



Bruce Velde  
Alain Meunier



# The Origin of Clay Minerals in Soils and Weathered Rocks

 Springer

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With 195 Figures and 23 Tables

 Springer

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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  $\mu\text{m}$  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  $\mu\text{m}$  for, geologists; 1  $\mu\text{m}$  for chemists; and 4  $\mu\text{m}$  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  $\mu\text{m}$ : for instance, 50  $\mu\text{m}$  sized kaolinites or illites are frequently observed in diagenetic environments. However surface alteration usually produces new phases almost always of less than 2  $\mu\text{m}$  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).

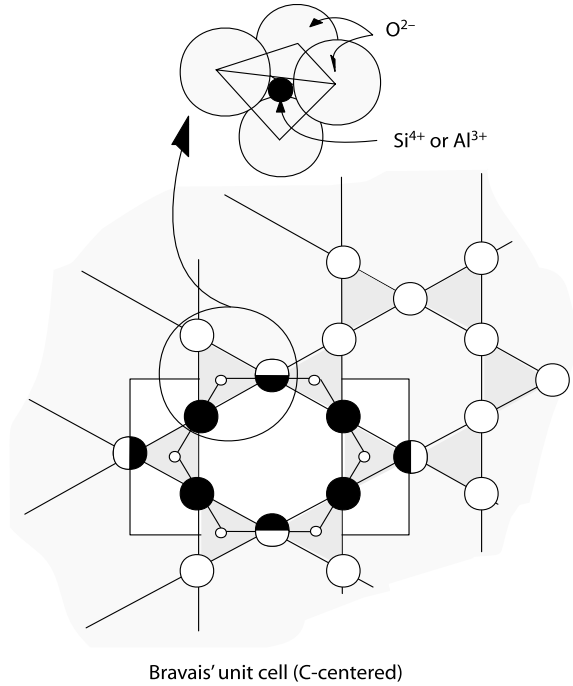
##### *The Tetrahedral Sheet*

The tetrahedral sheets of phyllosilicates are composed of  $\text{SiO}_4^{4-}$  or  $\text{AlO}_4^{5-}$  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  $\text{O}^{2-}$  anion bonds with a  $\text{Si}^{4+}$ - $\text{Si}^{4+}$  or a  $\text{Si}^{4+}$ - $\text{Al}^{3+}$  cation pair. The  $\text{Al}^{3+}$ - $\text{Al}^{3+}$  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).

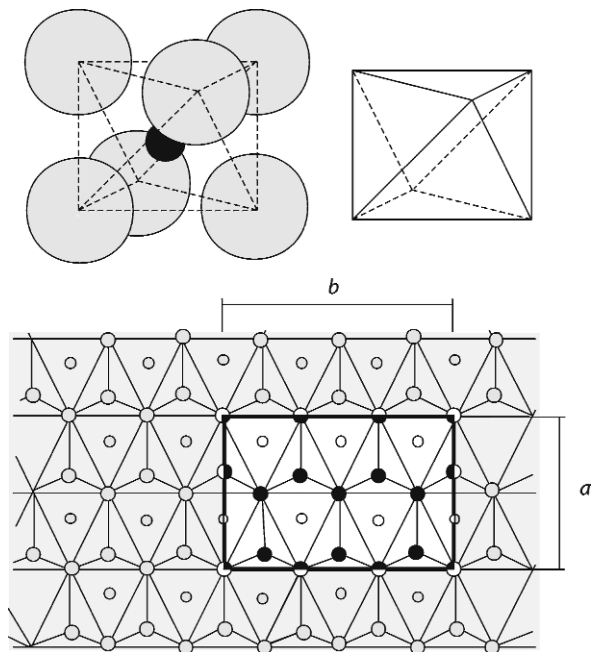
##### *The Octahedral Sheet*

According to their ionic radius, the  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$  cations exhibit a 6-fold coordination when bonded to  $\text{O}^{2-}$  or  $\text{OH}^-$  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  $\text{Al}^{3+}$  (dioctahedral) and  $\text{Mg}^{2+}$  (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  $10\text{O}^{2-}$  for  $4\text{Si}^{4+}$



**Fig. 1.2.** Structure of the octahedral layer. The  $b$  dimensions of the trioctahedral (brucite) and dioctahedral (gibbsite) unit cells are  $9.43$  and  $8.64 \text{ \AA}$  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  $\alpha$ ) and parallel (thinning angle  $\tau$ ) 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  $\psi$ ). 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

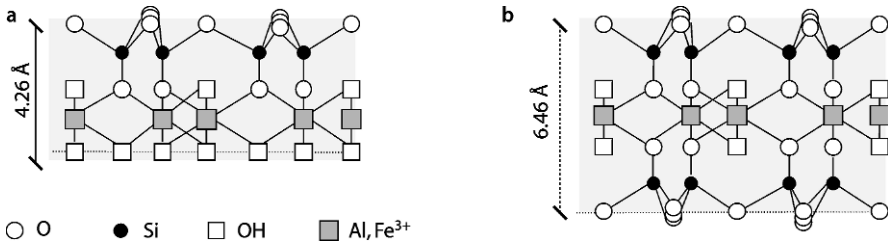
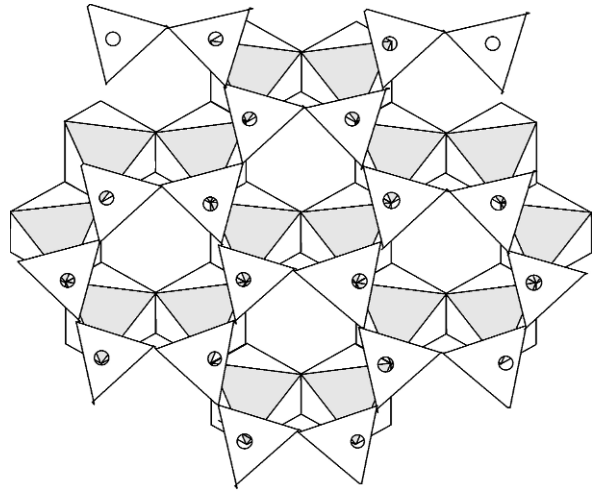


Fig. 1.4. The two crystal structure types of dioctahedral phyllosilicates; a 1:1 layer; b 2:1 layer

**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 Al<sup>3+</sup> cations while two of the six possible sites are vacant. The unit formula of kaolinite is: Si<sub>4</sub>O<sub>10</sub>Al<sub>4</sub>(OH)<sub>8</sub>. In the trioctahedral sheet of the high temperature mineral lizardite all six sites are occupied by Mg<sup>2+</sup> cations; the unit formula is: Si<sub>4</sub>O<sub>10</sub>Mg<sub>6</sub>(OH)<sub>8</sub>. 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 [Si<sub>8</sub>O<sub>20</sub>Al<sub>4</sub>(OH)<sub>4</sub>]. 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  $\text{O}^{2-}$  and  $\text{OH}^-$  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.

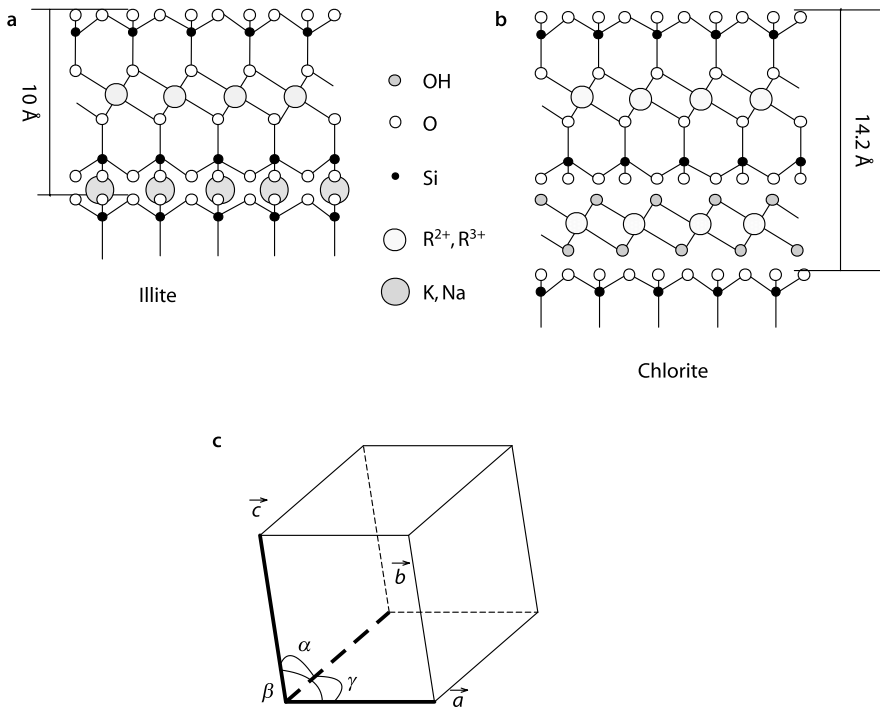
#### *The Cation Interlayer Sheet (2:1 Phyllosilicates)*

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 ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , 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  $\text{K}^+$  and  $\text{NH}_4^+$  (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  $\alpha$  angle is equal or lower to  $90^\circ$  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).

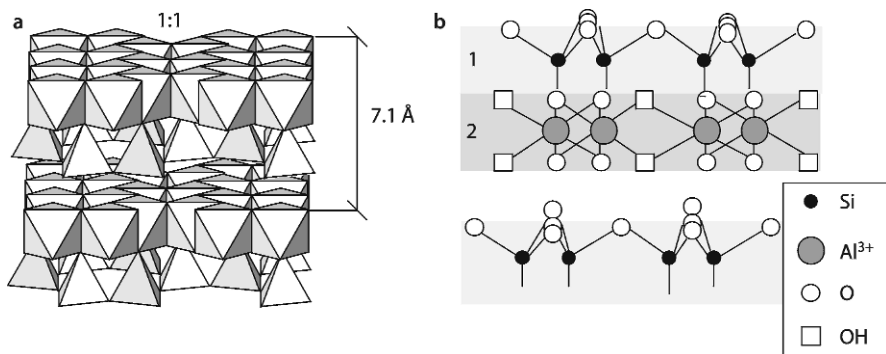
## 1.1.3

## The Different Layer-to-Layer Chemical Bonds

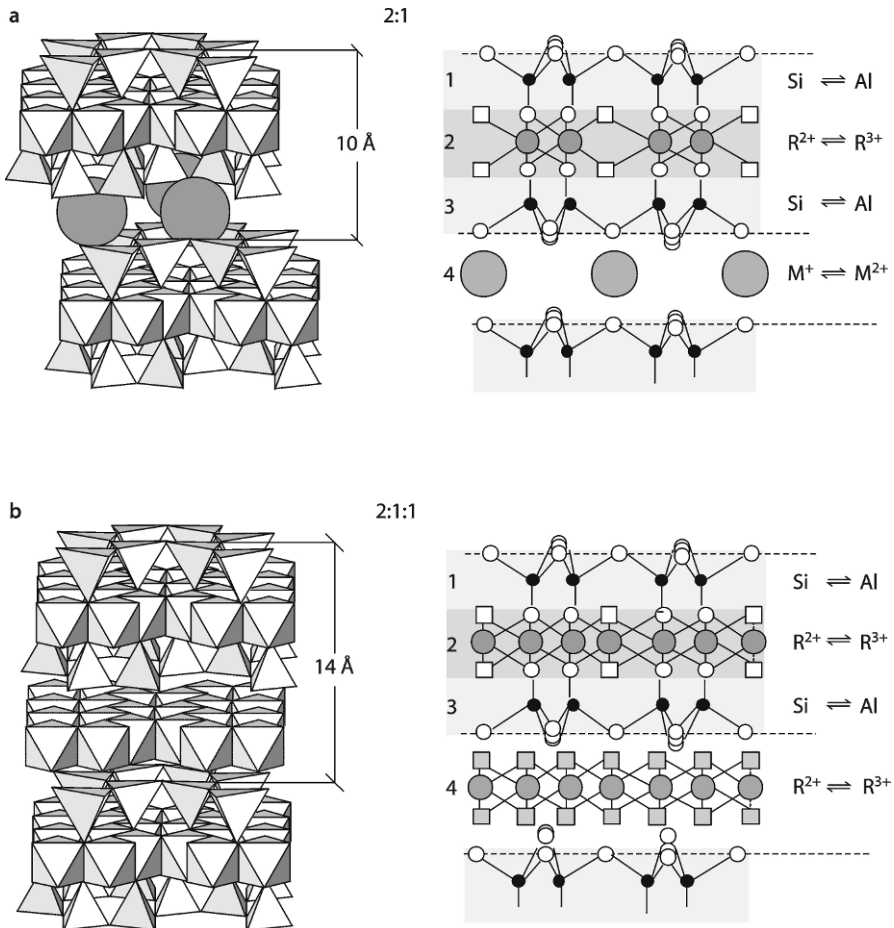
Some phyllosilicates are composed of layers which are electrically neutral because either there is no cation substitution in the tetrahedral and octahedral sheets (kaolinite, serpentine, pyrophyllite, talc) or because the negative charge in the tetrahedral sheet is compensated by a positive charge in 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<sub>1</sub> 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-

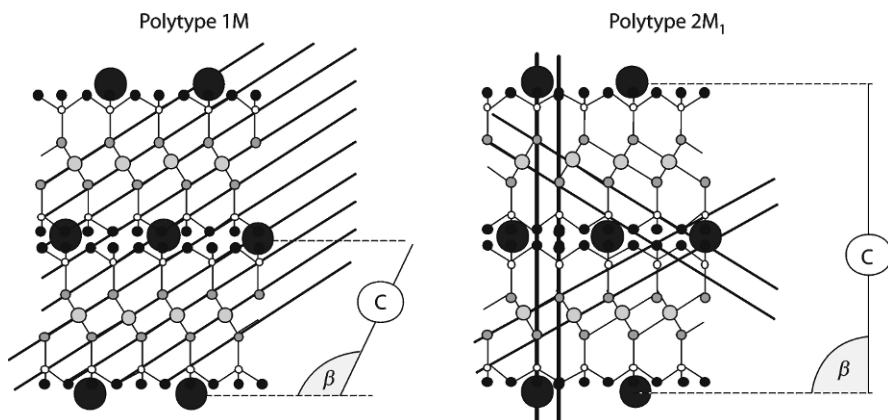
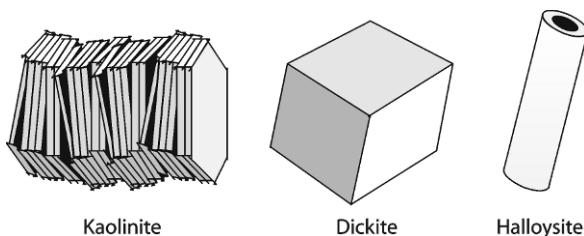


Fig. 1.8. Relation between the symmetry degree and the number of  $(hkl)$  planes in 1M and 2M<sub>1</sub> micas

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

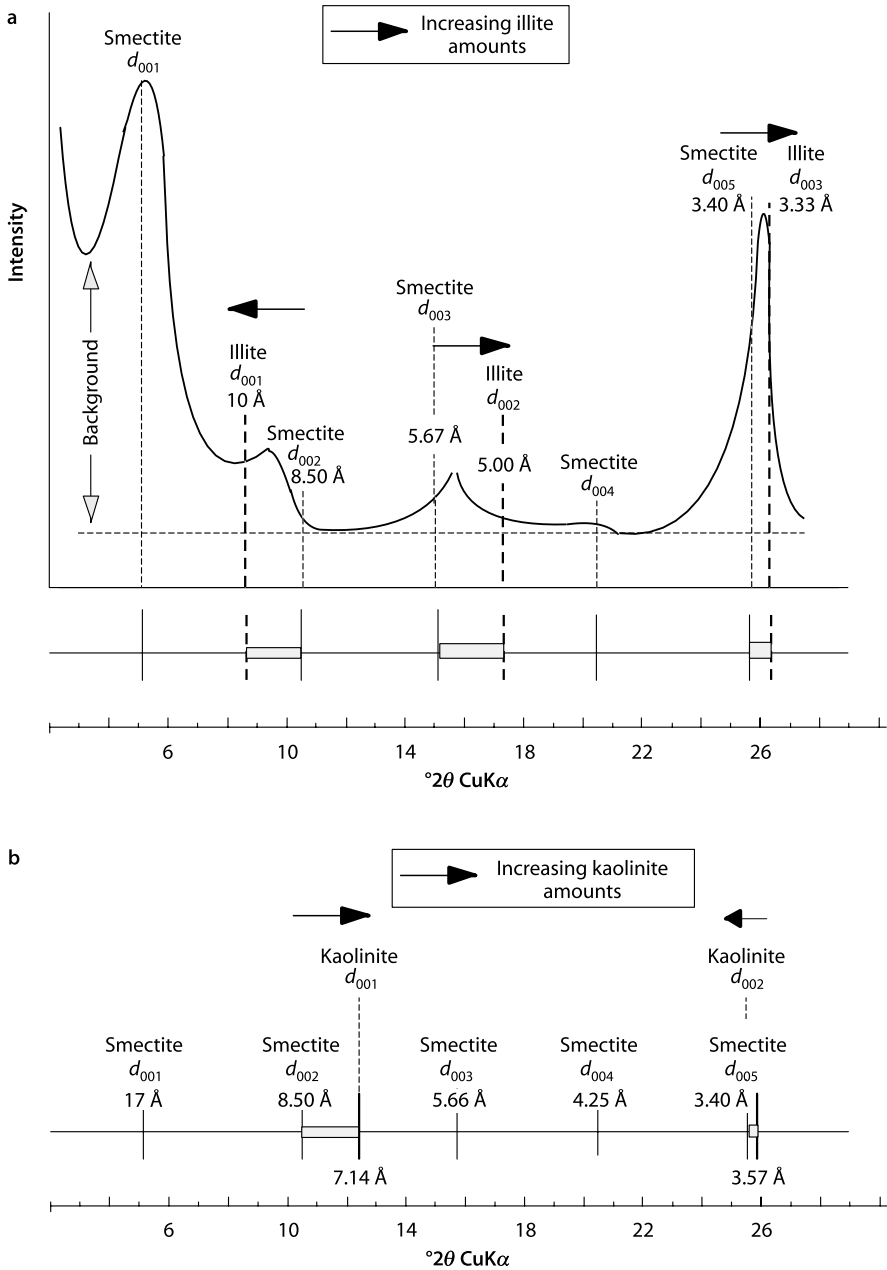
Mixed layer minerals (MLMs) are crystallites composed of two or more types of basic structural layers, 2:1 or more rarely 2:1:1 and 1:1. These minerals are most frequently found in the soil or upper parts of an alteration sequence. Their importance as far as mineral stability and transformation is not 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

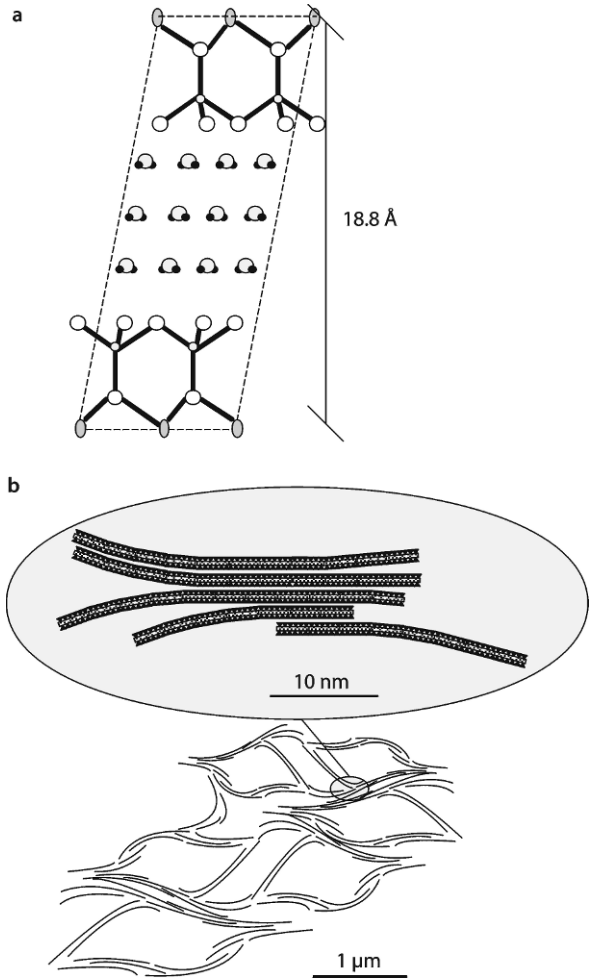
The term crystallite is used here for small dimension crystals. According to Putnis (1992), “a crystal is ideally made up of a repetition of identical building blocks, or unit cell, filling space, each unit cell in an identical orientation and related to the next by translation along of three crystallographic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



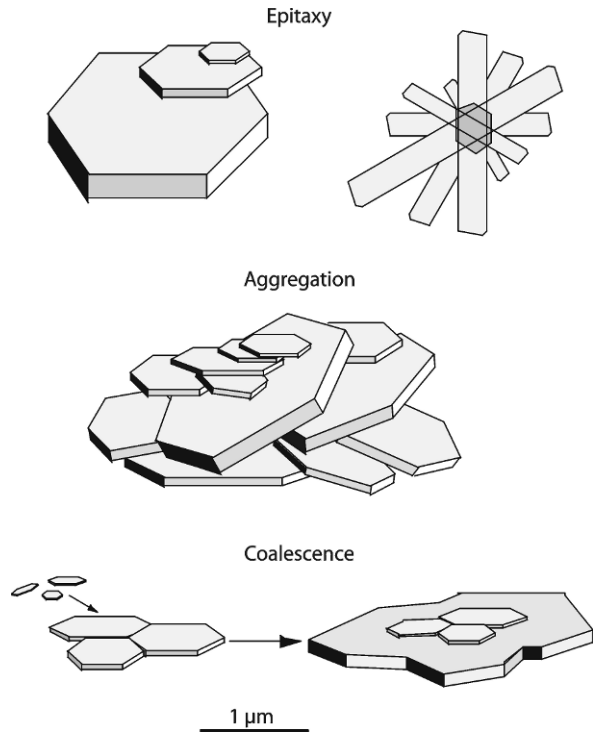
Generally, smectite crystals are small (crystallites below 1 μm) and very thin (a few nm, i.e. a few layers) while kaolinite and illite may reach higher dimensions (10 to 50 μm) and thickness (several tens of layers).

### 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  $\text{Fe}^{2+}$  replacing  $\text{Mg}^{2+}$  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  $\text{R}^{3+}$  for  $\text{R}^{2+}$  in the octahedral sheet imposes vacancies (symbolized by  $\langle \rangle$ ).

### ***Tetrahedral Substitutions***

In most of the 2:1 phyllosilicates,  $\text{Si}^{4+}$  may be replaced by  $\text{Al}^{3+}$  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  $\text{Si}^{4+}$  in 4 replaced by  $\text{Al}^{3+}$  (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  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$ , whose ionic radius is between 1.75 and 2.02 Å.
2. for 2:1 layer charge lower than about  $-0.75$  per  $\text{Si}_4\text{O}_{10}$  (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  $\text{Al}^{3+}$  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  $\text{Mg}^{2+}$  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

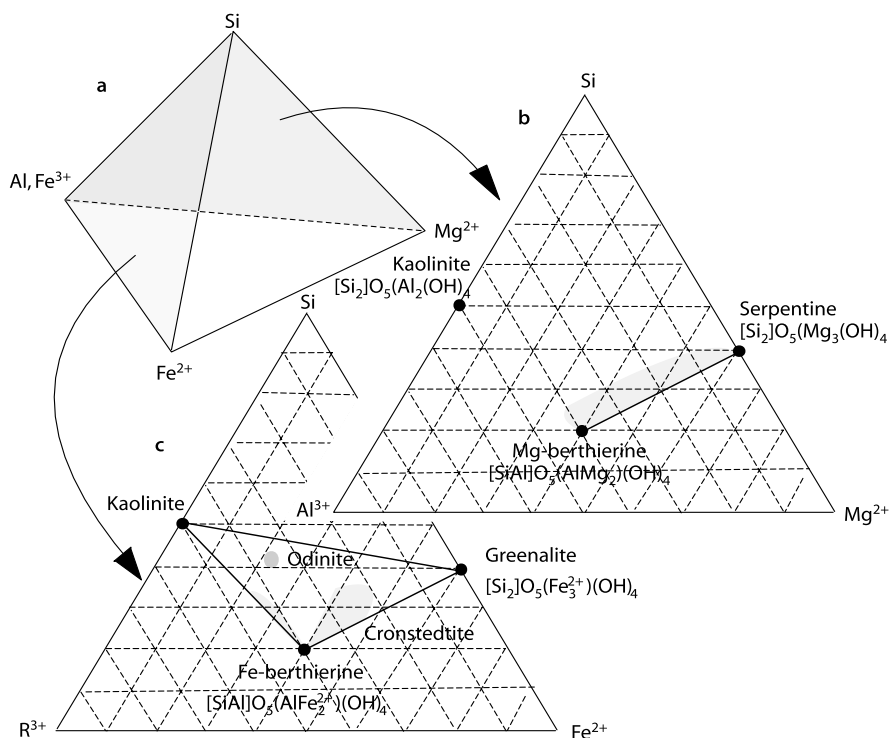


Fig. 1.13. Composition domains of 1:1 phyllosilicates in the Si–Al<sup>3+</sup>, Fe<sup>3+</sup>–Fe<sup>2+</sup>, Mg<sup>2+</sup> system; a the four component system; b the Si–Al–Mg system; c the Si–R<sup>3+</sup>–Fe<sup>2+</sup> system. The gray zones indicate the solid solutions

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  $3.0 \text{ \AA}$  according to Bailey 1980). The interlayer spacing of kaolinite is  $7.15 \text{ \AA}$ , that of lizardite  $7.25 \text{ \AA}$  for the pure magnesian end member; it increases with the substitution rate of Mg<sup>2+</sup> for Fe<sup>2+</sup>.

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-

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)<sup>-</sup> groups form one side of a triangular face on the right or on the left and 1 *trans*-octahedra (M1 site) in which (OH)<sup>-</sup> groups are located on the opposite vertices. Planes defined by the (OH)<sup>-</sup> 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).

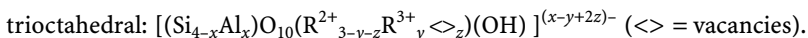
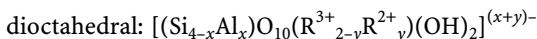
Pyrophyllite [Si<sub>4</sub>O<sub>10</sub>Al<sub>2</sub>(OH)<sub>2</sub>] is characterized by the presence of a vacancy in the *trans*-position. The actual unit cell dimensions are:  $a = 5.160$  Å;  $b = 8.966$  Å (angles  $\alpha$  and  $\gamma$  are close to 90°:  $\alpha = 91.03^\circ$  and  $\gamma = 89.75^\circ$ ). 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 [Si<sub>4</sub>O<sub>10</sub>Mg<sub>3</sub>(OH)<sub>2</sub>] 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<sup>+</sup> 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 Al<sup>3+</sup> for Si<sup>4+</sup> in the tetrahedral layer and of R<sup>2+</sup> for R<sup>3+</sup> 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 R<sup>3+</sup> substitution in the tetrahedral sheet; *y*: R<sup>2+</sup> for R<sup>3+</sup> substitutions in the octahedral sheet; *z*: number of octahedral vacancies (<>); *IC*: interlayer charge. Mineral types found in surface alteration are indicated in bold letters

<b>1:1 phyllosilicates ("7 Å phases")</b>		
Kaolinite	Si <sub>2</sub> O <sub>5</sub> Al <sub>2</sub> (OH) <sub>4</sub>	<i>x</i> = 0; <i>y</i> = 0
Chrysotile	Si <sub>2</sub> O <sub>5</sub> Mg <sub>3</sub> (OH) <sub>4</sub>	<i>x</i> = 0; <i>y</i> = 0
Antigorite	Si <sub>2</sub> O <sub>5</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>4</sub>	<i>x</i> = 0; <i>y</i> = 0
Nepouite	Si <sub>2</sub> O <sub>5</sub> Ni <sub>3</sub> (OH) <sub>4</sub>	<i>x</i> = 0; <i>y</i> = 0
Fraipontite	[Si <sub>2-x</sub> Al <sub>x</sub> ]O <sub>5</sub> (Zn <sub>3-y</sub> Al <sub>y</sub> ) <sub>3</sub> (OH) <sub>4</sub>	<i>x</i> = <i>y</i>
Amesite	[Si Al]O <sub>5</sub> (Mg <sub>2</sub> Al)(OH) <sub>4</sub>	<i>x</i> = -1; <i>y</i> = +1
Berthierine	[Si <sub>2-x</sub> Al <sub>x</sub> ]O <sub>5</sub> [(Fe <sup>2+</sup> ,Mg) <sub>3-y-z</sub> Fe <sup>3+</sup> <sub>y</sub> <> <sub>z</sub> ](OH) <sub>4</sub>	<i>x</i> = 6 + <i>y</i> - 2 <i>z</i>
Cronstedtite	[SiFe <sup>3+</sup> ]O <sub>5</sub> (Fe <sup>2+</sup> <sub>2</sub> Fe <sup>3+</sup> )(OH) <sub>4</sub>	<i>x</i> = <i>y</i> = 1
Greenalite	Si <sub>2</sub> O <sub>5</sub> (Fe <sup>2+</sup> <sub>3-y-z</sub> Fe <sup>3+</sup> <sub>y</sub> <> <sub>z</sub> )(OH) <sub>4</sub>	<i>x</i> = 0; <i>y</i> = 1/2 <i>z</i>
<b>2:1 phyllosilicates ("9 Å phases")</b>		
Pyrophyllite	Si <sub>4</sub> O <sub>10</sub> Al <sub>2</sub> (OH) <sub>2</sub>	<i>x</i> = 0; <i>y</i> = 0
Talc	Si <sub>4</sub> O <sub>10</sub> Mg <sub>3</sub> (OH) <sub>2</sub>	<i>x</i> = 0; <i>y</i> = 0
Minnesotaite	Si <sub>4</sub> O <sub>10</sub> (Fe <sup>2+</sup> ,Mg) <sub>3</sub> (OH) <sub>2</sub>	<i>X</i> = 0; <i>y</i> = 0
<b>2:1 phyllosilicates ("10 Å phases")</b>		
Muscovite	[Si <sub>3</sub> Al]O <sub>10</sub> Al <sub>2</sub> (OH) <sub>2</sub> K	<i>x</i> = -1; <i>y</i> = 0; <i>IC</i> = +1
Biotite	[Si <sub>3</sub> Al]O <sub>10</sub> (Fe <sup>2+</sup> ,Mg) <sub>3</sub> (OH) <sub>2</sub> K	<i>x</i> = 0; <i>y</i> = 0; <i>IC</i> = +1
Celadonite	Si <sub>4</sub> O <sub>10</sub> [(Al,Fe <sup>3+</sup> )(Fe <sup>2+</sup> ,Mg)](OH) <sub>2</sub> K	<i>x</i> + <i>y</i> = -1.0; <i>IC</i> = +1.0
Phengites	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> [(Al <sub>2-y</sub> (Fe <sup>2+</sup> ,Mg) <sub>y</sub> ](OH) <sub>2</sub> K <sub>x+y</sub>	<i>x</i> + <i>y</i> = -1.0; <i>IC</i> = +1.0
Glauconite	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> [(Al,Fe <sup>3+</sup> ) <sub>2-y</sub> (Fe <sup>2+</sup> ,Mg) <sub>y</sub> ](OH) <sub>2</sub> K <sub>x+y</sub>	<i>x</i> < -0.3; <i>y</i> < -0.6; <i>IC</i> ≅ +0.9
<b>Illite</b>	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> [(Al <sub>2-y</sub> (Fe <sup>2+</sup> ,Mg) <sub>y</sub> ](OH) <sub>2</sub> K <sub>x+y</sub>	-0.3 < <i>x</i> < -0.7; -0.2 < <i>y</i> < -0.6; <i>IC</i> ≅ +0.9
<b>Vermiculite (Diocahedral)</b>	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> [(Al,Fe <sup>3+</sup> ) <sub>2-y</sub> Mg <sub>y</sub> ](OH) <sub>2</sub> K <sub>x+y</sub>	-0.3 < <i>x</i> < -0.7; -0.2 < <i>y</i> < -0.6; +0.6 < <i>IC</i> < +0.8
<b>Beidellite</b>	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> (Al,Fe <sup>3+</sup> ) <sub>2</sub> (OH) <sub>2</sub> K <sub>x</sub>	-0.3 < <i>x</i> < -0.6; <i>y</i> = 0; +0.3 < <i>IC</i> < +0.6
<b>Montmorillonite</b>	Si <sub>4</sub> O <sub>10</sub> [(Al,Fe <sup>3+</sup> ) <sub>2-y</sub> Mg <sub>y</sub> ](OH) <sub>2</sub> K <sub>y</sub>	<i>x</i> = 0; -0.3 < <i>y</i> < -0.6; +0.3 < <i>IC</i> < +0.6
<b>Vermiculite (Triocahedral)</b>	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> [(Fe <sup>2+</sup> ,Mg) <sub>3-y-z</sub> (Al,Fe <sup>3+</sup> ) <sub>y</sub> <> <sub>z</sub> ](OH) <sub>2</sub> K <sub>x+y-2z</sub>	-0.3 < <i>x</i> < -0.7; -0.2 < <i>y</i> < -0.6; +0.6 < <i>IC</i> < +0.8
<b>Saponite</b>	[Si <sub>4-x</sub> Al <sub>x</sub> ]O <sub>10</sub> [(Fe <sup>2+</sup> ,Mg) <sub>3-y-z</sub> (Al,Fe <sup>3+</sup> ) <sub>y</sub> <> <sub>z</sub> ](OH) <sub>2</sub> K <sub>x+y-2z</sub>	-0.3 < <i>x</i> < -0.6; <i>y</i> + 2 <i>z</i> = 0; +0.3 < <i>IC</i> < +0.6
<b>Stevensite</b>	Si <sub>4</sub> O <sub>10</sub> [(Fe <sup>2+</sup> ,Mg) <sub>3-y-z</sub> (Al,Fe <sup>3+</sup> ) <sub>y</sub> <> <sub>z</sub> ](OH) <sub>2</sub> K <sub>x+y-2z</sub>	<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)	$[\text{Si}_{4-x}\text{Al}_x]_3\text{O}_{10}[(\text{Fe}^{2+}, \text{Mg})_{3-y-z}(\text{Al}, \text{Fe}^{3+})_y]_2(\text{OH})_2\text{AlMg}_2(\text{OH})_6$	$-0.3 < x < -1.0; 0 < y + 2z < -0.7;$ $I/C \equiv +1.0$
Sudoite (Di-Trioctahedral)	$[\text{Si}_{4-x}\text{Al}_x]_3\text{O}_{10}[(\text{Al}, \text{Fe}^{3+})_{2-y'}(\text{Fe}^{2+}, \text{Mg})_{y'}]_1(\text{OH})_2\text{AlMg}_2(\text{OH})_6$	$-0.3 < x < -1.0; 0 < y < -0.7; I/C \equiv +1.0$
Donbassite (Dioctahedral)	$[\text{Si}_3\text{Al}]_3\text{O}_{10}(\text{Al}, \text{Fe}^{3+})_2(\text{OH})_2\text{Al}_2(\text{OH})_6$	$x = -1.0; I/C \equiv +1.0$

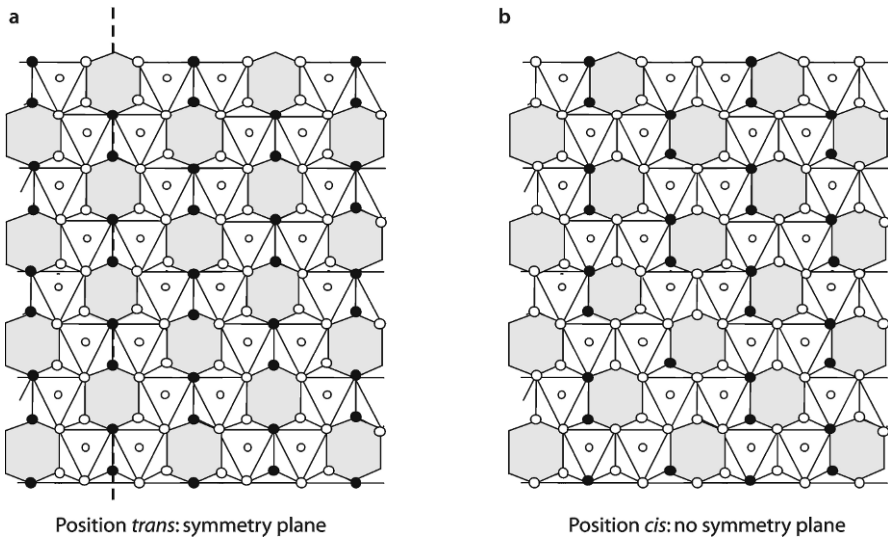


Fig. 1.14. Crystal structures of 2:1 dioctahedral phyllosilicates; **a** the octahedral vacant site is in the *trans* position inducing the presence of a symmetry plane in the octahedral sheet; **b** the octahedral vacant site is in the *cis* position, no symmetry plane

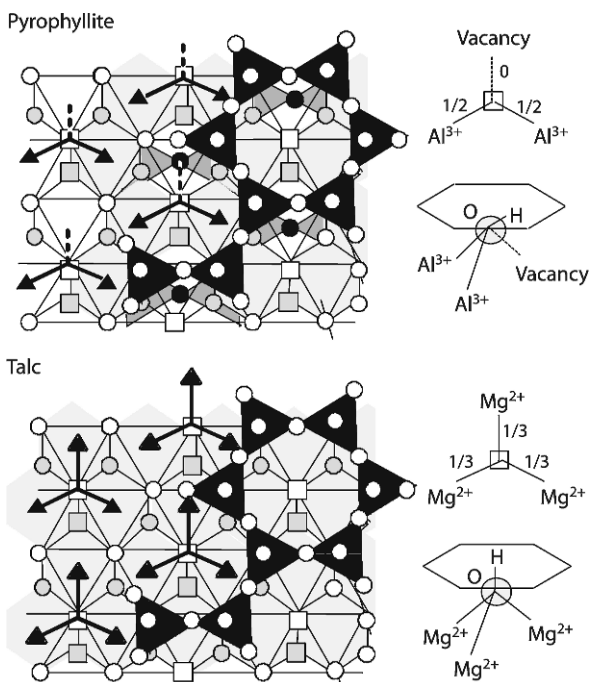
- dioctahedral minerals: brittle micas (margarite),  $x + y = -2$ , balanced by  $1 \text{ Ca}^{2+}$ ; micas (muscovite, phengite, celadonite),  $x + y = -1$ , balanced by  $1 \text{ K}^+$ ; vermiculites or dioctahedral smectites whose respective charge  $x + y = -(0.7-0.6)$  or  $x + y = -(0.6-0.3)$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

### 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  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  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  $14.2 \text{ \AA}$ ; 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

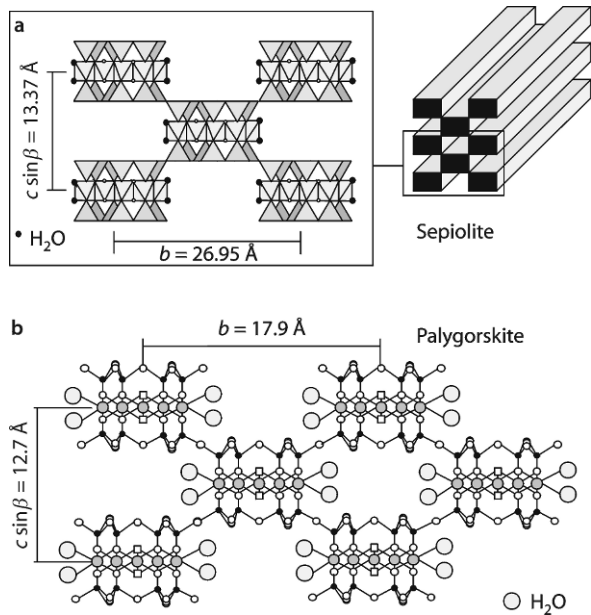
Sepiolite and palygorskite are considered to be clay minerals because they are always small sized crystals (most often less than 2  $\mu\text{m}$  long) and because they form in soils or sediments in surface conditions. Their crystal shape is typically that of fibers because of two particularities of 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,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  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

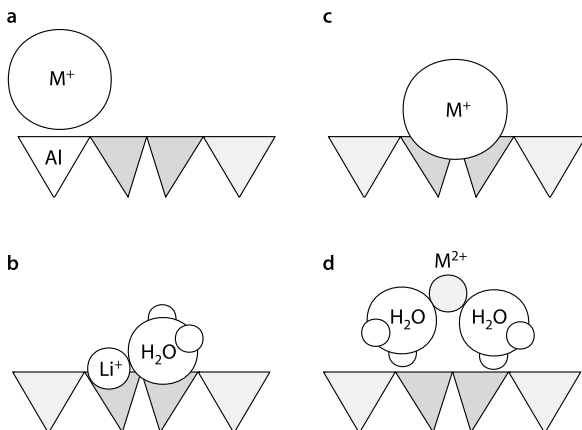
### 1.5.1 Hydration and Swelling

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.

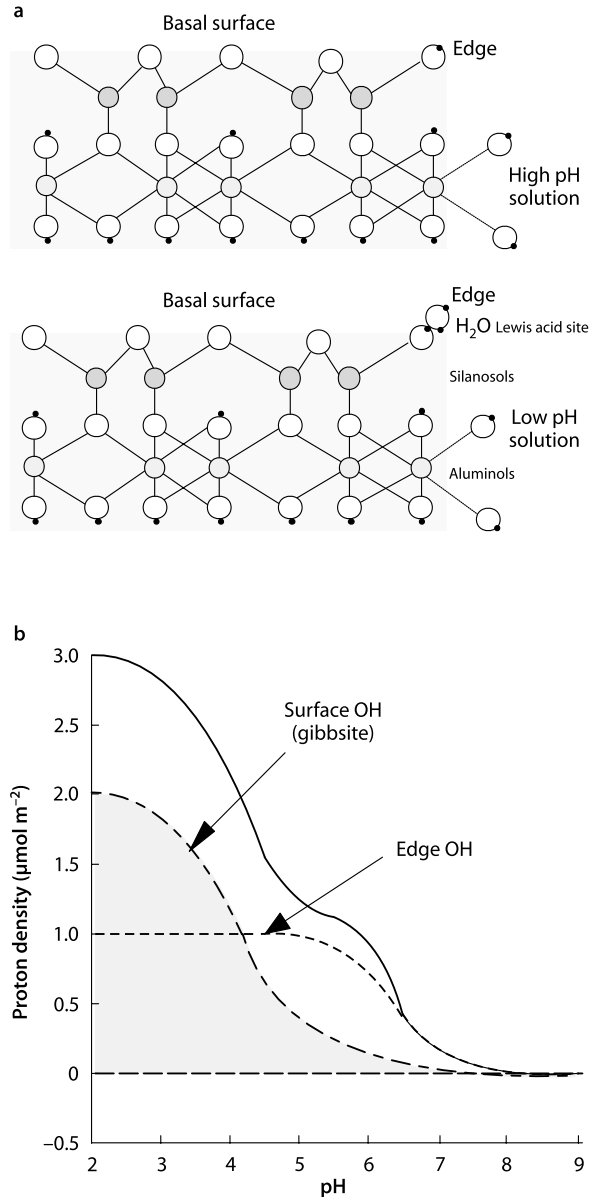
Molecular dynamics calculations show that the interlayer cations are located in different places according to their capacity to lose or conserve their water molecule “shell”. They are located near the negative charges when emerging at the surface of the 2:1 layer. If totally dehydrated, they are close 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



$\text{Ba}^{2+}$ ,  $\text{Na}^+$  and  $\text{Li}^+$  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  $\text{Li}^+$  ion is small enough to enter with water molecules (Fig. 1.18c).  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  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  $\text{H}^+$  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 cations, 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 <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
<b>Hydration state</b>						
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			
<b>Ethylene glycol saturation state</b>						
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 R<sup>2+</sup>-OH or R<sup>3+</sup>-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).

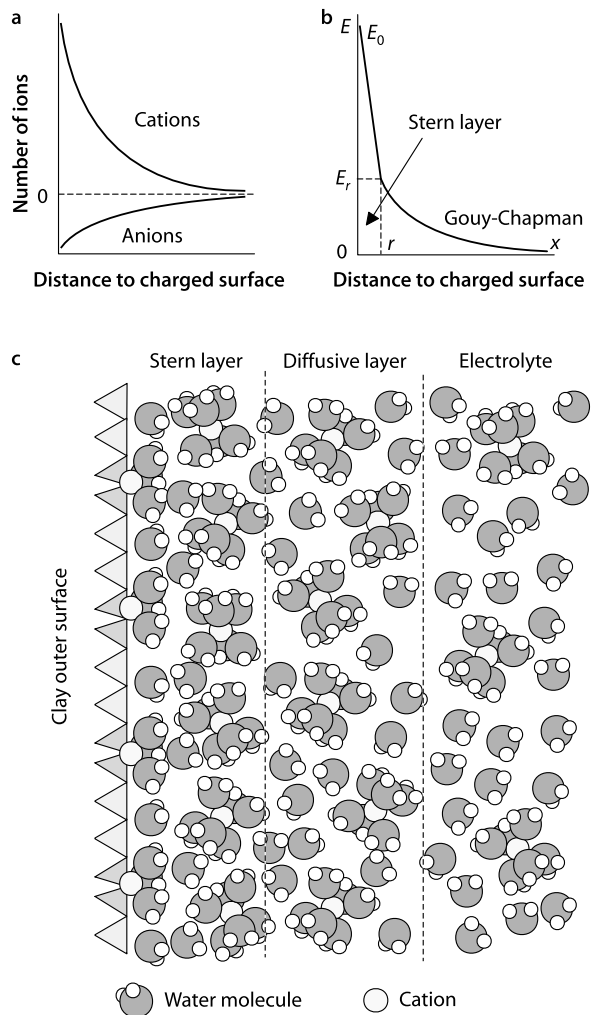
### 1.5.3

#### **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

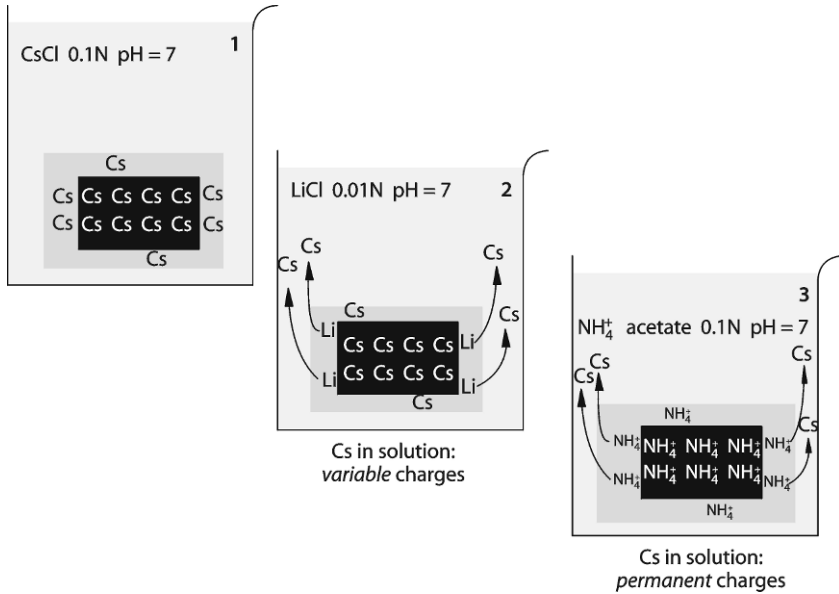
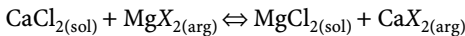


Fig. 1.20. Cation exchange controlled by variable and permanent charges

5 to 10 cmol kg<sup>-1</sup>. 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

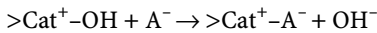
**Table 1.3.** Representative CEC values of the main clay species as measured at pH = 7 and 25 °C

Mineral	CEC (cmol kg <sup>-1</sup> )
Kaolinite	5 – 15
Illite	25 – 40
Vermiculite	100 – 150
Montmorillonite	80 – 120
Chlorite	5 – 15

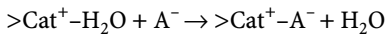
tend to use standard methods of determination, fixed solution concentrations and room temperature to determine the exchange phenomena of soil clays. Further information on the way cation selectivity operates is given in Annex 3.

