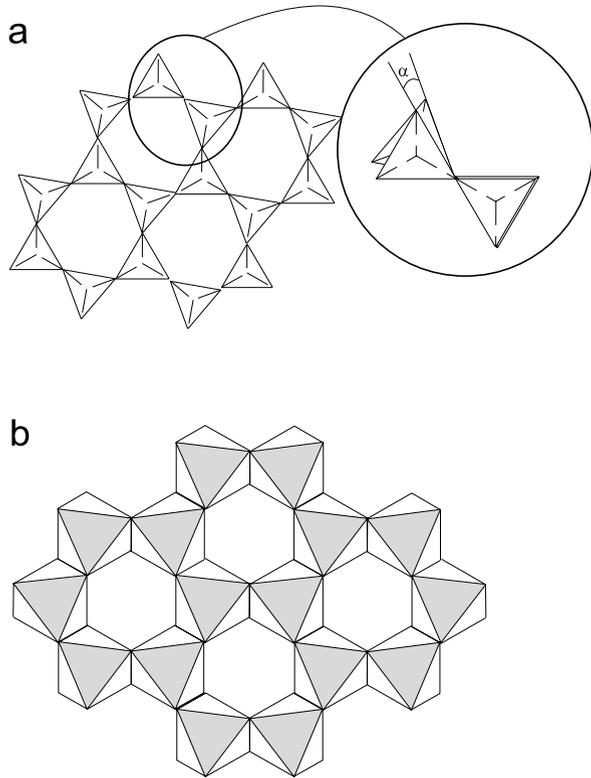


Fig. 1.3a,b. Deformation of sheets. **a)** Rotation of tetrahedra. **b)** Deformation of octahedra in a gibbsite-like structure

becomes ditrigonal and the rotation angle α can be estimated as follows:

$$\cos \alpha = \frac{b_{\text{measured}}}{b_{\text{theoretical}}} \quad (1.8)$$

Angle α can not exceed 30° for the repulsion that O^{2-} anions exert on each other. More complex distortions occur by rotation about axes that are contained in the plane and by deformation of the tetrahedra. The latter involve changes in the value of angles between the cation and the oxygens of the four vertices (theoretical value 109.47°) as well as in the bond length. Some of them shorten as shown by NMR spectroscopy (see Sect. 2.1.2.2).

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. 1.3b). 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 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 (Bailey 1980). Only the presence of bivalent cations with very different ionic diameter causes local changes in symmetry.

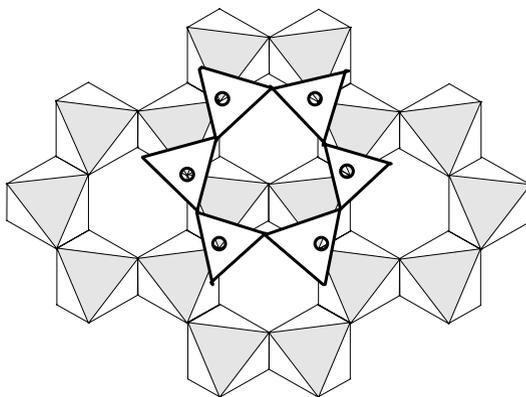


Fig. 1.4. The linkage between a tetrahedral sheet and a dioctahedral-type sheet necessitates their deformation. The hexagonal symmetry transforms into ditrigonal symmetry

The linkage between a tetrahedral sheet and a dioctahedral sheet requires a second type of rotation of the tetrahedra about axes in the basal plane (Fig. 1.4). The internal energy of the crystal is increased by the bond deformations (angles and length) through the addition of the elastic energy.

The Two Types of Layers: 1:1 and 2:1 Layers

The crystal structure of all phyllosilicates is based on two types of layers:

1. 1:1 layers in which one tetrahedral sheet is bonded to one octahedral sheet (Fig. 1.5a);
2. 2:1 layers in which one octahedral sheet is sandwiched between two tetrahedral sheets (Fig. 1.5b).

The theoretical structures (without deformations) of both types of layers depend on the hexagonal symmetry of the tetrahedral and octahedral sheets which are linked to each other. The apical oxygens of the tetrahedra become the vertices of the octahedra. Thus, the six vertices of the octahedra in a 1:1 layer are formed by 4 OH^- radicals and 2 apical oxygens of the tetrahedra. In 2:1 layers, they are formed by 2 OH^- radicals only because the other four vertices are the apical oxygens of the two tetrahedral sheets.