### *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



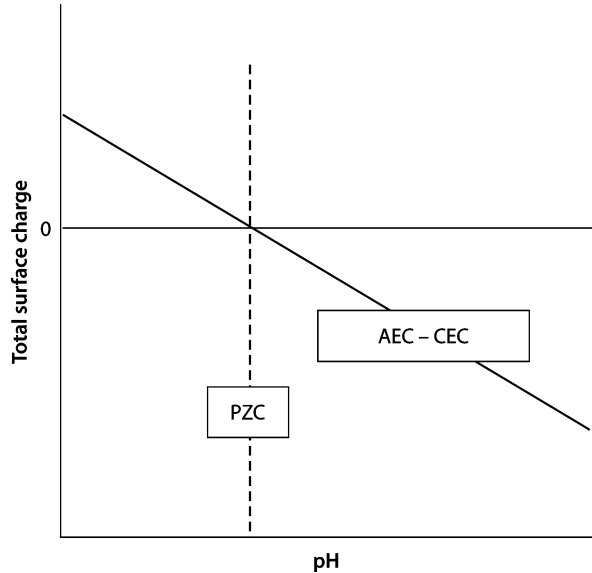
The AEC is obviously greater for minerals having a great number of interrupted bonds (allophanes and hydroxides).

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 R<sup>2+</sup>-OH or R<sup>3+</sup>-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?

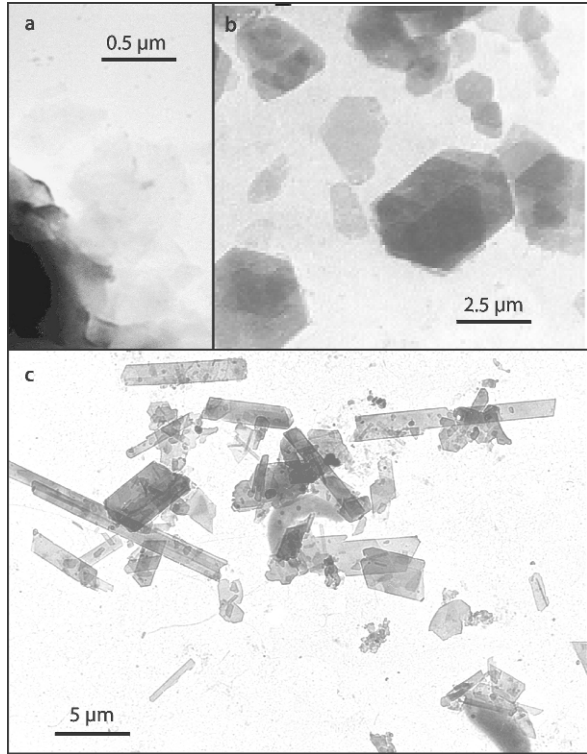
In order to attempt to answer this question we will often consider high temperature clay minerals, of diagenetic or hydrothermal origins in the discussion which follows. We assume that there is a strong parallel between these phases and those formed under conditions of lower temperature at the surface 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  $\text{nm}^2$  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  $\mu\text{m}$ . 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  $\mu\text{m}$  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 m<sup>2</sup> g<sup>-1</sup>. 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 m<sup>2</sup> g<sup>-1</sup> 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 m<sup>2</sup> g<sup>-1</sup>. 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<sup>-1</sup>),  
 $R_{p/A}$ : mean perimeter vs. area ratio (m<sup>-1</sup>),  
 $N_{oc}$  and  $N_T$ : site densities (mol m<sup>-2</sup>)  
 $\rho$ : clay density (g cm<sup>-3</sup>).

### 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 O<sup>2-</sup> and OH<sup>-</sup> 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.

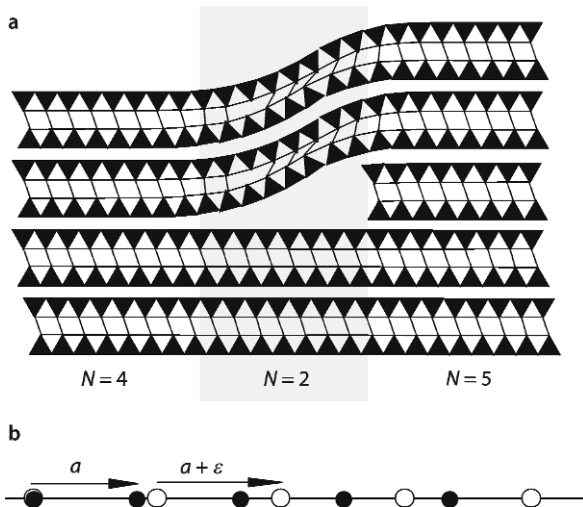
Crystal defects are theoretically disruptions of the 3D periodicity. The dimension scale of the defects is that of the unit cell. Because of their specific layer organization, the crystal defects for phyllosilicates have to be considered in the *a-b* plane (1:1 or 2:1 layers) and in the *c* direction.

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  $\alpha$  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.

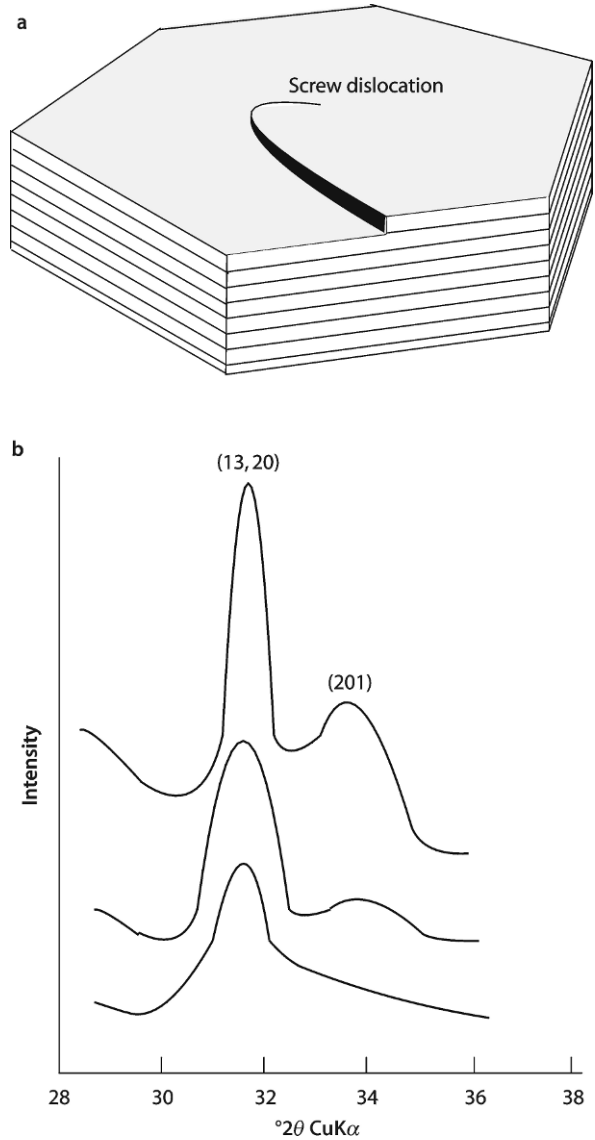
### ***Crystal Defects in Mixed Layer Minerals***

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)***

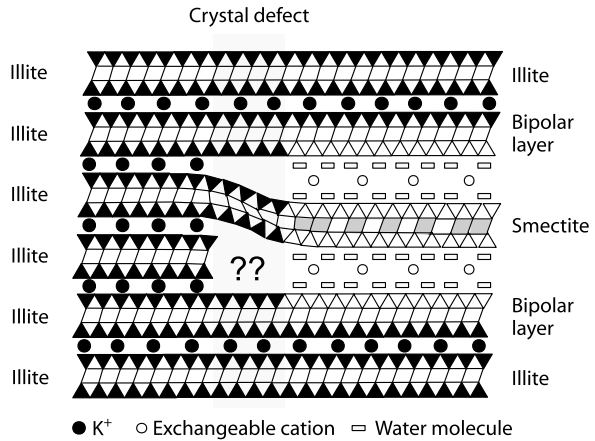
The variation of the layer thickness ( $d_{001}$ ) is related to the number and the spatial organization of water molecules in the interlayer zone. Thus, this kind of crystal defect is typical of smectites. The presence of these defects is detected by the modification

**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

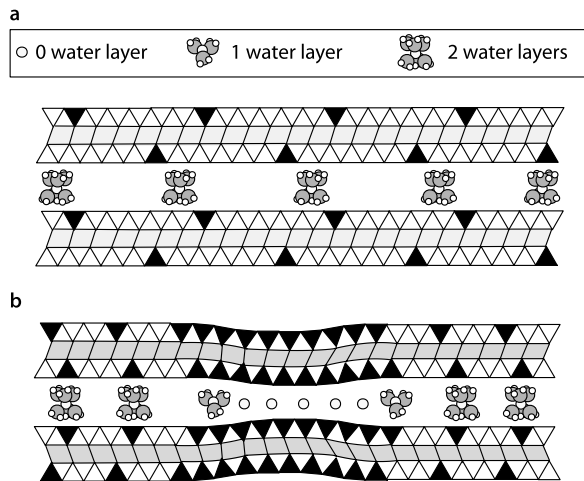


of the  $(00l)$  peak profiles of XRD patterns of oriented preparations. Ferrage et al. (2005, 2007) using XRD profile modelling showed the co-existence of smectite layers having contrasted hydration states: homogeneous 2 water layers (Fig. 1.26a) and variable number of water layers (Fig. 1.26b). The 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  $\mu\text{m}$  diameter is composed of about  $1.7 \times 10^6$  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  $\text{Al}^{3+}$  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  $\text{Al}^{3+}$  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  $\text{Al}^{3+}$  cations are dispersed. There is no requirement for long-range order.

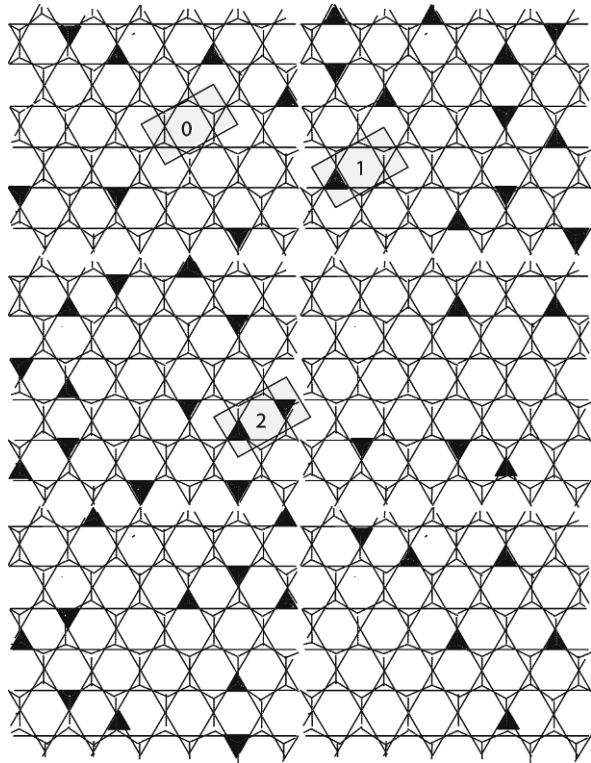
A typical  $\text{Al}^{3+}$  cation distribution in the tetrahedral sheet of phengite is given in Fig. 1.27. It theoretically allows three different sites having a unit-cell charge of 0, -1 or -2 respectively. The probability for the existence of -2 charged sites is weak.

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  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  which are present only in specific occurrences. The distribution of  $\text{Fe}^{3+}$  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  $\text{Al}^{3+}$  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

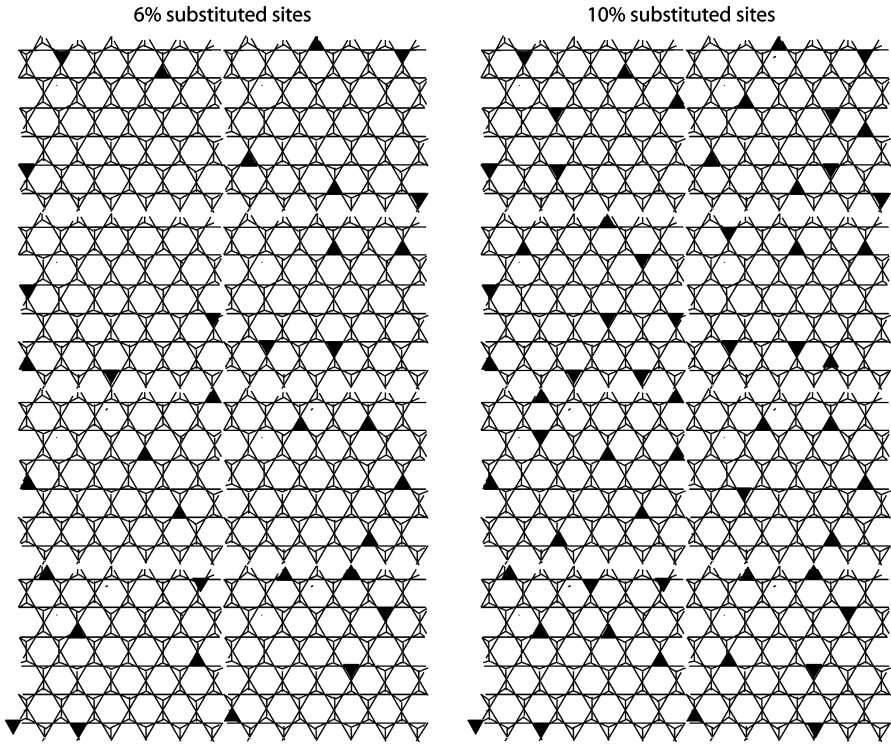
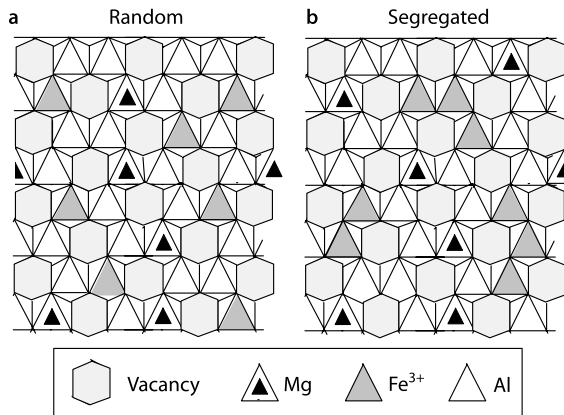


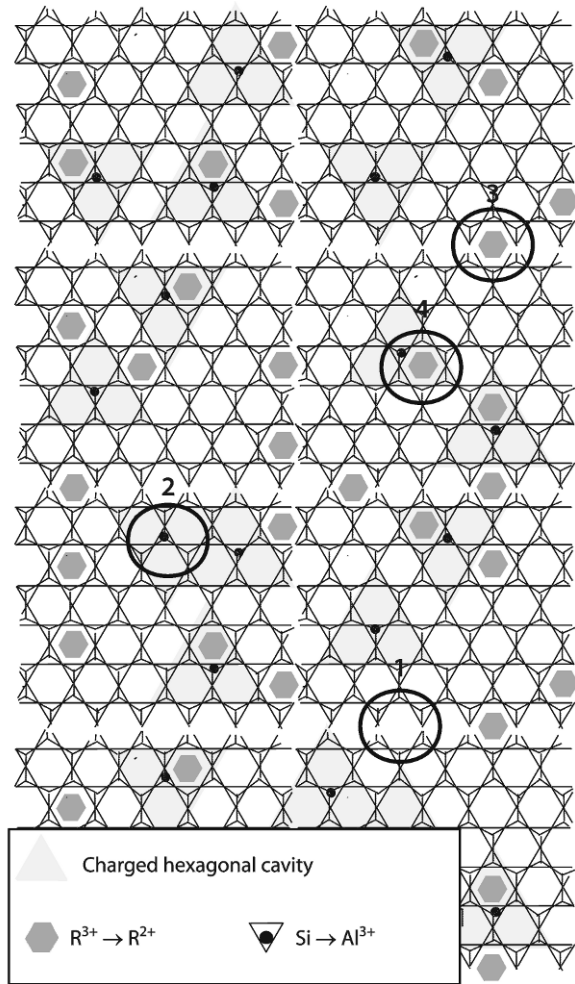
Fig. 1.28. Possible structures of the tetrahedral sheet according to different Al/Si ratios without long-range order

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 tetrahedral sheet,
- -1 charge originating in the  $R^{2+}$  for  $R^{3+}$  ionic substitution in the octahedral 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 ( $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ ) or in the octahedral one ( $\text{R}^{2+}$  for  $\text{R}^{3+}$ ). 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 ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ) 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  $\text{Al}^{3+}$  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.

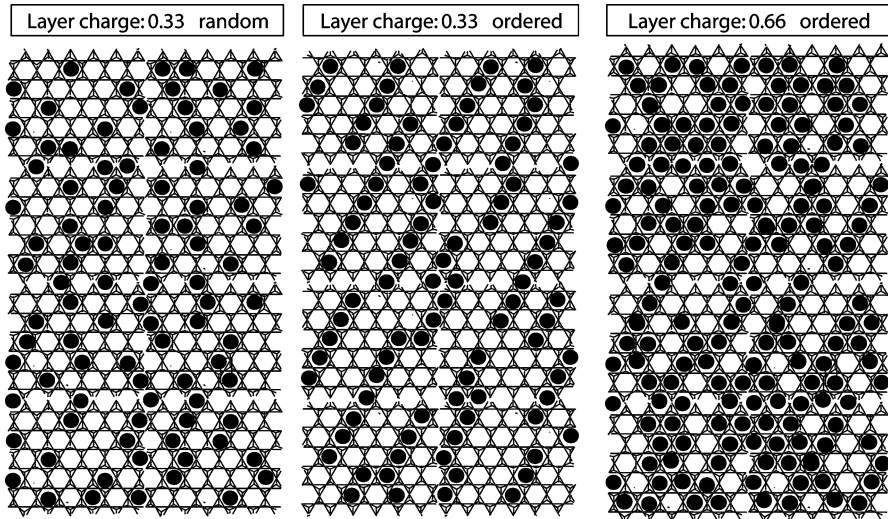


Fig. 1.31. Some possible interlayer cation distributions for different layer charges per  $O_{10}(OH)_2$ ; a  $LC = 0.33$ , random distribution; b  $LC = 0.33$ , ordered distribution; c  $LC = 0.66$ , ordered distribution

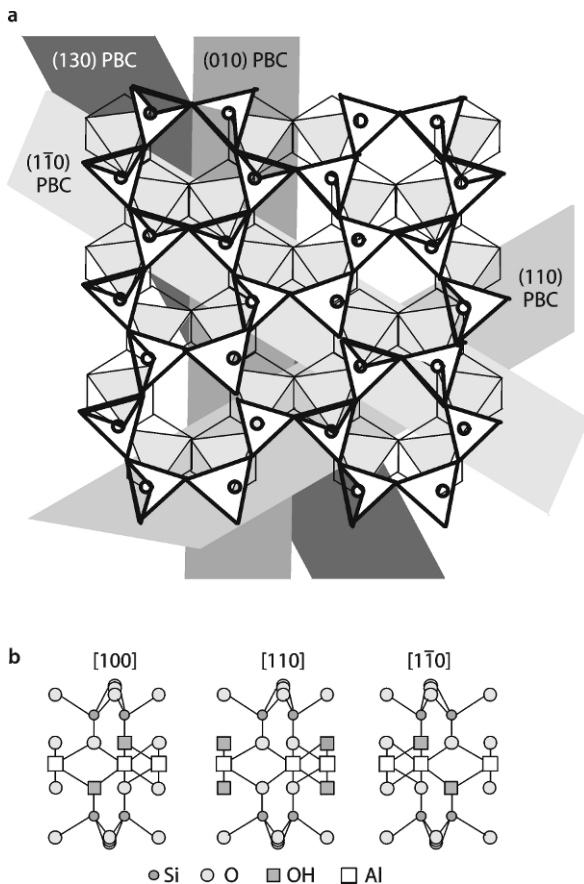
Crystal growth is approximated as the formation of strong bonds within the crystal structure (Periodic Bond Chains or PBCs). These chains must have the following characteristics:

- 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)



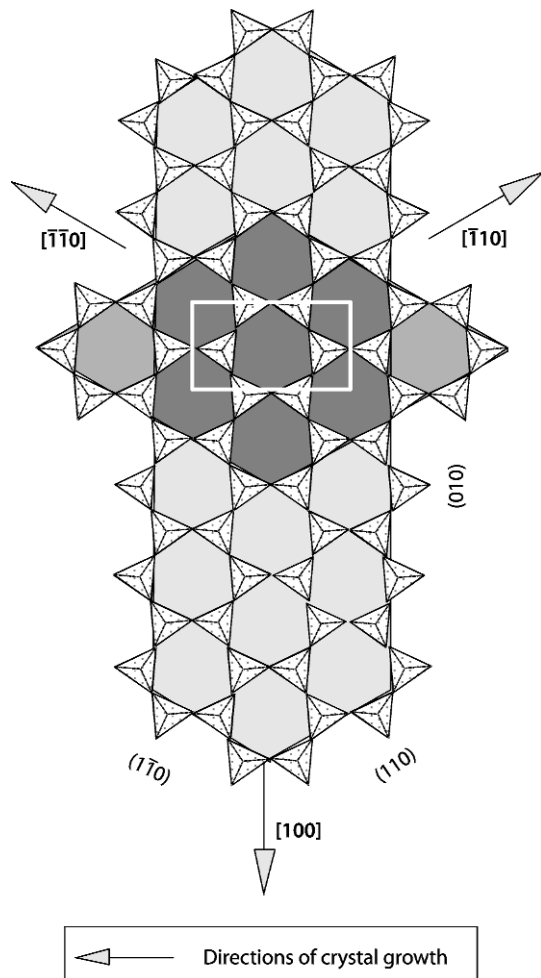
should be associated with that of the interlayer cations. Re-examining the distribution models of interlayer cations depicted in Fig. 1.31 shows that the random one cannot allow any PBC to develop. This could explain why the montmorillonite crystallites are always small and shapeless. On the contrary, 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).

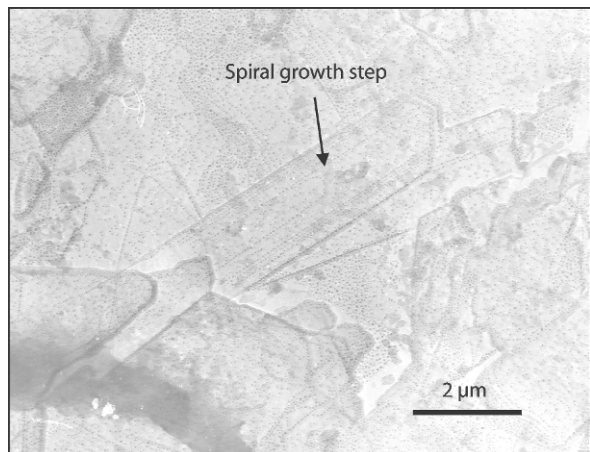
### 1.7.2

#### 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  $\text{Al}^{3+}$  cations are substituted by  $\text{Fe}^{3+}$  ions in the octahedral sheets (Muller et al. 1995; Balan et al. 1999). The presence of  $\text{Fe}^{3+}$  cations in place of  $\text{Al}^{3+}$  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)

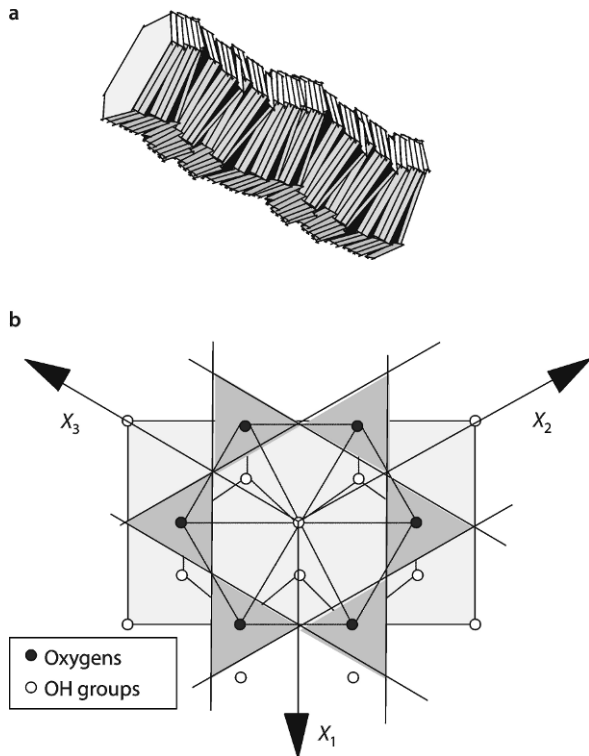


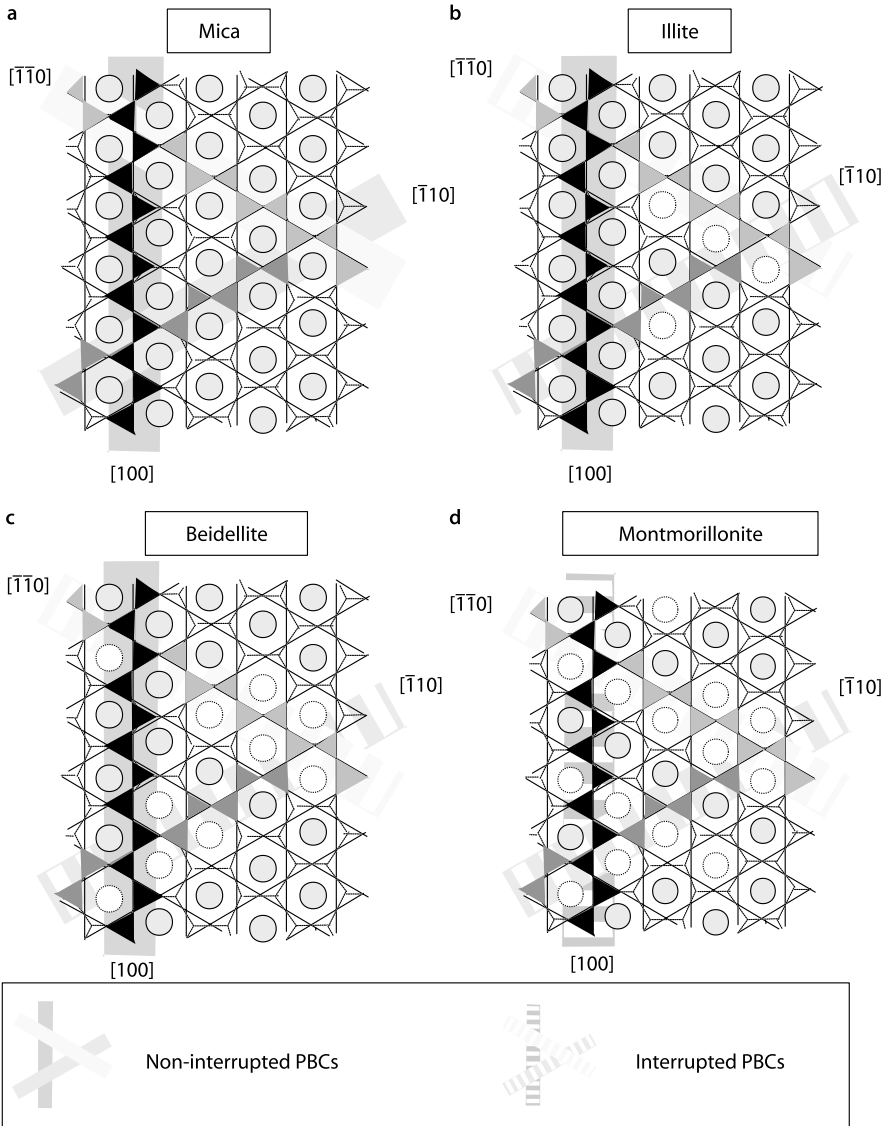
unit cells, the size difference induces the formation of crystal defects (Brindley et al. 1986) and the crystallites become shapeless (Petit and Decarreau 1990).

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

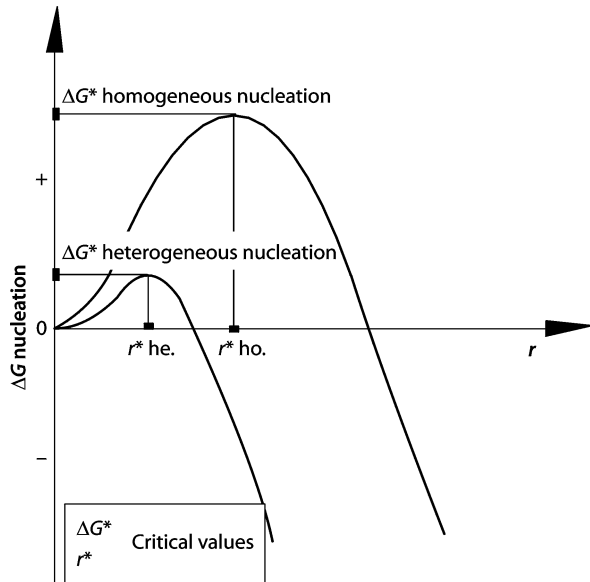
#### *The Energy Barrier for Nucleation*

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***

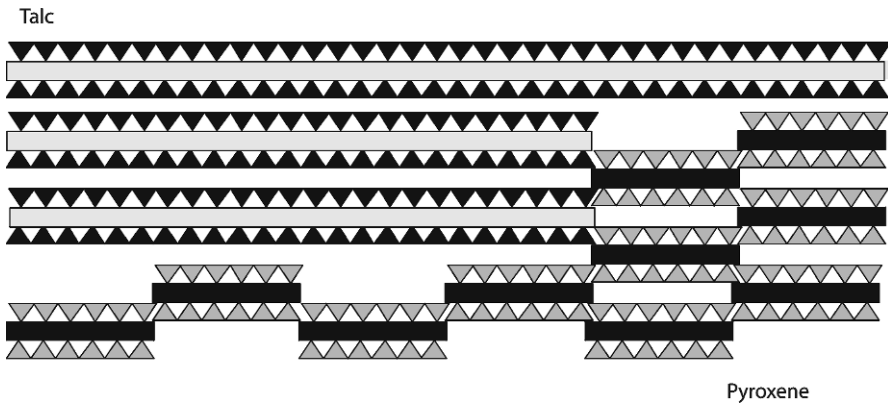
In any nucleation-growth process occurring in a closed system, the oversaturation ratio of the solution decreases with increasing amounts of crystals (Baronnet 2003). Several steps can be distinguished from the germination to the spiral growth stage (Fig. 1.39). For phyllsilicates (including clay minerals),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

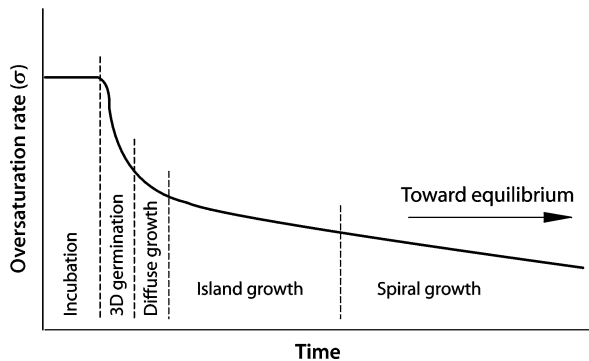
### ***Solution Oversaturation Ratio in Natural Environments***

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  $\mu\text{m}$  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,  $\text{NH}_4^+$  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.

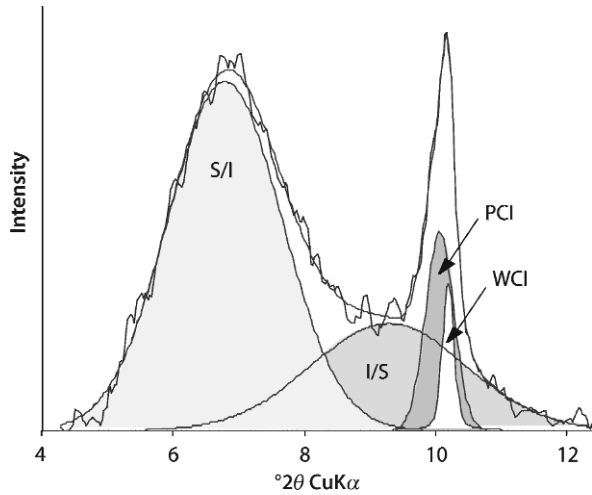
Using these designations, it is possible to establish the criteria which can be used to separate the different contributions to the intensity of the classical “illite” peak. In most cases a soil illite peak is composed of the two illite “phases” or diffraction peaks: PCI and WCI (Fig. 1.40a). Soil and 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

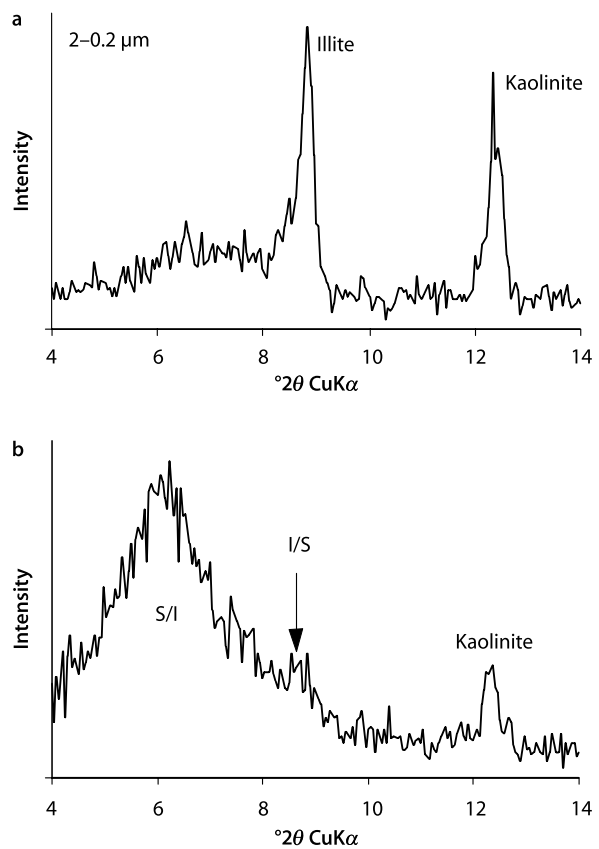
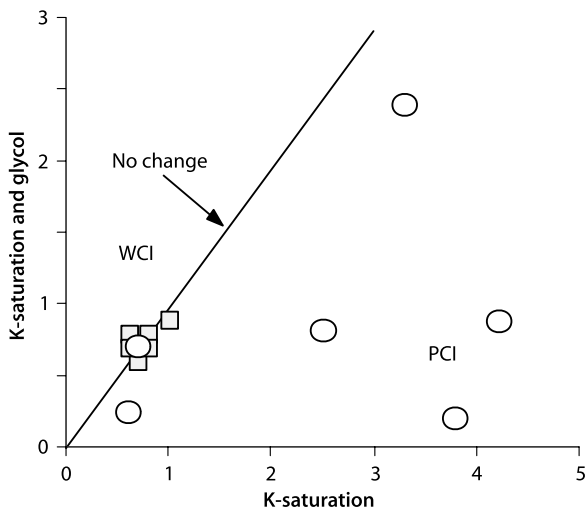


Fig. 1.42. Proportion of PCI and WCI compared to kaolinite for KCl treated samples before and after glycol treatment



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  $\text{K}^+$  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  $25^\circ\text{C}$  (Barnishel and Bertsch 1989, p. 748), but they do change basal spacing upon heating above  $300^\circ\text{C}$ . Vermiculites (Douglas 1989) are high charge smectites which expand in the Mg-saturated state under glycol saturation and which close to  $10\text{ \AA}$  upon potassium treatment at  $25^\circ\text{C}$ . Peak positions in the hydrated divalent cation state are above  $14.5\text{ \AA}$  (Ildefonse et al. 1979). Dioctahedral soil chlorites would be aluminous 2:1 minerals which do not close their interlayer spacing upon heating to  $300^\circ\text{C}$  whereas other hydroxyl interlayer minerals do (April et al. 1986). In order for the mineral to be considered a chlorite, the  $14\text{ \AA}$  peak should be of equal or lower intensity than the  $7\text{ \AA}$  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  $14.2\text{ \AA}$  non-expanding minerals (Mg and glycol saturation) collapses to  $10\text{ \AA}$  at  $25^\circ\text{C}$ . 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.  $14.2\text{ \AA}$  narrow peak, stable under exchange treatments and glycol saturation. Stable under heating to  $300^\circ\text{C}$ . This is a *soil chlorite*.
2.  $14.5\text{ \AA}$  or greater peak, near  $1^\circ 2\theta$   $\text{CuK}\alpha$  FWHM, expanding upon Mg and glycol saturation with collapse to  $10\text{ \AA}$  upon K treatment at  $25^\circ\text{C}$ . This is a *vermiculite*, high charge smectite.
3.  $14.2\text{ \AA}$  peak,  $1^\circ 2\theta$   $\text{CuK}\alpha$  FWHM, no expansion upon Mg and glycol treatment, collapse to  $10\text{ \AA}$  on K-saturation at  $25^\circ\text{C}$ . This is a *HI exchangeable mineral*.
4.  $14.2\text{ \AA}$  peak near  $1^\circ 2\theta$   $\text{CuK}\alpha$  FWHM, no expansion or collapse with CEC treatments at  $25^\circ\text{C}$  but collapse toward  $10\text{ \AA}$  upon heating to  $300^\circ\text{C}$ . 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.

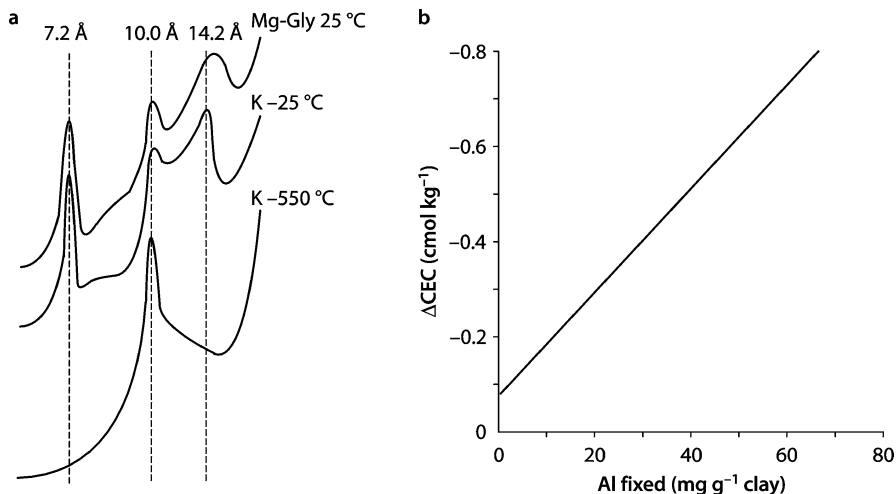
HI minerals and vermiculite then have peaks near 14.2 Å or slightly more and are relatively narrow (about  $1^\circ$   $2\theta$  CuK $\alpha$ ). Smectites (lower charge minerals) have a peak at 15.2 Å air dried state and are wide,  $>1.5^\circ$   $2\theta$  CuK $\alpha$ . HI minerals as well as smectites (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.

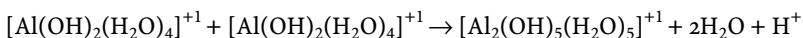
### *Al Ion Adsorption and Polymerization Processes*

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:

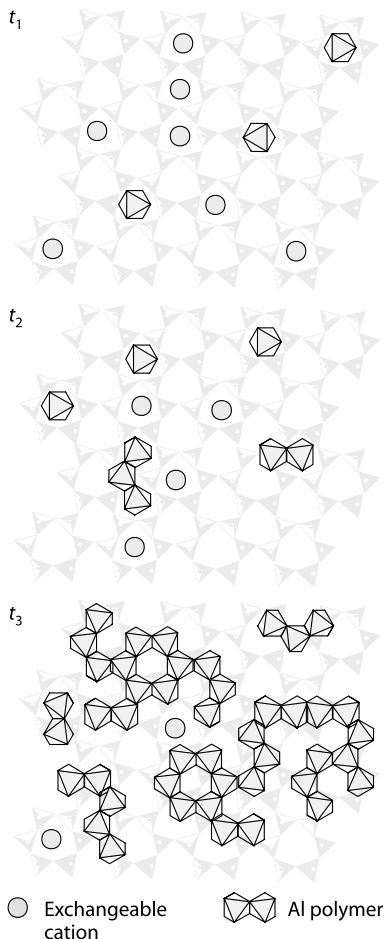
- *the incorporation of Al ions in the interlayer zone*: whatever the polymer state in solution, the incorporation is controlled by a cation exchange mechanism,
- *the polymerization of the adsorbed Al ions in the interlayer sheet of HIV or HIS minerals*: because the 2:1 layer has a given negative charge, 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  $\text{Fe}^{3+}$  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)*

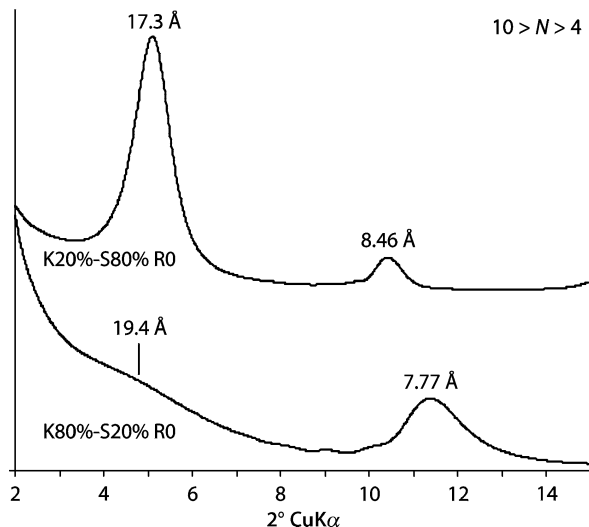
These minerals have been described in different sedimentary or pedogenetic environments (Hughes et al. 1993). Their chemical composition is highly variable since the smectite component can be beidellite or montmorillonite (see review in Meunier 2005). These minerals are certainly more common in soils 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



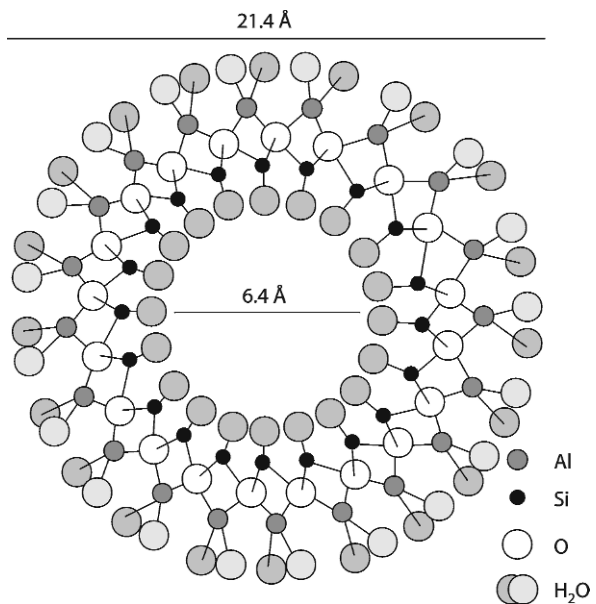


summarized in Table 1.5. Allophane is practically undeterminable using X-ray diffraction. On the contrary imogolite presents some broad diffraction peaks. Both minerals are currently detected in soils using a combination of infrared spectroscopy, thermal and chemical analyses. Even if still debated, 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 ( $\mu\text{m}$ )
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 $\text{cmol kg}^{-1}$	17 $\text{cmol kg}^{-1}$
AEC (pH 4.0)	5–30 $\text{cmol kg}^{-1}$	40 $\text{cmol kg}^{-1}$
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<sup>-1</sup>;
- pH = 8: the CEC is close to 30 cmol kg<sup>-1</sup>, 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 Fe<sup>3+</sup> cation is framed in different oxide or hydroxide crystal structures:

- the most important oxides are hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) or magnetite (Fe<sub>3</sub>O<sub>4</sub>),
- the hydroxides are goethite ( $\alpha$ -FeOOH), lepidocrocite ( $\gamma$ -FeOOH) and ferrihydrite (Fe<sub>2</sub>O<sub>3</sub>·2FeOOH·2.6H<sub>2</sub>O).

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,  $\text{Fe}^{3+}$  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 ( $\alpha$ -alumina trihydrate:  $\text{Al}(\text{OH})_3$ ) while its polymorphs bayerite and nordstrandite are much rarer. Boehmite ( $\alpha$ - $\text{AlOOH}$ ) 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 ( $\text{MnO}_2$ ), 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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- Newman ACD (1987) Chemistry of clays and clay minerals. Mineralogical Society (Monograph 6, 480 pp)
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# Basics for the Study of Soil and Weathered Rock Geochemical Systems

## Introduction

Clays minerals form and transform in many different environments at the Earth's surface or sub-surface such as soils, weathered rocks, oceanic and continental hydrothermal systems, sedimentary layers or diagenetic series. Whatever the environments, the common point is that aqueous solutions are always present and interact with rocks where clay minerals form. These solutions may be cold (few degrees at the ocean bottoms) or very hot (above 300 °C in the deep zones of hydrothermal systems). They may be diluted (meteoric water) or highly concentrated (brines). In all the cases, clay minerals adjust their composition and their crystal structure to the local conditions where they form or transform. At present, the numerous observations of their natural occurrences make the predominance of two factors obvious: the temperature and the chemical composition of both solids and solutions. Pressure seems to be negligible in the range of several kilobars since rather similar clay minerals may exist at the surface as well as deep in the oceanic or continental crusts. Consequently, before presenting the ways that clay minerals form or transform in different geological environments, the present chapter will focus on the definition of the driving forces at work.

The principal phenomena leading to the formation of clay minerals are the alteration processes (replacement of a pre-existing mineral) or the direct precipitation from solutions (homogeneous or heterogeneous nucleation and crystal growth, epitaxy, ...). Those mineral reactions are an exchange of matter and energy, they are typically in the scope of the chemical analyse of rocks and fluids and they can be studied through thermodynamic estimations. As for mineral reactions, if thermodynamic equilibrium is reached, the products must have specific compositions and be associated in adequate assemblages. If not, the departure from estimated equilibrium indicates that the reaction is incomplete and the presence of phases is governed by the kinetics of the incompleting reaction. This shows the importance of understanding the thermodynamic basics in clay mineral study.

Clays are very reactive minerals because of their huge outer and inner surfaces per mass unit. This characteristic is the source of many chemical and physical properties and enhance their capacity to adjust their composition and crystal structure when the local physicochemical conditions change. We will consider here that a clay mineral is transformed if the silicate layer (1:1, 2:1, or 2:1:1 type) is changed. This excludes the modifications in the interlayer zone related to the exchange capacity. One of the most documented transformation is the smectite to illite conversion in diagenetic series and geothermal fields. It has shown the importance of kinetic effects that is to say the influence of time.

Summarizing, the main factors to be considered in the clay mineral formation and transformation at the surface are: temperature, chemical compositions of solids and solutions, and time. The missing dimension is the scale of the geological object under consideration. This is the first step in our quest of the driving forces for clay mineral formation because the predominant factor changes with the size of the object. Indeed, at the scale of a continent, the thermodynamics of equilibrium may depict correctly the formation of the dominating mineral species in a weathered mantle for instance while at the scale of a crystal, electrical charges overcome short-distance interactions. This leads us to define the “system” under consideration that is to say the solids and the solutions interacting at specific temperature conditions in a given volume of the Earth’s surface. Then, the reasons why clay minerals are typically formed at the Earth’s surface conditions will be analysed. In alteration, the reactions are most often governed by the migration of elements in solution into or out of the system under consideration. This distinguishes alteration from diagenesis, metamorphic or igneous geologic systems.

## 2.1

### Definition of the Systems

#### 2.1.1

##### The Size of the Systems under Consideration

###### *Basic Principles for the Definition of Systems*

According to Atkins (1995) “A system is a part of the world in which we have special interest. [...] The surroundings are where we make our observation. The two parts are separated by a boundary and to specify the system and its surroundings we need to specify the boundary between them”. Natural systems, whatever their size, include solids (rocks, minerals, organic matter), fluids (solutions and/or gas) and eventually biota. A system is totally defined when all its components are known such as the chemical composition and the relative quantities of each physical component, i.e. phases (extensive variables) and when the exchanges (chemical components, energy) with the surroundings are known. Then, if pressure, temperature and chemical potentials applied to the system (intensive variables) are known, thermodynamics helps to compute the exchanges of matter and energy between the components of the system.

Natural systems are complex because of their high degree of heterogeneity whatever their size. At a large scale level, a continent is composed of contrasted areas such as mountains or plains. By contrast, at a low scale level, the atomic distribution inside a given mineral is frequently clustered or zoned. Consequently, the high degree of heterogeneity makes it difficult to define the boundaries of the system. However, even though empirical, this definition is necessary before any description of the geochemical processes at work. The size of a system will be defined by the size of the heterogeneity which is taken into consideration: it varies from the size of the mountain and plain areas in a continent to the size of the atomic layers in crystals. If the geochemical processes are investigated at the continent scale, then the transfer of chemical components at the crystal scale are negligible. Conversely, the mineral reaction at the muscovite-orthoclase interface in a weathered granite is independent of the global climatic conditions.

The size of the system determines the scale at which the transfers of chemical components and energy are considered. Thus, the scaling operation is the first task to do in any study of weathering or alteration processes (see Taylor and Eggleton 2001 for a review). However, because the systems to be considered for the origin of clay minerals are, for the most part, located at the Earth's surface, i.e. the atmosphere–ocean–continental or oceanic crust interface, their activity time is dependent on global tectonics. The “blue planet” is a living one; whatever the interface considered. No system is isolated.

### Scaling the Systems

Scaling the systems under consideration is a necessary preliminary for the study of natural systems. This has been particularly pointed out by White and Brantley (1995) for the calculation of the weathering rate. As many petrographers (perhaps a disappearing generation) we shall define the scale of the geological objects under study using the thin section as the reference. The thin piece of rock or soil of  $0.03 \times 20 \times 30 \text{ mm}^3$  will be the reference unit, i.e. a “system”. Figure 2.1 depicts schematically the way that “systems” can be scaled from that reference. For instance, the Earth's system or Global system is considered to be composed of different concentric envelopes from atmosphere outside to nucleus in the center. This system is isolated but not closed because the Earth receives matter (meteorites, cosmic dust) and energy (radiation) from outside (solar system) and losses matter (gas molecules) and energy (heat). Exchanges of chemical components and energy at the atmosphere/ocean/solid Earth's surface, can be calculated considering the mean composition of each member.

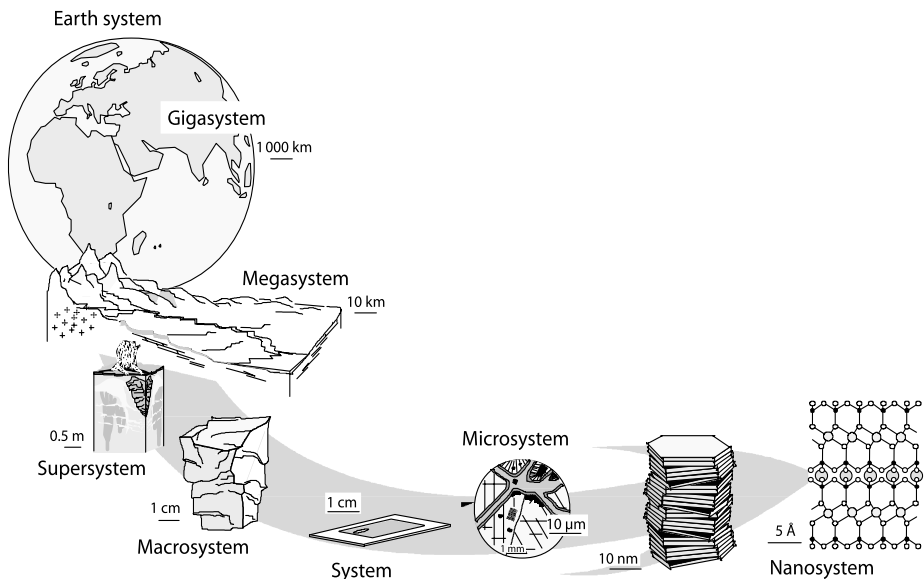


Fig. 2.1. Scaling of the systems from the planet (Earth's system) to the atomic size (nanosystems)

Zooming progressively from large to small sized objects, the next system to be considered has the size of a continent. Africa for instance is a gigasystem receiving energy (heat from solar radiation and heat due to radionuclide disintegration in the Earth's crust) and matter (rain, aerosols, ...). Interaction at the extreme leads to the formation of deep weathering mantles whose upper part is composed of laterites (Al and Fe oxides). The continent losses matter through rivers (Zaire, Nilus, ...) and winds (Scirocco, Harmatan, Monsoon, ...). The solid member of the gigasystem is a portion of the continental crust which can be represented by its average composition. The solution member is given by the average water composition of all the rivers which drain the plains and the mountains. The chemical mass balance at the gigasystem scale has been documented by Garrels and Mackenzie (1971) and Tardy (1992). More recent studies focused on the chemical budgets of alteration-erosion processes in order to calculate the denudation rate at the scale of continents. This has been done for instance for the Andes-Amazon basin (Dosseto et al. 2006) and the Himalaya-Brahmaputra basin (Galy et al. 1999, Galy and France-Lanord 2001).

If detailed, the anatomy of the Africa gigasystem appears to be composed of internally drained deserts and watersheds drained by rivers connected to oceans. Zooming again, each watershed can be considered also as an isolated megasystem receiving and losing matter and energy. The contribution of the different rock types represented in this area to the composition of the alteration solutions can be computed and compared to that of the river water (see Drever 1982).

Inside a given watershed, each alteration profile is composed of soils overlying weathered rocks. Each soil or weathered rock profile is a supersystem in which the fluids percolate through the different horizons or altered rock zones using the fractures and pore-micropore connected networks. A profile, considered as a homogeneous object is represented by an average composition for the solids and the spring waters for the solutions. Of course, as each horizon or zone is different from the others, we can zoom again to systems having the size of hand specimens each of them being a macrosystem. At this scale the soil horizon sample (1 kg) or the piece of rock (1 dcm<sup>3</sup>) for each zone appears to be homogeneous as perceived by the naked eye. The solutions can be sampled through lixiviation boxes or porous ceramics. This scale was preferentially used in most of the clay mineral studies which are based on crushing and separation of the <2 μm fraction from weathered rock or soil samples.

As expected, what looks homogeneous at a given scale, becomes heterogeneous at a smaller one. Thus, a piece of rock reveals the presence of different systems at the scale of the thin section observation. Indeed, it is possible to separate altered fracture wall rock from massive, unaffected parts. However, at this scale, the altering solutions are not easily sampled. Their study is increasingly difficult. Most often, their chemical composition is indirectly approached through thermodynamic calculations based on the mineral reactions observed in the system.

Using microscope observations of thin sections (vital reflex of petrographers!), the hand specimens appear to be highly heterogeneous. Several types of mineral reactions acting in numerous microsites inside the rock can be observed in a single thin section. Each of the reaction sites (few tens of micrometers) is a microsystem. If high resolution electron microscopy (HERTM) or atomic force microscopy are used to observe the crystal structure and the surfaces of minerals at the atom scale, one can define nanosystems.



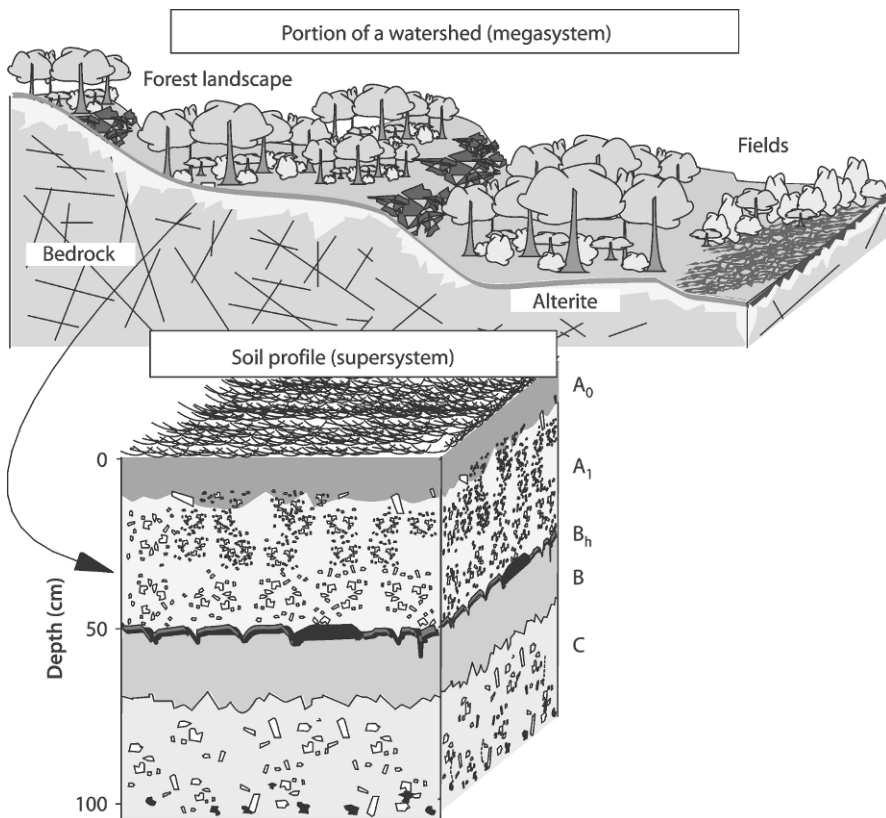
We shall focus here on the nano-, micro-, macro- and supersystems at the atmospheric Earth surface which are the appropriate sized systems for the study of clay origins. Nanosystems presented here will be chosen for specific cases which have been reasonably well documented. Of course, the consequences of phenomena described at higher scale systems (noticeably, megasystems) will be presented as far as they concern the chemical or matter exchanges at a more local scale. Nevertheless, it is not in the scope of this book to describe the mechanisms of matter and energy transfers at the scale of watersheds, and *a fortiori* at the scale of continents or the whole Earth. This has been done in other publications or books which are indicated in the recommended reading list.

### ***The Supersystems***

The basic unit for the supersystems is the soil or the weathering profile whose dimensions may vary from a few centimeters to near a hundred meters depending on the local climatic conditions. A soil profile is composed of several “horizons” while a weathering profile is composed of several “facies” or “zones” (see the definitions in Taylor and Eggleton 2001, p. 157). These different parts interact with each other through the circulation of water (soluble elements in solutions and clay and oxide particles in suspensions). A profile is an open supersystem which receives energy and matter from outside (biosphere, rainwater, aerosols, ...) and loses soluble elements and fine particles (Fig. 2.2). Mass balance calculations based on the solids have been developed since the pioneer work of Ebelmen (1847) using the volume conservative assumption. Several other methods have been proposed using chemical component conservative assumptions. Classically, the ratio between the amounts of inert components in rock and soils or weathered facies is used to calculate a relative mass balance of the alteration process (see White 1995 for a review). The chemical composition of the solutions is directly measured after sampling springs or pools or extraction from soil horizons or regolith facies either under field or laboratory conditions (White 1995; Drever and Clow 1995). The composition of the fluids is an average of all their local interactions with solids. The average composition is classically used through activity-activity thermodynamical diagrams to identify the stable phase or phases in the systems (Garrels and Christ 1965; Helgeson 1968; Tardy 1971). For instance, the spring waters from granitic massifs were shown to be in equilibrium with kaolinite (Feth et al. 1964; Garrels and Mackenzie 1967). This means that kaolinite is the dominant phase in the highly porous parts of the rock. In other words, the chemical trend of granite weathering is controlled by the formation of kaolinite. The more intense the alteration, the higher the quantity of kaolinite produced. The granitic rock which is heterogeneous at the mineral scale is transformed into a kaolinite-Fe-oxide new rock (laterite) which is much homogeneous at smaller scales. It is obvious that rocks formed in deep pressure-temperature conditions react at the Earth’s surface to give a more homogeneous new material.

### ***The Macrosystems***

The size of a macrosystem varies with that of the mineral or organic components. Most often, it varies between a few thousands to hundreds of cubic centimeters for weathered zones of granite or shale respectively. It corresponds to the size of the “represent-

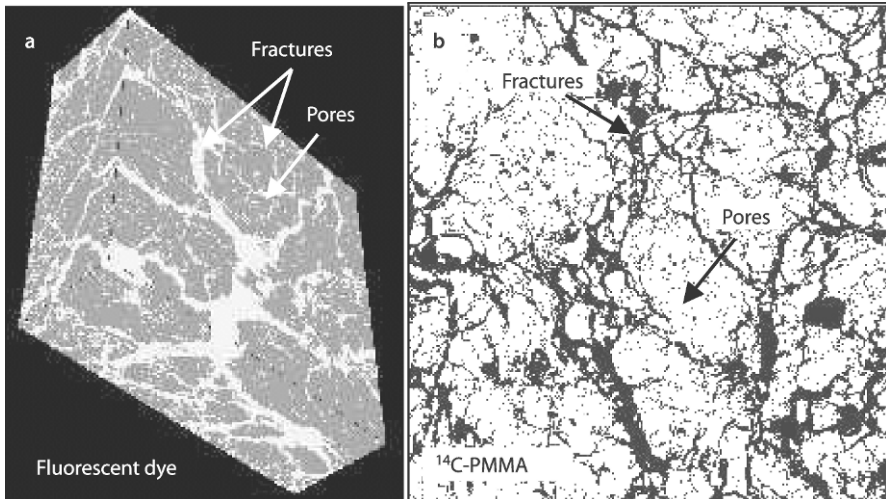


**Fig. 2.2.** A landscape as commonly observed is a portion of a watershed (megasytem). It is composed of different soil-vegetation association according to topography, human activity, etc. A given soil profile is considered as a supersystem composed of different horizons: here a podzolic soil in a forest

tative sample” whose chemical composition is identical to that of any bigger piece of the rock or soil. Any sample having smaller dimensions has a chemical composition significantly different. Thus, the size of a macrosystem can be considered as the critical size of “the representative sample”, that is to say, the lowest size for samples having the same average chemical composition.

The solution member in such macrosystems is necessarily represented by the solutions which impregnate the macrovoids (greater than 1  $\mu\text{m}$  diameter) of the material. These macrovoids are generally 3D connected (Fig. 2.3a) and connected to the dispersed porosity (Fig. 2.3b). The fluids can circulate inside the rocks or the soils and impregnate the porous zones (Moreau et al. 1996). These fluids can be extracted from the soil samples using suction or pressure devices. Based on their chemical composition, thermodynamic calculations determine the dominant secondary assemblage which characterizes the macrosystem.

Summarizing, at the macrosystem scale, the average trend of mineral reactions is correctly depicted by the fluid analyses and their thermodynamic consequences. The



**Fig. 2.3.** Distribution of fractures and pores in a vertisol; **a** reconstructed 3D fracture network using 2D images obtained from a series of sections made in a sample impregnated by a fluorescent dye (Moreau et al. 1996); **b** pores and fractures impregnated with a <sup>14</sup>C-PMMA resin (polymerized methylmetacrylate) in a 2D section

size of the representative volume or mass of rock depends on the scale of heterogeneities. It could be of few grams for the A horizon of soils to several tens of kilograms for altered rocks.

### *The Systems*

A system refers to a piece of rock having the dimensions of a thin section ( $0.03 \times 20 \times 30 \text{ mm}^3$ ). Most frequently, except for rocks of unusually large grain size, such systems are composed of a great number of crystals exhibiting different alteration states. Sometimes a thin section may be representative of a single soil horizon or weathered facies. In that case, it can be considered as the smallest unit of a macrosystem. However, they are more frequently composed of several regions which exhibit different microstructures and mineral alteration states. Then, the system is representative of the rock or soil local heterogeneity. The scale of such a system is rarely appropriate for the calculation of a chemical mass balance.

The fluids which impregnate the microporosity (less than  $1 \mu\text{m}$  diameter) flow very slowly because of the high tortuosity of the connected pore network. Their physical state is controlled by the capillary forces. Most often, these fluids are not analysable. The main question is how the connected porosity is distributed among the different mineral species which compose the rock. This has been investigated by Sardini and his co-workers who developed a specific petrographical method based on the combination of rock staining and impregnation by a <sup>14</sup>C doped resin (methylmetacrylate or MMA). After polymerization, the resin (<sup>14</sup>C-PMMA) hardens sufficiently to resist sieving and polishing actions. 2D images are obtained by autoradiography, i.e. activation

of a film in direct contact with the polished surface (Sardini et al. 2001a). The autoradiographs are superimposed on mineralogical maps obtained by mineral staining and chemical microanalysis (Fig. 2.4). Oila et al. (2005) used such combined mineralogical-permeability maps to calculate the porosity histograms for each primary mineral species (Fig. 2.5). The % porosity calculated from the autoradiograph is not equivalent to the pore size. It is only proportional to the quantity of tracer per pixel. In other words, a large number of impregnated small pores may give a darker pixel compared to few larger ones.

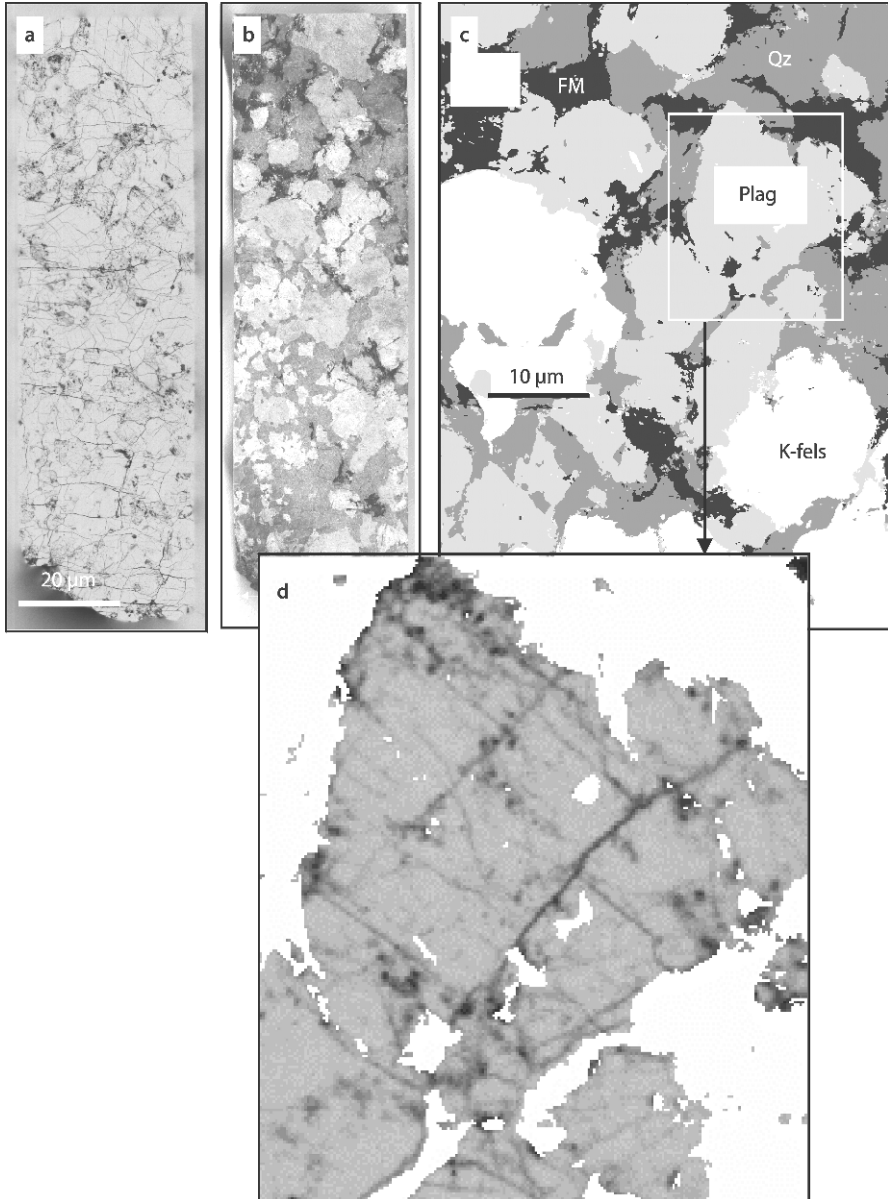
### *The Microsystems*

A microsystem is defined by the physical interaction of outer or inner mineral surfaces with water in its liquid state (Meunier and Velde 1979a). Thus, its size depends on that of the reacting solid phases: it varies from one to tens of micrometers. In weakly altered rocks, the microsystems are observable either at the contact between parent phases (contact microsystems) or inside single unstable phases (internal microsystems). The fluids cannot be sampled at this size scale. Nevertheless, their composition is indirectly approached by thermodynamical calculations based on the compositions of the secondary phases formed. Numerous microsystems exist in small volumes of rocks or soils such as that investigated through thin sections. However, in spite of their great number, these microsystems belong to only a few categories. For instance, in a weathered granitic rock, one sees:

- *contact microsystems*: illite formed along the mica-K-feldspar joints,
- *internal microsystems*: polyphased mineral assemblages replacing the crystals of K-feldspars, plagioclases and micas,
- *fissural microsystems*: clay-oxyhydroxide coatings on the microfracture walls (cutans).

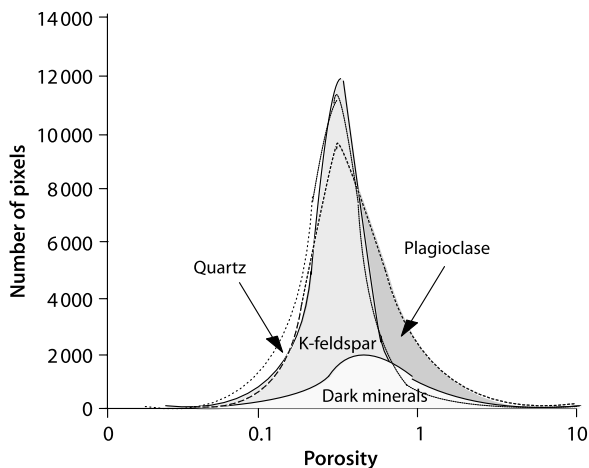
Theoretically, the greater the number of different microsystem categories, the higher the heterogeneity of the rock or the soil considered. Highly altered materials such as duricrusts in lateritic profiles are characterized by only one type of microsystems in which Al- and Fe-oxyhydroxides form.

Depending on their location in the altered rock, the microsystems are more or less open. For instance, some mineral reactions along narrow intergranular joints are triggered by the fluids introduced by capillary forces (Fig. 2.6). These fluids are very slowly renewed, i.e. resident fluids. On the contrary, other reactions are observed in large fractures where fluids may flow freely. The texture and crystallochemical characteristics of the secondary minerals assemblages are different in these two cases. Typically in weathered granite profiles; illite is formed in muscovite-K-feldspar intergranular joints while kaolinite + Fe-oxyhydroxides form cutans (oriented deposit texture) which coat the wallrocks of the largest water pathways. Illite is formed in the less open microsystems while kaolinite is the unique clay mineral phase which is stable in the totally open ones. Thus, the thermodynamics of all the microsystems cannot correctly be represented by the classical activity-activity diagrams which enhance the role of



**Fig. 2.4.** Imaged permeability of the Palmottu granite, Finland, using impregnation with the  $^{14}\text{C}$ -polymethylmethacrylate (from Oila et al. 2005); **a** a polished section of a 15 cm long drill core has been stained in order to contrast the granite primary components (quartz, orthoclase, plagioclases and dark minerals); **b** an autoradiograph is obtained using a direct exposition of a Kodak Biomax film to the polished sample surface; **c** a thresholded mineralogical map is obtained from the stained section; **d** the specific connected porosity is imaged for each crystal of the primary minerals

**Fig. 2.5.** Example of porosity histograms obtained from the aurodiograph of the Palmottu granite (from Oila et al. 2005). Porosity is given in %



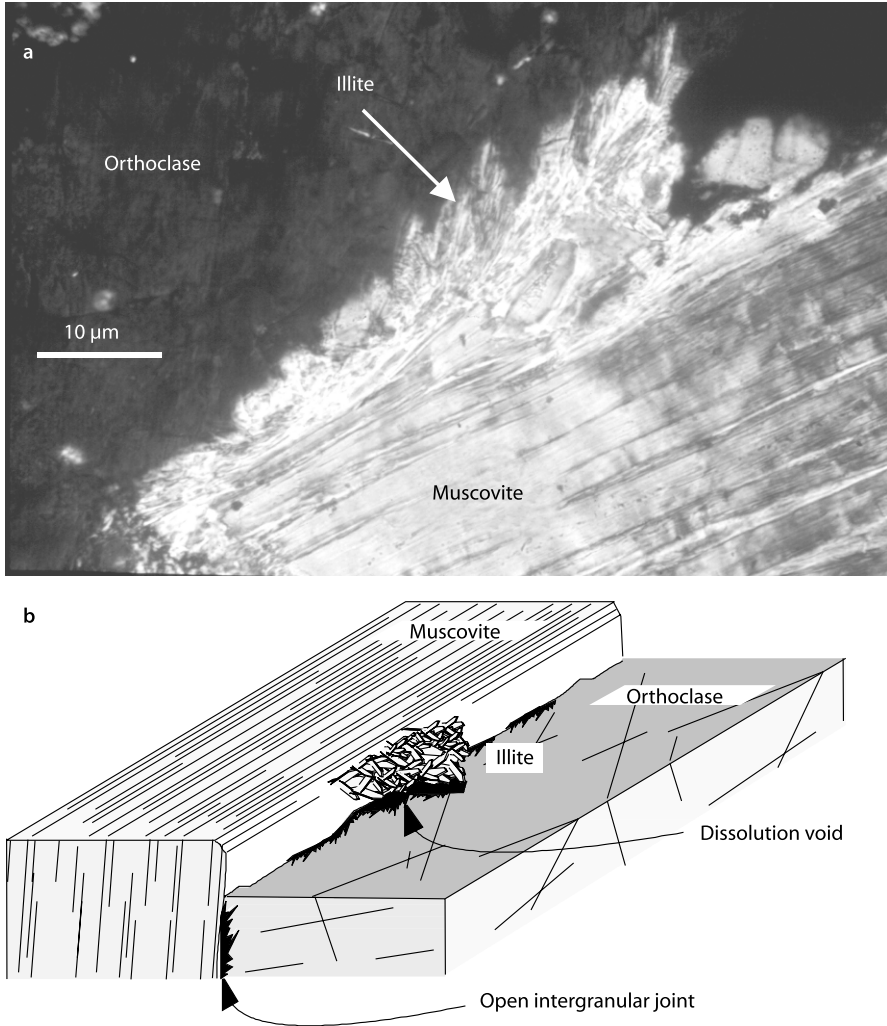
the fluids. These diagrams which depict correctly the fluid-mineral interactions in the totally open microsystems fail to represent the mineral reactions at work in the less open ones. For instance, illite is formed in the less open microsystems in which the reaction is controlled by the local rock composition. The chemical properties of such microsystems are governed by that of those solids. Therefore, the most adapted phase diagrams are composition ones (triangle in 2D space; Fig. 2.7a). Phase diagram principles are detailed in Annex 5.

Microsystems which form in the porous zones of altered rocks are semi-open. That means that both the rock composition and the activity of some components in solution are the controlling factors of the mineral reactions. The fluids are not quickly renewed. Thus, the fluid chemical composition is controlled by the surrounding solids. The mineral reactions are triggered by local chemical gradients. The migration of elements is controlled by chemical diffusion. Chemical activities (or chemical potentials) and inert components (rock composition) are intensive and extensive variables respectively. In that case, the most adapted phase diagrams are activity-composition ones (Fig. 2.7b).

Microfractures or pores forming a connected network are percolated by diluted meteoric solutions. These solutions impose locally specific conditions which are determined by the chemical activities of the dissolved elements. Thus, the microsystems can be considered to be totally open. They favor the formation of new mineral assemblages. Most often, the texture of these mineral assemblages exhibits sedimentation features (cutans). The most adapted phase diagrams are the activity-activity ones (Fig. 2.7c).

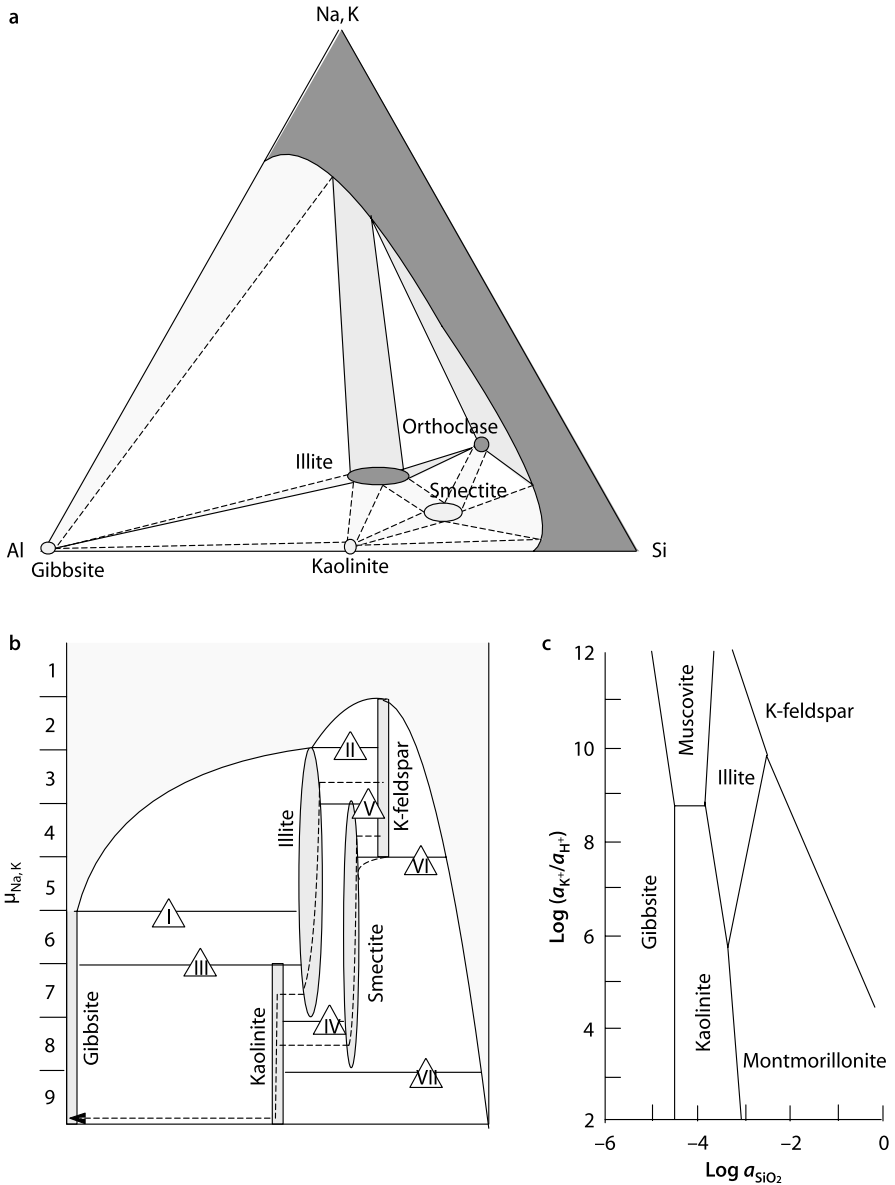
### **Nanosystems**

Nanosystems are investigated using high magnification devices such as scanning or transmission electron microscopy (SEM, TEM) which provide morphological and chemical data. For instance, the dissolution of the primary minerals can be quantita-



**Fig. 2.6.** Example of a microsystem in a weathered granite at the intergranular joint between muscovite and K-feldspar; **a** microphotograph from the La Rayrie altered granite, Deux Sèvres, France; **b** schematic representation of the contact microsystem

tively studied through the measurement of etch pits and the way they coalesce to give corrosion grooves. The chemical composition of the secondary mineral which forms in these nanosystems can be currently obtained now. Spectacular examples of the relation between microstructure and etch pit distribution in perthitic K-spars have been presented by Lee and Parsons (1995). The studies based on high resolution transmission microscopy observations (HRTEM) show how the crystal structure of the secondary minerals (mostly clay minerals) is controlled by topotactic growth processes (see Holchella and Banfield 1995 for a review).



**Fig. 2.7.** The different phase diagrams representing the alteration of granitic rocks in the Si-Al-K, Na system ( $\text{H}_2\text{O}$  in excess); **a** composition diagram; no mobile components; adapted to study the phase relations in nearly closed microsystems; **b** activity-composition diagram; mobile components: K, Na; inert components: Si and Al; adapted to study the phase relations in semi-open microsystems; **c** activity-activity diagram; mobile components: Si and K, Na; inert component: Al; adapted to study the phase relations in open microsystems (modified from Garrels 1984)



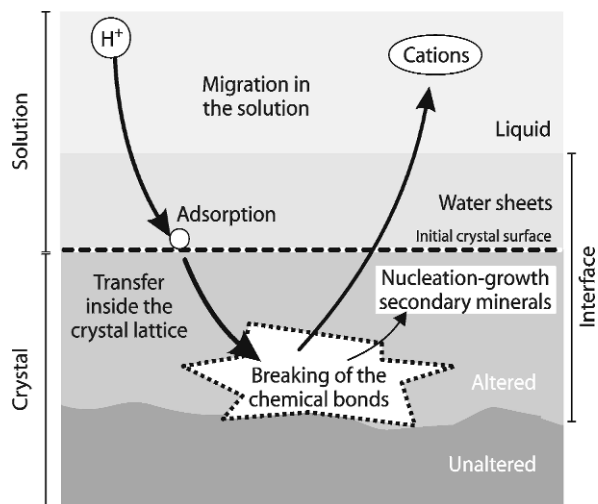
Nanosystems typically include the interface between the parent minerals and their secondary products with the solutions involved in the reaction (Fig. 2.8). The parent and secondary crystal lattices may be either connected (pseudomorphs) or totally disconnected (dissolution etch pits, nucleation-growth of secondary phases). At this scale, water is not in its liquid state because of the huge effects of the electric charge at the surface of the solids. Thus, water does not act as a solvent but rather as a molecular component. The classical macroscopic thermodynamic laws are no longer available because the threshold supersaturation required for nucleation and growth is much higher in nanovoids than in micropores (Worden et al. 1990; Putnis 2002).

### 2.1.2

#### The Solutions in Systems of Different Size

The solutions in soils or weathered rocks result from the reaction of rainwater with minerals and organic matter. The reaction proceeds through the connected porosity (permeability network) which is invaded by rainwater. Permeability is a physical parameter which appears simple to obtain since voids are easily identifiable in any material. However, it is difficult to measure because of the tortuosity and necking of the fluid pathways. Thus, permeability measurements give different values according to the probe used: mercury, water, gas. For example, the small voids which cause the turbidity of feldspar crystals appear to be unconnected using the classical technique of permeability measurement. However, they were shown to be connected by diffusion experiments of  $\text{H}_2^{18}\text{O}$  molecules (Walker 1990). Permeability is both a macroscopic and a microscopic parameter. This is the reason why it is important, even if difficult, to characterize it in a set of orders of magnitude from the hand specimen to the mineral-fluid interface scales.

**Fig. 2.8.** Theoretical representation of a nanosystem. The thickness of the altered zone inside the crystal varies with the crystallization of secondary products



### *Analysable Solutions*

The solutions can be sampled in soils or weathered rock profiles either directly in pools or springs or indirectly using lysimetric boxes (free water). The solutions which are highly retained inside the small pores can be sampled using porous probes or extracted using different suction or pressure methods. Both give different information on the solutions existing in the soils or the weathered rocks. The solutions flowing freely through connected large voids (macropores) are sampled directly. Their chemical composition is used to calculate the element loss (output) of the system. The residing solutions which are sampled in the second way correspond to solutions retained by capillary forces in connected small voids (micropores). For each pore diameter there corresponds a pressure that causes the expulsion of the fluid by gas replacement. That pressure gives the point of air entry. The diameter can then be determined by applying the Jurin-Laplace law:

$$P = \frac{2A \cos \alpha}{D}$$

*P*: gas pressure applied

*A*: surface tension

$\alpha$ : contact angle at the solid-liquid-gas interface

*D*: maximum pore diameter

The chemical composition of these solutions results from the addition of all the fluid-mineral interactions at a local scale. In other words, it is still an average composition.

It is to be noticed that capillary forces modify the activity of water. The lower the pore diameter, the higher the pressure to be exerted to extract the fluids and consequently the lower the water activity (Table 2.1).

When flowing inside a rock or a soil horizon, the slightly acidic rainwater interacts with the solids. The solution protons are exchanged for the mineral cations. The reaction is initiated by the diffusion of hydrogen ions into the crystal. Then, the exchange of alkali and alkaline earth ions can proceed. The composition of the solution depends on the respective rates of the water input (proton reservoir) on one hand and of the mineral dissolution (cation reservoir) on the other hand. The solutions circulating in the largest connected fractures are rapidly renewed. Thus, they are constantly diluted and their composition is maintained far from equilibrium with the dissolved mineral species. This kind of solution is sampled in the springs for instance. On the contrary, the solutions extracted in situ using porous ceramics are less rapidly renewed. Their composition approaches the equilibrium with the dissolved minerals (Fig. 2.9).

### *Non-Analysable Local Solutions*

The viscosity of water does not change significantly for capillary diameter higher than 1  $\mu\text{m}$ . It increases exponentially below this value (Derjaguin and Churaev 1986). Thus, the efficiency of the suction or centrifugation extraction procedures to extract the

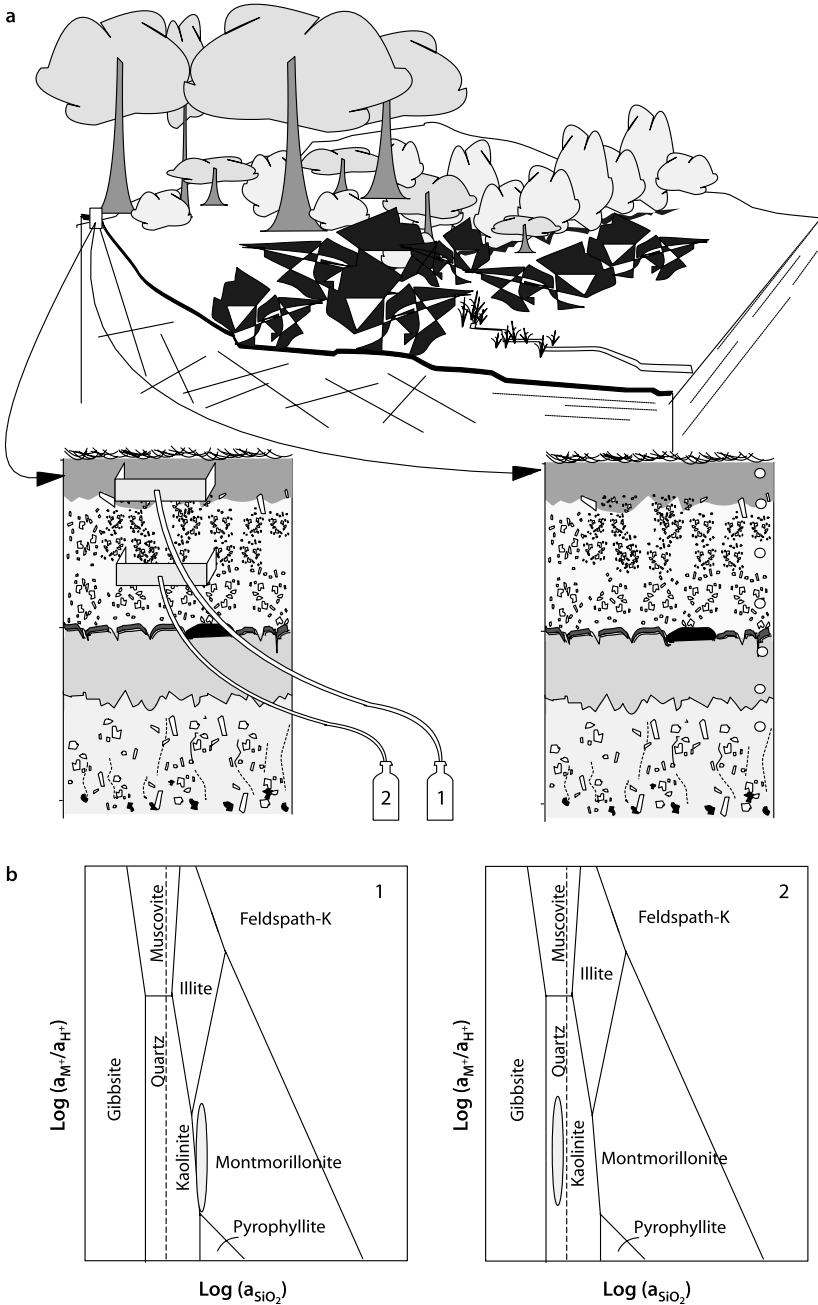
**Table 2.1.** Equivalence between pF, ionic strength of solutions, water activity ( $a_{\text{H}_2\text{O}}$ ) and pore size (pF: base 10 logarithm of the matrix potential, i.e. tension of soil water expressed in cm height of water column). Data from Tessier (1990)

pF	$a_{\text{H}_2\text{O}}$	Pressure (bar)	$D_{\text{max}}$ pores ( $\mu\text{m}$ )	Ionic strength
1	0.999993	0.01	150	$2.2 \times 10^{-4}$
2	0.999927	0.1	15	$2.2 \times 10^{-3}$
3	0.99927	1	1.5	$2.2 \times 10^{-2}$
4	0.9927	10	0.15	$2.2 \times 10^{-1}$
4.2	0.9888	15.8	0.095	$3.38 \times 10^{-1}$
4.67	0.9669	46.4	0.032	1
5	0.927	100	0.015	2.2
5.48	0.8	305	0.005	6
5.7	0.695	500	0.003	
6	0.484	1 000	0.0015	

solutions in a sample is limited to pore diameter greater than  $0.1 \mu\text{m}$ . Even if it is possible to measure the water content of the altered rock or soil impregnating pores of lower diameter (loss on ignition), it is not possible to analyze the chemical composition of the solutions involved in the micro- and nanosystems. At that scales, the physical state of the solutions is controlled by the capillary forces inside the pores and the coulombian forces close to the solid surfaces.

What is the physical state of the silicate surface at the atomic scale when in contact with aqueous solutions? At low pH conditions, because of the presence of  $\text{H}^+$  protons, the surface of the silicates is covered by silanol groups (Si-O-H). Because  $\text{H}^+$  protons are in excess in the solution, an additional  $\text{H}^+$  is fixed on the silanol groups: Si-O- $\text{H}_2^+$ . The resulting positively charged surface contributes to the organization of the diffuse double layer. The electroneutrality is insured by the presence of counter ions. On the contrary, in high pH conditions, the surface of the silicates being covered by Si-O $^-$  groups, it is negatively charged. The pH value at which the positive and negative charges are equal is assigned as the point of zero charge (PZC). As water molecules are polarized, they are necessarily organized in different ways according to the pH values at the very surface of minerals. They may form several sheets more or less in an ice-like configuration whose number depends on the pH.

The dissolution of a mineral corresponds to the break up of the ionic or covalent bonds that hold ions or atoms together within its crystal lattice. The dissolution of silicates in water involves the adsorption of water molecules and the hydrolysis of Si-O bonds (Dove and Crerar 1990). The dissolution is controlled by the coordination states of the chemical components at the surface of solids. According to Berger et al. (1994) and Berger (1995), the dissolution of silicates is controlled by two processes with different rates:



**Fig. 2.9.** The analysable solutions; **a** solutions quickly renewed are sampled in springs or inside the soil profile using lysimeter boxes; Solutions impregnating the porosity of the soil are sampled using porous ceramics; **b** the composition of solutions sampled in the lysimeter boxes number 1 (organic horizon) and 2 (eluvial horizon) are in equilibrium with smectite and kaolinite respectively

1. a rapid initial rate controlled by the silica concentration in the solutions diluted at a pH value close to neutrality;
2. a slower rate established over a longer period of time and controlled by the Al concentration of the solutions for acidic pH values.

All silicates are dissolved at the surface, quartz being the only residual mineral in temperate conditions.

The physical state of water determines its activity (Table 2.1). However, if fluids are more or less immobile, ions are able to move over short distances due to chemical diffusion processes between the solutions and the solids. How can one determine the solution chemical composition at these very local scales? Until now, only thermodynamic calculations may help us using nano-petrography observations to determine which phase is dissolving or crystallizing. The ion exchange between the solutions and the solids must take into account the forces acting at the atomic scale such as the energy of the chemical bonds or the polarization of water molecules. This is the field of molecular dynamics.

## 2.2 The Physicochemical Forces Acting in the Systems

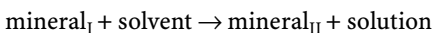
### 2.2.1

#### Basic Definitions

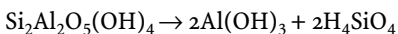
Clay minerals formed at the Earth's surface conditions are most often the products of the dissolution of unstable silicates which have crystallized in deeper zones of the crust. Clay minerals precipitate from the dissolved components after migration on variable distances and according to the local physicochemical conditions (Fig. 2.10). Most of the concepts used have been defined or described in numerous classical books or articles. It is not in the scope of the present book to give an exhaustive reference list. Among these references, few ones have been intensely used: Garrels and Christ (1965), Drever (1982), Stumm (1992), Putnis (1992). Some particular terms have to be precisely defined because they may have significantly different meanings according to some authors. This is the case for congruent and incongruent dissolution for instance. Some principles should be recalled such as crystallization and equilibrium definitions.

#### *Dissolution*

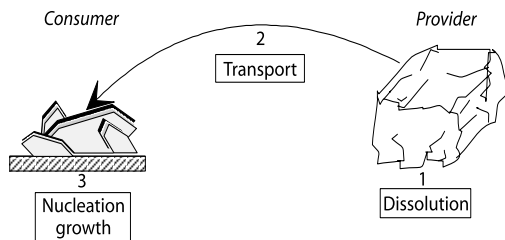
In weathering conditions, the rocks are affected by interaction with slightly acidic rain-water which triggers either a congruent dissolution of the unstable minerals or the formation of clay minerals. In that case, clay minerals are considered to be the residual portion of the an incongruent dissolution. Any incongruent dissolution is a reaction of the following type:



A typical case is the kaolinite dissolution:



**Fig. 2.10.** The three steps of a dissolution-precipitation process during clay mineral formation in the Earth's surface conditions



If we look in detail, this reaction is in fact more complex than a simple dissolution phenomenon. Indeed, kaolinite dissolves congruently but only silica remains in solution while aluminum precipitates giving a new mineral phase: gibbsite. Two other processes are involved in the reaction: nucleation and crystal growth. A true incongruent dissolution is normally characterized by stoichiometric relations different from those of the mineral (Stumm 1992). In such a case, some components remain attached to the solid phase as amorphous or pseudocrystalline gels. Thus, reactions similar to that of the kaolinite to gibbsite transformation will not be assigned here as an incongruent dissolution but rather as a dissolution-crystallization process.