However, the tetrahedral and octahedral sheets exhibit differing a and b dimensions. Thus, their linkage cannot possibly take place without deformation of the angles and lengths of some chemical bonds, as indicated previously. These deformations are significant in dioctahedral layers; they are minor in trioctahedral layers. In all cases, the 6-fold symmetry becomes 3-fold symmetry.

The symmetry group to which phyllosilicates belong depends on the way 1:1 or 2:1 layers are stacked. From the highest to the lowest they are: hexagonal (H), rhombohedral (R), orthorhombic (Or), ditrigonal (T), monoclinic (M) and triclinic (Tc). Therefore, the various layer-stacking modes determine distinct polytypes, the number of which is a function of the mineral species considered

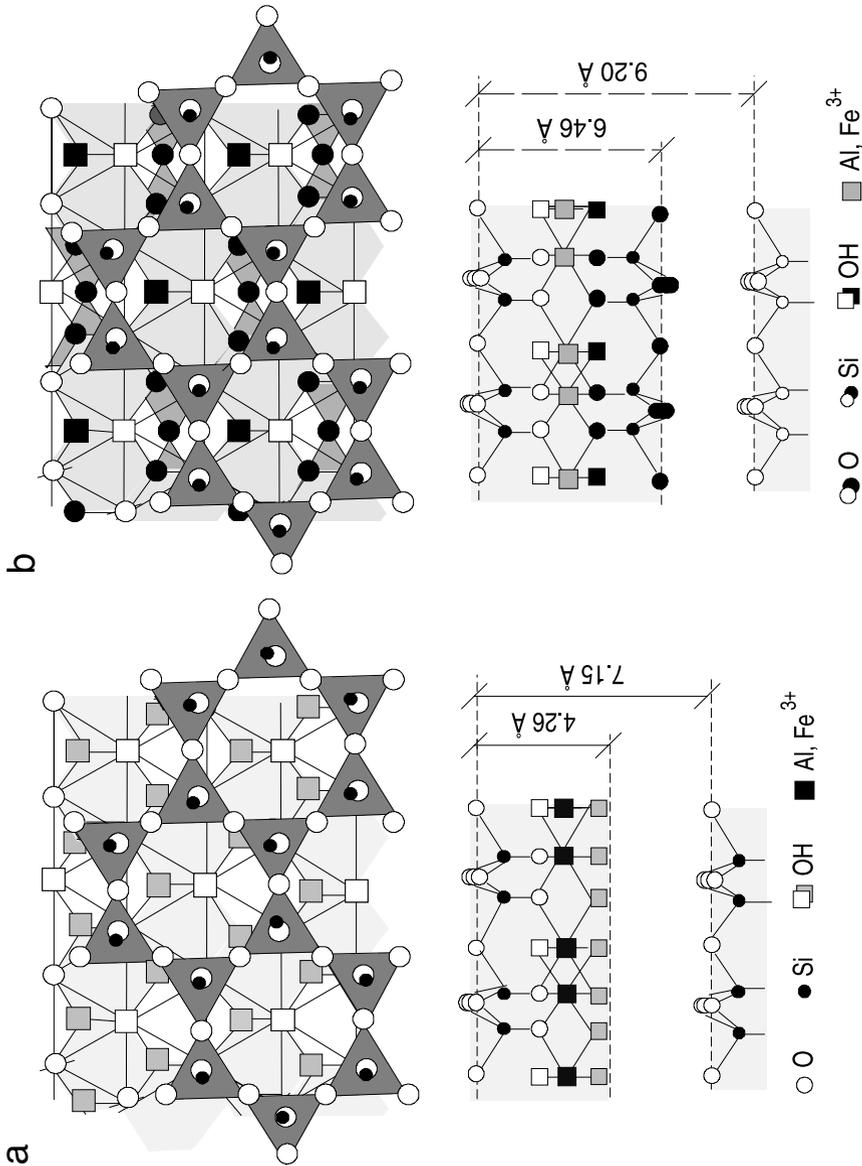


Fig. 1.5a,b. Crystal structure of dioctahedral phyllosilicates. a 1:1 layer. b 2:1 layer

(cf. 1.1.2.1). Let us consider that there are three possible ways to stack two consecutive layers:

- *no shift*. The symmetry becomes orthorhombic, pseudo-hexagonal or hexagonal;