Incongruent dissolution (amorphous layer) seems to be the rule rather than the exception even if the mechanism is still debated. Some researchers claimed that a gel is formed, others that the surfaces are armored by the precipitation of secondary oxides, others that the Si, Al framework is dissolved congruently after the alkalis have been exchanged (see Brantley and Chen 1995; Blum and Stillings 1995). However, if non-stoichiometric dissolution occurs under initial dissolution conditions, it approaches congruency when undersaturation is maintained. Nagy (1995) stated that at low temperature, phyllosilicates are incongruently dissolved at first. Then, they are congruently dissolved if the undersaturation with respect to the Al and Mg phases is maintained. This has important effects on the chemical properties of systems from nano- to mega-scales. Dissolution, whatever its mechanism, may locally induce a supersaturation with respect to some secondary phases. These phases form locally even if undersaturation is maintained in other microsystems having higher amounts of fluids.

The dissolution of any crystal in natural or experimental conditions begins by a chemical attack on nanosites having a higher energy than their surroundings: vertices, edges, lattice defects. This suggests that the dissolution rate could be controlled by the bulk dislocation densities. This has been shown for dissolution processes in near equilibrium conditions (Blum et al. 1990; Burch et al. 1993).

### *Transport*

The dissolved components may be displaced in solution according to two processes: they are carried away if the fluid is flowing or they diffuse if the fluid is immobile. The first process is largely dominant in the fracture networks. The driving force is gravity. The dissolved component may migrate over long distances from rocks to oceans or continental basins. The second process is active in the low porosity zones where fluids are resident. The driving force is the gradient of chemical potentials. The dissolved chemical components are displaced over short distances.

### Crystallization

We must recall that a phase is not formed at equilibrium with the solution but rather when the solution is supersaturated (see Sect. 1.7.3). In other words, the concentration of dissolved components in solution must be higher than the solubility product of the phase. This is the way for a nucleus to overcome the energy barrier (see Fig. 1.35), i.e. the critical radius and the critical energy (Putnis 1992). Supersaturation being reached at a fixed temperature, crystal nuclei tend to grow so that concentration is lowered, getting closer to the value of the equilibrium concentration at this temperature. Conversely, undersaturation conditions force crystals to dissolve so that the concentration of elements in solution increases until equilibrium has been reached. At equilibrium, the amounts of dissolved solid and precipitated solids are equivalent.

Crystal nuclei may grow if they overcome the energy barrier of nucleation (see Fig. 1.35). This barrier is high for a direct precipitation in a supersaturated solution (homogeneous nucleation); it is lowered by the catalytic effect of the solid support (heterogeneous nucleation). As soon as nuclei overcome the energy barrier, the growth of the new crystals proceeds by incorporation of some of the dissolved components. The energy of this process is also found in the supersaturation of the solution, but at a lesser degree than nucleation. Two growth processes have been classically distinguished according to the controlling factors:

- *Interface-controlled growth.* When the nucleus of a phase  $\beta$  starts growing on a phase  $\alpha$ , the size of the  $\alpha$ - $\beta$  interface is increased. The growth rate is controlled by the transfer of atoms from  $\alpha$  to  $\beta$  through the interface. This transfer comes up against an energy barrier which represents the resistance to atom incorporation in the growth sites,
- *Diffusion-controlled growth.* The process necessitates a transfer of atoms from the dissolution sites of the parent minerals to the growth sites of the secondary clay minerals. Near the clay-solution interface, this transfer takes place by chemical diffusion. Diffusion is activated when a concentration gradient of the involved chemical components exists within the solution far from the crystal surface ( $C_\infty$ ) and in contact with the crystal surface ( $C_{inter}$ ).

Detailed descriptions of these phenomena can be found in Putnis (1992) and Lasaga (1995).

### Epitaxy or Topotaxy Controlled Crystallization

Epitaxy and topotaxy are frequently encountered in weathering processes (see Nagy 1995 for a review). The nucleation energy barrier is lowered by the catalytic effect of the solid support (Fig. 1.35). Epitaxy is frequently observed in natural systems where clay minerals grow on altered parent crystals. For instance, kaolinite crystals are seen to grow on detrital micas in diagenetic sandstones (Pevear et al. 1991; Jiang and Peacor 1991; Lanson et al. 2002). Epitaxy has been experimentally reproduced (Manceau et al. 1999; Schlegel et al. 2001; Rainer et al. 2002).

According to the degree of unlocking of the primary and secondary crystal structures, three types of clay mineral formation have been described in rock alteration

through HRTEM studies.: (1) inheritance of primary structure elements; (2) no inheritance but lattice coherency; (3) no inheritance, no coherency. The first process is commonly observed in mica alteration (Fig. 2.11a). Banfield and Eggleton (1988) showed how vermiculite replaces biotite layer per layer in spite of significant changes of the chemical composition (Fe oxidation, K loss, addition of water in the interlayer). This has been confirmed later using experimental alteration of biotite and phlogopite by Murakami et al. (2003). The second process is typical of non-phyllsilicate alteration such as the replacement of enstatite by talc (Eggleton and Boland 1982) or amphibole by smectite (Banfield and Barker 1994). The secondary products are topotactically oriented with respect to the interface (Fig. 2.11b); no open pores have been observed (Banfield and Barker 1994). When formed by the third process, the crystal structure of the secondary minerals has no coherency with that of the primary ones. The secondary minerals nucleate and grow independently of the interface inside the corrosion sites. Eggleton and Buseck (1980) show the formation of illite in the etch pits of K-feldspars (Fig. 2.11c).

Classically, inheritance was considered to result from a solid state transformation. Oppositely, the non-inheritance was considered typical of a dissolution-recrystallization process. However, Putnis (2002) shows that even when the primary and secondary minerals have similar crystallographic properties, the replacement of the first by the second is always controlled by a dissolution-recrystallization process which produces a secondary porosity (see Fig. 1.36b). A particularly demonstrative example is the plagioclase pseudomorphosis by albite (albitization). The perfect coherency of primary and secondary crystal lattices is related to an autocatalytic effect of the interface. Thus dissolution occurs even for mica alteration which are replaced layer by layer by vermiculite.

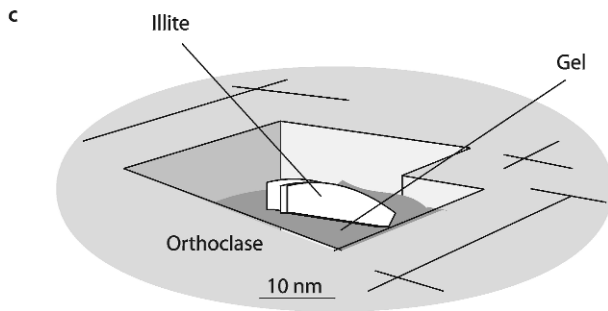
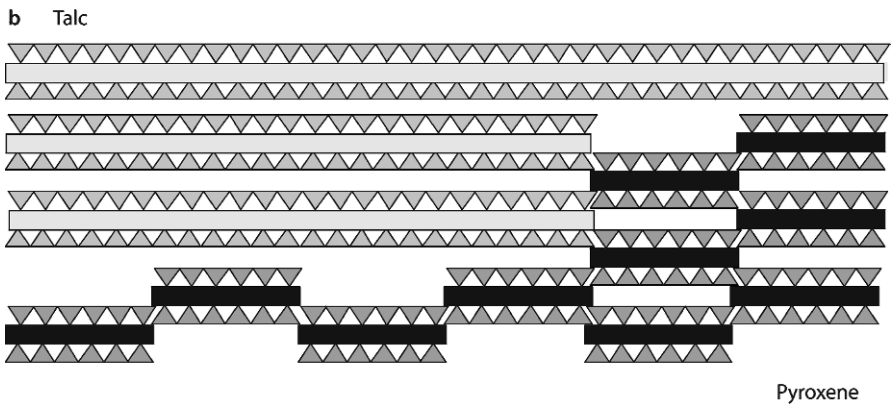
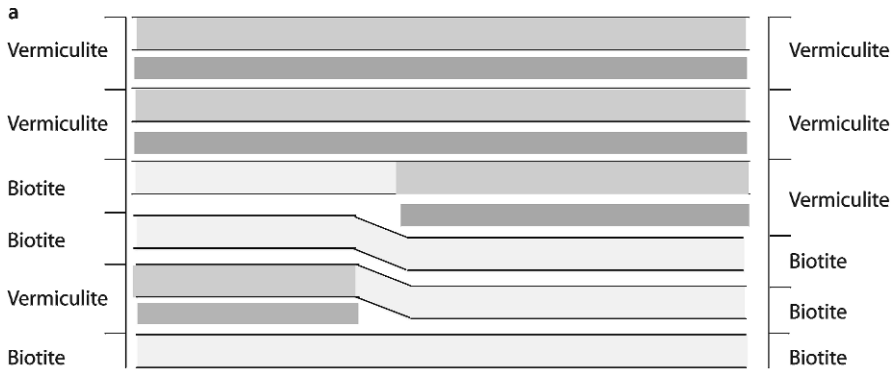
### 2.2.2

#### The Chemical Potential

##### *Chemical Potential and Energy*

The chemical potential differences between the flowing and the resident fluids are the general driving forces throughout the mega- to microsystem scales. Considering for instance, a granitic rock which outcrops in a typical “Gâtine” landscape (western France). It was brought to Earth’s surface with the potential energy of a rock formed in the continental crust at elevated temperature and pressure conditions. This potential energy is much higher than that of rocks formed at the Earth’s surface. Consequently, a series of mineral reactions is triggered to decrease this excess of energy. A part of the unstable minerals is dissolved creating new voids in the rock. The other part is recombined into new mineral phases which are stable or less unstable in the surface conditions. The remaining energy excess is reduced by the collapse of the original granite structure which is replaced by a new fine-grained rock. Then, because of climatic conditions, a soil forms with living organisms on the fine-grained rock. Biota and organic matter impose new conditions at the rock-atmosphere interface which trigger in their turn a new sequence of mineral reactions.





**Fig. 2.11.** The three types of formation of secondary minerals; **a** inheritance of some structural features of the primary mineral (biotite vermiculitization from Banfield and Eggleton 1988); **b** no inheritance but autocatalytic effect (pseudomorphosis of enstatite by talc, Eggleton and Boland 1982); **c** no inheritance and no autocatalytic effect: example of a K-feldspar altered to illite (from Eggleton and Buseck 1980)

According to Gibbs (1961), the chemical potential is the change of internal energy ( $\delta U$ ) that occurs in response to the addition of infinitesimal quantity of component  $i$  ( $\delta n_i$ ):

$$\mu_i = \left( \frac{\delta U}{\delta n_i} \right)_{n,V,n_{j \neq i}} \quad (2.1)$$

The Gibbs free energy ( $G = H - TS$ ) is equal to the sum of the chemical potential of all the components in the system:  $G = \sum \mu_i n_i$ . It is to be noticed that the Gibbs free energy of a system is an extensive variable which depends on the size (volume or mass) of that system. The chemical potential is an intensive variable which is independent of the size of the system. Temperature or pressure are also intensive variables.

For a given component  $i$ , the potential energy is:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (2.2)$$

where  $R$ : gas constant ( $8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$ : temperature (K),  $\mu_i^0$ : standard state chemical potential of the element  $i$  which is a function of temperature and pressure only ( $\text{J mol}^{-1}$ ), and  $a_i$ : chemical activity of component  $i$  (dimensionless parameter).

The  $RT \ln a_i$  member is necessary because the element  $i$  is not at its standard energy, i.e. combined with other elements for instance. This quantity corrects the Gibbs free energy introducing the activity ( $a_i$ ) in place of concentration ( $X_i$ ). For ideal mixtures  $a_i = X_i$ . For departure from ideal mixing,  $a_i = \gamma X_i$  where  $\gamma$  is the activity coefficient. According to the Debye-Hückel theory concerning solutions,  $\gamma$  is a function of the ionic strength of the solution and the charge of the ion  $i$ . It describes the depression of the free energy of ion  $i$  making it less likely to take part in chemical reactions.

The chemical potential refers to a standard state. For a component in an aqueous solution or in a solid solution, the standard state is that of the pure component at the same temperature and pressure conditions as those in the system under consideration. It is important to distinguish the solvent from the solute it contains. Indeed, in natural systems at the Earth's surface the solutions being aqueous, it is important to determine  $\mu_{\text{H}_2\text{O}}$ . If the solution is infinitely dilute,  $\mu_{\text{H}_2\text{O}}$  is close to the standard state  $\mu_{\text{H}_2\text{O}}^0$  and the water activity is equivalent to the concentration, hence  $a_{\text{H}_2\text{O}} = 1$ . Conversely, for the solute, the standard state is given by the infinite dilution because, activity approaches concentration.

### **Gradients of Chemical Potential: The Driving Force**

Considering a chemical element  $i$  in a two phase system (A + B), the equilibrium is reached when the difference of the chemical potentials of that component is null:  $\mu_{i(A)} = \mu_{i(B)}$ . That does not mean that there is no exchange of component  $i$  between phases A and B but rather that the energy balance of exchange is null ( $G$  does not vary). By definition, at equilibrium, the chemical potential of each component is the same in all the phases. For instance, when kaolinite is formed with goethite in a laterite soil,

the chemical potentials of Al are identical in the two phases even if their respective concentrations are highly contrasted.

If  $\mu_{i(A)} > \mu_{i(B)}$ , the system is not in equilibrium. Consequently, changes occur in order to reduce the difference between  $\mu_{i(A)}$  and  $\mu_{i(B)}$ . Physically speaking, as the difference of the chemical potentials is established between crystal bodies separated by a certain distance even if they have a common border, a gradient of chemical potential is established. It is the driving force leading the chemical component  $i$  to move from A to B in order that the difference  $\mu_{i(A)} - \mu_{i(B)}$  becomes null. A chemical gradient is stabilized in time until the two original A and B phases are present. It vanishes when, at least, one of them has disappeared or totally changed its composition.

By what means do the chemical components migrate from one point to another? Recall that at equilibrium, the chemical potentials of a given element in the solids and the solutions are equal whatever their respective concentrations in that element. Thus, any difference of chemical potential imposes a disequilibrium state which is reduced through migration of that component from the high to the low potential areas. Whatever the difference established inside a liquid or a solid, the migration is controlled by the chemical diffusion process. The diffusion is more rapid in a solution than in a solid. Most often, diffusion is efficient in solids only at high temperatures. The chemical diffusion has been early identified as the process by which elements migrates.

### *Effective Length of Action for Chemical Potential Gradients*

The distance of interaction and movement of material in static aqueous systems, those where convective transport is very small, depends upon chemical diffusion in the solutions. For a brief review of the principles of diffusions see Annex 6. The motor of diffusion is the chemical potential gradient in a system.

The chemical potential gradient is the major variable at the microsystem scale. However, it is not the unique thermodynamic parameter to be taken into account. At the nanosystem scale, it is associated with other forces which have almost the same importance such as surface tension, electrical forces, crystal defect density. Thus it is important to consider the effective distance of action for the different processes.

Comparing with astrophysics, the chemical potential gradient can be considered as the equivalent of the gravitational force which is weak but acts over long distances while the chemical forces at the solid-solution interfaces are strong but limited to very short distances from the interface (see Holchella and White 1990 for a review). The equivalent in astrophysics is the strong nuclear interactions which are very strong but act at very short distances. These short distance forces become preponderant in the nanosystems (Table 2.2).

**Table 2.2.** The driving forces controlling mineral reactions in the micro- and nanosystems

Energy source	Intensity	Distance of action	Control
Chemical potential gradient	Weak	Long	Microsystems
Surface energy	Strong	Short	Nanosystems

### Application to Weathered Rocks

During weathering, the primary minerals are progressively corroded and transformed into new ones which are of small size. The corrosion zones are filled by a new fine grained material assigned as “plasma”. The plasma is composed of newly formed secondary minerals mixed with fine debris of the parent ones. It is porous and the secondary porosity is interconnected to the rock initial fracture network. The total permeability of the rock increases with weathering. For instance, the  $^{14}\text{C}$ -PMMA impregnated samples of a fresh and an altered granite (Fig. 2.12) shows that alteration produces a secondary porosity (gray patches) which is connected to the primary network.

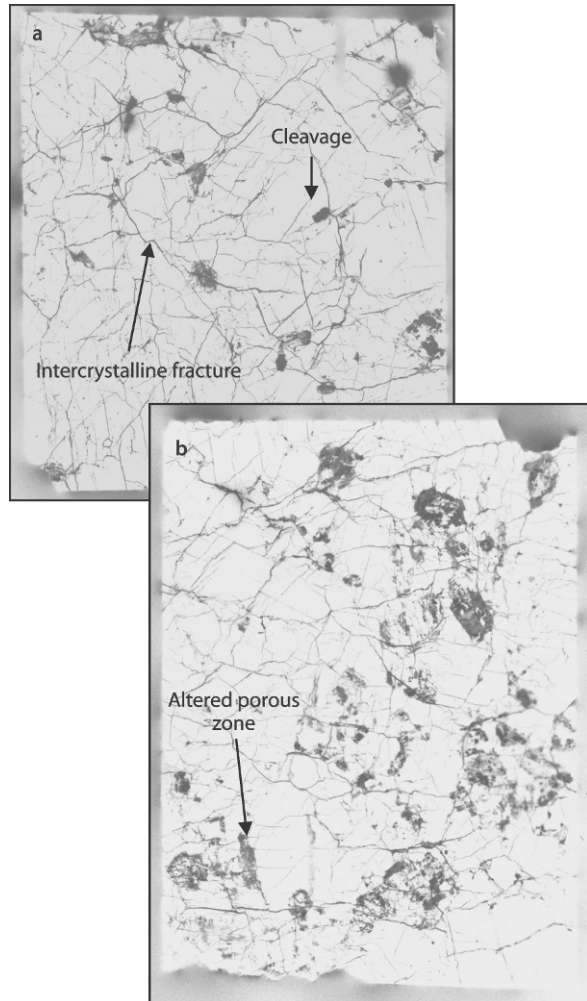
Summarizing, alteration induces concomitantly chemical and physical changes of the rocks. At a given weathering stage, the rock is composed of unaltered remains which conserve the initial fluid pathways (intergranular joints, cleavages, microcracks) and newly formed plasma in which the secondary porosity creates new pathways (Fig. 2.13). The rock becomes heterogeneous; it is composed of highly and weakly porous zones. These zones are physically and chemically contrasted. At this stage, the chemical potentials of the dissolved elements are particularly variable from point to point in the altered rock. Local gradients are established from high to low potentials triggering the transfer of these chemical components.

These theoretical considerations have been applied to the calculation of the flux of dissolved components. Holchella and Banfield (1995) proposed the following equation:

$$f = \frac{dq_i}{dt} = \frac{D_i(C_{\text{int}} - C_{\text{ext}})A}{l} \quad (2.3)$$

Considering a given chemical element  $i$  migrating by diffusion from the dissolution site ( $C_{\text{int}}$ : internal concentration) to the larger pores in which the solutions flow ( $C_{\text{ext}}$ : external concentration), the flux  $f$  ( $dq_i/dt$ : quantity per time) depends on the concentration gradient ( $C_{\text{int}} - C_{\text{ext}}/l$ : approximation of the chemical potential gradient), the effective pore area ( $A$ ) and apparent diffusion coefficient of species  $i$  ( $D_i$ ). The parameter  $l$  corresponds to the length of the diffusion path (Fig. 2.14). Parameters  $A$  and  $l$  are average values which change with the alteration progress. They are difficult to measure because they include voids whose size varies in a several order of magnitude range. The  $A$  and  $l$  parameters are determined by the geometrical characteristics of the fluid pathways. In other words, they quantify the dimensions of the connected pore network as it is pictured in  $^{14}\text{C}$ -PMMA impregnated samples (Fig. 2.12). The main geometrical characteristics of the rock permeability are the tortuosity and the connectivity. Connectivity may depend upon the size of the necks which bond the pores. The smaller they are, the more the electrical surface effects become important. In other words, connectivity depends on the physicochemical properties of the molecule or ion used as a probe. A demonstrative example is given by the study of the deuterium pores in feldspars by Walker (1990). Using the diffusion of  $\text{H}_2^{18}\text{O}$ , the authors showed that deuterium pores are connected in spite of the fact that they were considered commonly to be outside of rock permeability.

**Fig. 2.12.** Alteration increases the rock porosity. The autoradiographs of unaltered (a) and altered (b) Palmottu granite shows the increase of the diffuse porosity areas in the altered facies (from Siitari-Kauppi et al. 2003).



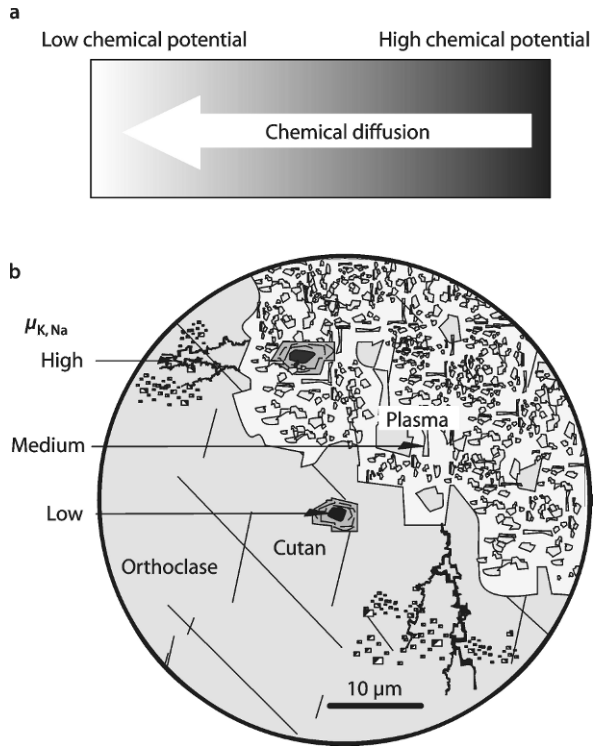
### 2.2.3

#### A Particular Chemical Potential: The pH

Some of the chemical parameters of the initial altering fluids (rain) are controlled from the outside of the macrosystems. This is particularly the case for the pH: rainwater dissolves the atmospheric  $\text{CO}_2$  and becomes acidic:  $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$ . According to Drever (1982), the pH of the most acidic waters in natural systems controlled by the  $\text{H}_2\text{O}-\text{CO}_2$  chemical interactions is about 5.5. That value decreases in soils because of the presence of organic acids (fulvic and humic acids) down to pH = 4 in podzols.

Considering the formation of clay minerals, the proton  $\text{H}^+$  (or its hydrated state  $\text{H}_3\text{O}^+$ ) has a double action. First, it breaks the cation-oxygen chemical bonds in the

**Fig. 2.13.** At a given alteration stage, gradients of chemical potentials are locally established; **a** diffusion direction; **b** gradients in altered rocks



crystal structure of silicates (dissolution). Second, it may compete with other cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , ... for the saturation of the exchangeable sites of smectites or vermiculites.

### ***What Is the Effect of pH in the Dissolution Processes?***

In weathering processes involving slightly acidic rainwater, there is an overall exchange of hydrogen for cations in the high temperature minerals. Basically the alteration process produces hydrous minerals (those containing hydrogen ions) from those that contain none or few of these ions. The products are clay minerals which have OH units in their internal structure. The hydrogen proton comes from the altering solutions. If no ion exchange occurs the minerals are dissolved, such as calcite and quartz.

The proton breaks the cation-oxygen bonds leading to the destruction of the silicate crystal framework. Dove and Crerar (1990) showed that the dissolution of quartz in water is a step-by-step process which involves the adsorption of water molecules and the hydrolysis of Si-O bonds (Fig. 2.15a). Thus, the adsorption of protons on the surface of the silicates is the controlling parameter of the dissolution rate. Numerous experiments have been conducted to measure the dissolution rate of silicates in conditions far from equilibrium (Casey and Ludwig 1995 and references therein). They show the pH-dependency of the dissolution rate: the lower the pH, the higher the rate.

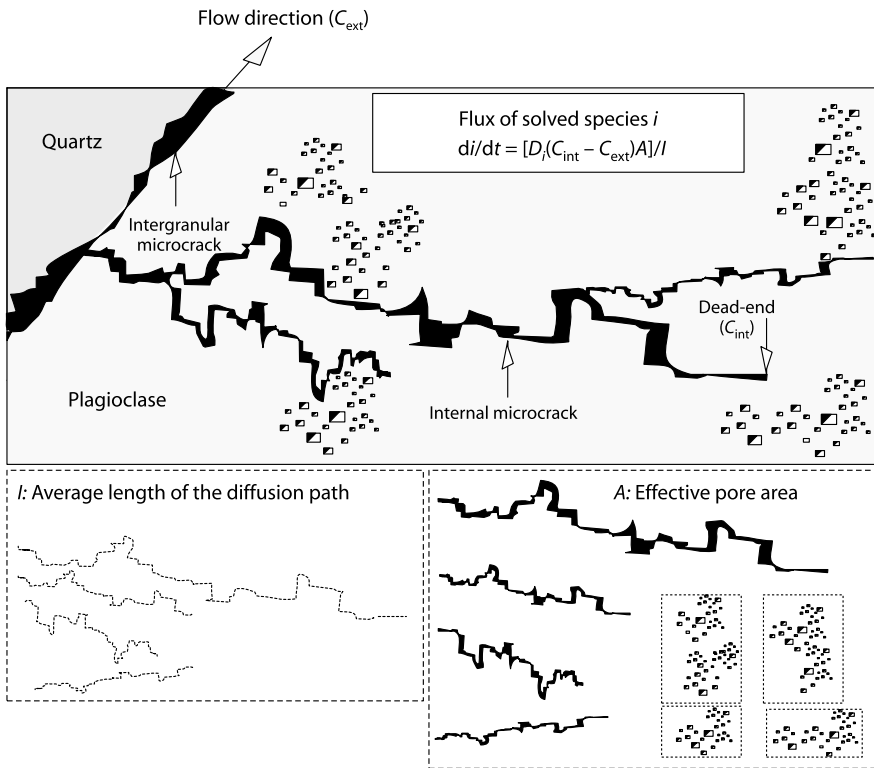
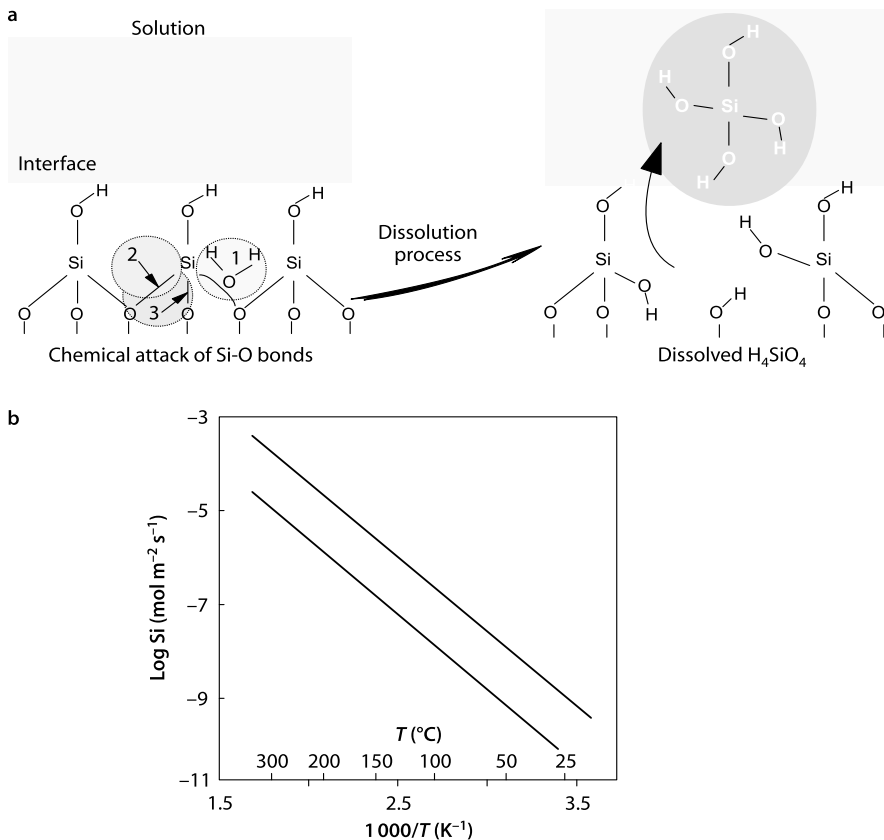


Fig. 2.14. Elements for the calculation of the flux of a given dissolved component (from Holchella and Banfield 1995).

However, conditions far from equilibrium are not stable everywhere inside weathered rocks. Particularly, they cannot exist for long periods of time in the most closed microsystems such as those prevailing in the earliest weathering stages.

The dissolution is controlled by the coordination states of the chemical components at the surface of solids (Berger et al. 1994). For example, two processes control the rate of the alteration of a basaltic glass: (1) an initial rate is controlled by the silica concentration in the solutions at a pH value close to neutrality; (2) a slower rate is established over a longer periods of time. It is controlled by the Al concentration of the solutions for acidic pH values. Figure 2.15b shows that the rates of these two processes are similar to the dissolution rates of glass in open systems (diluted solutions) on the one hand and of crystallized silicates (quartz, albite, anorthite, K-feldspar) on the other hand (Berger 1995). The role of the structure of the surfaces in contact with the solvent has been confirmed by comparative dissolution experiments of smectites and kaolinites (Bauer and Berger 1998). The tetrahedral and octahedral sheets of kaolinites are simultaneously submitted to the chemical attack whereas only the tetrahedral sheets of smectites are first exposed. For kaolinites, the dissolution of the octahedral sheet is faster ( $E_a = 33 \pm 8 \text{ kJ mol}^{-1}$ ) than that of the tetrahedral sheet ( $E_a = 0.51 \pm 8 \text{ kJ mol}^{-1}$ ).

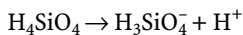


**Fig. 2.15.** The dissolution mechanism of silicates; **a** the dissolution of quartz (after Dove and Crerar 1990, modified): first, adsorption of water molecules on the crystal surface; second, break up of the three Si-O bond (hydrolysis) and release of a  $\text{H}_4\text{SiO}_4$  molecule into water; **b** Arrhenius diagram showing the dissolution rates of basaltic glasses and silicates (after Berger 1995)

The activation energy of the smectite dissolution is very close to that of the tetrahedral sheet of kaolinites ( $E_a = 0.52 \pm 4 \text{ kJ mol}^{-1}$ ).

### *Solubilities of Si and Al versus pH*

The solubility of crystalline and amorphous silica phases is constant up to pH 8.5 and increases dramatically at higher pH values (Stumm and Morgan 1981). The weak acid  $\text{H}_4\text{SiO}_4$  is dissociated at pH above 9 according to the following reaction (Fig. 2.16):





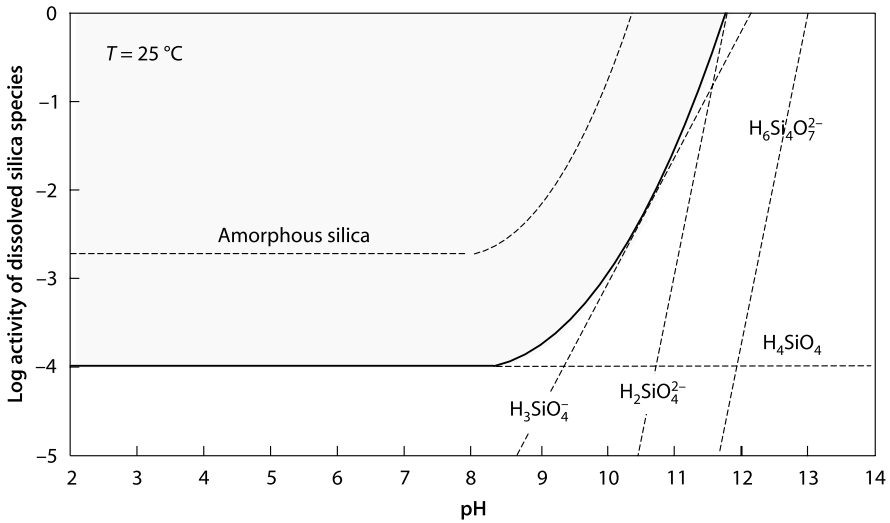
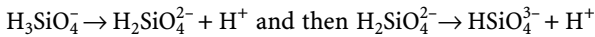


Fig. 2.16. Variation of the activities of dissolved silica species in equilibrium with quartz at 25 °C versus pH. The *heavy line* represents the total activity of dissolved silica species. The *gray zone* corresponds to the activity-pH domain supersaturated with respect to quartz. The *dashed line* indicates the equilibrium with amorphous silica (modified from Drever 1982)

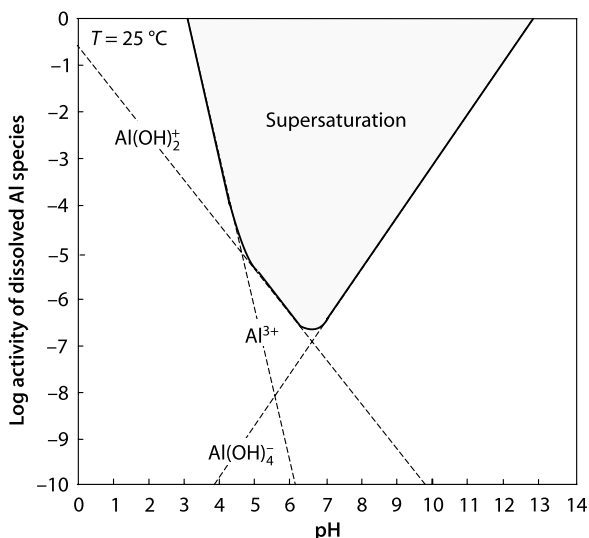
This reaction is a chemical buffer in natural macrosystems where zeolites are formed with clay minerals. It can locally be an important parameter at the scale of microsystems in some particular conditions (weathering of serpentinites for instance). In very high pH conditions, the  $\text{H}_3\text{SiO}_4^-$  acid is dissociated in its turn:



These dissociation reactions are not important in natural systems. However, it is possible that ionized polymers such as  $\text{H}_6\text{Si}_4\text{O}_7^{2-}$  play a significant role when clay minerals are formed in the presence of amorphous silica. Aqueous dissolved silica species are able to interact with organic substances to form complexes (Bennett et al. 1988; Bennett 1991). This has a huge importance in soils.

The solubility of aluminum is very low except at low and high pH values. The dominant species in solution are  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_4^-$  at  $\text{pH} < 4$ ,  $4 < \text{pH} < 7$  and  $\text{pH} > 7$  respectively (Fig. 2.17). The activities at equilibrium of each aluminum species decreases with increasing activity of dissolved silica. Thus, the amounts of dissolved aluminum species in natural waters in equilibrium with clay minerals such as kaolinite or smectite are extremely low: 0.1 to 1  $\mu\text{g}$  per liter (Drever 1982). Consequently, aluminum is considered most often as an immobile component. This is reasonable at the scale of the macrosystems but not adequate at the scale of the microsystems. Indeed, even if aluminum has a very low solubility, large quantities may move if a gradient of chemical potential is maintained somewhere in the rock. This is why smectites form-

**Fig. 2.17.** Variation of the activities of dissolved aluminum species in equilibrium with gibbsite at 25 °C versus pH. The heavy line represents the total activity of dissolved aluminum species. The gray zone corresponds to the activity-pH domain supersaturated with respect to gibbsite

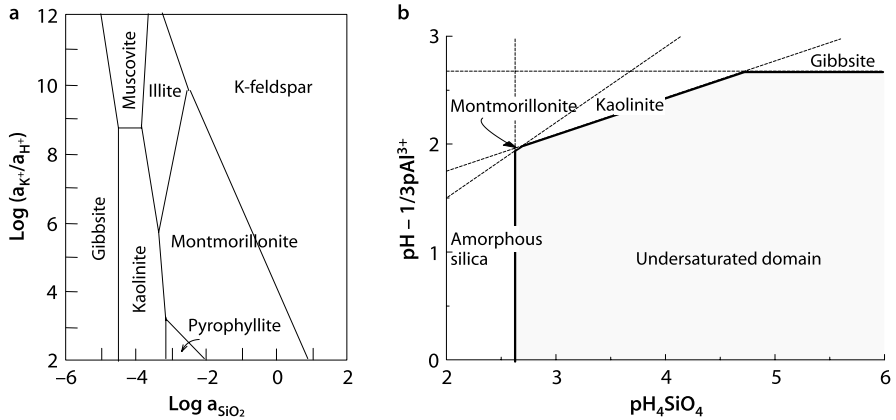


ing inside olivine in the early weathering stages of a gabbro may contain aluminum. Aluminum; in spite of its low solubility is not immobile but it is an inert component. Indeed, the aluminum chemical potential is rarely a decisive factor for the formation of clay minerals. Its presence determines the quantity but not the nature of secondary clay minerals.

### *The Stability of Clay Minerals Respective to pH*

It has been shown that the formation of clay minerals is strongly pH-dependent. Trioctahedral magnesium-rich clays are formed at pH above neutrality while dioctahedral aluminum-rich ones are formed under more acidic conditions. However, this does not explain how pH influences the stability of these minerals. Consider for instance the classical phase diagrams of Garrels (1984) which depict the stability of dioctahedral clay minerals in an activity-activity plot (Fig. 2.18a). Such a phase diagram is a useful tool to relate the observed assemblages in soils or weathered rocks with the conditions imposed by the fluids. It is also informative concerning the forbidden assemblages such as montmorillonite-gibbsite for instance. In such diagrams, the pH (negative logarithm of  $H^+$  activity) is included in the ordinate  $\text{Log}(a_{K^+}/a_{H^+})$ . The  $a_{K^+}/a_{H^+}$  quantity may vary only if one of two members varies:  $a_{K^+}$  or  $a_{H^+}$ . At a given alky activity, changes in mineral stability may happen due to pH variation. This point has been discussed in detail by Kittrick (1969c) who used another phase diagram (Fig. 2.18b).

The  $\text{pH} - 1/3\text{pAl}^{3+}$  variable is related to the chemical potential of hydroxide aluminum  $\text{Al}(\text{OH})_3$ . It is referred to as the aluminum hydroxide potential in soils (Schofield and Taylor 1955). The Al activity is controlled at very low levels in natural waters. However, as more Al is dissolved in acid than in neutral waters, the aluminum hydroxide potential is pH-dependent. Then, the dioctahedral phases which precipitate in the



**Fig. 2.18.** Phase relationships relative to the activities of  $H_4SiO_4$ ,  $Al^{3+}$ ,  $K^+$  and  $pH$ ; **a** phase diagram of the system  $K_2O-Al_2O_3-SiO_2-H_2O$  at  $25\text{ }^\circ\text{C}$  after Garrels (1984);  $Al_2O_3$  is considered as an inert component; **b** phase diagram in the  $pH - 1/3pAl^{3+}$  versus  $pH_4SiO_4$  coordinates after Kittrick (1969c)

microsystem are responsible for the  $pH$ -dependent control of  $Al$  at low levels. Coming back to the Garrels' phase diagram, this means that the  $Al$  activity is determined in each monophasic field by the mineral which is stable.

### *The Proton $H^+$ : A Cation among Others*

The soil acidity depends on the amounts of protons and aluminum cations in the solutions. Protons are produced by water hydrolysis and by biological activity ( $pH \geq 6$ ):  $Al^{3+}$  cations are produced by the destabilization of silicates including clay minerals ( $pH \leq 6$ ). The proton does not exist freely in solution as a cation; it is linked to a water molecule, i.e. hydrated as are the other cations in solution such as  $Na$  or  $Ca$ . The three O-H bonds are equivalent in the hydronium cation ( $H_3O^+$ ). The proton  $H^+$  in its hydrated state ( $H_3O^+$ ) behaves as a cation competing with others such as  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , ... for the saturation of the exchangeable sites in clay minerals. However, its preference degree of adsorption by clays is the weakest compared to other commonly exchangeable cations (absorption of  $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ \cong NH_4^+ > Na^+ > H_3O^+$ ). This implies that it is adsorbed in the interlayer zones of clays only when highly concentrated in the solutions. Such hydrogenated clays are probably short lived because the hydronium ions decompose into a proton and a water molecule.

#### 2.2.4

### The Oxidation-Reduction Potential (Redox)

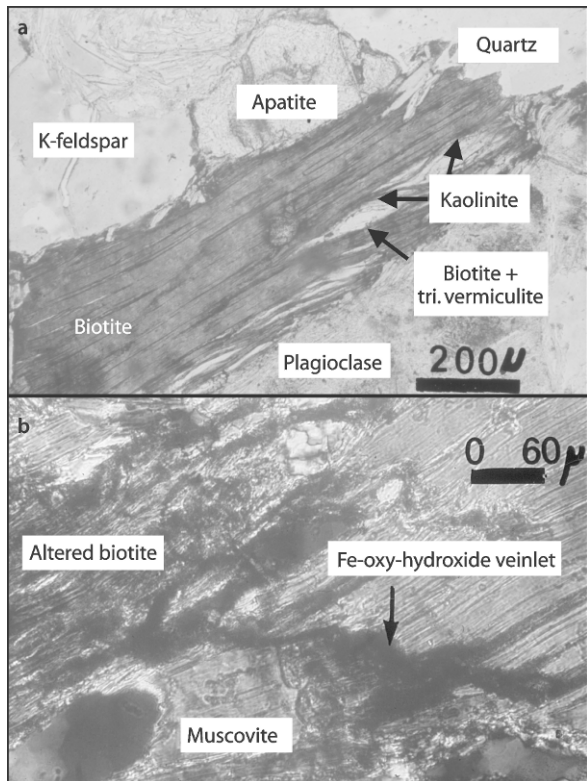
#### *Redox Effects on Alteration Processes*

The redox conditions in natural environments may vary at different system scales. For instance, the sediments in the bottom of a lake are transformed by anoxic waters (kilometer scale). Some soils exhibit a mosaic of bleached and colored zones which are

low or high in Fe oxide content (meter scale). Reduction reactions may be observed in the vicinity of organic matter debris at the micrometer scale (glauconite grain formation). In all the cases, the chemical elements which have different oxidation states such as iron or manganese are dissolved in some places and precipitated in others according to the anoxic-oxic transition (redox gradients). This is particularly well shown in weathered granites where biotites are the unique iron bearing mineral species. Iron is extracted from the lattice during the mineral reactions and precipitates locally with the secondary silicate phases (Fig. 2.19a). In certain conditions, iron may migrate over longer distances as shown by the invasion of non-Fe bearing primary minerals by Fe-oxyhydroxide which precipitates in the rock microcracks (Fig. 2.19b).

The Fe oxy-hydroxides are commonly found in soils and weathered rocks. They have been studied in detail for decades (see Schwertmann and Taylor 1989 for a review). The Fe ions at the surface of the minerals are hydroxylated or hydrated and extracted from the crystal lattice. They migrate in solution mostly in the  $\text{Fe}^{2+}$  state. Then they are incorporated in secondary silicate and/or oxy-hydroxide phases. At equilibrium,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  cations are shared between the aluminous phases, i.e. gibbsite and kaolinite, and Fe-oxy-hydroxides (Trolard and Tardy 1989).

**Fig. 2.19.** Redox effects in a weathered granite; **a** a biotite is altered into a vermiculite + kaolinite assemblage along an internal microcrack which is outlined by Fe-oxide deposits; **b** when strongly altered, biotites lose Fe ions which form Fe-oxyhydroxide deposits in the surrounding microcracks whatever the host mineral



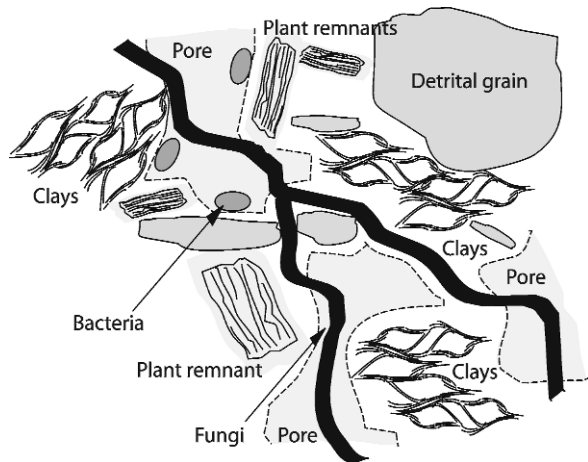
### *Redox Effect on Clay Minerals*

Redox is an important factor which controls the formation and the composition of the Fe-bearing clay minerals. Much of the available literature is related to the works of Stucki and his co-workers. Stucki (1988) shows that two processes are involved during the oxidation of  $\text{Fe}^{2+}$  cations in dioctahedral smectites: (1) the loss of an electron which decreases the layer charge of the 2:1 unit, (2) the sequence of de-protonation and hydroxylation reactions. These reactions have been shown to modify not only the crystal structure of the clays (octahedral sheet configuration, layer charge) but also the cation exchange and retention capacities, the specific surface and the layer stacking order (see Stucki et al. 2002 for a compilation). Surprisingly, the experimental oxidation of smectites conducted by Stucki et al. (1984) shows that the decrease of the layer charge is not linearly related to the  $\text{Fe}^{3+}$  content. Similar observations were made on natural weathering systems in which chlorite has been transformed into vermiculite (Proust et al. 1986). The reduction-reoxidation experiments conducted on the Garfield nontronite (Fialips et al. 2002) show that the modifications experienced by the crystal lattice are not fully reversible. Reduction creates defects in the octahedral sheet (Manceau et al. 2000a,b) which do not disappear after re-oxidation.

### *Microbial Interactions in Soils*

The huge external surfaces of clay minerals multiply their capacity to interact with organic substances and micro-organisms. Among all the mineral compounds of a given soil horizon, clays are by far the most sensitive to the pH and Eh variations induced by the presence of organic acids and bacteria or fungi (Fig. 2.20). Indeed, bacteria or fungi often need Fe. They cannot find Fe in oxygenated water because of its very low solubility. They find Fe in specific complexes and in the redox sites within minerals (Banfield et al. 1999). The chemical exchanges occur on the walls of the pores through

**Fig. 2.20.** A schematic representation of a rhizosphere environment where mineral and organic compounds interact with biota (inspired from Chenu and Stotzky 2002)



the resident fluids where the bacteria can develop (see Chenu and Stotzky 2002 for a review). The impact of organisms living in such specific environments on the weathering processes is much more important than that of the inorganic reactions.