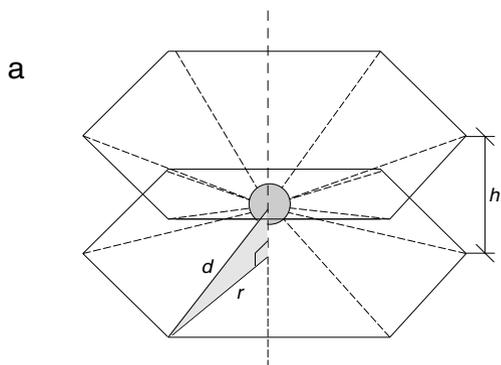
- *a:3shift*. If no rotation occurs, the symmetry is monoclinic. If rotation occurs, angle β may be near 90° and the symmetry close to the orthorhombic;
- *b:3shift*. If no rotation occurs, the symmetry remains monoclinic. If rotation occurs, angle α may be near 90° and the symmetry close to the orthorhombic;

This point is explained in more details in Sect. 1.1.2.1. (polytypes) and annex 2.

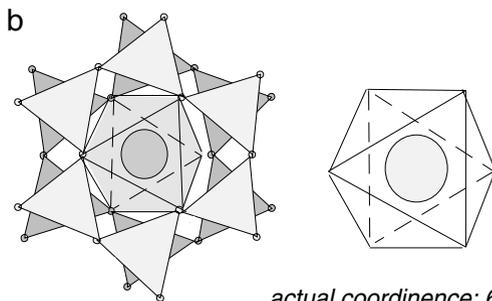
The Interlayer Sheet

In some 2:1 phyllosilicates, the electrical neutrality of crystal structures is ensured by the addition of a cation interlayer sheet: interlayer sheet of smectites, vermiculites and micas (cations not bonded to each other) or brucite-like sheet of chlorites (cations forming an octahedral sheet without any shared vertex with tetrahedral sheets). In interlayer sheets, cations are housed in hexagonal or ditrigonal cavities formed by the O^{2-} anions of the opposite tetrahedral sheets (Fig. 1.6a). Therefore, disregarding distortions, these cations have 12-fold coordination. Through simple geometrical relationships, the length of the bonds between oxygens and interlayer cations can be calculated:

$$d = \sqrt{\frac{h^2}{4} + r^2} \quad (1.9)$$



theoretical coordination: 12



actual coordination: 6

Fig. 1.6a,b. Structure of the interlayer zone. a) Thickness h depends on the bond length between the interlayer cation and the O^{2-} anions of the tetrahedra (d). b) Distortions of the tetrahedral sheets brings the coordination from 12 down to 6

where

h : interlayer spacing (shortest distance between the oxygens of the two tetrahedral sheets).

r : distance from the centre of the hexagonal cavity to the oxygens of the plane in a tetrahedral sheet.

In case of deformation of the tetrahedral sheets by rotation of angle α , r is shown to vary as follows (Decarreau 1990):

$$r = \frac{b}{6 \cos 30^\circ} - \frac{b \cdot \tan \alpha}{6} = \frac{b}{6} (\sqrt{3} - \tan \alpha) \quad (1.10)$$

The actual coordination is no longer 12 but 6 (Fig. 1.6b). The structure of the brucite-like sheets is discussed in a further paragraph (Sect. 1.1.1.2)

At this point, it is possible to find out how the tetrahedral, octahedral and interlayer sheets form different patterns of layer structure. The calculation of the “unit cell” dimensions and volume is accordingly facilitated. The “unit cell” concept will be used throughout this book; here, it is considered as the smallest volume repeated in the two-dimensional space of the layer. The calculation of the cell unit dimensions and volume will help in understanding why some dimensional parameters are useful criteria for the X-ray diffraction identification of clays, on the one hand, and how mineral density is determined, on the other hand.

1.1.1.2

The Different Patterns of Layer Structure

1:1 Structure (no Interlayer Sheet): Kaolinite and Lizardite

In the unit cell of a kaolinite, four sites of the dioctahedral sheet are occupied by Al^{3+} cations and two are vacant (Fig. 1.6a). 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 six 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 five ionic planes. The actual a and b unit cell dimensions are, respectively: $a = 5.15$; $b = 8.95 \text{ \AA}$ for kaolinite and $a = 5.31$; $b = 9.20 \text{ \AA}$ for lizardite.