## 2.3 Mineral Reactions in Alteration Systems

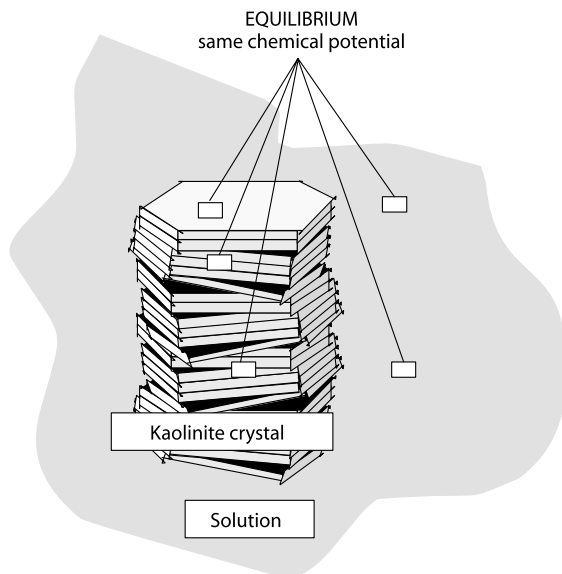
### 2.3.1 Conditions at Equilibrium

#### *Fundamentals*

A consequence of the second law of thermodynamics is that, at equilibrium, the chemical potential of a substance is the same throughout the co-existing phases regardless of how many are in the system (Fig. 2.21). In other words, at equilibrium, the chemical potential of any element composing the solution and the minerals is the same throughout the liquid and each of the solid phases and the same in the liquid as all the solid phases. This is the ideal situation which is reached for gas and liquid phase equilibrium. It is almost never perfectly realized with solids which are frequently heterogeneous (zonations, clustering, ...). However, in spite of approximations, the definition of equilibrium was fruitfully applied first to mineral equilibria in metamorphic or magmatic environments, then to mineral-fluid equilibria in alteration systems (see Meunier 2005 for a review).

Assuming that the chemical and structural heterogeneity of clay minerals is not an insurmountable obstacle to the use of the classical thermodynamic rules, it is possible

Fig. 2.21. At equilibrium, the chemical potential of any element composing the solution and the mineral are the same throughout the liquid and the solid phases and the same in the liquid as in the solid phases



to apply the Gibbs' phase rule to clay mineral assemblages. This method has been fruitful for the petrographical analysis of altered rocks. Particularly, it helps to predict the maximum number of mineral phases which form the stable assemblages in a given chemical system. The number of phases present depends on the number of extensive and intensive variables which characterize the system. Using the general formulation of Korzhinskii (1959), the variance  $F$  (or degree of freedom) of the system is given by  $F = V_{\text{ext}} + V_{\text{int}} - p$  where  $V_{\text{ext}}$  and  $V_{\text{int}}$  are the number of extensive and intensive variables respectively and  $p$  the maximum number of phases. A detailed presentation of the Gibbs' phase rule for soils can be found in Chesworth (1980, 2000).

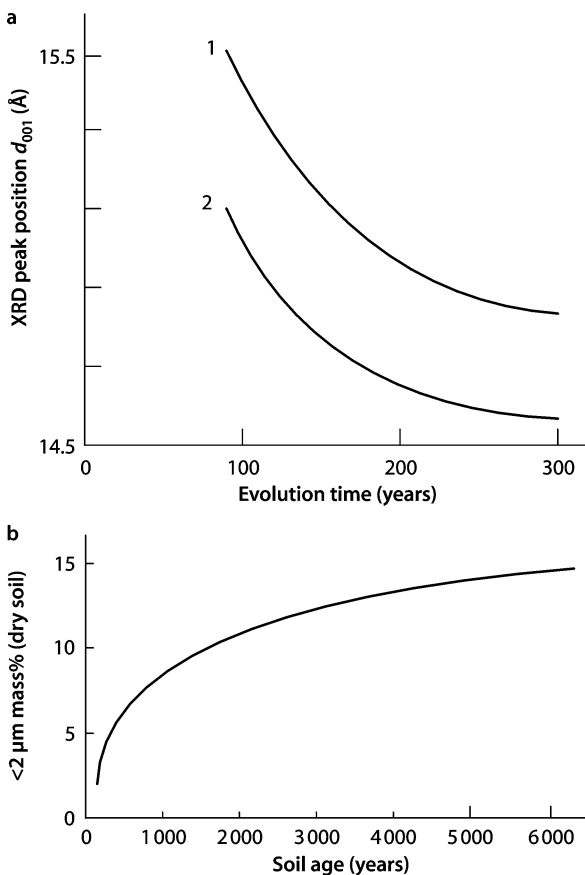
Extensive variables depend on the system size (enthalpy, entropy, volume or mass). For a given chemical system at fixed pressure and temperature, the number of extensive variables is equal to the number of inert components. An inert component is a chemical component for which only the amount plays a role and which determines the quantity of each phase formed. Note that, despite the qualifying term *inert*, these elements are not immobile; they can be drained off (leaching) or concentrated in a given system.

Intensive variables in natural systems where energy is not dependent on temperature and pressure variations, are typically the chemical potential of "mobile" component. Mobile components are elements whose chemical potential determines the nature of mineral phases and not their quantity. An element can be inert under certain circumstances and become mobile under others. For weathering systems, the Korzhinskii's relation can be written as follows:  $F = C_{\text{mobile}} + C_{\text{inert}} - p$ .

### ***Application to Weathered Rocks: Phase Diagrams***

At the nanosystem scale, the formation of the secondary phases is kinetically controlled by different processes (atom diffusion in the solution or at the mineral surfaces, autocatalytic effect, ...). The mineral assemblages are generally monophased at the fluid-parent mineral interface: pyroxene  $\rightarrow$  talc for instance. However, as the mineral parents dissolve congruently, the chemical components are recombined into a polyphased assemblage far from the mineral/fluid interface. The transition from nano- to microsystems has been illustrated by Eggleton and Boland (1982) who show that a complex transitory assemblage of smectite + chlorite + magnetite is formed near the interface. In their turn the transitory phases are destabilized giving talc + spinel. Thus, the internal destabilization of enstatite gives a polyphased secondary assemblage. As, the fluid composition is controlled by the primary minerals in the altered zones of the early stages of weathering, several secondary phases are generally formed. For instance, biotites in weathered granite are replaced by a vermiculite + kaolinite + Fe-oxyhydroxide assemblage. Monophased secondary assemblages are sometimes formed in specific conditions where only one chemical element behaves as an inert component. This is the case of plagioclases in granitic rocks which are altered into kaolinite. All these observations can be represented in different kinds of phase diagrams. The basics for phase diagrams construction have been summarized for clay-bearing rocks by Velde (1985), soils (Chesworth 2000) or altered rocks (Meunier and Velde 1986; Meunier 2005). They are presented in Annex 5.

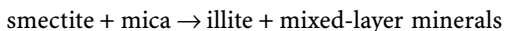
**Fig. 2.22.** Soil chronosequences; **a** sodic and acqic entisols from the Marais Poitevin (western France). Migration of the XRD peak position of the Ca-saturated and air-dried  $<2 \mu\text{m}$  fraction as a function of time; *1*: smectite, *2*: illite/smectite mixed layers (from Righi et al. 1995); **b** logarithmic increase of the clay mass as a function of time in soils developed on the Mont-Blanc massif moraines (from Righi et al. 1999)



### 2.3.2

#### Kinetics of Alteration Reactions

The fundamentals of reaction kinetics are presented in Annex 5. The measurement of time duration of natural processes is difficult. However, it is made possible in some particular circumstances such as soils formed in historical sites or on dated formation (glacier moraine for instance). Historical documents have been used in the Marais Poitevin (western France) to study a time sequence of clay soils (over 60% clay) developed in similar pedogenetic conditions (sodic entisols – aquic entisols). Seven polder events from 1665 to 1912 have been used to establish a soil chronosequence from 330 to 80 years. A mineral evolution is observable in the  $<0.1 \mu\text{m}$  clay fraction which was extracted from soil samples collected at a given depth (36 cm from soil surface). Righi et al. (1995) show that the potassium of the micaceous phases has been transferred to the expandable phases according to the following reaction:





The progress of the reaction is not a linear function of time (Fig. 2.22a). Rapid at first, it approaches equilibrium after 200 years.

Podzol chronosequences have been described in post-glacial environments of Finland from 0 to 10 000 years (Gillot et al. 1999, 2000) and 80 to 6 600 year old moraine deposits in the Mont-Blanc massif (Righi et al. 1999). Both examples show the effects of different time dependent mineral reactions:

- Finland: disappearance of high-charge smectite layers after 6 000 years in the E horizon (eluvial horizon). In the same time, the amount of mixed-layer minerals decreases with time until only beidellite remains in the most ancient soil (10 000 years).
- Mont Blanc: disappearance of the trioctahedral primary phases (biotite + chlorite) within 1 000 years, yielding mica/smectite dioctahedral mixed layers. The dioctahedral primary phases do not disappear but are transformed into mica/smectite regularly ordered mixed layers. Both mineral reactions are intense in eluvial horizons (E horizons) and caused a logarithmic increase in the soil clay mass as a function of time (Fig. 2.22b).

Other examples of reaction progress as a function of time are given in various chapters to follow.

## Suggested Reading

- Drever JI (1982) *The geochemistry of natural waters*. Prentice-Hall, Englewood Cliffs, 388 pp
- Holchella MF Jr, White AF (eds) (1990) *Mineral-water interface geochemistry*. Mineralogical Society of America, Washington (Reviews in Mineralogy 23)
- Taylor G, Eggleton RA (2001) *Regolith geology and geomorphology*. John Wiley and Sons, Chichester, 375 pp
- White AF, Brantley SL (1995) Chemical weathering rates of silicate minerals: an overview. *Rev Mineral Geochem* 31:1–22

## The Development of Soils and Weathering Profile

### Introduction

Weathering processes and soil development have been classically considered as two aspects of a single phenomenon which is the transformation of rocks under climatic conditions (meteorization). White (1995) gave a clear definition of what is classically considered as a soil profile: *“The soil profile is generally considered to make up the upper part of a much thicker weathering profile. A more inclusive definition of a soil profile is the vertical section that includes all the layers that have been pedologically altered during chemical weathering. Soil horizons defined within such profiles clearly recognize the vertical transition in the degree of weathering from the intensively altered A and E horizons through the moderately weathered B, to the relatively unaltered C horizons to bedrock (Buol et al. 1989). Such an approach encompasses the entire span of chemical weathering occurring at the earth’s surface including both the distribution of primary silicates as well as secondary clay and oxyhydroxide minerals”*. This definition opens a fundamental question: do soil and weathering belong to a same alteration phenomenon at the Earth’s surface, the soil being the most altered level? If not, are soil formation and rock weathering different Earth’s surface phenomena? The idea that they are different phenomena has been proposed by Ildefonse et al. 1978). It is supported by Taylor and Eggleton (2001) who proposed that: *“The distinction from regolith is, in general subtle, but the relationship with the surface is distinctive. To amplify the difference it may help to suggest that soils develop horizons from a regolith parent, while regolith develops from in situ or transported weathered rock material to form zones”*.

Until now, it has not been possible to find an unambiguous definition of soil and weathered rocks in spite (or because) of the huge literature dedicated to the study of alteration. This is essentially due to natural and Gulliver factors. The first factor is imposed by natural environments, either in tropical or temperate climatic zones, in which the soils appear superficially to be in a continuum between clay-rich materials and with weathered rocks. For this reason weathering has been considered to be concomitant with the soil development. The Gulliver factor results from the choice of the side by which the egg is eaten! Indeed, pedologists study the soil downward: the A horizons are at the very surface of solid Earth while geologists begin their investigation upward from the unaltered rocks. Even if this looks like a student joke, it is certainly one of the major reasons why the two scientific communities have had so little collaboration in the past.

We can try to reduce this secular gap if soils and rocks are considered from a physical and chemical point of view. Starting from the simplest observations, it becomes easy to distinguish two environments which have contrasting properties:

- the *soil* is limited at the top by the interface with atmosphere. This interface plays a specific role because of the presence of living organisms (plants, bacteria, animals). It is the organic matter reservoir at the Earth's surface. A soil is organized in horizons whose limits are more or less parallel to the atmosphere interface. Soils involve plant and plant debris interaction with silicate and oxide materials.
- *rocks* are weathered along fluid pathways (fractures, joints, faults, ...). Weathered rocks are not necessarily covered by a soil. They do not contain large quantities of organic matter or living organisms. The alteration process occurs between rain-water and rock.

The long history of continent alteration on Earth since the Archean era shows that weathering has affected rocks for a long time before life appeared. Weathering (interaction between slightly acid rainwater and silicate minerals) can transform rocks independently of soil formation. Conversely, after each volcanic eruption, plants and micro-organisms are able to colonize fresh ash or lapilli deposits. This is the first step of the development of a soil on a rock which has not been previously altered. Thus, soils and weathered rocks may be considered as independent open systems. Soils imply plant and animal activity while altered rocks imply interaction between atmospherically equilibrated water and silicate materials.

### 3.1

## Physical Description of Soils and Weathering Profiles

Soil develops downward from the rock-atmosphere interface. With increasing time, the soil material is progressively differentiated into entities of similar properties which are more or less parallel to the interface topography, i.e. the horizons. On the contrary, weathering does not depend much on the geometry of the rock-atmosphere interface but rather on that of the fluid pathways which crosscut the rock. Friable zones are frequently observed beneath unaltered ones. Weathering and soil formation have been considered to be concomitant because soil develops faster on permeable rocks than on hard ones. In fact, there is an interface between the base of the soils and the rocks whatever their alteration degree. With increasing time, a soil deepens while weathering progresses downward into rocks along the fluid pathways. In both cases, any given point in the soil or the rock experiences the propagation of the interactions between fluids (with or without the chemical control of organic matter) and silicates. Consequently, any given point is submitted to changes in local chemical conditions.

#### 3.1.1

### The Development of Weathering Profiles

The definition of rock facies or zones can be considered from the bottom upwards. The analysis which follows treats the alteration process and development of alteration zones from the bottom upwards. Initially one must define the zones concerning the alteration of coherent, high temperature silicate materials which can form clay minerals: rocks.

### *Previous Definitions of Rock Facies or Zones*

During weathering the fabric of the parent rock changes progressively from the unaltered to the most clay-rich zones or facies. The definition of the term regolith was given by Taylor and Eggleton (2001, p. 157–159). These authors consider that the regolith is composed of saprock + saprolite where saprock is the altered coherent rock (structure conservative) and the saprolite: is the altered soft rock (also structure conservative). Above the saprolite, the altered soft rock which is a non-conservative zone is assigned as the pedolith. These definitions are a bit confusing at least for the weathering profiles developed under temperate climates, for two reasons:

- the pedolith could be considered as being concomitantly formed with the soil. This is not the case,
- the limits between zones where the rock structure is conserved and that where it is lost is not sharp. Most often non-conservative zones are observed inside the saprock itself. Conversely, saprock or unaltered rock pieces are conserved in the saprolite.

Saprock and saprolite form the residual regolith (see regolith definition in Taylor and Eggleton 2001, p. 1–3). In many publications, the term alterite is used as an equivalent of residual regolith.

### *New Definitions for Altered Rock Materials*

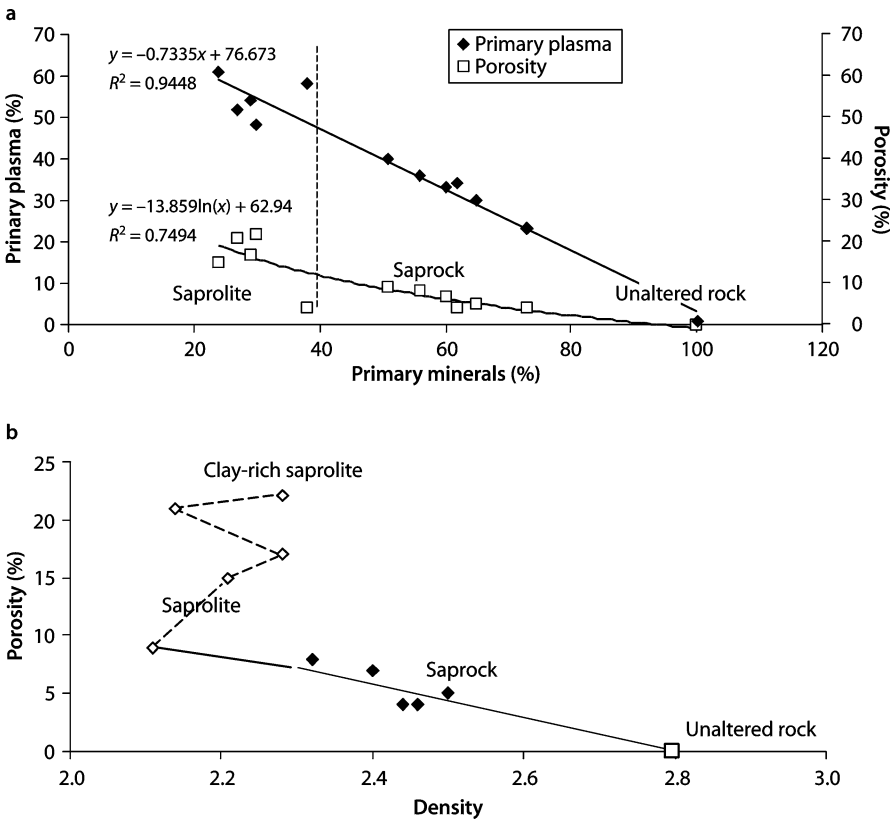
Considering these observations we propose other definitions for altered rock facies based on the physical properties that are easily observable in the field: conservation or destruction of the primary rock structure and physical resistance (coherent, friable, soft, clay enriched). Weathering profiles developed under temperate climate exhibit two altered rock types: the coherent rock which may be sampled as self-sustained pieces conserving original rock texture and the friable rock which when sampled becomes gravel. According to these observations, one can distinguish three facies using the following features:

- *the altered coherent rock*: the original structure of the rock is perfectly maintained, although some primary minerals show pockets of alteration in which their debris are mixed with newly-formed clays,
- *the saprock* (friable) in which the original rock structure is conserved: the structure of the rock is maintained although its mechanical strength is very reduced. The porosity ranges from 10 to 20%. It results from the dissolution of primary minerals and the formation of new fractures generated by local variations in the stress state.
- *the saprolite* (friable) in which the original structure is erased: it forms more or less continuous zones above and within the saprock. In tropical climates, saprolite is the most developed facies of the weathering mantle (Nahon 1991; Tardy 1993). The mechanical strength and Young's modulus are very low and correspond to those of unconsolidated rocks. However, in specific cases, the upper levels of some laterite profiles are strongly indurated by the precipitation of Fe-oxyhydroxides. Their mechanical resistance is higher than the uncemented saprolite (duricrusts or cuirasses).

### Propagation of the Weathering Mineral Reactions

The primary minerals are progressively replaced all along the weathering process by a microporous material composed of fine parent crystal debris and newly formed minerals such as clays and oxy-hydroxides. The microporous material is assigned as *the primary plasma*. As expected, the quantity of the primary plasma in an altered gabbro (volume approximated by point counting on petrographic thin sections) increases linearly with decreasing amounts of primary minerals (Fig. 3.1a). However, the relation indicates that only 75% of plasma is formed when the primary minerals have totally disappeared from the rock. That means that 25% of the parent components have been dissolved. This is coherent with the measured porosity.

The continuous functions (linear or logarithmic) depicted in Fig. 3.1a support a progressive alteration process in spite of the contrasted aspect of the different zones



**Fig. 3.1.** Variation of rock components during gabbro weathering (amounts are expressed as % surface by point counting); **a** the primary plasma formation is a linear function of the disparition of the primary minerals. At 0% primary minerals, the primary plasma represents about 75% of the solids; **b** macroscopic structure changes in the saprolite correspond to an increase of density. Data from Ildefonse (1978)

in the alteration profile. The fabric of the parent gabbro is conserved at all observation scales (from macroscopic to microscopic) in the altered coherent rock and the saprock. It is conserved at the macroscopic scale but erased from place to place at the microscopic scale in the saprolite. At least, it is totally erased at all scales in the clay-rich saprolite. Again, the clay-rich saprolite facies is not considered here as the transition to soil through a B horizon. On the contrary, it is a step in the weathering process as shown by Fig. 3.1a. The density decreases progressively from unaltered rock to saprolite, but increases to clay-rich saprolite (Fig. 3.1b). This reversal is related to the macroscopic structure changes.

It could seem strange that density and porosity increase concomitantly in the clay-rich saprolite. In fact, the density of the newly formed clay material is higher than that of the primary plasma because of compaction and closure of voids. The new material is assigned as *the secondary plasma*. The rock structure collapses under its own weight as its mechanical resistance is considerably lowered by the formation of the primary plasma (Righi and Meunier 1995). This physical process is totally independent of pedological ones.

Because alteration increases the porosity, the density decreases concomitantly with the amount of remaining primary minerals in the rock structure conservative facies. Figure 3.2 shows that the relation is roughly linear and has more or less the same slope for a gabbro (Ildefonse 1978) and a granite (Meunier 1977). In spite of the fact that pyroxene and plagioclase are more sensitive to meteoric alteration than K-feldspar and micas, the gabbro and the granite experiment the same type of mineral reaction: high-temperature silicates  $\rightarrow$  clays + oxyhydroxides. For a given density, the gabbro is more altered than the granite. In other words, during alteration, the gabbro produces more clay minerals than granite. The difference is due to the presence of quartz in granite rocks. Quartz does not contribute to the formation of clay minerals.

This description is in fact brief and will be considered in greater detail in Chap. 4.

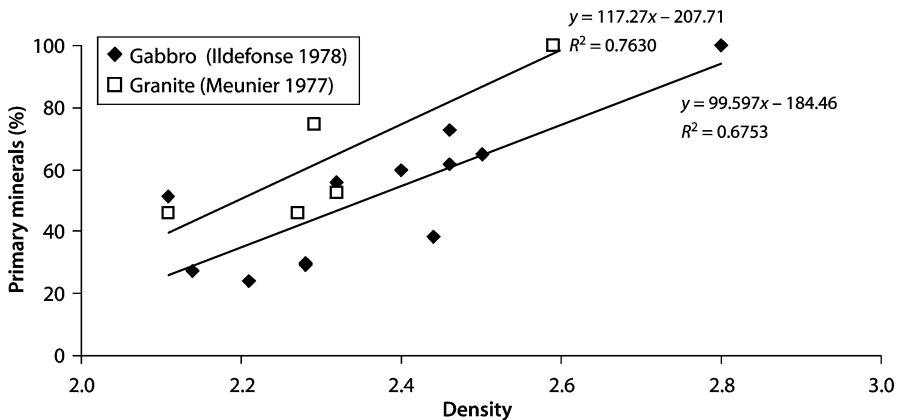


Fig. 3.2. Variation of the amount of primary minerals (% surface by point counting) with density for two magmatic rocks: gabbro (data from Ildefonse 1978) and granite (data from Meunier 1977)

### 3.1.2

#### The Development of Soils

One of the key points to study in the development of soils is to reconsider the definition of the C horizon. The C horizon is classically included in all soil profile descriptions as a transition with the substratum. Its lower limit is never indicated. This is a consequence of the current definition of the C horizon.

#### *What Is the C Horizon?*

The definition of C horizon is still debated (see the Geoderma Special Issue, May 2005). According to the Keys to Soil Taxonomy (1998), the present day definition is: “*Horizons or layers, excluding strongly cemented and harder bedrock, that are little affected by pedogenic processes and lack the properties of O, A, E, or B horizons. Most are mineral layers. The material of C layers may be either like or unlike the material from which the solum has presumably formed. The C horizon may have been modified, even if there is no evidence of pedogenesis. Included as C layers are sediment, saprolite, bedrock, and other geologic materials that are moderately cemented or less cemented. The excavation difficulty in these materials commonly is low or moderate. Some soils form in material that is already highly weathered, and if such material does not meet the requirements for A, E, or B horizons, it is designated by the letter C. Changes that are not considered pedogenic are those not related to the overlying horizons. Some layers that have accumulations of silica, carbonates, gypsum, or more soluble salts are included in C horizons, even if cemented. If a cemented layer formed through pedogenic processes, however, it is considered a B horizon*”.

The B horizon is the zone of illuviation, or translocation. It is formed by an accumulation of clays, Fe-oxyhydroxides, humic substances or carbonates derived from soil horizons above.

The above definition and the description of the C horizon are not perfectly clear and a bit contradictory. Some parts have to be carefully re-examined:

- what does “*little affected by pedogenic processes*” mean? Is the lack of requirements for O, A, E or B horizons an appropriate definition?
- why are the effects of deep roots of trees or plants which crosscut the soil and penetrate inside the substratum far away from A, E or B horizons ignored? Are they considered to be in contact with the bedrock without any altered layer?

The definition of the C horizon in the french taxonomy (Référentiel Pédologique, INRA 1995, p. 44–45) is a bit more explicit. The C horizon differs from the A, E or B because it does not have a generalized pedogenic structure. The original lithologic structure is the dominant feature. However, the C horizon may present some dispersed pedogenic features such as illuviation (carbonate, sulfate, salts or clay deposits) or lateral eluviation.

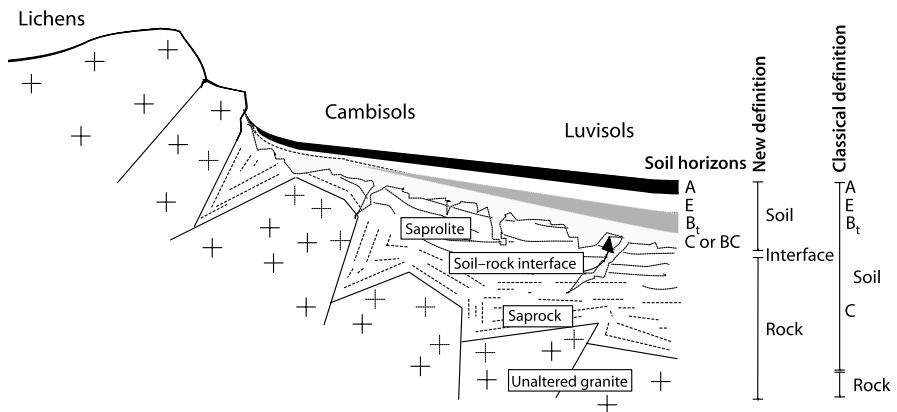
The definition of the C horizon is made difficult because of the static analysis of soils. If considered as a dynamic process, the formation of the C horizon can be better understood. Particularly, dynamics implies that the C horizon would have an interface with the substratum even if difficult to locate precisely in the profile. This inter-

face necessarily migrates downwards as the soil develops with time. Then, the C horizon may be seen as a transition between the A, E or B horizons and the substratum whatever its alteration stage. the pedogenic features progressively disappear toward the interface. This is the meaning of “*little affected by pedogenic process*”. What are the characteristics of the interface?

### The Soil-Altered Rock Interface

The soil may exhibit a sharp interface when developed on hard rocks but this is not a rule. The transition between the C horizon and the saprock or the saprolite may be progressive suggesting that soil formation and weathering are a single phenomenon. This is supported by Taylor and Eggleton (2001) who claimed that “*The changes that transform the saprolite are largely the same as those that form soil. In some profiles this region where the parent fabric begins to be lost can be viewed as the base of the B horizon*”.

The depth at which the soil-rock interface is found in a given landscape varies from place to place. It may be located at only a few millimeters depth on hard rocks (boulders) or at several tens of centimeters in friable materials. The soil-rock interface depends on different parameters such as the permeability of the rock, the position in the topography where the alteration occurs and the time during which the alteration conditions remain stable enough for the soil to develop. Consider for instance a cambisol to luvisol soil sequence in which the eluvial and accumulation horizons are progressively differentiated (Fig. 3.3). The pedological horizon limits remain approximately parallel to the surface. Most often, soil descriptions do not give a lower limit of the C horizon. This habit intuitively comes from the idea that the soil is the most altered stage of a weathering profile. This is not correct and must be reconsidered because a soil develops from the atmosphere interface. Consequently, the C horizon would have a lower limit (sharp or progressive) which is assigned as the soil-rock interface.



**Fig. 3.3.** Schematic representation of the position of the soil-rock interface in a granitic landscape. A: organic horizon, E: eluvial horizon present in acid soils, B<sub>t</sub>: texturally observable accumulation horizon; C or B-C: transition horizon where the hydraulic conductivity is the lowest through the profile



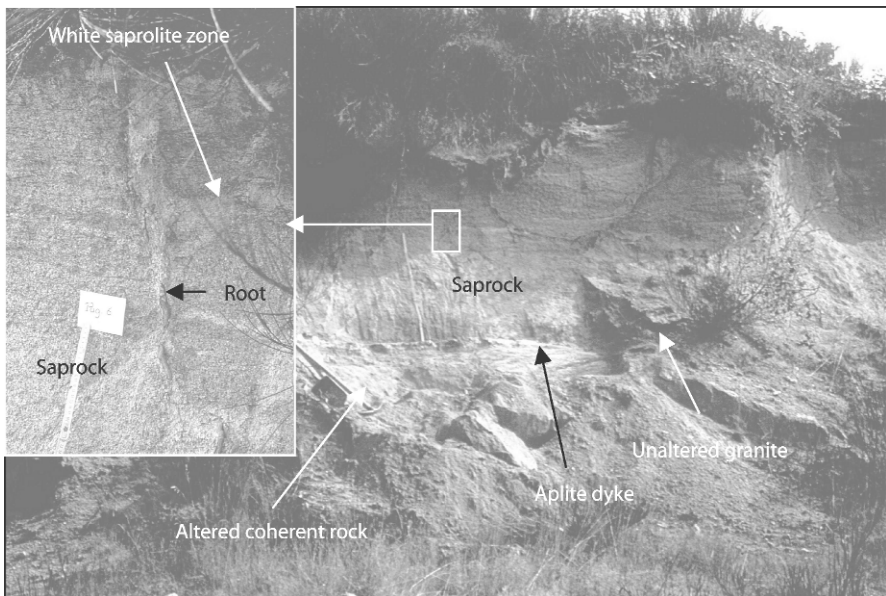
Buol and Weed (1991) proposed the interface as a BC transition horizon in which the hydraulic conductivity is the lowest in the profile. Using thin section observations, they related the low conductivity to the absence of continuous pores and to the formation of thick cutans of clay translocated from the overlying soil. The soil-saprolite boundary may be identified through hydrology parameters such as the water saturation and the matric potential, i.e. tension forces (White et al. 2002).

Even if the location of the soil-rock interface is difficult to observe at a given place at the scale of the landscape, the C or BC horizon is seen to crosscut either saprolite, saprock or hard rock. Consequently, the soil-rock interface can be roughly located as shown in Fig. 3.3. Whatever the difficulties encountered to locate the soil-rock interface, we must keep in mind that the C or BC horizon is not the most altered stage of a weathered rock profile.

The C horizon systematically exists even in young soils in which the B horizon is absent or very thin. It may be reduced to a few millimeters forming a weathered skin on the hard surfaces of the substratum. On the contrary, in old thick soils formed under forest, the tree deep roots invade the substratum and locally induce an alteration. This altered zone does not have any of the characteristics of the A, E or B horizons. It should be considered as a C horizon exhibiting a sharp interface with the substratum (Fig. 3.4).

#### *The Evolution of the Physicochemical Conditions During the Formation of Soil Horizons*

Soils are shown (see Sects. 2.3.2 and 3.2.2) to need hundreds to thousands of years to be formed. This means that the sequence of soils shown in Fig. 3.4 results from a time-



**Fig. 3.4.** Bleached zones around deep roots forming a C horizon inside saprock-saprolite formed on a granitic rock

dependent evolution. As an example of soil evolution, we shall consider the acid soil sequence. With time, the A, E and B horizons are formed. They are clearly identifiable in the most evolved stage (ulvisol). One can reconstruct the evolution during time as shown in Fig. 3.5a:

- $t_0$ : the saprolite is covered by lichens which trigger the first soil dissolution processes. The A and C horizons are millimeter thick,
- $t_1$ : vegetation grows on undifferentiated soil (cambisols). Chemical interactions between organic matter and silicates produce clay minerals while dissolution increases,
- $t_2$ : clay minerals are translocated from the A horizon. During the development of acid soils, they are dissolved. Then, an eluvial (E) and an accumulation ( $B_t$ ) horizons appear. At this stage (young luvisol), the dissolution of silicate is intense,
- $t_3$ : clay translocation and silicate dissolution are active. The soil has attained its maximum development before degradation begins (old luvisol).

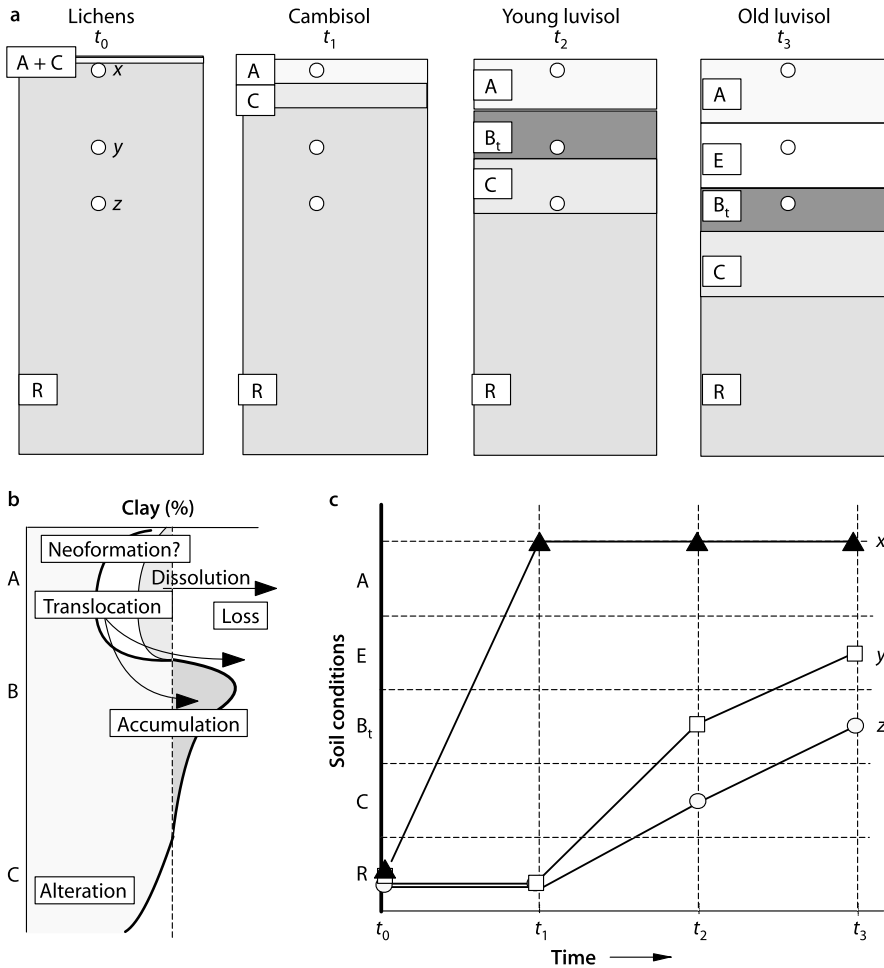
Because of translocation and dissolution, the amount of clay varies with depth. It is the lowest in the E horizon where eluviation is intense and the highest in the  $B_t$  horizon where particles sediment from the suspensions. Figure 3.5b shows how dissolution, translocation and accumulation affect the distribution of clay minerals in the soil profile during its development. Several consequences can be deduced:

- There is more clay in the A than the E horizon. The recycling of silica, potassium and other components through the vegetation sufficiently modifies the chemical conditions to stabilize the clay minerals in the upper part of the A horizon (see Sect. 8.5).
- As translocation progresses downward, it necessarily superposes on clay accumulation zones previously formed.

Considering the  $x$ ,  $y$  and  $z$  points located at different depths in the profile, they will experience contrasted chemical conditions during the progressive deepening of the soil (Fig. 3.5c). At  $t_0$ , the chemical conditions for all points are that of the rock or the C horizon. Then, point  $x$  will experience the chemical conditions imposed by the chemistry in the organic A horizon during all the soil evolution. Point  $y$  will experience first the  $B_t$  conditions and then the those in the E horizon where clays are actively dissolved. Point  $z$  remains in the C conditions from  $t_0$  to  $t_2$ , then those of  $B_t$  at  $t_3$ .

The three active horizons in soil zones are A, where clays are abundant but also eluviated downward (i.e. physically transported in flowing solutions) E, when present, where clays are actively dissolved by acid conditions engendered by organic acids and B where the eluviated clays are accumulated.

One should remember that soils can be formed on other substrates than hard, high temperature rocks. Soils can develop on poorly indurated sediments, gravel or sand terraces, on salt marsh clay-rich sediments, and so forth. The processes and alteration zones are the same as those found for the alteration of hard, indurated rocks. However, their expression (seen in the field) is more difficult to observe and determine. For the most part, the A horizon is clearly present, identified by a darker color due to humic matter. The E horizon, when present, is indicated by a very light, sand-rich layer. However the C-alterite boundary is more difficult to identify.



**Fig. 3.5.** A schematic representation of the development of a soil with increasing time from  $t_0$  to  $t_3$ . The effects are considered at different depths ( $x$ ,  $y$  and  $z$ ); **a** the progressive differentiation of A, E and B horizons in a luvisol; **b** dissolution and translocation during the soil development; **c** modification of the physicochemical conditions for points  $x$ ,  $y$  and  $z$  during the soil development

**3.1.3**

**Conclusion in a YES or NO Question Series**

**Are rock weathering and formation of soil independent?** YES they are independent. In the Earth’s early history alteration was active before life appeared.

**Do weathered rocks and soils form closed independent systems?** NO, they form open systems which exchange minerals and chemical components.

**Do alteration and pedogenesis contribute to reduce the rock heterogeneity?** YES both transform the structure and the composition of rocks to approach the ideal equilibrium with surface conditions. As soil develops on altered rock by biological activity this process is intensified. The homogenization increases toward the atmosphere interface.

**Are there limits to rock alteration and soil formation?** YES even if altered profile may be several order of magnitude thicker than soils, both are limited in their development because of internal and external reasons:

- internal reasons: weakening of the driving force with increasing distance to the interface; chemical potential gradient and biological activity for altered rocks and soils respectively.
- external reasons: no systems at the Earth's surface may offer stable conditions for a long period of time because of climate change and/or, rejuvenation by erosion.

**What are the rates of soil and alterite formation?** The rate of soil formation is independent of that of weathering. Both are controlled by global (climatic) and local conditions (topography or position relative to the water table). Soils are formed during hundreds to thousand year periods; weathered mantles are formed during hundred thousands to million year periods.

Because classical definitions are sometimes ambiguous, we shall use here new ones (Table 3.1). When little information is present which would allow a determination of C-saprolite categories, we will use the term alterite to signify a material dominated by clays and oxides formed under conditions of water/rock interaction.

### 3.2

## **Dynamics of the Alteration Process under Temperate Conditions: An Investigation Comparing Soil and Rock Alteration in Profiles**

### 3.2.1

#### **Alteration in Temperate Climates**

In the preceding section we have considered the physical description of alteration profiles, that proposed classically by pedologists and a new structural concept. The lower portions of alteration are dominated by rock water interaction where the pathways of water circulation determine the zones where alteration takes place. The result is an irregular spatial distribution of alteration zones where new clays minerals are found. The collapse of the old rock structure brings about a more homogeneous physical distribution of new clay minerals and the initiation of a horizon structure. A horizon, in the pedological concept, is the expression of general homogeneity on a horizontal scale.

In fact, the occurrence of clays in the classical description of soil profiles is dominated by the top most level, that of plant/silicate interaction. Here clays play a great role in the physical and chemical properties of the altered matter. The A (organic) and

**Table 3.1.** Summary of the definitions used in the literature and in the present book. The differences come from distinct interpretations of the development of soils and weathering mantles: two parts of a single continuous system (classical) or two independent open systems (concept developed here)

		Classical definitions		Definitions used here
Weathering profile (water/rock interaction)	Zones or facies	<i>Residual regolith</i>		<i>Alterite</i>
	Unaltered rock	Bedrock (consolidated rocks)		Unaltered rock (hard and soft substratum: granite, limestone, mudstone, mud, sand, ...)
	Conserved rock fabric	Coherent	Saprock	Coherent altered rock
		Friable	Saprolite	Saprock
	Non-conserved rock fabric	Pedolith		Saprolite
Soil profile (pedological alteration)	Horizons	<i>Horizon characteristics</i>		<i>Horizon characteristics</i>
	C	Limited upwards by the interface with the B horizon (no clear limitation downwards)		Limited by two interfaces – upwards with the B horizon – downwards with the saprolite
	B	Accumulation		Accumulation
	E	Lixiviation – dissolution		Lixiviation – dissolution
	A	Organic		Organic

B (clay rich) horizons begin the profile. Under conditions of high acidity, a clay-poor horizon (E) develops between the A and B horizons by clay dissolution processes. Below these zones one finds, usually, a C zone of clay-rich altered rock with varying amounts of rock particles, unaltered or partially altered high temperature minerals and clays formed through rock/water interaction. We would like to investigate the clay mineralogy of alteration by comparing the A-B horizon clay minerals and the C horizon clay minerals as reported in the literature. The reason for doing this lies in the question, do plants have a significant impact on clay minerals? We have established that high temperature minerals form clay minerals through the exchange of hydrogen ions with alkali and alkaline earth ions in high temperature minerals. Further alteration is effected by oxidation processes of iron in silicate minerals which destabilize them electro-chemically allowing the formation of new, more stable minerals. Once formed, the low temperature minerals such as clay phases would be the stable minerals as expected. However, in most mineralogical studies of alteration profiles one finds a continuing change in minerals, clays included, up to and within the A horizon. Why do these changes occur?

The initial assumption of clay change in alteration profiles is that the clays interact with rainwater, as do the underlying rocks, to form less alkali-rich and less siliceous minerals. However, under conditions of temperate climates the clays persist and one finds the alkali silicic clay mineral illite which is often the dominant clay mineral. We will consider the clay facies under conditions of temperate climate alteration.

The adjective “temperate” is important here in that our analysis considers initially only places where rainfall is in reasonable abundance and a very large portion of the year is “frost free”. This excludes deserts and tropical rain forests. Plants are an important part of the surface horizon in the alteration profile. Here the action of aqueous fluids on rocks is important but in the weathering profile the upper portions are occupied by a three-phase system, silicates (solids), water and air. Such a system insures a high and regular growth of plants and an equilibrium between plants, rock alteration and soil development. If the climate is too cold, not enough water/rock interaction will occur and the impact of plants is relatively small. If the climate is too dry only sporadic patches of plant life are installed. The altered surface is dominated by water/rock interactions and physical disaggregation of rock materials. In tropical climates, the very high rainfall tends to dominate with the result that the clay formation and transformations are dominated by unsaturated solutions bringing about the end of alteration, oxide and hydroxyoxides (gibbsite, ferri-hydrates, kaolinite) with the elimination of the 2:1 minerals. Only a very thin layer of material at the surface is occupied by plant/silicate interaction. Temperate climates, not too hot, not too cold, not too much rainfall, lead to optimum conditions of plant growth and plant/soil development. It is not an accident that the temperate climate zones of continents have supported the major development of the human species, where the ability of the Earth to give sustenance (agricultural productivity per surface area) is greater than in other areas. Ideal conditions are not all that common. Not all of the soils of the world can be used to produce grains, those plants capable of sustaining both human and animal populations which lead to the inevitable development of large, concentrated populations.

The richness of the Earth for agricultural mankind resides in the presence of 2:1 clay minerals; illites, smectites, mixed layer minerals and to a lesser extent HI minerals. Such situations require that the plants can grow and prosper and that the soils can furnish the needed sustenance and structure for the effective growth of these plants. However, even though high altitude, mountain prairie soils in Colorado (USA) produce interlayer illite-smectite minerals, this is not enough to give a high agricultural productivity to the soil because of the climatic limits. The lower, plain areas next to these massifs are better adapted to produce crops and they also have a mixed layer mineral mineralogy (see Birkeland et al. 2003 for an overview of the clay mineralogy of these climatic zones).

In order to understand the relations between plant/silicate interactions which form the upper part of alteration profiles and the rock/water interactions of rock alteration we shall consider the differences in the clay minerals which represent the surface mineralogy in the two zone A-B and C divisions and we shall consider the rate of change of minerals in the two zones in order to establish whether or not there is continuity between the two portions of soil profiles.

### 3.2.2

#### Kinetics of Alteration Processes

##### *The Effect of Climate*

As we have seen in the preceding section, water/rock interaction is the alteration mechanism which forms clay minerals first. The mineral type formed is determined

by the host or unstable silicate mineral in the rock substrate. These minerals are subsequently mixed intimately through the action of compaction as the rock structure is lost when the materials move upward towards the surface as a result of the action of surface erosion. The surface, or interface between the plant biosphere (root zone and surface vegetal detrital layer) leads to, as we hope to demonstrate, a new chemical structure or system where clay minerals react not only to the impact of slightly acid water, as is the case for the rock/water interaction zone, but more importantly with the complex of root exudates and bacteriological modification of this material which forms the humus and dissolved organic material of surface soil media.

One must keep in mind that climate (the external forces acting upon alteration systems), is the prime agent of alteration and it is basically governed by two variables: temperature and rainfall. One can simplify this to the variables of temperature and the concentration of chemical elements in the altering solutions. The more the solution has a high concentration of dissolved elements, the slower the process of mineral destabilization. The solution is tending towards saturation with dissolved material. Hence at high rainfall levels, one will have more alteration and above all mineral dissolution because of dilute solutions. The pertinent relation of reaction is  $k = 1 / (A)$  where  $A$  is the concentration of dissolved matter in solution (Ritchie 1966). The amount of reaction ( $k$ ) is linear with time and concentration. However the relation with respect to temperature is  $k = A \exp^{-E/RT}$ . Here the reaction relation with temperature is exponential as temperature increases. Roughly one can visualize these two relations as in Fig. 3.6. Such relations have been demonstrated by observations relating clay content of top soils (humic horizon) and rainfall (Jenny 1994, p. 155).

The effect of climate is then complex, a linear function of rainfall and an exponential one with temperature. In general, there is much more water-rock alteration in hot, wet climates than in cold ones, wet or not. Of course if there is little water available, hot or cold, the chemical alteration is very small. As a result in latitudes approaching the poles or on mountains, alteration is weak. As one comes down off the polar caps or from the mountain tops two possibilities are evident, either higher alteration rate with high rainfall or little under desert conditions.

The formation of the alteration and soil structure takes some time to become established in nature. Some chrono studies indicate just how much.

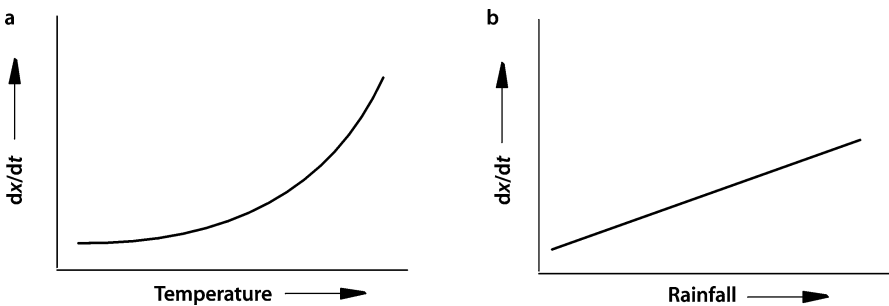


Fig. 3.6. Indication of probable relations between rainfall (a) and temperature (b) as they affect reaction rate ( $dx/dt$ ) for the formation and alteration of silicate minerals at the surface

### *Initial Water/Rock Interaction*

Establishing the rate of weathering is not an easy problem to solve. The most important point to resolve is the starting point, determined by unweathered material, and establishing the point in time at which weathering begins. Several approaches have been made.

First of all a very important experiment was carried out using crushed granite which was subjected to rainwater interaction for 30 years (reported in Millot 1964, p. 117–119). Investigation of the material after this period shows a reduction in grain size, with 2% entering the clay size category ( $<2 \mu\text{m}$ ). However careful investigation shows that no clay minerals crystallized. Similar results were obtained in laboratory simulations. Physical breakdown of rock particles occurs (2% in the clay sized fraction produced in 30 years) but no new minerals were formed. This indicates that the water which flows freely through a rock system (macropore gravitational flow) did not become saturated with chemical elements that will form clay minerals but the near totality of the water/rock reaction is dissolution. Thus the first step necessary in soil clay mineral formation is obtaining water that approaches saturated with dissolved elements. This does not occur in macropore or free flowing water but in the capillary water. The first step in alteration is the dissolution of unstable minerals.