The distance between two neighbouring 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 is added the thickness of the interlayer spacing. The latter depends on the length of the hydrogen bonds connecting the tetrahedral sheet in one layer to the octahedral sheet in the neighbouring layer (about 3.0 \AA according to Bailey 1980). The interlayer spacing of kaolinite is 7.15 \AA , and that of lizardite 7.25 \AA for the pure magnesian end member; it increases with the substitution rate of Mg^{2+} for Fe^{2+} .

Table 1.2. Calculation of the unit cellmass of kaolinite (M_{vk}) and lizardite (M_{vA})

Element	Mass	Stoich.coef	Kaolinite	Stoich.coef.	Lizardite
Si	28.09	4	112.36	4	112.36
Al	26.98	4	107.92		
Mg	24.30			6	145.8
O	16	18	28.8	18	28.8
H	1	8	8	8	8
Total			516.28		554.16

To make it simpler, let the unit cell be considered for a single layer, independently of polytypes (annex 2) as indicated in Fig. 1.1a. The a and b dimensions correspond to the actual ones and the c dimension is equal to the distance between two consecutive layers (actual value: $c \cdot \sin \beta$); the calculation of its volume is given by: $a \times b \times c$. For kaolinite it is $329.83 \times 10^{-30} \text{ m}^3$; for antigorite: $361.35 \times 10^{-30} \text{ m}^3$. The density of these two minerals (ρ_{vk} and ρ_{vA} for kaolinite and antigorite respectively) may be calculated considering a number of unit cells equal to the Avogadro number ($N_A = 6.02252 \times 10^{23} \text{ mol}^{-1}$) as shown in Table 1.2

The densities ρ_k and ρ_A expressed in grams per cubic meters are calculated as follows:

$$\rho_k = \frac{\text{unit cell mass}}{\text{unit cell volume} \times N_A} \quad (1.11)$$

and so

$$\rho_k = 259.91 \times 10^4 \text{ g} \cdot \text{m}^{-3} \quad (1.12)$$

$$\rho_A = 254.64 \times 10^4 \text{ g} \cdot \text{m}^{-3} \quad (1.13)$$

2:1 Structure (Without Interlayer Sheet): Pyrophyllite and Talc

The structure of 2:1 layers consists of seven ionic planes (Fig. 1.7a). The octahedral sheet in 2:1 layers is formed by two kinds of octahedra: cis-octahedra (2 M2 sites) in which (OH^-) groups form one side of a triangular face on the right or on the left, trans-octahedra (1 M1 site) in which $(\text{OH})^-$ groups are located on the opposite vertices (Fig. 1.7b). Planes defined by the $(\text{OH})^-$ groups when they are in the trans-position become planes of symmetry of the octahedral sheet (Fig. 1.7c). This is not true for the cis-position.

Pyrophyllite $[\text{Si}_4 \text{O}_{10} \text{Al}_2 (\text{OH})_2]$ is characterised by the presence of a vacancy in the trans-position. The actual unit cell dimensions are: $a = 5.160$; $b = 8.966 \text{ \AA}$ (angles α and γ are close to 90° : $\alpha = 91.03^\circ$ and $\gamma = 89.75^\circ$). Bonding between neighbouring layers (from tetrahedral sheet to tetrahedral sheet) depends on van der Waals bonds. These bonds have a stable configuration when two neighbouring 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 $c \cdot \sin \beta = 9.20 \text{ \AA}$ ($c = 9.33 \text{ \AA}$; $\beta = 99.8^\circ$).