#### 3.2.3

### **Kinetics of Soil Formation**

#### *Water-Rock Interaction*

Colman (1986) uses measurements of weathering rinds (zones of partial mineral transformation) on boulders buried in glacial deposits to establish weathering rates. This is the initial rock/water interaction outside of the presence of plants and soils. Observations were made on boulders deposited by glacial action in moraine deposits. As can be expected, weathering rates decrease as the process proceeds. However the data gathered indicate very low rates of alteration, on the order of millimeters per  $10^5$  years. Whitehouse et al. (1986) indicate that weathering rinds on sandstone boulders in New Zealand where rainfall is abundant is on the order of millimeters per  $10^4$  years. Birkeland (1984, p. 94) indicates a rate of several millimeters per  $10^3$  years for alteration of a granite boulder in Colorado. Boulad et al. (1977) estimate that the advance of the alteration front into underlying granite in a soil in tropical Cameroon as being 70 mm per  $10^3$  years. The estimation is based upon disequilibrium dynamics of uranium in the altered and unaltered materials (Thomas 1994). These measurements indicate the penetration of the early stages of alteration into a heretofore unaltered rock which is unstable at Earth surface conditions. The values vary then from several millimeters per 1 000 years to millimeters per 100 000 years. The most rapid rates occur in hot, wet climates and the lowest in cold climates.

#### *Soil Development (Water/Rock and Plant/Silicate Interaction)*

Direct observations of soil formation are reported by Evans and Cameron (1979) who indicate that the rate of weathering resulting in the thickness of solum formation (the



sum of weathered material both new minerals and small grain sized particles due to physical weathering) occurs at a value of near 10 mm per  $10^3$  years on moraine material of Baffin Island. Observations are made on initially denuded rock surfaces which were left open to atmospheric effects with glacial retreat. The soil material develops, of course, in the presence of plants, mostly grasses (Fig. 3.7). Thus soils develop more rapidly than does an alteration front in a rock, given similar climatic conditions.

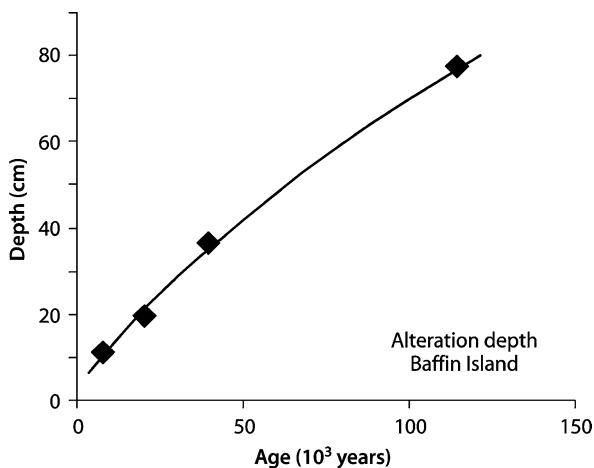
Another method of establishing weathering rate is to calculate chemical loss in a zone undergoing alteration within a mature profile context. Such measurements indicate rate of loss by both erosion but mostly by dissolution of high temperature minerals. Calculations of transport using dissolved matter in streams released from profiles 3 meters thick in Rhodesia (Owens and Watson 1979) suggest weathering rates of granite to be about 8 millimeters per  $10^3$  years. Dethier (1986) calculates that the loss from the saprolite and bedrock of volcanic rocks in the Pacific Northwest USA is on the order of 30 mm per  $10^3$  years.

The conversion of rock to clay, i.e. total reaction, can be measured as percent clay in the A horizon material. Righi et al. (1999) found a value of near 12% after 7 000 year weathering under alpine weathering conditions. From the shape of the curve of clay formation as a function of time, it appears that the rate slows greatly after 3 000 years (Fig. 3.8).

Thus total conversion to clays will be almost impossible under geologic conditions of erosion in such an area. However alteration of tephra in different parts of New Zealand, described by Lowe (1986), indicates a continuing change to clay of up to 85% conversion after nearly 750 000 years (Fig. 3.9).

Under these conditions the rock to clay conversion takes nearly a million years, a geologic number. Jahn quoted by Star (1994, p. 118) indicates that weathering of volcano-clastic materials under a semi arid climate may take 4 Ma to reach 80% conversion to clays. Hence total conversion of a rock to clay takes a significant period of time, somewhere between 1 and 4 Ma. Accomplishment of such a conversion necessitates that the soil be little eroded and the profile stable for long periods of time to be entirely transformed by weathering process.

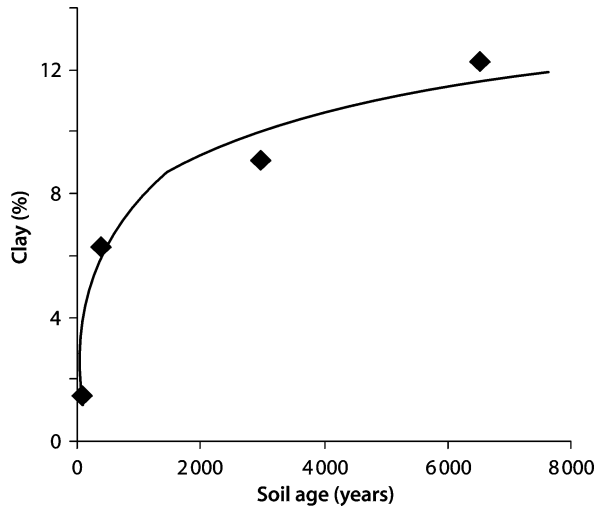
Fig. 3.7. Depth of solum formation observed on Baffin Island as a function of soil formation time (data from Evans and Cameron 1979)



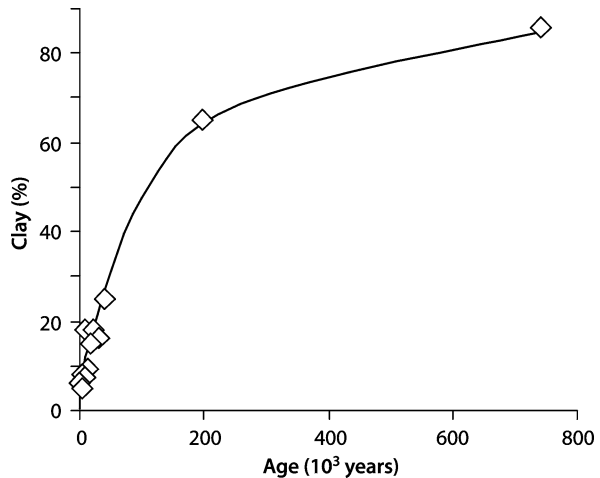
The above estimations of weathering rate are direct observations of processes under various climates (arctic to tropical) where the process is observed very locally (weathering rinds) or as an overall process in developing solum material. Jenny (1980, p. 242) has proposed a similar schematic description of weathering rates for the different parts of soil profiles under a variety of climates.

Considering these various studies which use different methods of observation to determine weathering processes under different climates, we can assume that the initial rate of development of clays in the first stages of weathering (water/rock interaction) is variable and rather slow when disconnected from plant activity, millimeters of alteration in hundreds of thousands of years. Climate and rock type can vary the absolute values greatly. Given these estimations, it would take between 6 000 to

**Fig. 3.8.** Proportion of clay in alpine soils as a function of time (data from Righi et al. 1999)



**Fig. 3.9.** Proportion of clay in the upper portion in tephra soils as a function of time (data from Lowe 1986)



4 000 000 years to form 40 cm of altered material, clay and disaggregated rock, by water rock interaction depending upon the climate and other factors such as the intensity of erosion by physical transport, and plant activity. Layers of solum as thin as 40 cm are those of rather young profiles which are usually not well differentiated into A, B and C structures. One would expect to encounter the faster rates estimated in tropical climates and those slower in temperate to mountain climate alteration processes.

The formation of clay minerals, rock + water to clay, takes on the order of 1 Ma under conditions of moderate climates.

### *Establishing Clay Mineral Facies in Soils (Plant/Silicate Interaction)*

There are some estimations of the time necessary to establish an equilibrium clay mineralogy in the upper portions (B, A horizons) of a soil. This information is extremely important as a basis in understanding the kinetics of soil mineral formation after rock alteration. Bain et al. (1993) give data comparing loss of Ca (which can be interpreted as the weathering of primary minerals) from the A horizons in Scottish soils and cation exchange capacity (formation of clays). The curves of measured values against age of the soil indicate stabilization after 40 000 years. Amounts of clays are small, on the order of several percent. Righi et al. (1999) indicate that the formation of the stable smectite S/I mineral in the upper horizons of a prairie podzol as well as gibbsite in the high altitude Swiss Alps is complete after about 3 000 years of weathering of glacial moraine material. Observations used to determine this time frame range from 80 year old moraine materials subjected to weathering to those of 6 500 year age.

Egli et al. (2004) demonstrate the formation of smectite S/I minerals in the upper zones of glacial moraine material in similar situations to those of Righi et al. (1999). Here the relative proportion of the different new minerals was compared in the upper portion of soils over an 11 500 year time span for two sites. The change in abundance of the new minerals begins to become very small after about 2 000–3 000 years of development, a conclusion very similar to that showed by Righi et al. (1999). The shape of the curve clearly indicates an exponential function, compatible with kinetic formulations. These two studies indicate that it takes near 3 000 years to establish clay mineral assemblages in a soil profile under alpine prairie conditions where the substrate is granitic moraine material. Mahaney and Halvorson (1986) indicate similar time scales for soils developed on a variety of rock substrata in the Wind River Mountains (WY).

Thus it appears that the stabilization of soil clay mineralogy occurs at a rather more accelerated rate than that of water/rock interaction, thousands of years compared to a million. However, one should note that all of the studies available are made under conditions of new soil formation at low temperatures, mountain climates. The temperature factor will be quite important. Soils forming at lower altitudes, and in warmer climates will develop faster.

### *Formation of Humic Layers*

The humic layer is a direct expression of plant activity in the alteration profile.

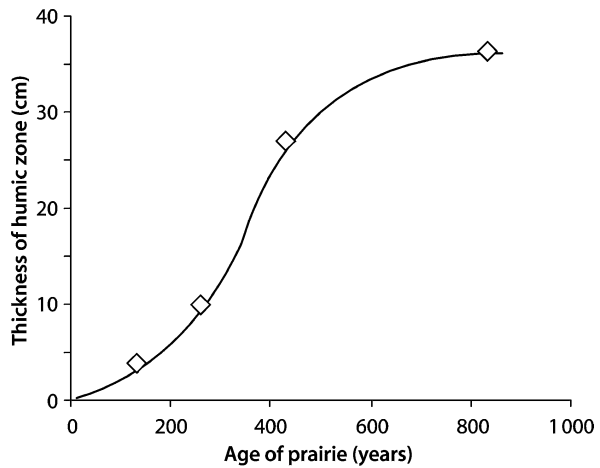
Observations of color change in poldered sediments kept in prairie over different periods up to 850 years (Velde et al. 2003) indicate that after the maximum period observed, the humic zone continues to develop only slowly under prairie in sediments

(Fig. 3.10). It is probable that the development of the humic horizon will stabilize at near 1 000 years. This is towards the upper limit indicated by Birkeland (1984, p. 225). Data from Egli et al. (2002) indicate that both N and C content in alpine prairie soils reaches a more or less stable content after 4 000 years development (Fig. 3.11). It is clear that the effect of temperature is important in establishing the stable humic layer chemistry, varying the time necessary to reach equilibrium by a factor of four.

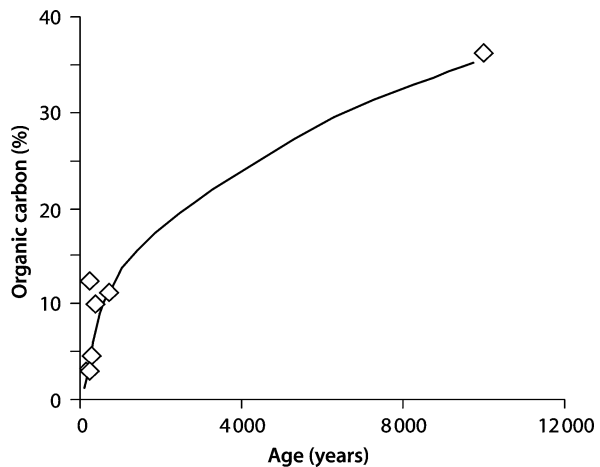
### *Comparison of Reaction Rates in the Different Parts of an Alteration Profile*

In the above summary of several studies, it appears that the formation of the different parts of an alteration-soil profile occur at different rates. The initial stages of rock weathering (altered rock zone) have rates of formation of millimeters per  $10^3$  years and hence  $10^{4-5}$  years are needed to form a minimal solum under intense weathering

**Fig. 3.10.** Observed thickness of humic layer in soils developed on clay-rich sediment (data from Velde et al. 2003)



**Fig. 3.11.** Portion of organic carbon in surface soils in Alpine environment as a function of time (data from Egli et al. 2002)



conditions. Formation of stable clay mineral suites in the C-B horizons take near  $3 \times 10^3$  years to reach a steady state. The formation of the humic layer takes less than  $10^3$  years. These numbers are only indicative in that the examples are taken from very different climatic sites, mostly in mountain areas. The time scale of mineral formation and mineral interactions in weathering necessary is given in Table 3.2.

The above hierarchy of reaction rate is important in further considerations of soil profile development and mineral equilibrium. Initially, it is clear that the water-rock interaction is the slowest process and thus will determine the extent of solum development, i.e. the amount of material converted to minerals (essentially clays) stable at the Earth's surface. Next the clay species and assemblages appear to develop in the soil (A-B) zone at a faster rate. Most rapid is the development of the humic, plant-soil interface. It seems clear that the development of an alteration profile is not one single, inter-connected sequence. The several zones react at very different rates. The slowest is at the bottom and the most rapid is related to plant/silicate interactions.

### 3.3 The Inter-Relation of the Dynamics of the Alteration-Soil Profile Sequence

#### 3.3.1

##### Overview of Soil and Weathering Mineralogy

In Chap. 2 one finds that rocks alter to clays under specific conditions of interaction between aqueous solutions and unstable minerals. The sequence of rock to altered rock to saprock to saprolite is one of progressive change in the density of the material, signifying the dissolution and transport of material in solution out of the immediate alteration zones. New silicate minerals occur as a result of the interaction of slightly acidic aqueous solutions with the minerals present which were formed at higher temperatures than those of the surface. This process leads to the loss of divalent and monovalent ions, such as K, Na, Ca, Mg. The end result is the concentration of the major elements Al, Si and Fe. The balance of mono and divalent ions determines the fertility of the alteration products. Most common agricultural crops need some mono and divalent ion sustenance. This is of course especially true in temperate climates where plants derived from grasses are the major source of agricultural benefit. It is clear that trees can thrive more easily on substrates containing less 2:1 phyllosilicate material. They are planted, in temperate climates, on soils containing less 2:1 silicate material, and especially that of the smectite-illite type.

In the initial stages of alteration, excepting desert environments, plants install themselves on rocks. Here we have the interaction of plants (and the organic matter associated with them such as leaf litter, roots, and root exudates) in direct contact with the unstable silicate material. In almost all situations the first step in alteration is the formation of the soil (plant/silicate) interaction zone. The chemical action of plant material dominates in the soil or fine material of the A horizon. However, the initial stages of alteration in rocks are dominated by microsite reactions within the coherent rock itself, where the presence of unstable minerals dominates the mineral reactions. The production of 2:1 minerals dominates in such reactions. However, one finds the illite, smectite, vermiculite 2:1 minerals most often accompanied by the 1:1 mineral kaolinite.

**Table 3.2.** Time scale of mineral formation and mineral interactions in soils

Horizon	Action	Time (years)
C	Water/rock interaction	1 000 000
B	Clay mineral facies in A-B horizons	3 000
A	Stable formation of the humic horizon	1 000

Depending upon the initial rock composition one can find other phases, talc, chlorite, zeolite among others, which can at times be important in quantity but which rapidly become unstable as the altered material becomes saprock and saprolite. Rocks containing metamorphic and diagenetic phyllosilicates such as chlorite, biotite and muscovite change to a lesser degree because the minerals present are less in disequilibrium with the surface chemical forces than higher temperature phases such as feldspars or pyroxenes. They are already phyllosilicates. The relative instability of minerals at the Earth surface reads in the same sense as Bowen's reaction series for minerals at high temperature. Sedimentary rocks show less of a tendency to change in that the material is even closer in mineral nature and thermodynamic stability to soil clays, i.e. fine-grained illite, mixed layer minerals and chlorite, kaolinite assemblages. The difference between the free energy of these minerals and that of the new or eventual clay minerals under surface conditions is less than that of say an olivine grain or a plagioclase and a clay mineral. Nevertheless chlorite, muscovite, diagenetic illite, and diagenetic illite/smectite minerals are not stable in the alteration environment. This is witnessed by the fact that soil clays change mineralogy with burial near 50–80 °C to become a full smectite mineral (Meunier and Velde 2004, p. 82). Surface clay minerals have a specific stability field of temperature and are modified by prolonged heating above about 50 °C.

The microsystems in the old rock structure are gradually effaced through the collapse of the old mineral structure pseudomorphing the initial rock mineralogy. The saprolite structure becomes more prevalent in the middle zones of an alteration profile. In the saprolite zone the clay minerals of surface origin become more intimately mixed and lose the chemical specificity of their microsite configuration. This structure is destined to progress downward with time into the rock substrate. In situations of low erosion rate such alteration can be traced to depths of tens of meters or more (see Millot 1964). Thus under conditions of normal or rather high rainfall, the alteration of rocks proceeds downwards with time. Saprolite and saprock are extended downwards.

If there is uplift, erosion becomes important and the surface layer of an alteration profile is taken away at various rates depending upon slope or the difference between the flowing river structure and the surface of the profile. Here the surface approaches the rock, or the rock "moves upward" depending upon the relativistic point of view one has. Under high rates of erosion, rock bodies appear at the surface. On average, where granular, macrocrystalline rocks are concerned, the rock alteration interface is quite irregular. In the case of sedimentary rock of low grade metamorphism, the interface is less irregular. This interface determines the richness of the soil. If it is too near the surface the farmer says that it is rocky, it is too far below the soil of the Earth he farms it is too "heavy" i.e. rich in clay.

### 3.3.2

#### The Mineralogy of Soil Horizons

##### *The C Horizon Mineralogy*

This is the top of the water/rock interaction zone. In pedology the altered rock (saprock) and more fine-grained layers (saprolite) have often been combined into one horizon for consideration in a nomenclatural scheme: C horizon (see Sect. 3.1.2). However the differences are great between the two concerning structure and water flow. The characteristics of the C horizon are based upon grain size distribution (stages of rock alteration since alteration materials are normally more fine grained than the source rocks) and dispersed pedologic features (presence of scarce clays or organics deposits from upper horizons; alteration around deep roots). One must remember that soils can develop on all sorts of geologic material; sand dune, sediments, sedimentary rocks and eruptive rocks for example, and hence the starting materials can be in the form of a rock, a transported sediment or soil. Hence the transformation from source material to soil is diverse and varied. However, considering a solid, metamorphic, sedimentary or crystalline rock, one can describe a succession of stages in alteration progression.

In macrocrystalline rocks, the effects of microsystem alteration are primordial. They are less evident in rocks with smaller initial crystallites but nevertheless the microsystem reactional scheme is operative. The most striking effect in the C horizon is the loss of density. Much material is dissolved and transported out of the initial system. This can be seen in the conductivity or permeability curves in soil profiles on alteration profiles (see Chap. 4).

The C horizon is dominated by minerals stable under conditions of interaction of surface (free flowing) aqueous solution and unstable high temperature minerals.

##### *The B Horizon Mineralogy*

In ideal, "average" conditions, one has a reasonable saprock and saprolite zone, called the C horizon by most pedologists, and a plant interaction horizon, the A horizon, at the interface with the atmosphere. In between these two zones is the B horizon where a portion of the clay material in the upper A horizon is concentrated through downward water flow until it is stopped by lowered pore space. This is the zone of accumulation where clays and some organic matter are accumulated. However if this is a zone of clay accumulation, not all clay mineral material present comes from above. The B horizon is a transit zone where the C horizon clays will move upward to reach the surface through erosion. They are mixed with clays from this upper, erodable A horizon.

As far as clay minerals are concerned, the B horizon is a zone of mixture of surface (soil) and subsurface (C horizon, saprolite) clay minerals.

##### *The E Horizon Mineralogy*

This zone, present in acid soils, is dominated by the development of a clay-free system where alumino-silicates and oxides are largely absent due to dissolution processes.

### *The A Horizon Mineralogy*

Clays here are dominantly the result of plant/clay interaction. This is governed by the chemistry engendered by plant detritus decomposition and transformation as well as root exudation material and its decomposition.

The clay minerals in the A horizon where plants are established reflect the new chemistry and chemical equilibria engendered by plant activity. This portion of the alteration profile is by far the most complex, where plants (roots and litter) are modified by bacteria, fungi, burrowing animals and other living organisms. The variety of chemical products is multiplied greatly compared to the rock/water regime. Much work has been done on the interactions of the living or organic material but relatively little has been done on the organic-clay complexes. Thus we ask more questions than can be answered reasonably in this domain. This is not due to a lack of scientific effort, the agronomic community has been active for more than a hundred and fifty years to be sure. The system is however extremely complex, variable and the objects to be observed are normally of extremely small size. Recent improvement in instruments have allowed immense progress but these have been available on a routine basis only for several decades and we are only beginning to make significant strides in understanding the processes operative in the A soil horizon.

Overall, in the A horizon bacterial and other actions change the organic matter to a large extent. The main action is oxidation of a large portion of the carbon and nitrogen. This is called mineralization. This effect is measured in a relative manner by observing the elemental ratio of nitrogen to carbon (C/N ratio). The ratio is not an absolute measure of carbon loss in that much nitrogen is lost through the production of gas also. However, one consistently sees a change in C/N ratio which indicates the humification of the soil organic matter (Stevenson 1986). Besides the C and N ratio, humification increases the amount of carbon relative to oxygen present in the organic matter as larger molecules are produced which contain fewer radicals. Humus is associated with soil fertility in agricultural terms. In the A horizon, soils tend to form stable aggregates, conducive to good plant growth. They promote capillary retention of water. Thus the soil horizon is or was the focus of research into the fertility of soils for agronomists.

An interesting point, made by Dethier (1986) considering mass balance studies of weathering is that the loss of material by dissolution from the A horizon is small compared to that from the zone of water-rock interaction. It would appear that the soil zone is one of conservation of material due to dissolution while that below is one of great loss.

The A horizon is the agricultural one. It determines the fertility of crop growth and the mechanical conditions under which the land can be utilized. Changes in agricultural practice can change the mineralogy and the soil structure, rendering it less amenable to crop growth or more amenable and more fertile. However the A horizon is the most susceptible to physical erosion, and hence the most fragile in the short term. It is this effect that lets the clays from the C horizon move upwards to the surface soil horizon.

#### 3.3.3

#### **Mineralogical and Chemical Differences between Alteration and Soil Zones**

In Sect. 3.1 we have seen the physical and structural relations between the different parts of an alteration profile. Since our main objective is to describe the clay formed



in surface environments, it is useful to establish the differences between the lower C horizon and the upper A-B horizons which are influenced by plant/silicate interaction. Given that the soil horizon interface between plants and weathering clay minerals is one where new chemical forces (organic matter) come into action as compared to those of water/rock interaction at the bottom of the weathering profile, how can one establish this contrast?

In the plant/soil interface we have the interaction of mineral and organic material which reacts to form new minerals according to chemical potentials engendered by the activity of plants at the surface; roots and decomposition of detrital organic matter. This soil horizon designated as A by classical pedology is at times sub-divided into different categories. If the weathering of rocks to form clay-rich strata is well understood, or accepted as presented in the preceding chapters, the plant/clay interface which we call soil horizon in this discussion is less accepted as a specific system producing new clays or at least less considered as a special part of an alteration profile even though it was proposed as such by Duchaufour (1979). Most pedologists consider the rock to organic-rich surface zone as a continuum of inter-related reaction horizons. However, if one considers the structure of a soil profile, one sees an upper, organic-rich zone (A), a horizon of clay concentration due to physical displacement of fine particles (B) and a gradation of zones with decreasing clay content toward the rock (C).

The upper, A, horizon is not only one of high organic matter content but also the zone where much of the biological activity in a soil is concentrated. Plant roots are in high concentration. In general more than 50% of the root mass of plants is found in the topmost 20 cm of the profile (Schenk and Jackson 2002). The exudates of these roots are strongly present. Bacteria are especially active here also, where they transform leaf and other plant litter (entering the soil from the surface). Burrowing animals continually work and re-work this portion of the alteration profile. This horizon is one where mineral encounters living matter.

In considering the whole soil, Oh and Richter (2005) present data indicating variable behavior of different elements in deeply altered profiles, 4 to 5 meters thick. Phyllosilicate rock loses relatively little potassium but most of its Na, Ca and Mg is lost. Gneiss loses about one third of K, and almost all of the Na and Ca present. Diabase rock loses two thirds of its K, three quarters of Ca and Na, but almost all of the Mg present. By contrast, the typical profile of overall potassium content in intensely weathered tropic alteration is one of continual potassium loss (Mohr and Van Baren 1959, data p. 142). The same trend is seen for an alpine fir forest alteration profiles from low altitude forests (Egli et al. 2002, 2004). Depending on rock type, climate and plant regime the loss of alkali and alkaline earth ions is more or less great.

As we have seen in the preceding chapter the alteration reaction zone (water/rock interaction) is first governed by microsite reactions effected by descending, gravity-driven aqueous solutions. These processes are the slowest to proceed in the alteration process. At the lowest levels of the alteration profile the interactions are those driven by the instability of high temperature minerals, often anhydrous ones such as feldspars, and slightly acidic aqueous solution. In the upper reaches of such reaction zones one finds faster reactions which develop inter-stability of clay mineral species which were produced by the first reactions in micro-sites of deeper sub-surface origin. New phases occur and relative proportions of old minerals change. Normal surface erosion brings these clay zones, formed at depth, up to the surface and hence into the zone of interaction with

plants at the surface. The reaction times in the upper most horizon, A, are the most rapid and hence new equilibria determine the minerals which will be present.

### 3.4 What Are the Clay Mineral Assemblages?

#### 3.4.1 Formation of Different Clay Mineral Phases in A Horizon

In order to establish the new chemistry affecting clay minerals in the soil, plant zone, one should look at published work on clays in alteration profiles in order to see whether or not the clay mineralogy does in fact change in the root, organic-rich part of the profile compared to that in the lower zones. To do this we must often “re-read” published data because it is rare that authors have considered this possibility. Thus we look at published X-ray diffraction diagrams to see whether or not changes in mineralogy occur at the interface of the high density root zone, the A horizon in most cases. Some examples of such interpretations are given below.

#### *Smectitic, S/I minerals in Soil (A) Horizons*

Fichter et al. (1998) indicate that there is a strong change in mineralogy in the clay-rich upper horizons in acid, forest soils developed on hydrothermally altered granite in the Vosges mountains, France. New expanding mixed layer clays occur rather abruptly in the upper horizons at the expense of smectite in lower zones.

Righi and Lorphelin (1987) present data for a toposequence of prairie soils developed in the Himalayas where clay minerals change rather abruptly in the upper B-A horizons compared to those present in deeper portions of the profiles. Mixed layer minerals become very important in a podzol but are lost in a brown acid soil in the A-B horizons. Gibbsite, found in the lower portion of the profile (aluminum hydroxide), is lost in the upper A horizon.

Olsson and Melkerud (1989) give XRD spectra which indicate the formation of a smectitic mineral in the E horizon of podzol soils (part of a complex A horizon) based on till in Southern Sweden. The lower portions of the profile show chlorite and vermiculite with minor amounts of illite. One can assume the formation of smectitic material from vermiculite in this upper, plant influenced horizon.

Ross et al. (1987) indicate that the mineralogy of the A horizon of soils developed from marine clay for 8 000 years near Ottawa (Canada) shows a loss of illite and a strong gain of smectitic mixed layer mineral compared to lower horizons.

Takahashi et al. (1993) give data which indicate a strong loss of illite from the clay assemblages in going from C and B to A horizons in soils on volcanic materials in California. The plant cover is conifer. Much of the silicate material has been transformed into hydroxyl-oxides and forms of kaolinite. However, it appears that illite is replaced by a HI or smectitic mineral in the A horizon.

Alpine profiles studied by Egli et al. (2004) indicate that vermiculitic material is lost at the expense of smectite in the AE or E (upper plant influenced) horizons of soils developed on rhyolite. The amount of smectite present appears to be related to climate differences.

Harris et al. (1987) indicate that the A and E horizon mineralogy of Ultic Haplaquods developed on Plio-Pleistocene sediments in Florida woodlands present a kaolinite/smectite mineralogy whereas the lower horizons show HIV mineralogies. These authors invoke mineral reactions to produce the smectite in the upper soil horizons.

April et al. (2004) indicate that in spodosols formed on crystalline rocks in the Adirondack mountains, smectite is prevalent in the A, E horizons while HI minerals are present below these horizons.

Buurman et al. (1976) present data which indicate that smectite forms at the expense of chlorite and HI minerals in calcareous micaschists forming cryorthod soils under alpine conditions. Mica seems to be stable for the most part. The vegetal cover is prairie and grazed conifer forest.

Tevelde et al. (1990) give data which indicate a loss of a hydroxy-interlayered mineral (vermiculite) and a gain of smectite in the E-O layer of a spruce forest on sandy soil in Norway.

Droste et al. (1962) indicate that smectitic S/I forms from illitic I/S minerals in soil horizons in alteration profiles developed on Wisconsin till and limestone in Indiana.

### *Illite, Illitic I/S Minerals in Soil (A) Horizons*

An example is given by Kuzila and Lewis (1993) where loessal soils in Nebraska were studied. Here we see a smectite-rich interlayered mineral (S/I) of loessal parent material origin transformed to a more illitic I/S mineral in the upper horizon of a prairie soil.

Spiers et al. (1984) show data which indicate the strong shift in illite content of mixed layered minerals and the formation of vermiculite in the A horizon of Solenetz soils in Alberta (Canada). The zeolite clinoptilolite was identified in this horizon also.

Badraoui et al. (1987) show RXD spectra which indicate an increase in illite content of the S/I mineral and the appearance of illite in the A horizon of tall grass vertisol soils in Minnesota.

Tice et al. (1996) give data which indicate the formation of illite in the A horizon of a sandy loam based upon diorite rock in the San Gabriel mountains, California. The study reports results on a comparative study of the effect of either oak or pine forest planted on essentially scrub soils. In the A horizon of the oak forest, 41 years after planting, one finds a strong illite peak along with the initial HI mineral found in the original soil as well as in the lower portions of the profile. The pine forest showed no change in clay mineralogy between the initial state or at different points at depth.

Madsen and Nornberg (1995) also demonstrate that the type of vegetal cover can influence the clay mineralogy of the A horizon in soils derived from glaciofluvial material in Denmark. Grass cover favors the formation of illite while spruce shows a strong tendency to produce HI minerals. The lower portions of the soil profiles show I/S and S/I plus illite as the major clay minerals.

Boettinger and Southard (1995) present data which indicate a change of smectitic I/S minerals into more illitic I/S minerals in the upper horizons of sage and grass desert soils derived from granitic materials.

### *Vermiculite and Hydroxy-Interlayered (HI) Minerals in A Horizons*

Hussain et al. (1984) show XRD spectra which indicate a change of a smectitic clay assemblage (S/I) to one with a strong vermiculite component in the A horizon of chestnut soils in Iraq. Parent material is unidentified. These soils are now farmed.

Pevear et al. (1984) show data indicating that HI mineral (HI expandable) is present in glacial marine drift soils in the Pacific Northwest at the surface (A and upper B horizon) at the expense of smectite in lower portions of the profiles.

Ransom et al. (1988) present data suggesting that smectite (S/I) is lost to the advantage of HI in the upper B horizon of an Aqualaf soil in Southwestern Ohio. This is especially important in the coarse clay fraction ( $<2-0.2 \mu\text{m}$ ). The clays collapse upon potassium saturation suggesting that the HI is an HI of smectitic character with exchangeable interlayer alumina.

Graham et al. (1990) indicate that weathering profiles on micaceous colluvium and serpentine show a change of smectite to HI in the A horizon of Argixeroll soils developed under sparse shrub growth in northern California.

Soller and Owens (1991) give X-ray data which indicate a loss of mixed layer (I/S and S/I) minerals from the B horizon of a sandy soil in Maryland USA and an increase in HI mineral in the upper horizon.

Millot and Camez (1963) indicate that HI mineral is the product of transformation of illite in sandstone rocks under forest in Alsacian alteration profiles.

In old soils formed under humid conditions in the Southeastern United States one finds gibbsite and kaolinite dominant at depth while HI minerals are dominant at the surface under forest soil conditions (Norfleet and Smith 1989; Bryant and Dixon 1964).

### *Summary of Possible Mineral Changes in A Horizons*

The major mineral changes cited above are summarized in Table 3.3.

It is clear that almost all clay species appear in the A horizons compared to other minerals found below in the alteration clay materials in an alteration profile. That is, almost all types of minerals appear to be formed from other types if one considers that the evolution of clays is from the bottom of a profile upwards. Such a variety of changes can most likely be attributed to changes in soil chemistry (organic and inorganic) in the A horizon but which do not pertain in the lower zones of the alteration profile.

Given the wide variety of apparent mineral reactions observed in going from altered rock or parent material to upper horizon soil clay mineralogy, some the reverse of others, it appears that the change in chemical and mineral stability is not the same in all types of soil (A) horizons. The only variable possible, obvious at that, is the type of plant present which forms or influences the A horizon. If plants can influence the clay minerals present they must be creating a specific chemical environment typical of their species or group. This situation is indicated in the work of Madsen and Nornberg (1995) where they compare the clays developed under different plant regimes in sandy soils in Denmark. They find that the type of plant cover can determine the type of clay mineral developed from essentially the same subsoil. Spruce develops HI, grass illite and oak or heather effected little change in the clays.

**Table 3.3.** Summary of major mineral changes from C to upper horizons in soils

C horizon-alterite material	Soil clays
Illite	Smectitic mixed layer mineral
Illite	Vermiculite
HI plus gibbsite	I/S
HI	Illite
HI	Smectite
I/S and/or S/I	Illite or HI
Smectitic S/I	Illitic I/S and/or HI
Chlorite,HI	Smectite
Gibbsite, kaolinite	HI

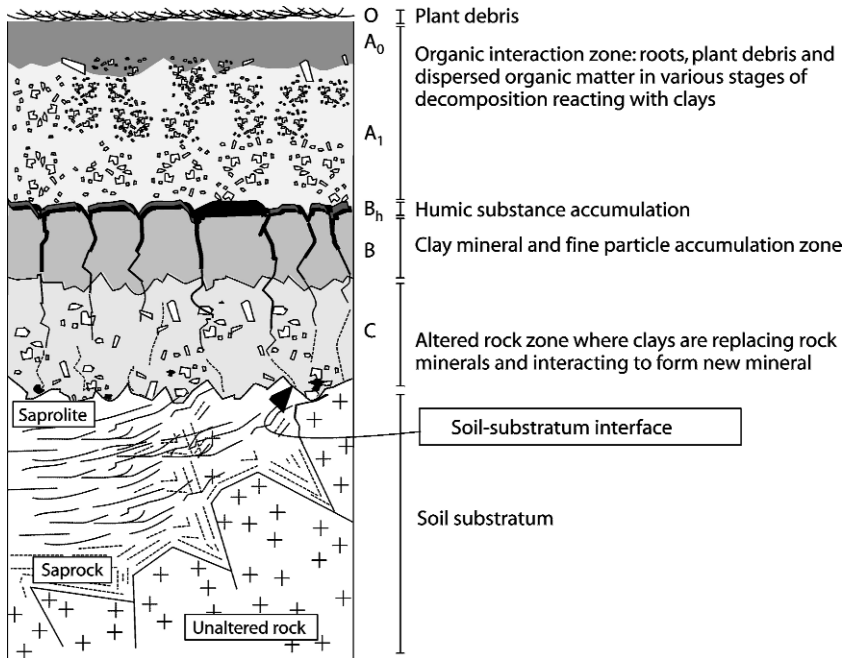
The contrast between soil clay mineralogy (A horizon) and that of the lower B, C horizons in the profiles cited above indicates that the chemistry of the aqueous solutions (capillary) in soil and alteration profile is not the same. This reflects the difference between free or bulk water which flows freely downward in the profile due to gravitational forces and the capillary water which is more strongly held in the alteration material and which in fact moves upward in the profile. Depending upon the rate of rainfall, bulk water, flowing in pores and fractures is essentially in equilibrium with the atmosphere, having but little chemical exchange with the capillary water intimately held by the clay particles or it is in various stages of equilibrium with the clays in the soil zone. Data of Ranger (2002) support this view. In this work forest soils were investigated for pore water and capillary water. Significant differences in the concentration of dissolved elements can be seen as well as specifically different elemental ratios between the two water types. The chemistry of alteration and clay stability in the B-C horizons is that of the capillary water. Hence the alteration process in each portion of an alteration profile is governed by microsite chemical reaction and, in the case of the soil horizon, by the transformation of other non-mineral material which interacts with the silicate matter. Here the chemical forces which dominate are other than those of the alteration horizons.

### 3.4.2

#### General Schema of Alteration Zone and Soil Relations

Figure 3.12 shows the relations of rock, saprock, saprolite, clay accumulation and plant/clay interaction. These are considered in the context of the present definitions of the A, B and C horizons and the interface with the substratum.

In the lower most part of the alteration profile the water/rock interaction is initiated. Here clays are formed under essentially mineral chemical constraints. These processes are generally considered to be slow demanding several thousand years or several tens of thousands of years to come to chemical equilibrium by the transformation of rock to clays. The major process in this zone is that of hydration and chemical



**Fig. 3.12.** Schematic representation of the components of a soil profile and different chemically active parts of the profile

dissolution. The initial source minerals are normally less hydrated ( $H_2O$  and  $OH$  molecules) than the soil clay minerals which form from them.

By contrast, the A horizon is one of relatively rapid change necessary to come to an equilibrium between plant chemical regime and that of the silicates. The starting material for reaction in this zone comes from the rock (altered or not) through erosion of the surface soil layer and from other clays which have been moved down in the soil profile by water flow gravitational movement and subsequently mixed with the C horizon clays, largely dominated by minerals formed by water/rock interaction but still influenced to a certain extent by the presence of organically derived chemical components (essentially roots).

The B horizon is one of mixing, the surface clays and the alteration clays finding themselves physically mixed and eventually brought to the surface. The B is the re-cycling horizon where illuvial transport of clays puts them in contact with new, water/rock interaction clays. This mixture is gradually cycled upward when the A horizon is taken away by erosion. The clays reaching the A soil horizon are a mixture of old, equilibrated clay minerals and new, unequilibrated minerals.

The most important aspect of this schematic representation is the reality of two different reaction rates, slow in the substrate and the rather rapid reaction in the A horizon. This is the plant interface. The energy of plant and living material is very great. Clearly the input of living organisms can strongly affect the stability and the kinetics of mineral reactions.

### 3.4.3

#### Overview of Alteration in the Soil Zone in Temperate Climates

The adjective “temperate” is important here in that our analysis considers only places where rainfall is in reasonable abundance and a large portion of the year is “frost free”. Here the action of aqueous fluids is important but in the weathering profile the upper portions are occupied by a three-phase system, silicates (solids), water and air. Such a system insures a high and regular growth of plants and an equilibrium with rock alteration and soil development. If the climate is too cold, not enough water/rock interaction can occur and the impact of plants is relatively small. It is not an accident that the temperate climate zones of continents have supported the major development of the human species, where the ability of the Earth to give sustenance (agricultural productivity per surface area) is greater than in other areas. Ideal conditions are not all that common. Not all of the soils of the world can be used to produce grains, those plants capable of sustaining both human and animal populations which lead to the inevitable development of large, concentrated populations.

The richness of the Earth for agricultural mankind resides in 2:1 clay minerals; illites, smectites and to a lesser extent HI minerals. Such situations require that the plants can grow and prosper and that the soils can furnish the needed sustenance and structure for the effective growth of these plants. Thus, even though high altitude, mountain prairie soils in Colorado (USA) produce interlayer I/S minerals, this is not enough to give a high agricultural productivity to the soil. The lower, plains areas next to these massifs are better adapted to produce crops and they also have a mixed layer mineral mineralogy (see Birkeland et al. 2003 for an overview of the clay mineralogy of these climatic zones).

Alteration in very dry climates is largely determined by different processes of rock fragmentation, due to differential thermal expansion of constituent minerals. It is mechanical without the formation of new clay minerals. At the other extreme, alteration under conditions of very high rainfall for long periods of time produce at a final stage hydrous oxides of iron and alumina, hematite-goethite and gibbsite. In both of these extreme soil conditions, plants are overwhelmed by climate, either too little water or too much.

The following chapter gives the processes of clay formation in the rock/water interaction zone.

#### Suggested Reading

- Birkeland PW (1984) *Soils and geomorphology*. Oxford University Press, 372 pp  
Duchaufour P (1991) *Pédologie. Sol, végétation, environnement*, 3rd edn. Masson, Paris, 289 pp  
Jenny H (1994) *Factors of soil formation*. Dover, New York, 281 pp  
Meunier A (2005) *Clays*. Springer-Verlag, Berlin, 472 pp  
Millot G (1964) *Géologie des argiles*. Masson and Cie, Paris, 499 pp (English translation 1970: *Geology of clays*. Springer-Verlag, New York, 429 pp)  
Stevenson FJ (1986) *Cycles of soil: carbon, nitrogen, phosphorous, sulfur and micronutrients*. John Wiley and Sons, New York, pp 356

# Clay Mineral Formation in Weathered Rocks: Water/Rock Interaction

## Introduction

The greatest part of the geological formations are altered when outcropping. Formed under temperature, pressure and chemical conditions different from those prevailing at the interface with the atmosphere, the rocks are transformed into a softer material. Their physical and chemical characteristics are changed because new minerals are formed, new passageways for water are opened and most of the chemical components are leached out. The altered mantle is in its turn covered by soils when the climatic and topographic conditions are favorable for the life of plants and trees. During and after their life, these organisms locally modify the chemical conditions (pH, complexation) at the rock-atmosphere interface inducing specific mineral reactions. The macro- and microbial activity contributes to chemical exchanges with the atmosphere. The result is the *SOIL*.

A soil has totally different mineralogical and textural properties from the weathered rock. Organic compounds and microbial activity impose particular chemical conditions in the surface horizons. The release of organic and inorganic components by plant debris on the very surface of the soil inverses the chemical impoverishing trend of the weathering processes. The soil and weathering sequences of primary mineral alteration products must be considered apart (Wilson 2004).

Because of the importance of weathering and soil development processes in human environments and agricultural resources a huge amount of work has been published on that topic during the two last decades. Part deals with experimental alteration of different mineral species in order to measure their dissolution rates (see White and Brantley 1995). In spite of their fundamental interest, these experimental results are somewhat difficult to connect to natural weathering profiles. Considering the feldspar alteration processes, Wilson (2004) explains very clearly how difficult it is to relate experimental geochemistry to optical, SEM, TEM or HRTEM observations of the mineral reactions in weathered rocks.

The purpose of this chapter is to propose a multiscale method of investigation of the weathered rocks from the profile to the thin section which is the universal tool of all the petrographers over the world. The description of the alteration zones at the scale of the watersheds, the continents or the planet is beyond the scope of the present book. From a geochemical point of view, the weathering processes will be described from the supersystem scale to that of the micro- or nanosystem.



## 4.1 Weathered Rock Profiles in Temperate Climates

### 4.1.1 Weathering at the Landscape Scale

#### *Typical Landscape of Granitic Countries*

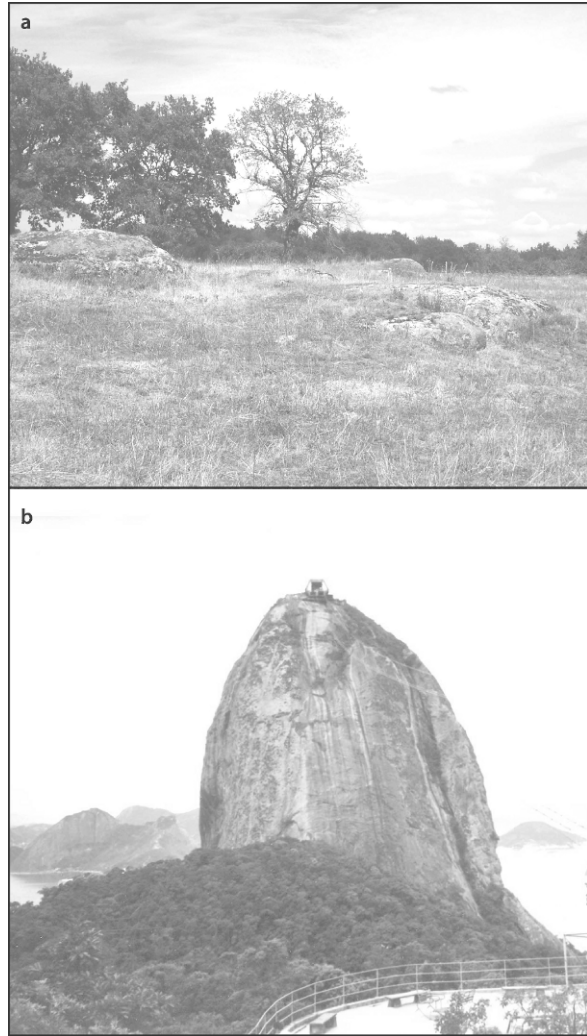
Weathering and erosion processes played a major role in the geomorphological evolution of the European continent. Weathering mantles which are observed even in northern countries have been formed from Late-Cretaceous to Pleistocene (Migon and Lidmar-Bergström 2001). They have been partly eroded during the alternating cold and warm periods. A typical landscape in granitic areas of the southern part of the Massif Armoricain in France is low hills covered by meadows surrounded by hedges. From place to place, rounded granite blocs outcrop (“chirons” in local dialect) in the hill slope profiles (Fig. 4.1a). The soils form toposequences from shallow acidic brown to thicker gley soils from hill tops to valley bottoms respectively. Under the soil, the granite is altered forming a soft grained material whose thickness varies from zero near the “chiron” to several meters deep in intensely fractured zones. The thickness of the weathered rock is totally independent of the thickness of the soil which overlays it. The porous “coat” forms a superficial water reservoir which is used in each farm to give water for cattle. During the summer, most of these pools are dried off. The water table is lowered to the bottoms of the fractured zones.

In wet tropical countries, similar heterogeneities are observed. Their effects are simply multiplied by the intensity of the alteration process. Indeed, one of the most famous inselberg is the “Pao de Açucar” which dominates the Rio de Janeiro city (Fig. 4.1b). The altered mantle is also variable in thickness but it may reach several tens of meters deep above fractured zones. These simple observations indicate that granite weathering whatever the place in the world does not form a continuous regular mantle over the hard rocks. Thus, a vertical zoning leading to horizons is not to be expected except in the upper soil itself. The petrographical study of the alteration process must take into account that alteration intensity does not necessarily increase upwards. In other words, it must be based on rock facies rather than on horizons.