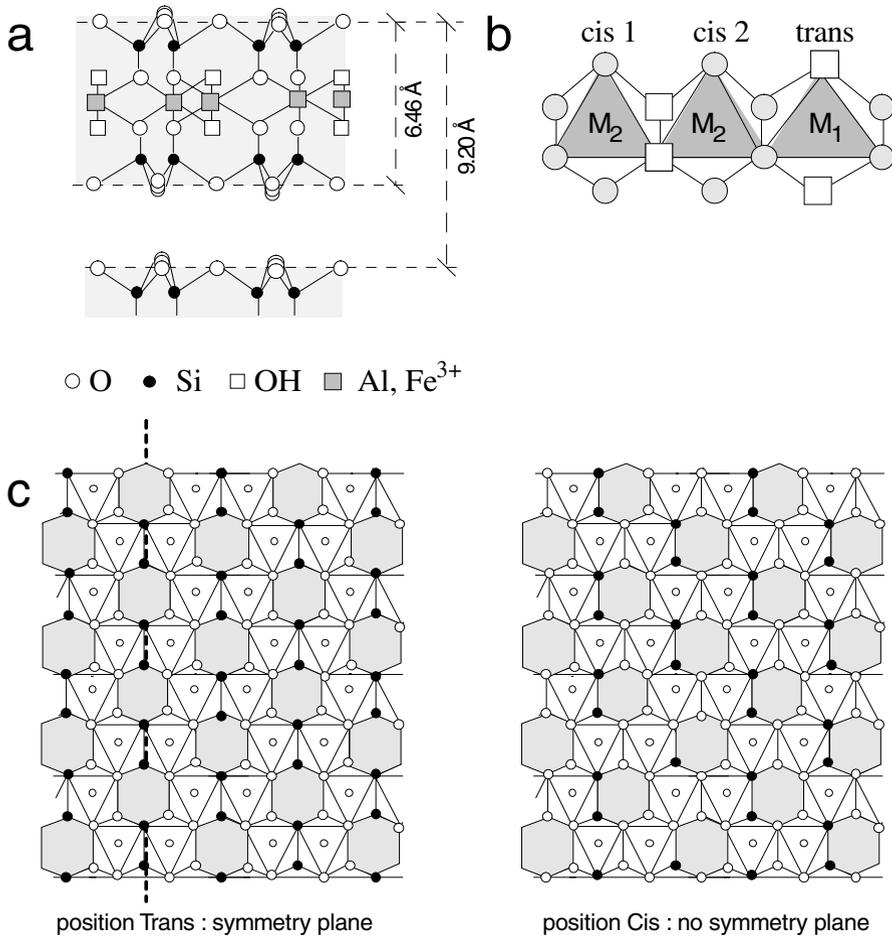


Fig. 1.7a-c. Structures of 2:1 dioctahedral phyllosilicates. a) Projection of the unit cell in the b-c plane (pyrophyllite). b) The three types of octahedra. c) Only the trans-position introduces a plane of symmetry in the octahedral sheet

The talc half-unit formula $[\text{Si}_4\text{O}_{10}\text{Mg}_3(\text{OH})_2]$ points out the absence of 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: $a = 5.29$; $b = 9.173 \text{ \AA}$. The c dimension is 9.460 \AA .

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 two neighbouring cations, each of them providing one-half of positive charge. As the vacancy breaks the balance of the repulsive forces, the O-H bond is inclined to its direction (Fig. 1.8a). In the tetrahedral structure, each OH is balanced by three bivalent cations, each of them providing one-third of the positive charge. In the latter case, the H⁺ pro-

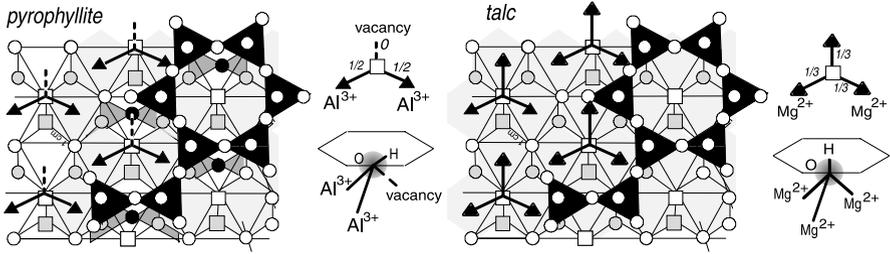


Fig. 1.8a,b. Position of cation – OH – cation bonds. **a)** Case of a dioctahedral structure (pyrophyllite). **b)** Case of a trioctahedral structure (talc)

ton is systematically perpendicularly oriented in the centre of the hexagonal cavity of the tetrahedral sheet (Fig. 1.8b). This short explanation 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 (refer to Sect. 2.1.2.2).

The unit cell volumes of pyrophyllite and talc are $425.63 \times 10^{-30} \text{ m}^3$ and $459.05 \times 10^{-30} \text{ m}^3$ respectively. The densities of pyrophyllite (ρ_{VP}) and talc (ρ_{VT}) are respectively:

$$\rho_{VP} = 277.21 \times 10^4 \text{ g} \cdot \text{m}^{-3} \quad (1.14)$$

$$\rho_{VT} = 274.36 \times 10^4 \text{ g} \cdot \text{m}^{-3} \quad (1.15)$$

2:1 Layers with an Interlayer Sheet: Micas, Vermiculites, Smectites

The crystal structure of micas and dioctahedral clays derives from that of pyrophyllite through cation substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer and of R^{2+} for R^{3+} in the octahedral layer (Méring 1975; Walker 1975). These substitutions lead to a positive charge deficiency in the 2:1 layer: $[(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{R}_{2-y}^{3+}\text{R}_y^{2+})(\text{OH})_2]^{(x+y)-}$ per half-cell. The crystal structure of micas and trioctahedral clays derives from that of talc through tetrahedral and octahedral substitutions. In the latter, bivalent cations may be replaced by trivalent cations and vacancies (\square). The general unit formula becomes: $[(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{R}_{3-y-z}^{2+}\text{R}_y^{3+}\square_z)(\text{OH})]^{(x-y+2z)-}$.

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

- 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

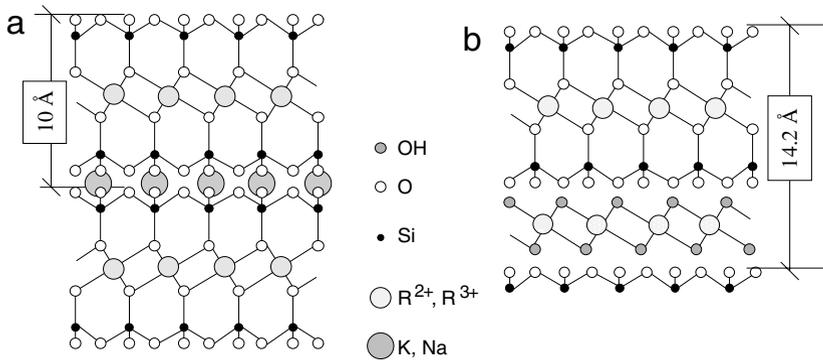


Fig. 1.9a,b. Crystal structures derived from the 2:1 layer. a) Presence of an interlayer sheet (micas, vermiculites, smectites). b) Presence of a brucite-like sheet (chlorites)

$$x - y + 2z = -(0.7 - 0.6) \text{ or } x - y + 2z = -(0.6 - 0.3) \text{ is balanced by } K^+, Ca^{2+}, Mg^{2+} \text{ or } Na^+.$$

The interlayer cations are situated in the ditrigonal cavities outlined by two opposite tetrahedral sheets (Fig. 1.9a). If the negative charge of the 2:1 layer is high, they serve as “locks” strongly bonding these layers together. No expansion of the interlayer sheet is possible.

The *a* and *b* dimensions as well as angle β of the unit cell (for a single 2:1 layer whatever the polytype is; annex 2) depend on the substitution rate in tetrahedral and octahedral sheets (Table 1.3). The *c* dimension of vermiculites and smectites varies as a function of the number of sheets of polar molecules such as water, glycol, glycerol, and alkylammonium (refer to Sect. 1.1.1.3).

The unit cell molar volumes of muscovite $[(Si_6Al_2)O_{20}(Al_4)(OH)_4K_2]$ and phlogopite $[(Si_6Al_2)O_{20}(Mg_6)(OH)_4K_2]$ are respectively:

$$V_{mus} = 5.19 \times 9.04 \times 10.04 = 471.05 \times 10^{-30} \text{ m}^3 \tag{1.16}$$

$$V_{phlo} = 5.314 \times 9.204 \times 10.171 = 497.46 \times 10^{-30} \text{ m}^3 \tag{1.17}$$

These values have to be multiplied by 2, 3 or 6 for 2M and 2Or, 3T or 6H polytypes respectively). Their density is given by:

Table 1.3. Unit cell parameters of 2:1 phyllosilicates with an interlayer sheet

Parameter	Dioctahedral			Trioctahedral		
<i>a</i> (Å)	5.19	5.23	5.18	5.17	5.33	5.34
<i>b</i> (Å)	9.00	9.06	8.99	9.08	9.23	9.25
<i>c</i> (Å)	20.00	10.13	9.6; 14.4; 16.8	9.6; 15.4; 17.1	20.1	9.6; 14.9; 16.4
β	95.7°	100.92°	–	–	95.1°	97°

$$\rho_{\text{mus}} = \frac{796.62}{471.05 \times 10^{-30} \times 6.02252 \times 10^{23}} = 280.81 \times 10^4 \text{ g} \cdot \text{m}^{-3} \quad (1.18)$$

$$\rho_{\text{phlo}} = \frac{834.5}{497.46 \times 10^{-30} \times 8.02252 \times 10^{23}} = 278.54 \times 10^4 \text{ g} \cdot \text{m}^{-3} \quad (1.19)$$