#### *Examples of Weathering Profiles of Crystalline Rocks in France*

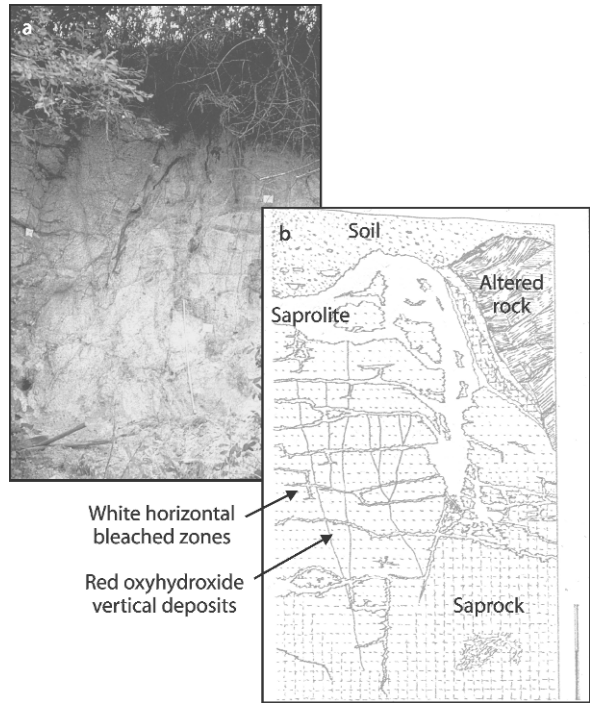
Typical weathered profiles developed on crystalline rocks in the Hercynian massifs in France exhibit the following facies sequence (Meunier 2005): fresh rock, coherent slightly altered rock (altered bedrock), saprock (structure conservative but friable material) and saprolite (restructured clayey zone). The coherent slightly altered rock is not systematically found at the bottom of the profiles and large blocks may outcrop through the soil cover. The weathered granite profile at La Rayrie, France (Fig. 4.2) shows that the friable alterite can be locally found under the hard bedrock (Meunier 1980). The thickness of the slightly altered facies depends on the local fracture distribution and the type of the parent rock. It may vary from a few meters in granite to a

**Fig. 4.1.** Typical landscapes of granitic areas; **a** in temperate countries, hills covered by meadows are punctuated from place to place by unaltered boulders of granite which are called “chirons” (picture from La Poupelinière, southern Massif Armoricain, France); **b** in tropical areas, inselbergs may form sharp slope hills such as the famous “Pao de Açucar” in Rio de Janeiro city



few centimeters in serpentine alteration. The thickness and limits of the saprock (friable structure-conservative facies) also depend on the fracture distribution in the parent rock. It frequently coats rounded unaltered core stones giving boulders typical of granite areas or the “onion” shapes in basalt flows (Fig. 4.3). The saprolite (friable non structure-conservative facies) is of variable thickness depending on the parent rock composition and the fracture distribution. In granitic areas, the thickness varies from a few centimeters along the major fractures to few meters in some profiles on hill slopes. The parent rock structure collapsed because of weakening of the mechanical resistance. Other forces may contribute to erase the original rock structure in clay-

**Fig. 4.2.** The weathered granite profile of la Rayrie, western France from Meunier (1980); **a** a photo of the outcrop; **b** cartography of the macroscopic features of the alteration profile



rich zones. This is particularly observed in mafic crystalline bodies (Fig. 4.4) or ultra-mafic ones (Fig. 4.5) where the saprolite is a clay-rich material. It systematically exhibits a prismatic newly formed structure. The micro- and macro-fractures (from micrometer to centimeter widths) are found throughout the profiles in all the alteration facies (slightly altered rock, saprock, saprolite). They are always coated with clay deposits which have been transported by the aqueous flow.

#### ***Examples of Weathering Profiles Formed on Sedimentary Rocks in France***

Weathering does not affect only crystalline rocks. When outcropping at the Earth's surface, all the geological formations are altered. The largest sedimentary basins in France were formed after the Hercynian orogenesis. From Triassic sandstones at the base to Oligocene lacustrine limestones at the top, they exhibit a large variety of sediments which outcrop in more or less concentric areas, the oldest terrains partly covering the bordering crystalline rocks. During the Tertiary, the weathering products of the crystalline basement have been flooded over the marine or lacustrine sediments. Then, at the end of the Pliocene and during Pleistocene glaciations, the landscapes have been dissected by rivers which deposited sands and gravels in terrasses. Several loess deposits covered most of the flat surfaces. All sediments have experienced weathering during more or less long periods from Tertiary to Holocene. Most often, the soil cannot be distinguished from the weathering profile. This is particularly the case for

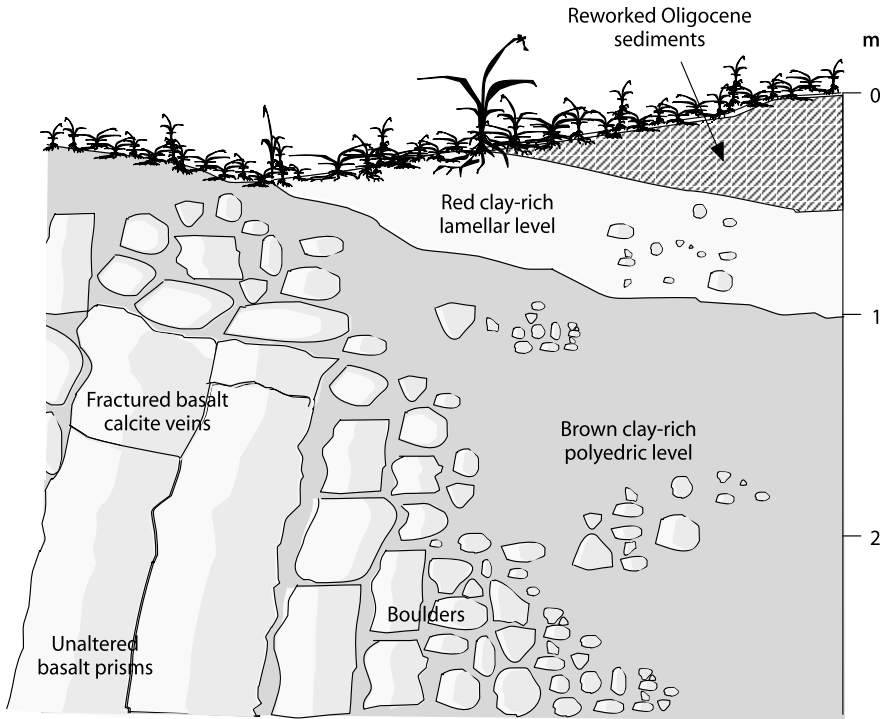


Fig. 4.3. Weathered basalt profile of Belbex, Massif Central, France (from Ildefonse 1987)

the limestone formations or the loess deposits. In some rare occurrences, the different steps of the soil-weathering profile development are marked by paleosols of superimposed pedogenesis. Tertiary lateritic formations have been dismantled for the most part. Some remains are still observable near the Hercynian massifs (Thiry et al. 2001).

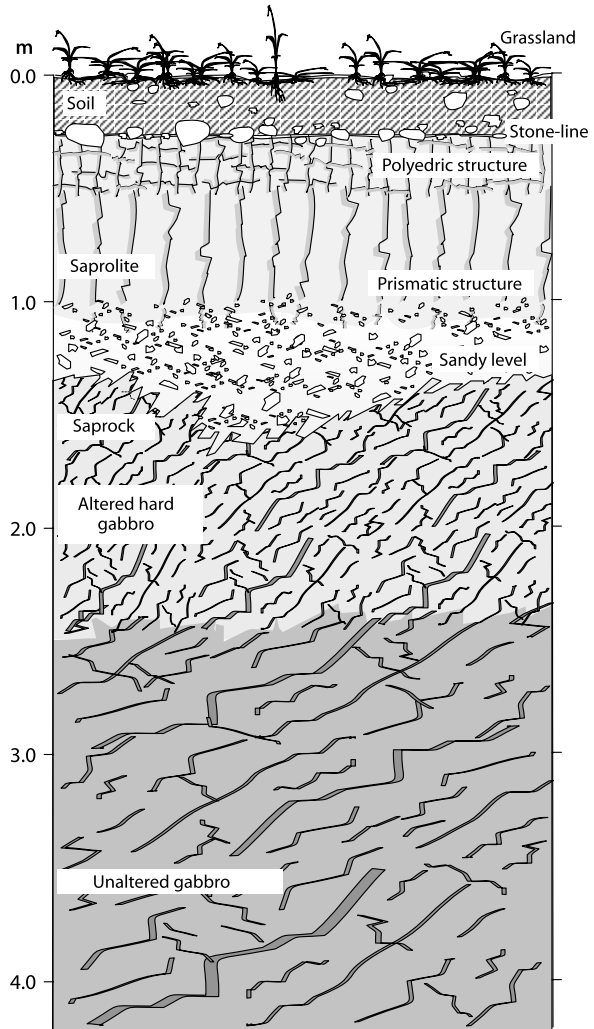
Some of the soils on the limestone formations are intensively farmed. The clays are ordinarily considered to be inherited from the insoluble fraction of the carbonate sediment. However, most often, these carbonate deposits do not contain enough clays. This indicates that the soil, even if apparently developed on the limestone, has integrated the weathering products of a formation which has totally disappeared. In France or Italy, the “terra rosa”-like soils have inherited their clay components from the weathering of glauconite-bearing formations (Colombo and Terribile 1994). This is why we have chosen to consider here only the weathering of silicate-bearing sedimentary rocks.

#### 4.1.2

##### The Parent Rock Control on Weathering Profiles

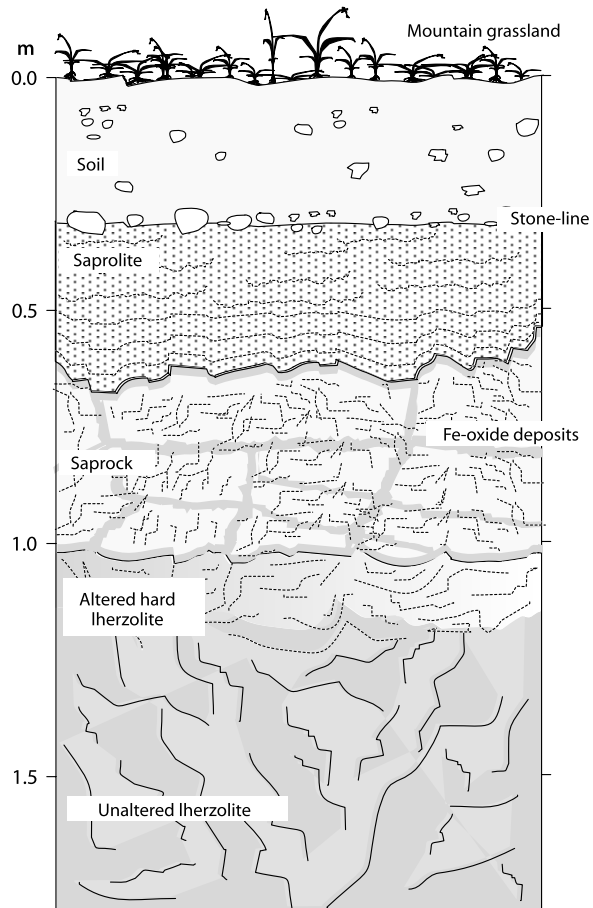
Whatever the rock considered, the weathering process systematically induces a decrease of the density and an increase of the clay fraction. The density decreases be-

Fig. 4.4. Weathering profile of a metagabbro at Le Pallet, France (from Ildefonse 1980)



cause a secondary porosity is formed by the primary mineral dissolution. The crystallization of clay minerals in the place of anhydrous pre-existing ones increases the amount of OH groups linked to the silicate crystal structure. The amount of OH is measured by the loss on ignition, i.e. the  $\text{H}_2\text{O}^+$  %. This method is pertinent for anhydrous rocks but inappropriate for hydrated ones such as serpentine. Thus, both density and clay content directly ( $<2 \mu\text{m}$  fraction amount) or indirectly measured ( $\text{H}_2\text{O}^+$ ) can be used to compare the weathering profiles developed on different parent rock types. This is particularly useful to investigate the large variability of clay production in similar climatic and topographic conditions.

**Fig. 4.5.** Weathered Iherzolite profile at Lers, Pyrénées, France (from Fontanaud 1982)

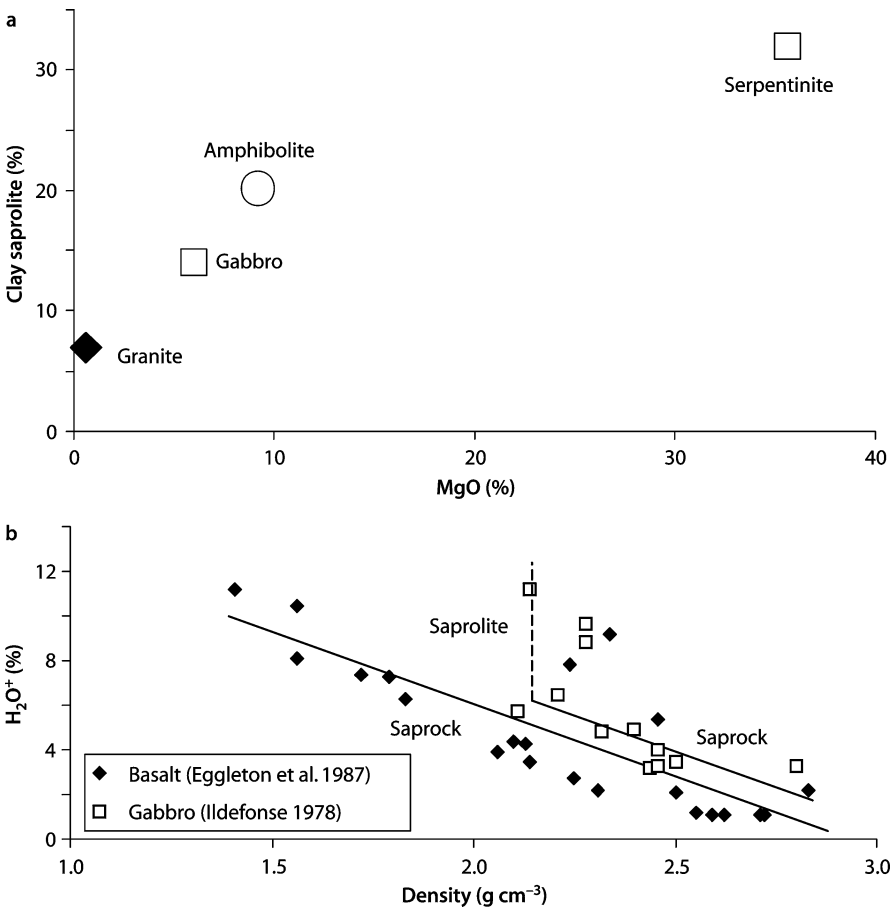


### ***Weathering Profiles on Crystalline Rocks***

The effect of the chemical composition can be investigated through the comparison of crystalline rocks having similar microstructures. This is the case for granite and gabbro which have contrasted chemical compositions but which both exhibit a granular microstructure. From unaltered rock to saprock (structure-conservative alteration), the density decreases 18.5 or 24.6% and the clay fraction ( $<2 \mu\text{m}$ ) varies from near 0% to 5% or 15% in granite or gabbro weathering profiles respectively. This means that the amount of clays produced by alteration of a gabbro is more than twice that of a granite. This difference is considered to be due to different “alterability” degree of the primary minerals. In the present case, it is clear that the alterability degree depends on the chemical and mineralogical composition of the two rocks: (1) quartz does not contribute to the formation of clay minerals and K-feldspars are much more resistant

than plagioclases; (2) highly alterable Fe-Mg-bearing minerals are more abundant in a gabbro than a granite.

Saprolite (non structure-conservative alteration) is the most altered facies in the weathering profiles under temperate climates. Large differences in clay content are observed in saprolites from granite, gabbro, amphibolite or serpentine. These rocks have different microstructures, hence different permeability distributions. However, in considering the global clay production at a macroscopic scale (supersystem), it seems that the amount of clays produced in these highly altered facies depends particularly on the MgO content of the parent rock (Fig. 4.6a). This could be related to the enhancing effect of Mg ions for nucleation and growth of clay minerals (Grauby et al. 1993, 1994).



**Fig. 4.6.** Amounts of clays produced by weathering of different crystalline rocks; **a** relation with MgO content of parent rocks (weathering profiles in ancient eroded crystalline massifs in France); **b** relation with density for a gabbro (Ildefonse 1978) and a basalt (Eggleton et al. 1987)

The gabbro and basalt chemical compositions are rather similar. The main difference between the two rock types is their microstructure. The clay content measured by  $\%H_2O^+$  in the structure conservative facies of a basalt alteration profile (Eggleton et al. 1987) varies with density according to a roughly linear inverse relation (Fig. 4.6b). The same inverse relation with the same slope is observed in the saprock (structure conservative alteration) of a gabbro profile (Ildefonse 1978). The amount of clay formed in the altered facies is higher in the gabbro than in the basalt for equivalent densities. This could be due to a higher permeability through connected microcracks in the granular microstructure than in the microlithic one. The slope of the curve abruptly changes in the non structure-conservative facies of the gabbro profile. The amount of clay increases at roughly constant density.

Figure 4.6b shows that above 6%, equivalent clay amounts are formed either in the basalt or the gabbro profiles at very different density values in conservative and non conservative-structure facies respectively. The parent microstructure persists in a wider range of densities for the basalt compared to the gabbro: the granular microstructure collapses when the density decreased by about 20% while that of the basalt is maintained even after a decrease of 50%.

### *Weathering Profiles Formed on Silicate Sedimentary Rocks*

Compared to crystalline rocks, most sedimentary rocks exhibit a different pattern of porosity distribution. In the former, the porosity is mainly dependent on a microfracture network whose characteristics depend on the size of the crystals and on the thermal and mechanical events experienced by the rock. The porosity of sedimentary rocks is more homogeneously distributed. Its physical characteristics such as pore size and shape depend on the sedimentation and diagenetic processes which have been experienced by the sediment. Consequently, in sedimentary rocks, the weathering reactions occur in microsites which are homogeneously distributed in a porous matrix and which have more or less the same chemical properties.

The pore size and shape depend on the type of sedimentary rock. They are small and irregular or big and rounded in fine- or coarse grained rocks respectively. The influence of the pore size on the weathering processes can be pictured by the comparison of two contrasted sedimentary rocks: a marl (Laffon and Meunier 1982) and a glauconite sandstone (Courbe et al. 1981). Both are phyllosilicate-bearing sedimentary rocks which have been weathered under similar climate conditions (western France). The amount of secondary clay minerals produced by the alteration reactions as estimated using the difference of  $H_2O^+$  amounts between unaltered and altered samples ( $\Delta_{H_2O} = H_2O^+_{\text{altered sample}} - H_2O^+_{\text{unaltered rock}}$ ). It varies from zero to about 10% and 0 to 22% for the glauconite sandstone and the marl respectively. The chemical changes experienced by the two sedimentary rocks during weathering is represented by the variation of the  $SiO_2/Al_2O_3$  ratio. This ratio does not significantly change in the marl while it decreases about 65% in the glauconite sandstone. The amount of secondary clays in the marl increases under constant chemical conditions (trend 1, Fig. 4.7). This is not the case for the glauconite sandstone where  $\Delta_{H_2O}$  and  $SiO_2/Al_2O_3$  are negatively correlated (trend 2, Fig. 4.7).



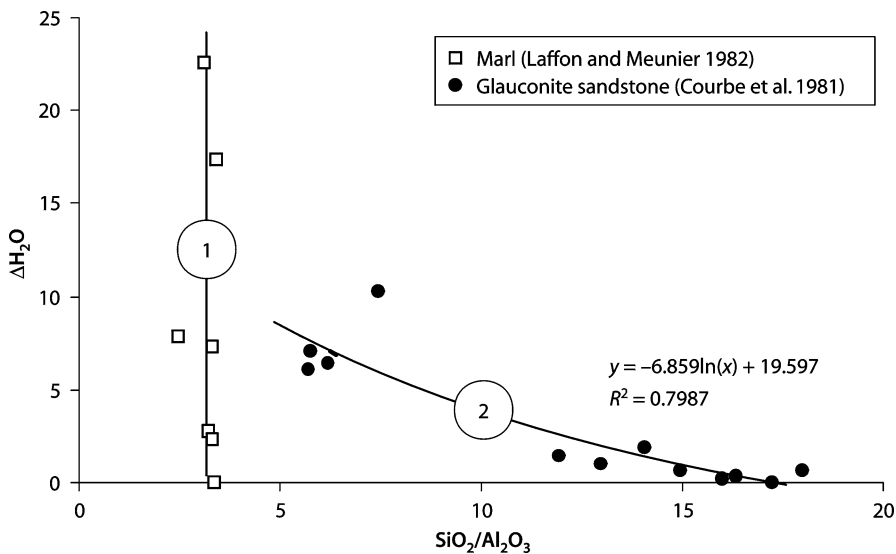


Fig. 4.7. Variation of the amount of secondary clay minerals ( $\Delta_{\text{H}_2\text{O}} = \text{H}_2\text{O}^+$  sample -  $\text{H}_2\text{O}^+$  unaltered rock) with the chemical changes experienced by two sedimentary rocks during weathering ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ); 1: marl, 2: glauconite sandstone (data from Laffon and Meunier 1982 and Courbe et al. 1981)

### 4.1.3

#### The Climate Control on Weathering Profiles

##### *The Effect of Climate on Weathering*

At a global scale, the climatic effect (temperature and precipitation) on weathering processes has been shown to overcome all the other factors such as the topography or the extent of the last glaciation (White and Blum 1995). The thickness of the altered mantle is classically thought to decrease with increasing latitude. Because, thick laterite profiles are observed today in the intertropical countries, they are considered typical of these climates. On the contrary, thin alterites are considered typical of temperate climates. Such a simplistic approach frequently leads to misunderstanding of the weathering phenomenon at the geological time scale. First, climatic conditions have necessarily changed whatever the place in the world. For instance, laterite remains are frequently found at unusual high latitudes (Tabor and Yapp 2005). Second, weathering is a kinetically controlled process. The main factor is not uniquely temperature but *temperature × time*. In other words, the saprolites that concentrate secondary minerals which are considered typical of laterite such as gibbsite or goethite, can form under temperate conditions if the alteration process is maintained active for a long time. Consequently, unequivocal proofs of the climate influence are more difficult to establish than ordinarily thought.

In spite of the difficulties explained above, some effects of the climate influence can be grasped if weathering profiles formed on identical rocks are compared. For instance, basalt weathering profiles from Australia and New Zealand (Eggleton et al. 1987; Moon

and Jayawardane 2004) exhibit similar evolution trends: in both cases, the rock density decreases and the  $\%H_2O^+$  increases from fresh to altered zones. However, the negative correlations shown in Fig. 4.8 indicates that the amount of secondary clays increases with rock dissolution but not in the same proportions for the two profiles. The amount of secondary clays in New Zealand is twice that in Australia for the same 2.8 to 2.2 density decrease. Even if the topographical position of the profile is not identical, such a difference is at least partially related to climatic parameters (amount of rainwater).

Berre (1970) compared serpentinite weathering profiles formed under different climatic conditions in France. The serpentinite bodies are located in Brittany and Limousin (3 profiles; oceanic climate) and Provence (1 profile; mediterranean climate). The profile thickness varies from 40 to 60 cm in the former but reaches 140 cm deep for the latter. The amount of clay is about 30% in the oceanic profiles and the upper part of the mediterranean one. However, it reaches 60% at 1 meter depth in the latter (Fig. 4.9a). Topographical conditions being nearly identical for all the profiles, the difference observed is obviously an effect of the climate. Using the amount of clay as a qualitative indicator of alteration intensity, it appears that the magnesium content does not decrease under 20% of the parent rock in oceanic and mediterranean conditions whatever the amount of clay (Fig. 4.9b). This indicates that the MgO concentration in altered rocks is buffered by the secondary phases, i.e. the clays. In other words, these clays are always Mg-bearing. Concomitantly, the  $SiO_2$  increases to 10–15% or 30% in the Mediterranean and oceanic conditions respectively (Fig. 4.9c). This difference is related to the chemical composition of the dominant clay fraction. Vermiculite forms in the Provence weathering profile while saponite crystallizes in the oceanic climate profiles.

#### *Uncertainty of the Reconstitution of Ancient Climatic Conditions*

Most often, the soils and alterites which are presently observable result from a long evolution history. Climatic and topographic conditions may have changed during their

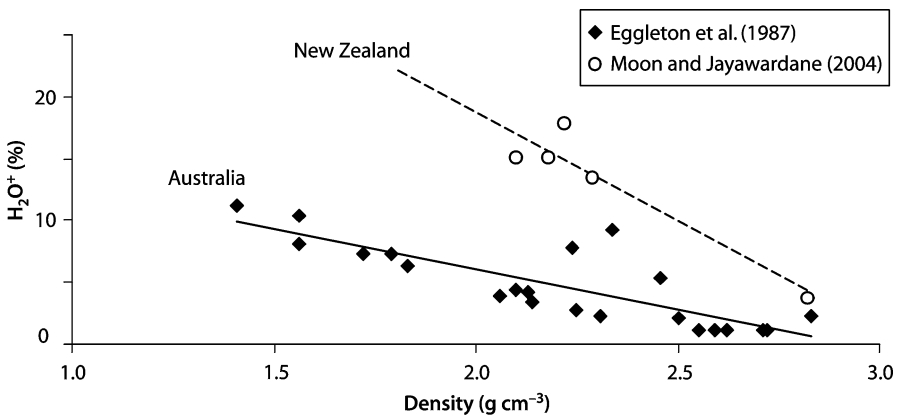
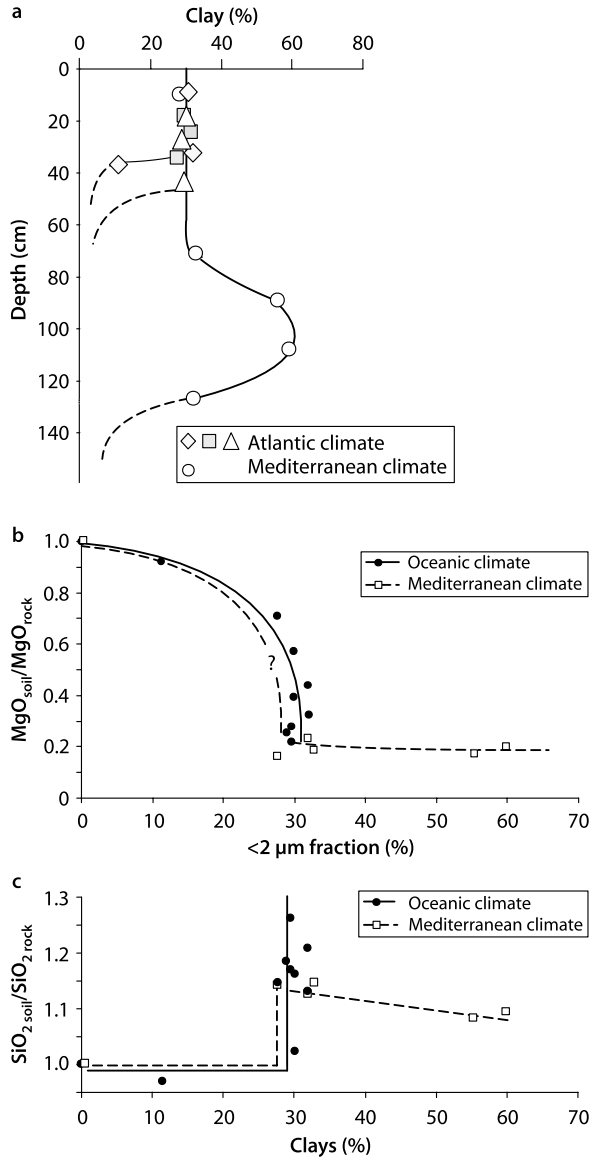


Fig. 4.8. Effect of the climate on the relation between clay amount and density for altered basalts from Australia (Eggleton et al. 1987) and New Zealand (Moon and Jayawardane 2004)

**Fig. 4.9.** Effect of climatic conditions on the weathering processes of serpentinite bodies in France (from Berre 1970). Four profiles have been studied: two from Brittany (*diamonds, squares*), one from Limousin (*triangles*) and one from Provence (*full circles*); **a** variation of clay amount with depth; **b** relative variation of the MgO loss versus clay amounts; **c** relative variation of the SiO<sub>2</sub> loss versus clay amounts



development: erosion may have truncated the profiles, or, on the contrary, sedimentation may have buried them. In fact, it is quite rare to find soils or alterites resulting from a single weathering or pedological event. Soil and Earth scientists must be aware that the clay mineral assemblages they determine in profiles may have been formed in successive events. This is particularly obvious for deep weathering profiles observed in northern latitudes or paleosols buried under loess or colluvial deposits. Unfortu-

nately, it is not always easy to identify the products of each pedological or weathering event involved because the profiles were truncated and reworked.

Examples of deep weathering are not rare in Europe even in its northern part. Alteration profiles are seen to be formed on a great variety of rocks during a large period of time from Mesozoic to recent (Migon and Lidmar-Bergström 2001). Most of them have been eroded even when they are still several tens of meter thick. Complete laterite profiles such as those described by Bestland et al. (1996) on the Eocene-Oligocene Clamo-John Day formation in central Oregon or in northern Ireland (Hill et al. 2000) are exceptions. Particularly in France, the Hercynian basement which outcrops in ancient massifs and Paleozoic zones of the Alps have been altered to laterite or bauxite during late Cretaceous to Early Tertiary (Thiry et al. 2001). These thick alteration mantles have been dismantled during late Tertiary giving a sequence of clay deposits in the sedimentary basins, i.e. Aquitanian, Paris and Rhodanian in the southwest, north and southeast of France respectively. Concomitantly, the Mesozoic calcareous sediments of these basins have been out of water during the major sea regression at the end of the Cretaceous. They were affected by a karst alteration type. Palaeo-profiles observable in sinkholes are characterized by flint-rich red clay deposits (Blanc-Valleron and Thiry 1997).

Thiry et al. (2001) showed that clay minerals formed during short periods of time are difficult to relate to climate. The presence of kaolinite or gibbsite in a weathering profile does not mean that alteration proceeded under tropical conditions. Dejou et al. (1970) and many others discovered gibbsite in the granite grus formed in the coldest areas of France (Massif Central, Limousin). The recent weathering profiles which can be observed now formed during the Holocene period because the glacier cap has completely renewed the rock surfaces during the last glaciation. The weather of these countries where the landscapes are deeply dissected by rivers is particularly rainy. Soils and grus are abundantly drained near the hill slopes along which many springs outcrop. The formation of gibbsite under these conditions is an effect of the intense leaching of the altered rocks rather than a remain of past rainy climates. Portugal and central Spain have not experienced the presence of glaciers. The old weathering profiles were not much eroded. Here the presence of gibbsite is thought to be related to a long duration of the weathering processes under climatic conditions similar to the present ones (Torrent and Benayas 1977).

#### 4.1.4

##### From Macro- to Microscopic Scale

In order to understand how rock weathers one needs to relate field observations to petrographical analysis. In other words, the rock disintegration is a multiscale phenomenon which can be studied from watersheds to atoms. Most often, it is rather difficult to integrate observations at the microscope scale in the calculation of a global mass balance concerning hundred of square kilometers. Dramatic errors resulted from excessive extrapolations in which microscope studies were used to estimate a global mass balance and, conversely they also occur when mass balances at the watershed scale were used to determine the weathering mineral reactions in the rock under concern. In spite of significative recent progress for a multiscale integrated interpretation of weathering (Bowser and Jones 2002; White et al. 2002), much remains to be done in that field.

Our purpose here is to describe the weathering phenomenon from profile to mineral scales. To simplify, one can consider that most of the weathering profiles exhibit two principal facies: the saprock (rock structure conservative altered zone) and the saprolite (non-conservative rock structure altered zone). The limit between these two facies may be progressive (granite) or sharp (serpentinite). Remains of saprock are frequently observed inside the saprolite. Also, saprolite microzones may appear inside the saprock. Petrographical observation reveals a similar mixture of conservative and non-conservative rock structure micro-zones at the thin section scale. The macroscopic aspect of the altered rock depends on what is the dominant microscopic facies. This does not exclude the presence of other facies at any scale of observation.

Thus, it is necessary to determine as precisely as possible the typical petrographical characteristics of the conservative and non-conservative rock structure alteration facies. In both cases, the new material which replaces the parent rock-forming minerals is microcrystalline and microporous. It has been assigned the term “*plasma*”. Plasma is formed inside myriads of microsites, each of them being related to microfractures which have conducted water to the mineral surfaces (intergranular joints, microcracks, cleavages). Two different kinds of plasma can be distinguished:

- *primary plasma*: observed in the internally destabilized primary minerals. The microporous material is composed of fine debris of the parent crystal mixed with its own secondary products (Fig. 4.10a),
- *secondary plasma*: observed in zones where the rock structure has been disintegrated. It is a polymineral microporous material composed of fine debris of several parent mineral species mixed with their respective secondary products (Fig. 4.10b).

The terms primary and secondary plasmas should be preferred to *alteroplasma* and *pedoplasma*. Indeed, alteroplasma and pedoplasma are more ambiguous and confusing because they suggest a genetic origin: alteroplasma is considered to be formed exclusively inside the saprock zone and pedoplasma implicitly indicates a relation with the soil. In fact, primary plasma can be formed everywhere inside the alteration profile even in saprock remains in the soil itself while secondary plasma may appear early in the less altered facies far away from the soil. According to the definitions presented in Sect. 2.1.1, the primary and secondary plasmas are formed in “microsystems”.

## 4.2

### The Internal Destabilization of Primary Minerals (Primary Plasmic Microsystems)

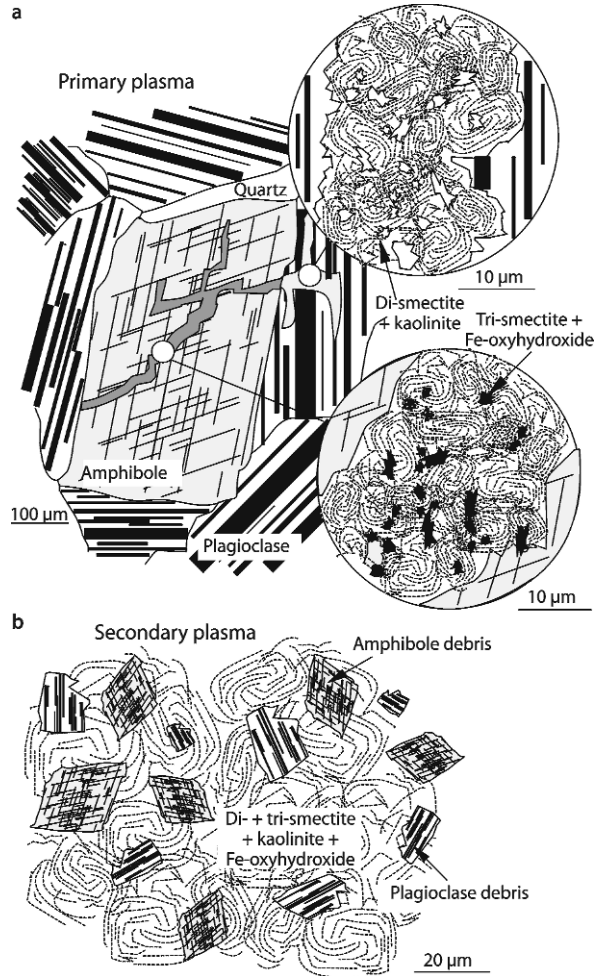
#### 4.2.1

##### Porosity-Permeability and Microsystems in Crystalline Rocks

###### *Micro-Cracks and Pores: The Connected Porosity*

Most often, a granite body is crosscut by large fractures which isolate massive blocks. The large fractures form a connected network in which water flows freely. On the contrary, the permeability of the massive blocks is very low ( $10^{-18}$  to  $10^{-20}$  m<sup>2</sup>). Consequently, the transport properties are highly contrasted according to the scale of the

**Fig. 4.10.** Schematic representation of primary (a) and secondary (b) plasmas formed in a weathered amphibolite



investigation, i.e. at the catchment or the mineral scales (see Taylor and Eggleton 2001, p. 241–247). Micro-cracks are elongated voids. They are the most important small scale fluid vector of unaltered granite rocks (Simmons and Richter 1976; Sausse et al. 2001). They are genetically related to the thermal and mechanical stress history of the rock from the cooling stage of the magma to the decompression of the solid rock body at the Earth's surface. When outcropping, crystalline rocks exhibit different types of micro-cracks:

- *inter-granular joins*. Whatever the minerals in contact, voids are open at the grain boundary,
- *intracrystalline micro-cracks*. Whatever the mineral species, the micro-crack extension is limited to a single crystal body,
- *intercrystalline micro-cracks*. They crosscut several crystals whatever their mineral species.

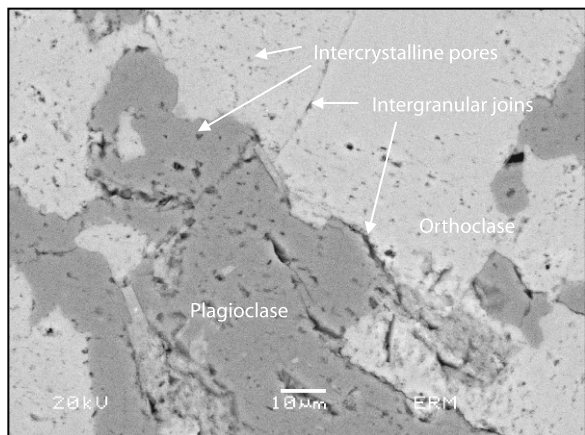
Pores are distinguished from micro-cracks by their non elongated morphology (Fig. 4.11). Some pores are formed early during the post-magmatic history of the rocks (Wong et al. 1989). This is typically the case for the pores inside plagioclases. Using morphometric analyses of SEM images, Sardini et al. (1997) showed that the pore size distribution in plagioclases is log-normal. Secondary pores are formed later during hydrothermal alteration events before the rock outcrops at the Earth's surface.

Meteoric water enters the rocks through a connected microcrack network. Connectivity is essential for permeability. Unfortunately, it is not an easy physical parameter to measure because microcracks or pores are difficult to observe in 3D space at the hand specimen scale. Most studies are based on sample impregnation using different polymers. The quality of impregnation depends on two factors:

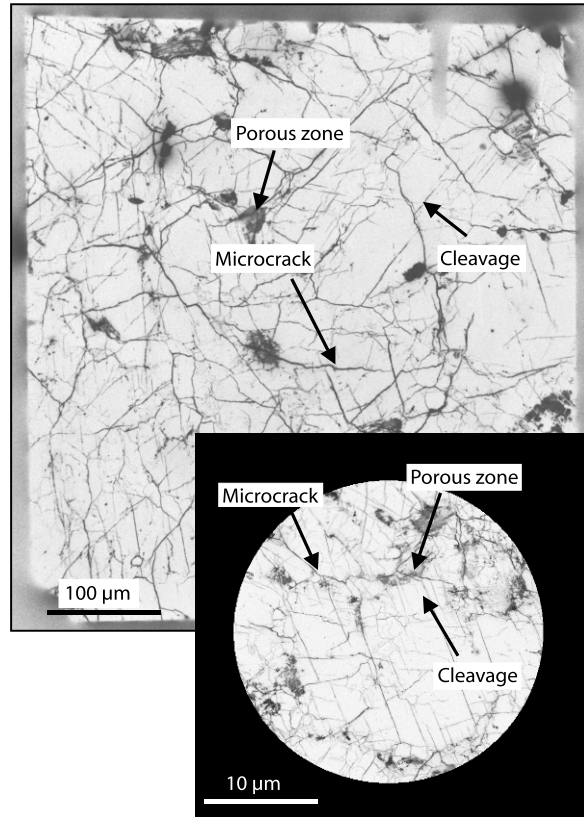
- *the size of the molecules used as a probe.* The methylmetacrylate resin (MMA) has been chosen because of its low viscosity at room temperature (similar to that of water). However, the dimensions of the MMA molecule (0.4 and 1.0 nm for thickness and length respectively) are significantly different from that of water (0.19 nm in diameter),
- *the duration of impregnation.* The impregnation quality is measured by the mass of MMA absorbed. The time after which the absorbed mass reaches a plateau varies with the rock porosity-permeability characteristics.

After polymerization, thin sections are made in the impregnated rocks. Then, a polished surface is covered with a film which is sensitive to the  $\beta$  particles emitted by the  $^{14}\text{C}$ -PMMA. An example of autoradiograph is given in Fig. 4.12. Recent studies are based on image analyses of combined autoradiograph pictures and mineralogical maps. The spatial distribution of the connected porosity of a  $^{14}\text{C}$ -PMMA impregnated granite is largely dependent on the mineral components of the rocks (Sardini et al. 1999; Oila et al. 2005). Using combined mineral maps and autoradiographs of unaltered Kivetty granodiorite samples (Finland), Sardini et al. (2006) measured the connected porosity for each mineral components of the rock. They have shown that the

**Fig. 4.11.** Palmottu granite (Finland). SEM microphotograph showing pores and intergranular micro-cracks in the unaltered rock (courtesy of Paul Sardini)



**Fig. 4.12.** The connected porosity. Autoradiographs of a polished section from an unaltered sample of the Palmottu granite previously impregnated with  $^{14}\text{C}$ -PMMA. Micro-cracks are observed as open inter-granular joins and feldspar cleavages. Porous zones are also observed in some parts of feldspar crystals (courtesy of Paul Sardini)



most porous are the biotites and amphiboles. The micropore size distribution whatever the primary mineral species, is a log-normal one (see Fig. 2.5).

### ***Connected Porosity and Chemical Microsystems***

The propagation of weathering in the early stages depends on the way that the fluids invade the rocks. Of particular importance for chemical interaction processes is the relative ease with which those fluids can move in and out the rocks. They can use two different pathways: fractures (macro-permeability) and micro-cracks and pore network (micro-permeability). In the former, water circulates freely under the normal pressure difference. The residence time inside the rock being relatively short, the solutions are diluted and far from equilibrium with the primary minerals. In the second, the water movements are ruled by capillary forces. The solutions are not rapidly renewed. They approach equilibrium with the primary minerals. Consequently, at a given time, fluids interact with rock in different microsystems whose degree of opening varies from place to place. The first mineral reactions to occur in macrocrystalline rocks (granite, gabbro, amphibolite, ...) are observed in two types of chemical microsystems which appear along micro-cracks:



- *contact microsystems in open intergranular joins*: growth of secondary phases into one or the two neighboring parent crystals;
- *internal microsystems in open inter- or intracrystalline microcracks*: destruction of the crystal body and replacement by a porous fine-grained material (plasma) composed of debris of the parent mineral and secondary phases (clays, oxyhydroxides).

The spatial distribution of the connected porosity inside an unaltered rock is a determinant parameter for the location of mineral-water reactions. The reactions happen first at a local scale and depend on the rate of renewing of the solutions. Renewal leads to dilution in meteoric alteration processes. Consequently, differences of concentration are stabilized between solutions flowing freely and those which reside at the contact with the crystal surfaces. The  $^{14}\text{C}$ -PMMA impregnation experiments show how the smallest pores or microfractures inside each mineral species are connected to larger avenues in which the aqueous fluids can flow by gravity. It is predictable that, at a given time and for a given parent mineral species, several different reactions can happen simultaneously according to the position of reacting crystals with respect to these largest avenues. The chemical attack on the crystal surfaces exposed to water molecules liberates ions to the solutions. If the pore aperture and the tortuosity of the connected voids forbid any fluid circulation, the solutions are locally at or near equilibrium with the dissolved mineral. On the contrary, the solutions in contact with crystals neighboring large passageways are constantly diluted by meteoric water inputs. Evaporation during dry seasons eliminates first free water before capillary water and changes the saturation of the dissolved components.

Differences of chemical potential of mobile components are established at a local scale (microsystem). Their amplitude varies according to the way that the microsystems are connected to the water passageways in the rock, i.e. the length of the diffusion path (Fig. 4.13a). At a given time, the intensity of the driving force which triggers the mineral reaction is not identical in all microsystems. Consequently, different mineral reactions may proceed simultaneously. Because the alteration reactions do not modify the original structure of the parent rock in the first stage of weathering (saprock), they necessarily increase the local porosity. Then, more water can enter inside the microsystems. This modifies the composition of the solutions and specifically the chemical potential of the mobile components. In other words, in a given place the chemical potential difference increases with time. This means that the secondary products which have been formed in the early stages may be destabilized in the later ones (Fig. 4.13b). As soon as the original rock structure collapses (saprolite), new conditions are established. In the most compacted zones, the chemical potential difference can recover a low amplitude in some particular new microsystems.

The example of the K-feldspar alteration in a granite saprock illustrates the discussion above. Its dissolution liberates Si, Al and K ions in the solution. Three petrographical situations can be distinguished at a given time (*variation in space*):

1. The residence time of the solution is long enough to consider it as almost immobile (narrow intergranular joints). In that case, its chemical composition is close to equilibrium with K-feldspar. However, at Earth surface conditions in the presence of water, a new phase different from K-feldspar is formed: illite. Illite crystallizes through a heterogeneous nucleation process on the mica surfaces in contact with K-feldspars.

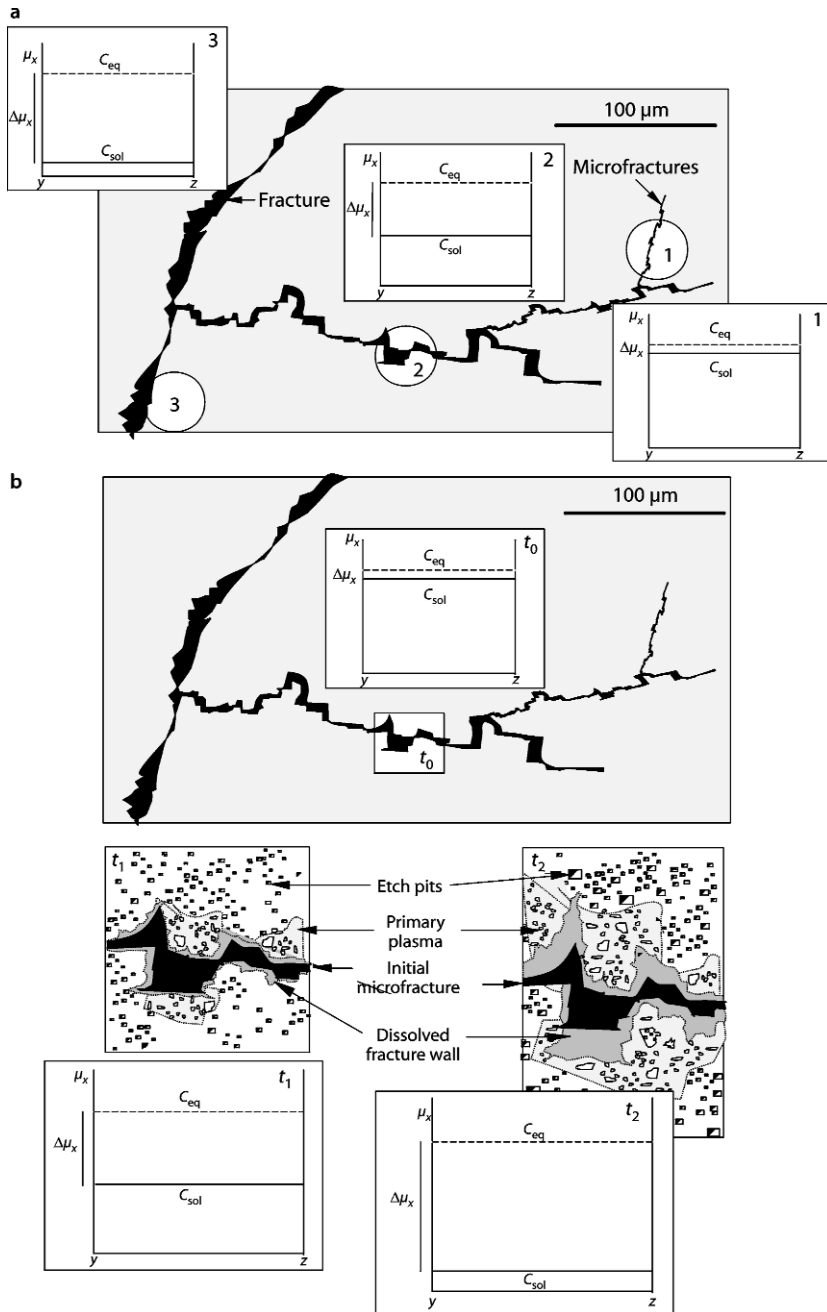
Considering the properties of the corresponding microsystem, one deduces that some elements behave as inert components (Si and Al) acting by their relative amounts while K behaves as a mobile one acting by its chemical potential.