2:1:1 Layers (Brucite-Like Sheet): Chlorites

Trioctahedral chlorites are the most common representatives (Bailey 1975). Their crystal structure derives from the combination of a talc-like 2:1 layer with a brucite-like octahedral sheet (Fig. 1.9b). 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 means. 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 ($\text{R}^{3+} = \text{Al}^{3+} + \text{Fe}^{3+}$). According to Deer et al. (1962), the unit cell parameters of single chlorite layers (whatever the polytypes) are: $a = 5.3$; $b = 9.2$ and $c = 14.3 \text{ \AA}$, $\beta = 97^\circ$. The unit cell volume is then $697.27 \times 10^{-30} \text{ m}^3$. The density of this “theoretical” chlorite is $\rho_{\text{chl}} = 264.68 \times 10^4 \text{ g} \cdot \text{m}^{-3}$.

The two other varieties of chlorite 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 pyrophyllite-like layer with the addition of a brucite-like octahedral sheet.

Structure with Channelways: Palygorskite and Sepiolite

The crystal structure of these two minerals differs from that of 1:1, 2:1 or 2:1:1 phyllosilicates. The $[\text{SiO}_4]^{4-}$ tetrahedra periodically point outward and inward in groups of four (palygorskite) or six (sepiolite), thus making the octahedral sheet discontinuous. Therefore, tetrahedra form chains that are similar to those of amphiboles (Fig. 1.10). These chains extend along the x -direction (i.e. parallel to the a unit cell dimension), which gives the crystals a fibrous appearance. The octahedral sheet is close to the dioctahedral type. Its constituent cations Mg, Al, Fe^{2+} and Fe^{3+} are so ordered that the vacant site is at the centre of the chain. The overall negative charge results from substitutions of Al for Si in tetrahedra and of R^{3+} for R^{2+} in octahedra and is generally weak.

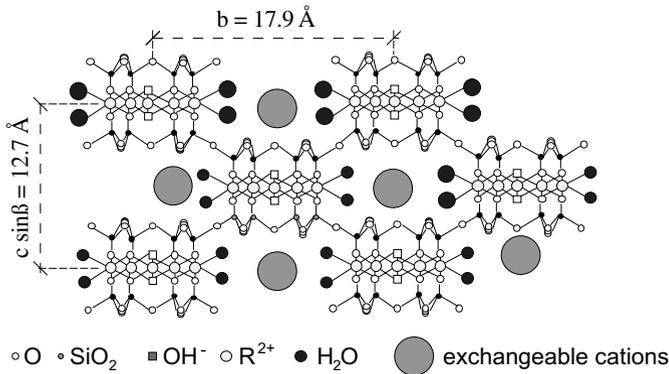


Fig. 1.10. Crystal structure of palygorskite. Channelways of rectangular section contain molecules of water and exchangeable cations that compensate for the positive charge deficiency of the tetrahedral and octahedral sheets

It is balanced by exchangeable cations that are located in channelways with water molecules.

1.1.1.3

A Strange Clay Mineral Property: the "Swelling" of the Interlayer Sheet

The "swelling" property is determined by the ability of cations to retain their polar molecule "shell" (water, glycol, glycerol) within the interlayer environment (Douglas et al. 1980). This property does not exist if the charge of the layer is too high (micas, chlorites) or zero (pyrophyllite, talc). More simply, this property is characteristic of di- and trioctahedral smectites and vermiculites (Table 1.6). Polar molecules are organised into layers whose number varies inversely with the interlayer charge:

1. charge contained between 0.8 and 0.6: 1 layer of polar molecules (di- or trioctahedral vermiculites and high-charge beidellites). High-charge saponites absorb 1 to 2 layers of polar molecules.
2. charge contained between 0.6 and 0.3: 2 to 3 layers of polar molecules (beidellites, montmorillonites and saponites, stevensites);

In the interlayer zone, cations are framed by ethylene glycol molecules, which are weakly bonded to the surface of tetrahedral sheets (hydrogen bonds). Like the water molecules, they are organised into more or less continuous layers.

Adsorption of polar molecules (water or organic molecules) alters the c dimension either progressively and regularly or in stages (Fig. 1.11). The total expansion is equal to the sum of the individual expansion of each layer able to absorb a varying number of water (0 to 3) or ethylene glycol layers (0 to 2). For clay with layers having a given charge, the number of absorbed water layers depends on two factors: the nature of the interlayer cation (Table 1.4) and the

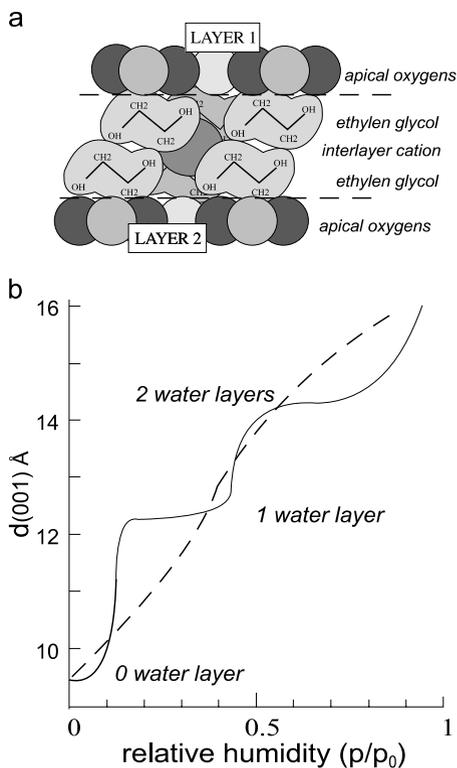


Fig. 1.11a,b. Adsorption of polar molecules. a) Two ethylene glycol layers; b) Relations between the crystal c dimension and the water saturation state of the interlayer zone. p/p_0 : partial pressure of water

Table 1.4. 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

Hydration state	c dimension (Å)	Li ⁺	Exchangeable cations			
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
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	c dimension (Å)	Li ⁺	Exchangeable cations			
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
2 glycol layers	16.9–17.1	M	MB	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		

partial pressure (p/p_0) of water or ethylene glycol. A stage variation of the total expansion implies that all the layers behave homogeneously and fix 1 or 2 water or ethylene glycol layers for a given range of p/p_0 . On the contrary, a progressive variation implies that clay behaves as a mixed-layer mineral composed of layers having 0, 1 or 2 polar molecule interlayer sheets.

Now that the main types of phyllosilicate layers have been determined, the investigation scale can move from one angström to one nanometer, and the way they are stacked in the phyllosilicate crystals can be addressed. At this scale, we will discover the huge diversity of clay species. This will lead us to discriminate between crystals, particles and aggregates. The X-ray diffraction identification of clay minerals remains the guiding principle.

1.1.2

Crystal – Particle – Aggregate

A crystal, even as tiny as commonly found in clay species, is a three-dimensional object. It is composed of several layers that can be stacked in different ways. Theoretically, the number of layers should determine the crystal thickness. However, as simple as it may sound, the thickness of clay mineral crystals is difficult to measure routinely because of the presence of crystal defects. One must keep in mind that XRD only determines the size of the scattering coherent domains. Initially, the stacking sequences will be considered perfect and the effects of the presence of crystal defects will be ignored. Accordingly, emphasis will be put on the two typical structures that are commonly found in clay species depending on layer composition.

1.1.2.1

Stacking Sequence of Layers of Identical Composition: Polytypes

Phyllosilicates form crystals that are limited externally by crystalline faces whose shape and dimensions depend on growth processes (see Sect. 1.2.3). The thickness depends on the number of stacked layers. Simple-species crystals are composed of layers of identical chemical composition. For a given composition, different stacking modes are possible; each of them corresponds to a polytype. A polytype is considered here as a one-dimensional polymorph: the density stays constant, because the unit cell dimensions of each layer remain unchanged. On the contrary, the “structural formula” depicts the composition of the “over-unit cell” and changes with the polytype (annex 2).

For a given layer, octahedra show two different positions referred to as I and II in Fig. 1.12a. Position II can be superposed on position I after a rotation of 60° . Tetrahedral sheets, represented by hexagons formed by apical oxygens, exhibit a $\frac{a}{3}$ spacing shift whose direction depends on the position of the octahedral sheet (I or II). The angle between both directions of this shift is 60° . The nomenclature of polytypes is standardised: the number on the left indicates the number of layers per over-unit cell in the stacking sequence, the letter indicates the crystal system, the indexed number on the right gives the number