2. The solution is always almost immobile but the connection with larger fractures maintains a continuous migration of the mobile components by diffusion. The difference of chemical potential is great inside the corresponding microsystems. Consequently, the dissolution of K-feldspars progresses and new phases are formed which are stable at lower K potentials than illite: smectite or smectite + kaolinite.
3. The solution is continuously diluted by meteoric water input. The potential difference for the mobile component is very great. Some inert components then change their chemical behavior: they act in the microsystem as mobile ones. This is the case for Si ions; Al remaining inert. New phases are formed which are stable at the lowest K chemical potential: kaolinite and gibbsite.

Consider now the evolution during time of the conditions inside a given microsystem (for instance microsystem number 2 in Fig. 4.13b). At  $t_0$ , the K-feldspar are internally replaced by a smectite + kaolinite secondary assemblage. The reaction inside the primary plasmic microsystems is controlled by chemical diffusion. From  $t_0$  to  $t_2$ , the porosity increases because larger volumes of K-feldspar are transformed into a microporous material (primary plasma) and fractures are enlarged by dissolution of their walls. Consequently, more water enters in the microsystem and diffusion pathways are more and more easily connected to the large avenues.  $K^+$  ions are leached out of the microsystem. The chemical potential is dependent of the solution renewing rate in the fractures (advection control). The potassium chemical potential decreases. The secondary phases previously formed are destabilized in their turn to the benefit of new ones. The smectite + kaolinite assemblage is replaced by new ones: kaolinite or kaolinite + gibbsite with loss of silica.

### *From Nano- to Microsystem Scale*

Typically any weathering reaction transforms a compact primary mineral into a porous secondary mineral assemblage (secondary porosity). Three processes are activated during the reaction: (1) the dissolution of the primary mineral which occurs at the solid-solution interface, (2) the transport of the dissolved chemical species (hydrated ions or polymers) at a variable distance from their origin, (3) the growth of one or several new crystal structures. The reaction rate is determined by the slowest process. The interaction between the solution and the mineral (process 1) was shown to be largely dependent on the microtopography of the solid surface (Holchella and Banfield 1995 and references therein). This parameter has been integrated in the calculation of the dissolution rate of the main silicate species using Brunauer-Emmett-Teller (BET) method for surface area measurement (Brunauer et al. 1938). The BET area is corrected by a roughness coefficient (White and Brantley 2003). The diffusion of the dissolved components (process 2) on a nanometer scale is not fully understood at present. In the case of topotactic crystallization such as the formation of clay minerals on the dissolution surfaces of olivine, pyroxene or amphibole, the distance of diffusion is very short. However, as the reaction is not perfectly stoichiometric, a part of the dissolved components must be leached out of the system while water and some



**Fig. 4.13.** Schematic representation of the amplitude of the chemical potential difference of a given mobile component ( $\Delta\mu_x$ ) in systems where  $y$  and  $z$  are inert components; **a** variation according to the connection degree with the large water passageways of microsystems reacting simultaneously; **b** variation with time of  $\Delta\mu_x$  in a given microsystem

components originating in other mineral reactions are provided from outside the microsystem. Consequently, even the topotatic replacement of a primary mineral species by secondary ones implies chemical diffusion. Thus, diffusion rate is an important parameter which must be taken into account for the global reaction rate. The rates of nucleation and crystal growth of the secondary minerals (process 3) are practically unknown for topotatic replacements. The nucleation is certainly favored by a catalytic effect of the dissolution surface (Putnis 2002). The formation and the incorporation of the building blocks in a topotatic replacement remain mysterious (see Sect. 1.7.2).

It was constantly observed that silicate alteration rates in experimental and natural weathering conditions differ by several orders of magnitude. The natural processes are much slower than the experimental ones (Casey et al. 1993). White and Brantley (2003) show that fresh and weathered plagioclases do not react similarly in identical experimental conditions. These authors suggest that weathering in natural environments is more closely simulated by reactions near the thermodynamic equilibrium than by those which are activated in highly undersaturated conditions. This is certainly true at the super- to megasystem scales at which the weathering phenomenon is seen through calculation of average mass balances. However, this does not correctly depict the phenomena at the macro- to microsystem scales because different chemical conditions may be established concomitantly in a given weathering profile. Near thermodynamic equilibrium conditions prevail in contact microsystems and some but not all of the primary plasmic microsystems according to their relative position with respect of the large water passageways (Fig. 4.13). Consequently, it is predictable that a given mineral species will not alter at a constant rate in every microsystem. The dissolution rate for crystals crosscut by large fractures is close to the values measured in experiments using highly diluted solutions. The global alteration rate at the sample scale is a statistical average of the alteration rates of all the active microsystems. It is close to that of the dominant microsystem type.

Because a crystalline rock does not weather at the same rate in all the microsystems, the heterogeneity of the porosity distribution and the local mechanical resistance vary increasingly from point to point. The high contrast of physical properties at a local scale leads to partial collapse of the original structure and favors the formation of secondary plasmic microsystems. Primary and secondary plasmic microsystems can co-exist even in the less altered zones such as the coherent rock facies of the saprock. That means that distinct clay mineral assemblages can be formed at the same time.

#### 4.2.2

#### Petrography of Contact Microsystems

##### *Clay Mineral Growth in Non-Phyllosilicate Primary Minerals*

Neoformed clay minerals have been optically observed from point to point inside the intergranular joints in the early weathering stages of magmatic rocks (granite and gabbro). In both cases, the feldspars, i.e. orthoclase or labrador, are locally replaced by illite or beidellite respectively. The mineral reactions (dissolution of feldspars and crystallization of clay minerals) are due to water infiltration in the open spaces of

the mica-K-feldspar and labrador-amphibole intergranular joints respectively. Microsystems have been activated at each of these particular places (see Sect. 2.1):

- *Muscovite or biotite-orthoclase contacts* (Meunier 1977; Meunier and Velde 1979b). Autoradiographs show that the intergranular joints between K-feldspars and micas are at least partially open in the unaltered rocks. In some places, one can observe small birefringent crystallites which develop from the mica surface inside the feldspars (Fig. 4.14a). The composition of these minerals is clearly illitic (Fig. 4.14b, Table 4.1).
- *Labrador-amphibole* (Ildefonse 1978, 1980). Smectite platelets appear along the amphibole-labrador inter-granular join. They are slightly pleochroic (colorless to pale yellow) and present third order colors under crossed nicols. These platelets grow from the amphibole outer surface into the labrador body. In some places they invade the internal micro-fractures of the feldspar.
- *Forsterite-orthopyroxene* (Nahon et al. 1982). The chemical composition of smectites formed along the forsterite-orthopyroxene (OPX) intergranular joints of a tephroite-bearing ultramafic rock indicate that they grow inside the pyroxene. Indeed, they contain  $\text{Cr}^{3+}$  ions which do not exist in the forsterite. These ions are provided by the dissolution of the OPX crystals.

### *The Chemical Composition and Crystal Structure of Clays in Contact Microsystems*

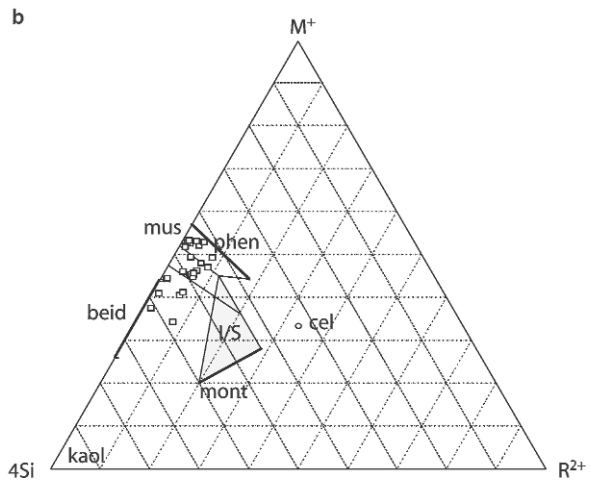
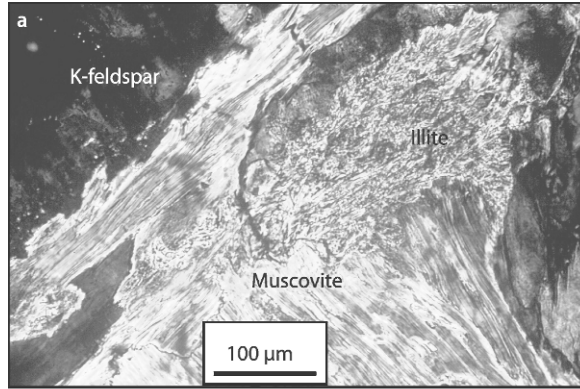
As muscovite does not appear to be weathered (Fig. 4.14a), it was deduced that the solution was locally undersaturated with respect to K-feldspar but close to equilibrium with respect to mica. The  $\text{K}^+$  activity is high enough for illite to form locally in replacement of K-feldspar (Meunier and Velde 2004 and references therein). However, the mineral reaction does not occur in a perfectly closed microsystem since Mg ions are incorporated in illite crystals. These ions necessarily come from biotite destabilization. The amount of Mg in illite is highly variable from place to place. However, it is systematically higher for illite growing at the biotite-orthoclase intergranular interface (Fig. 4.15a). Identically, the beidellites which crystallize in the place of labrador in the gabbro are rich in Mg and Fe ions (Table 4.1) indicating that the microsystems were partly open. In both cases, the ion migration is probably controlled by a chemical diffusion process rather than by fluid circulation.

The secondary minerals formed inside the contact microsystems of the early weathering stages of granite or gabbro rocks have two common characteristics: they are high charge clays and the layer charge originates for the major part from the Al for Si substitutions in the tetrahedral sheets (Fig. 4.15b). The local composition of the fluids involved in the microsystems being unmeasurable, one can only deduce some of their properties from the clay minerals which have precipitated. The tetrahedral coordination of the Al ions formed during the dissolution of K-feldspar or plagioclase must be favored by the local pH conditions.

### *Replacement of Primary Phyllosilicates along Intergranular Joints*

In the early weathering stages of granite or amphibolite, the mica or chlorite are altered from place to place along their intergranular joints whatever the species of the

**Fig. 4.14.** Contact microsystem in the La Rayrie weathered granite profile; **a** micrographs of secondary illitic phases growing from muscovite into K-feldspars; **b** chemical composition of the illitic phases



neighboring crystal. Except for quartz, these joints are outlined by local alteration features of the two crystals facing each other each of them being partly replaced by its own secondary minerals without any apparent mixing. This is typically the case of the joints between biotite, muscovite and plagioclase in granites. Different polyphased mineral assemblages are observed on the two sides of the intergranular joint:

- *biotite-plagioclase joint*: trioctahedral vermiculite + Fe-hydroxide + kaolinite in the biotite, kaolinite in the muscovite plagioclase (Fig. 4.16a),
- *muscovite-plagioclase joint*: dioctahedral vermiculite + kaolinite in the muscovite and kaolinite in the plagioclase (Fig. 4.16b),
- *biotite-muscovite joint*: trioctahedral vermiculite + Fe-hydroxide + kaolinite in the biotite, dioctahedral vermiculite + kaolinite in the muscovite.

The simultaneous alteration of chlorite and andesine along their intergranular joint has been described in a weathering profile of glaucophanite (Proust 1983). The chlo-

**Table 4.1.** Chemical compositions of clay minerals formed in contact microsystems in granite and gabbro; **a** illite in the muscovite-orthoclase inter-granular join; **b** illite in the biotite-orthoclase inter-granular join; **c** beidellite in the amphibole-labrador inter-granular join; gabbro from Le Pallet, France (from Ildefonse 1980)

<b>a Illite in the muscovite-orthoclase intergranular joints, saprock (Meunier and Velde 1979a)</b>												
Si	3.26	3.33	3.18	3.11	3.14	3.23	3.09	3.15	3.17	3.74		
Al	2.32	2.25	2.37	2.49	2.37	2.29	2.52	2.39	2.83	2.11		
Fe	0.17	0.18	0.22	0.18	0.23	0.23	0.19	0.23	0.00	0.00		
Mg	0.23	0.22	0.24	0.20	0.27	0.26	0.20	0.24	0.04	0.04		
Mn	–	0.01	–	–	0.01	0.01	0.01	–	0.01	0.01		
Ti	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01		
Ca	0.05	0.01	0.03	0.02	0.07	0.03	0.03	0.02	0.02	0.00		
Na	0.04	0.03	0.05	0.06	0.03	–	0.04	0.06	0.05	0.01		
K	0.85	0.85	0.88	0.92	0.83	0.87	0.83	0.81	0.35	0.59		
<b>b Illite in the biotite-orthoclase intergranular joint, saprock (Meunier and Velde 1979b)</b>									<b>c Beidellites amphibole-labrador (Ildefonse 1980)</b>			
Si	3.26	3.33	3.18	3.11	3.14	3.23	3.09	3.15	3.24	3.32	3.37	3.30
Al	2.32	2.25	2.37	2.49	2.37	2.29	2.52	2.39	1.59	1.72	1.42	1.69
Fe	0.17	0.18	0.22	0.18	0.23	0.23	0.19	0.23	0.80	0.68	0.82	0.68
Mg	0.23	0.22	0.24	0.20	0.27	0.26	0.20	0.24	0.44	0.32	0.37	0.34
Mn	–	0.01	–	–	0.01	0.01	0.01	–	0.01	0.01	0.01	0.01
Ti	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ca	0.05	0.01	0.03	0.02	0.07	0.03	0.03	0.02	0.27	0.25	0.31	0.28
Na	0.04	0.03	0.05	0.06	0.03	–	0.04	0.06	0.24	0.22	0.24	0.26
K	0.85	0.85	0.88	0.92	0.83	0.87	0.83	0.81	0.10	0.09	0.05	0.08

rite is transformed into a regular tri-vermiculite/chlorite mixed layer while the andesine is transformed into kaolinite.

Why do the neoformed clay minerals grow only along the mica-K feldspar joints and not along the mica-plagioclase ones? We saw above that the dissolution of the K-feldspar locally oversaturates the solution with respect to the mica phase. Then, the low temperature equivalent of the micas precipitates on the surface of the parent mica which acts as a catalyst. In the absence of potassium in a system, no low temperature Na and Ca mica equivalent phase can be formed. Therefore, the solution remains undersaturated with respect to the mica as well as the plagioclase. The two primary minerals react internally giving their typical secondary secondary products respectively. This is also the case for chlorite-andesine joints: none of the two primary phases are in equilibrium with the solution inside the intergranular joint. In all the cases, the min-

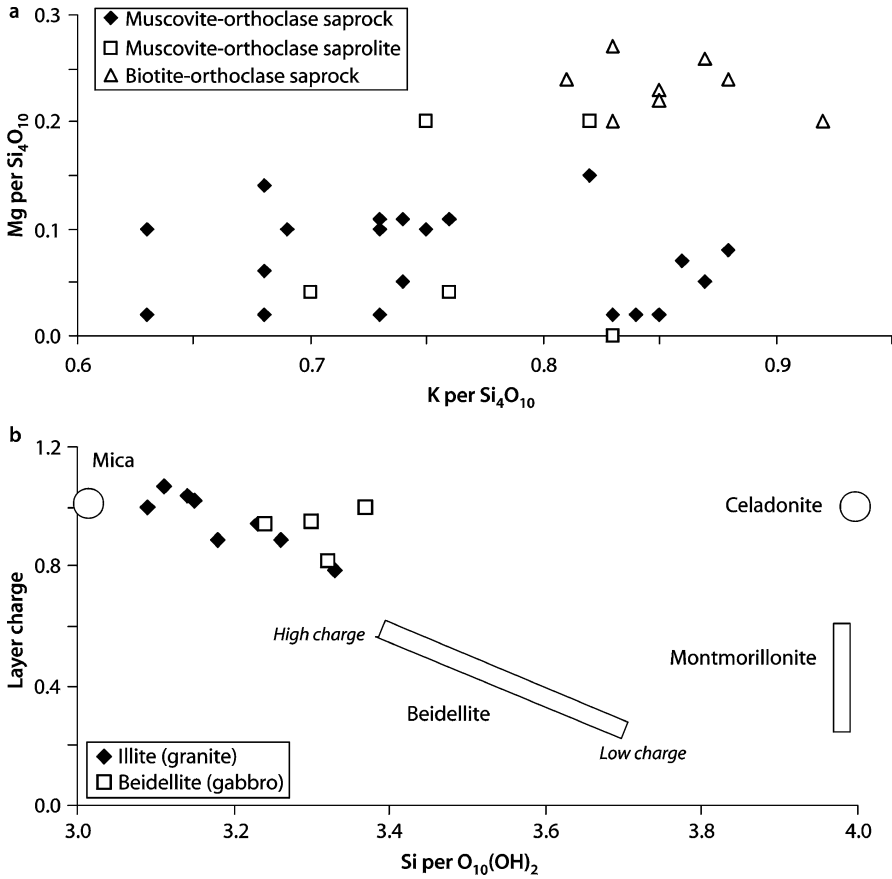


Fig. 4.15. Chemical composition of illite and beidellite formed in contact microsystems in weathered granite and gabbro respectively

eral reactions along the intergranular joints foreshadow that operating in primary plasmic microsystems which progressively transform each parent crystal into a microcrystalline material.

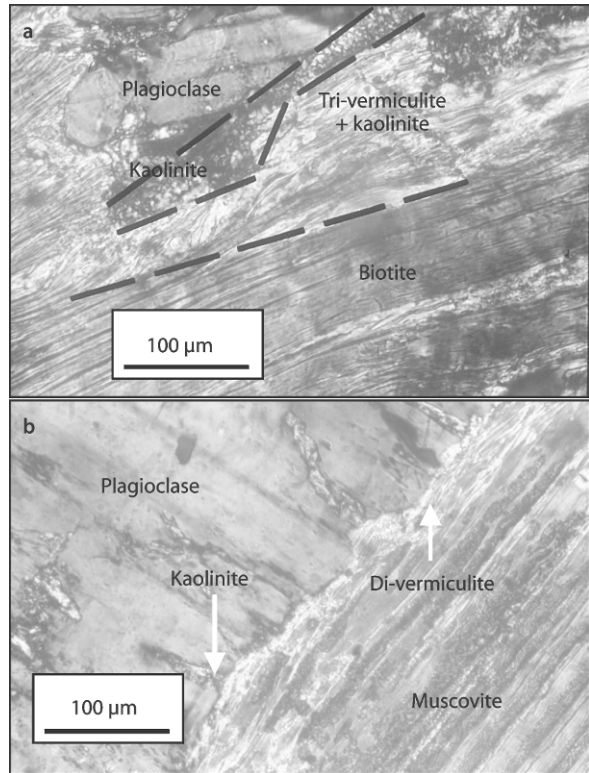
### 4.2.3

#### Petrography of the Primary Plasmic Microsystems

Whatever the crystalline rock type, the primary minerals are progressively replaced by a porous microcrystalline material in the saprock. Each primary crystal alters inside its own body. Consequently, the original microstructure of the parent rock is conserved. In other words, myriads of microsites begin to transform the mineralogy and the porosity of the rock in an apparent volume conservative process. Even if these microsites are innumerable, they belong to only a few categories of microsystems which depend essentially on the crystallochemical properties of the parent minerals. Most



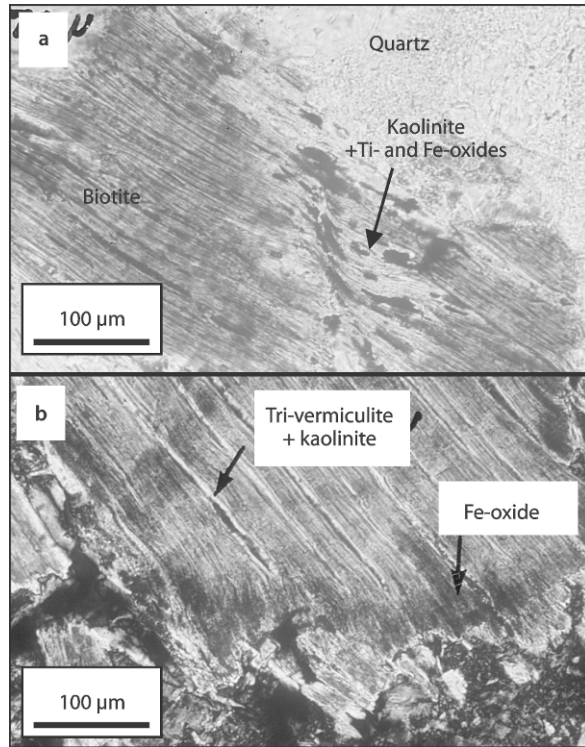
**Fig. 4.16.** Simultaneous destabilization of primary minerals along their intergranular joint (example of the La Rayrie granite, France);  
**a** biotite-plagioclase contact;  
**b** muscovite-plagioclase contact



often in the literature, microsystems are ignored and the weathering progress is described by a sequence of neofomed minerals. The alteration for each primary components such as micas, feldspars, chlorites, garnets are described separately (see the review of Wilson 2004). Unfortunately, because of the difficulty to correctly identify the secondary minerals in microsites, many discrepancies appear in the reported sequences formed in different climatic or topographic conditions. This gives an apparent chaotic picture of the weathering processes. We shall preferentially use here the mineralogical data controlled by a precise petrographical analysis.

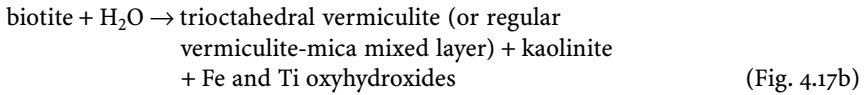
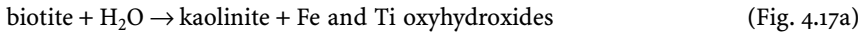
A general fact emerges from literature: when the parent crystals alter inside themselves during the early stages of the weathering, their secondary products are not always the same even in a single alteration profile. In other words, for a given parent mineral species, the corresponding plasmic microsystems which are at work concomitantly do not produce the same secondary mineral assemblages. It is obvious that this apparent random behavior is, in fact, controlled by the way that microsystems are connected to the major fractures. These fractures form the water avenue network through the rock. The solutions which flow inside the network are constantly diluted by the meteoric water input. They are a permanent sink for the dissolved components and they contribute to leach them out of the rock.

**Fig. 4.17.** Weathered biotites from weathered granite; **a** a kaolinite + Fe and Ti oxyhydroxide assemblage replaces the biotite along the microfracture; **b** formation of Fe-oxyhydroxides deposit at the margin of the biotite crystal which is partly transformed into a trioctahedral vermiculite + kaolinite assemblage



### ***Biotite Microsystems***

Biotite exhibits the most spectacular alteration features in the weathering profiles of granitic rocks even under temperate climates. Biotite alteration has been described in many papers (Coleman et al. 1963; Gilkes and Suddhiprakarn 1979; Meunier and Velde 1979b among others) and it is used to calculate the weathering rate in watersheds (Murphy et al. 1998 and references therein). Figure 4.17 shows some petrographical microsites selected in the La Rayrie and La Pagerie granite profiles in which a biotite crystal is transformed either into a kaolinite + Fe,Ti oxide assemblage or in tri-vermiculite along the cleavages. The first transformations are observed along the open intergranular joints whatever the crystal face orientation, e.g.  $(001)$  and  $(hko)$ , or along microfractures which crosscut the biotite crystal. Then, the cleavages are progressively opened. The layers partly conserve the original optical properties of the mica (pleochroism and polarization colors) but K ions are replaced by hydrated Ca or Mg ones. The newly formed expandable layers appear as sinuous layers. They are typically trioctahedral vermiculite or regularly interstratified vermiculite-biotite. The voids created by the distortion of the layers are filled up by a colorless microcrystalline mineral assemblage (kaolinite + Fe and Ti oxyhydroxides). Summarizing, the mineral reactions shown in Fig. 4.17a and 4.17b are the followings:

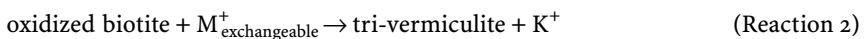


As we saw above, several processes are involved in the weathering reaction: dissolution, solid state transformation, crystallization of secondary products. Banfield and Eggleton (1988) using HERTM show that the first step is a chemical attack on crystal defects leading to a localized congruent dissolution of the biotite. Vermiculite develops by a direct modification of the biotite structure in a second step. The biotite is progressively transformed according to two processes:

1. one biotite layer is replaced by 1 vermiculite layer inducing a volume increase of 40%,
2. two biotite layers are replaced by 1 vermiculite layer inducing a volume reduction of 30%. A regularly interstratified biotite-vermiculite is formed which has been called as hydrobiotite (Coleman et al. 1963; Wilson 1970).

Combined with dissolution, the two processes do not produce an overall expansion of the biotite crystal. On the contrary, a secondary porosity appear inside the parent crystal body. Kogure and Murakami (1996) show that the two processes coexist in vermiculitized biotite crystals.

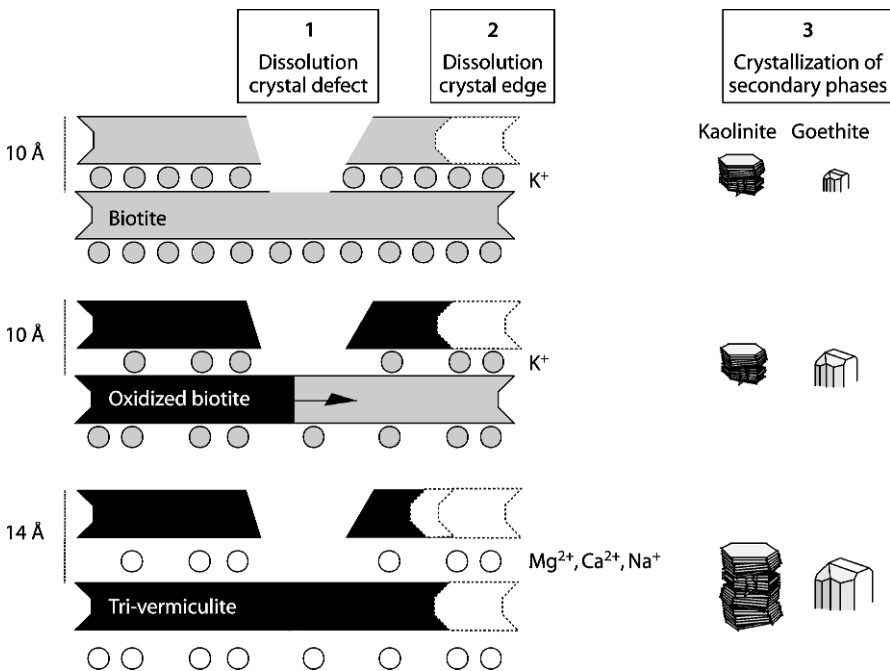
Most often, the biotite crystals do not totally disappear even in the most altered zones of deep weathering profiles. Some pleochroic layers remain but they do not conserve the original biotite chemical composition. The major transformation is the total oxidation of  $\text{Fe}^{2+}$  ions (Jeong and Kim 2003). Because the  $d_{001}$  remains at 10 Å, these layers are considered as oxidized biotite. According to the authors, the crystal structure of the oxidized biotite remains trioctahedral but the octahedral occupancy decreases by about 12% (the  $d_{060}$  values decreases from 1.542 to 1.533 Å). Concomitantly, the total Fe, Mg and K amounts decrease by about 13, 9 and 20% respectively. A great effort has been made to calculate of the chemical mass balance of the biotite vermiculization process. The reaction has been experimentally reproduced in many studies because of its potential role as a K ion source for plants (see the review of Wilson 2004 and references therein). The oxidation process changes the composition of the octahedral sheets but not that of the tetrahedral ones: the Al variation is always less than 3%. It is to be noticed here, that vermiculite is not formed at this stage in spite of the fact that the layer charge of the parent biotite decreases by more than 16%. The interlayer being entirely saturated with  $\text{K}^+$  ions, the  $d_{001}$  remains unchanged at 10 Å. The expansion to 14–15 Å necessitates an exchange of  $\text{K}^+$  for hydrated cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{Na}^+$ . Thus, the biotite vermiculization process depends not only on the  $\text{Fe}^{2+}$  oxidation but also on cation exchange:



The formation of vermiculite being favored by high amounts of exchangeable cations in the solution, it is more intense in Mg-rich than Fe-rich biotites (Murakami et al. 2003).

Kaolinite or halloysite and Fe-oxyhydroxides are classically considered to be the ultimate weathering stage of biotites. They are indeed the last silicates and oxides surviving in the ghost structure remaining when the mica has totally disappeared. However, they begin to form in the early weathering stages in the voids formed by the mica dissolution or the deformation of the layers. Most often, kaolinite and goethite or lepidocrocite crystals grow epitactically on the mica layer surfaces. Topotactic-like growth of kaolinite was described by Ahn and Peacor (1987). Titanium is recombined into anatase (more rarely rutile). All these secondary products co-exist with tri-vermiculite in the saprock. Banfield and Eggleton (1988) showed that the volume of the solid decreases by 23% when the *biotite* → *kaolinite* + *goethite* reaction is completed. If the rock structure is conserved, this means that the secondary porosity of the primary plasma represents 23% of the initial biotite volume. The complete alteration process is summarized in Fig. 4.18.

Are Reactions 1 and 2 necessary steps in the alteration process of biotite? Certainly not since the direct transformation of biotite to kaolinite has been observed (Ahn and



**Fig. 4.18.** Schematical representation of the early stages of the weathering of biotite layers by secondary products formed by topotactic replacement (tri-vermiculite) and separate crystallization as observed using HRTEM

Peacor 1987). Even if the description does not document the composition of the biotite-like layers, HRTEM analyses show that kaolinite forms 50 to 300 Å thick packets of layers intercalated within biotite. An irregular 2 kaolinite for 1 biotite layer transition has been observed also. The authors concluded that kaolinite in free or interstratified layers is formed by a dissolution/crystallization process. These observations indicate that the plasmic microsystems developed inside biotite crystals produce different secondary mineral assemblages in the early weathering stages. This is made possible if the difference in chemical potential varies inside the rock according to the more or less direct connection of the microsystem with the major water passageways as summarized in Fig. 4.19. The smallest difference leads to the formation of illite overgrowth inside the K-feldspar body (see Sect. 4.2.2: Contact Microsystem). The intermediate difference leads first to the replacement of biotite layers by tri-vermiculite,

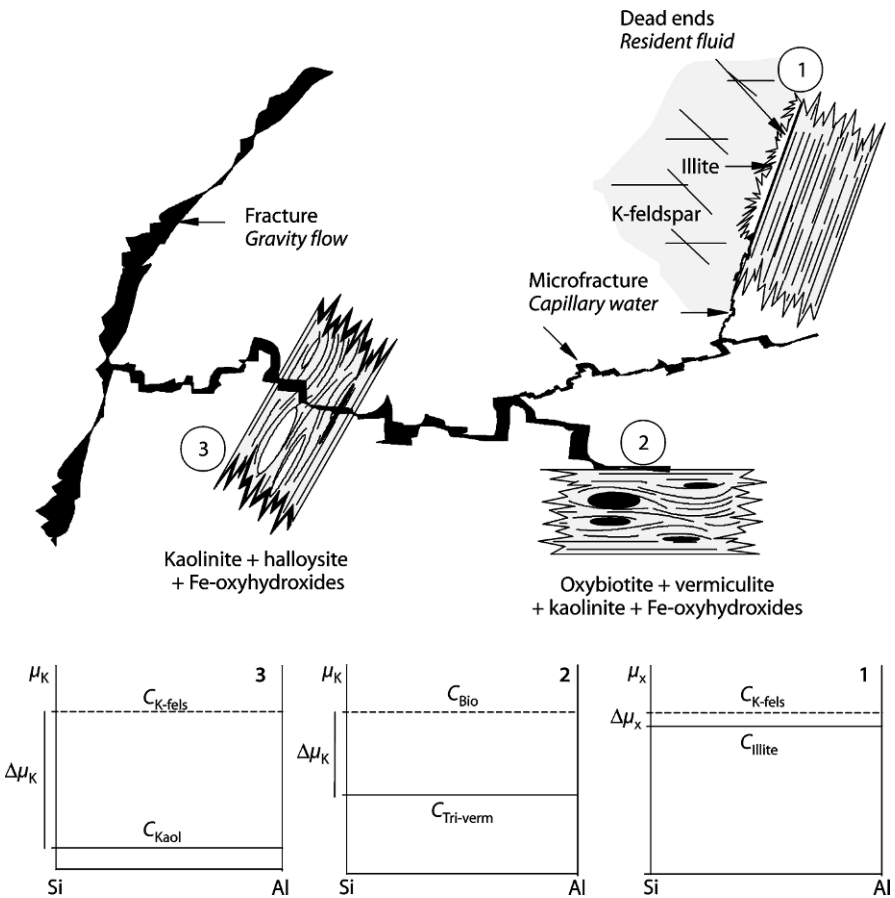


Fig. 4.19. Schematic representation of the relation between the composition of the secondary mineral assemblages and the possible connections between the biotite microsystems with the major water passageways in a granite

then by the crystallization of a Fe-di-vermiculite + kaolinite assemblage. The greatest difference leads directly to the formation of kaolinite + Fe and Ti oxyhydroxides.

### Muscovite Microsystems

The dioctahedral aluminous micas are by far more resistant to alteration than their trioctahedral equivalents. This is not only due to the fact that the effects of Fe oxidation are limited or absent but rather to the oblique orientation of the hydroxyl groups with respect to the (001) planes (Bassett 1960). However, muscovites are not unalterable. They appear to be partly transformed into a kaolinite ± expandable phase mineral assemblage in weathered granites. The nature of the expandable phase can be either a dioctahedral vermiculite (Meunier and Velde 1979a) or a dioctahedral Al-bearing smectite (Banfield and Eggleton 1990). The analysis of both the altered layers and the secondary products in two granite weathering profiles (Meunier 1977) indicate that muscovite alters according to a two step process (Fig. 4.20). The 2:1 layers lose a part of their potassium before transforming either to kaolinite (La Pagerie granite) or into an Al-rich vermiculite (La Rayrie). This is coherent with the data presented by Singh and Gilkes (1991) in figure 8 of their paper. These data are best fitted by a two step process.

The crystallization of the secondary phases from altered muscovites is not fully understood until now because it may involve different processes which are simultaneously activated such as the topotactic replacement and the epitaxial crystal growth. The topotactic transformation of mica into expandable phases on one hand or kaolinite on the other hand has been documented by the HERTM studies of Singh and Gilkes (1991) and Robertson and Eggleton (1991). The geometry of the topotactic replacement can be oblique (Fig. 4.21a) or straight (Fig. 4.21b). It implies necessarily the presence of mica-kaolinite interfaces. The structure of such interfaces remains somewhat enigmatic. Indeed, the potassium interlayer cations which compensate the charge deficit of the 2:1 layers are ordinarily located in the hexagonal cavities of the tetrahedral sheets of the two facing mica layers. How can this specific position be respected with a neu-

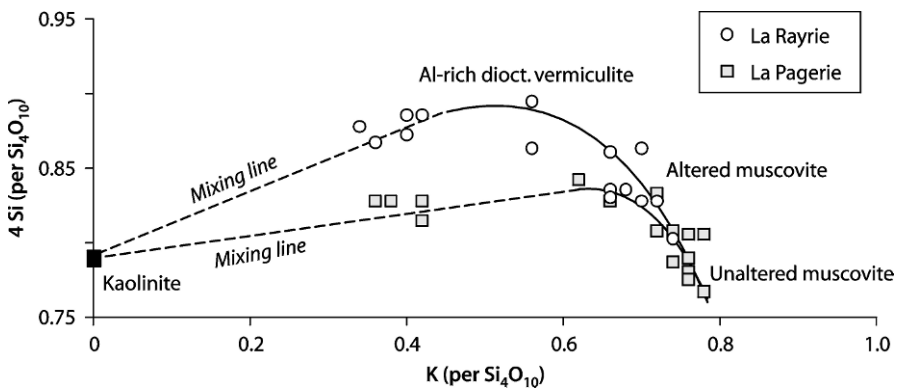
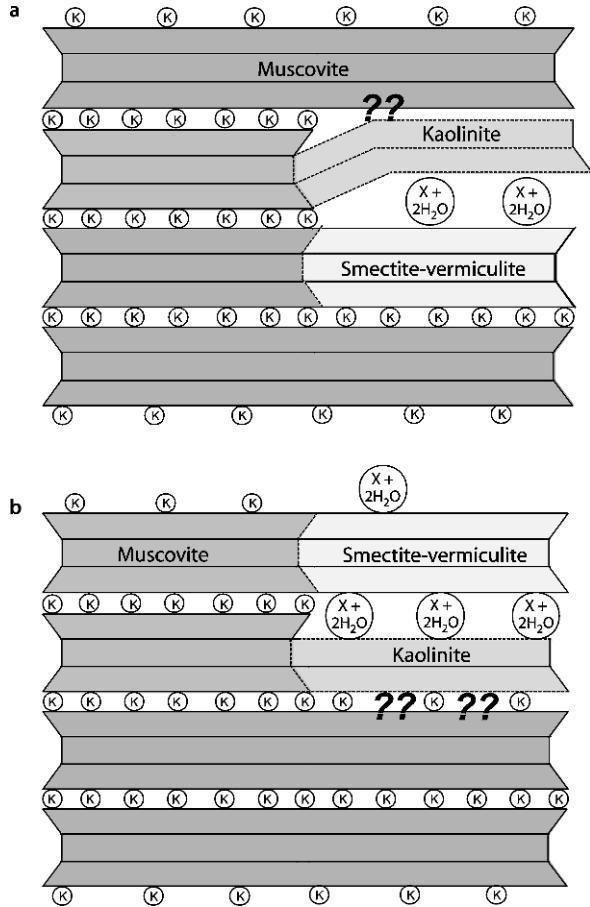


Fig. 4.20. Chemical composition of altered muscovite and their secondary products in two granite weathering profiles (from Meunier 1977)

**Fig. 4.21.** Hypothetical schematic representation of topotactic replacement of muscovite layers by kaolinite ones; **a** oblique boundary (from Robertson and Eggleton 1991); **b** straight boundary. Problematic interfaces are indicated by ?? symbols



tral tetrahedral sheet of the 1:1 kaolinite layer? On the other side of the kaolinite layer, the interlayer region is bordered by the octahedral sheet of the 1:1 layer and the tetrahedral sheet of the mica layer. The octahedral sheet has no room to locate cations as big as potassium, so the thickness of this type of interlayer is greater than that of the unaltered mica. Where are the K<sup>+</sup> ions located? Are they hydrated? The mechanism of the 1:1 for 2:1 layer topotactic replacement remains enigmatic.

Why are the expandable phases formed from muscovite: Al-rich dioctahedral vermiculite (Meunier and Velde 1979a,b), I/S and smectite (Banfield and Eggleton 1990)? In both cases, the charge deficit of the 2:1 layers decreases inducing the loss of K<sup>+</sup> ions and which are exchanged with hydrated cations. The presence of water molecules triggers the expansion of the interlayer region. Figure 4.21a,b does not take into account the deformation of the 2:1 layers induced by their expansion. When repeated, the deformation overcomes the mechanical resistance of the 2:1 layers leading to fracturing. These features are observable at a larger scale under the optical microscope: altered muscovite crystals exhibit deformed and open cleavages, fractures and decreasing

polarization colors. The muscovite alteration processes is not volume conservative at the HRTEM scale nor at the optical microscope scale. A secondary porosity is formed during the transformation. Additionally, kaolinite may epitaxially crystallize on the outer surfaces of the altered muscovite giving overgrowth features (Singh and Gilkes 1991).

The distribution of muscovite microsystems (internal destabilization) is related to the connected porosity in the same way as is biotite (Fig. 4.19). The muscovite microsystems produce different secondary mineral assemblages according to the distance to the large water passageways. The driving force is the chemical potential differences of  $K^+$ ,  $H^+$  and  $Si^{4+}$  ions. The constant dilution of the flowing solutions by meteoric water input entrains a high difference in microsystems close to the large passageways. Thus, kaolinite or halloysite are directly formed without any intermediate phases such as Al-rich vermiculite. On the contrary, if the microsystem is almost isolated as it is the case for narrow intergranular joints between K-feldspar and muscovite, the difference of  $K^+$  chemical potential remains low because the  $K^+$  concentration in solution is locally controlled by the dissolution of the K-feldspar. Thus, illite can form as a secondary product having the highest amount of alkalis. It has been observed as epitaxial growth on the outer mica surface (see Sect. 4.2.2).

### Chlorite Microsystems

Chlorite is classically considered to weather according to the following secondary mineral sequence: chlorite → regular chlorite-vermiculite mixed layer (C-V MLM) → tri-vermiculite → di-vermiculite (intergrade) → kaolinite + Fe-oxyhydroxides (see Wilson 2004). The process, which is assigned as “the vermiculitization”, is triggered by two chemical transformations: (1) the oxidation of the  $Fe^{2+}$  ions; (2) the loss of  $Mg^{2+}$  cations (Fig. 4.22). However, some petrographic and nanopetrographic work shows that this process is more complicated than originally thought since the secondary mineral assemblages produced by vermiculitization are not always the same (Table 4.2). First of all, the decrease of  $Fe^{2+}$  ion content cannot be simply reduced to oxidation. A part is leached out of the chlorite plasmic microsystem before oxidation

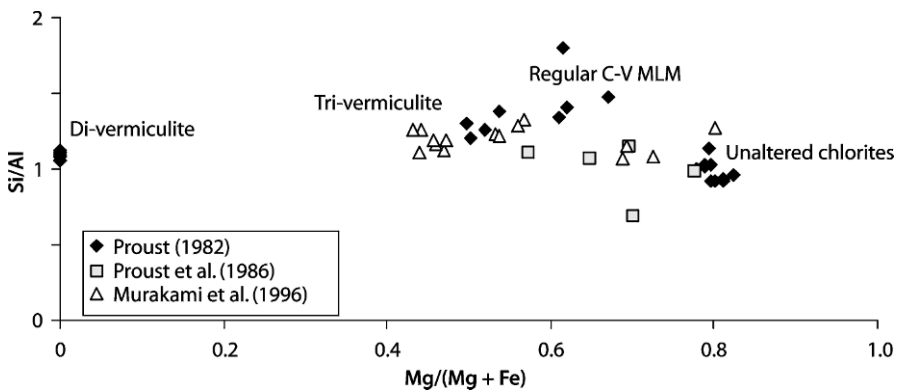


Fig. 4.22. General chemical trend of the chlorite vermiculitization process. C-V MLM: regular chlorite-vermiculite mixed layer mineral



**Table 4.2.** The major secondary mineral assemblages produced in chlorite microsystems during weathering and soil formation

Mg-chlorite	Fe-Mg chlorite	References
<b>Water/rock interaction</b>		
Regular vermiculite-chlorite mixed layer		Proust (1982)
1 Regular vermiculite-chlorite mixed layer 2 Di-vermiculite		Proust et al. (1986)
	Random vermiculite-chlorite mixed layer	Gilkes and Little (1972)
	1 Chlorite-vermiculite intergrade 2 Regular vermiculite-chlorite mixed layer 3 Tri-vermiculite 4 Kaolinite + goethite-hematite	Murakami et al. (1996)
Regular vermiculite-chlorite mixed layer		Banfield and Murakami (1998)
1 Regular vermiculite-chlorite mixed layer 2 Vermiculite 3 Vermiculite + goethite		Aspandiar and Eggleton (2002a,b)
<b>Soil (C horizon)</b>		
Intergrade vermiculite + kaolinite		Bain (1977)
	Regular vermiculite-chlorite mixed layer Nontronite + kaolinite	Herbillon and Makumbi (1975)

(Proust et al. 1986). Then, chlorite destabilization gives either C-V MLMs and tri-vermiculite in nearly closed microsystems or directly a kaolinite-halloysite + Fe-oxyhydroxides mineral assemblage in more open ones. Aspandiar and Eggleton (2002a,b) clearly show how the secondary products depend on the degree of opening of the plasmic microsystems, i.e. the way they are connected to the large water passageways in the rock. As seen for mica alteration processes above, here again, the differences of chemical potentials are the driving forces which control the formation of the secondary products. For chlorite weathering, the chemical elements whose chemical potential are active are Si, Mg and Fe<sup>2+</sup>; Al and Fe<sup>3+</sup> ions behaving as inert components.

The original chlorite transforms into a new mineral whose composition is almost the same: the regular (or semi-regular) chlorite-vermiculite mixed layer mineral (C-V MLM) in the nearly closed microsystems. The C-V MLMs are sometimes called corrensite. However, in spite of similar XRD patterns, these MLMs are different from corrensite whose domain of stability (diagenetic or hydrothermal conditions) and crystal structure have been defined by Beaufort et al. (1997) and Meunier (2005). The C-V MLMs do not form by the growth of a 24 Å unit. Their “corrensite-like” structure

is due to the periodical conservation of the brucite sheet which is imposed by an energy minimization process (Banfield and Murakami 1998). Consequently, the C-V MLMs should be considered as an intermediate step during the vermiculitization process, the new phase being a trioctahedral vermiculite. The whole process involves the solid-state-transformation of the 2:1 units and a non-stoichiometric dissolution of the brucite sheets. The vermiculite layers which are interstratified in the C-V MLMs or which form coherent stacks are trioctahedral, Mg-rich and high-charge. During the early weathering stage, the observed decrease of  $\text{Fe}^{2+}$  is probably due to interlayer diffusion and transport by solution to more oxidizing microsites where Fe-oxyhydroxides precipitate. Concomitantly, exchangeable sites are formed in the interlayer region which are opened after the dissolution of the brucite sheet. Then,  $\text{H}_2\text{O}$  molecules forming the hydrated shell of the exchangeable  $\text{Mg}^{2+}$  or other cations enter in the interlayer region:  $\text{H}_2\text{O}$  increases while that of the OH group decreases.

As the oxidation of  $\text{Fe}^{2+}$  ions and the leaching of the  $\text{Mg}^{2+}$  progress, the vermiculite layers become increasingly dioctahedral. The dioctahedral vermiculite is  $\text{Fe}^{3+}$ -rich. The complete transition from tri- to di-vermiculite is observed in recrystallized zones inside the chlorite crystals. It is accompanied by the formation of kaolinite and Fe-oxyhydroxides. The tri- to di- transition results from a dissolution-crystallization process. We shall see further that the di-vermiculite becomes an Al-rich dioctahedral phase in the secondary plasmic microsystems in the saprolite (Proust 1982). Then aluminum polymers are fixed in the interlayer region giving an “intergrade” property to the di-vermiculite. This process is totally completed in the soil horizons (Bain 1977).

### ***K-Feldspar and Plagioclase Microsystems***

An abundant and contradictory literature has been devoted to the study of the alteration of alkali feldspars and plagioclases under natural and experimental conditions (see the review of Wilson 2004 and references therein). The contradictions between petrographic observations at the micro- and nano-scales of natural weathered feldspars and experimental alterations evokes a more general problem: to what extent do experiments reproduce natural phenomena? In the present case, most of the dissolution experiments concern isolated crystals which are chemically attacked on their entire outer surface by solutions of constant composition. In natural occurrences, the feldspar-solution interface area is much more limited because of the geometry of the connected rock porosity. The resulting regime of the solutions varies in space (microenvironment petrographical characteristics) as well as in time (seasonal alternance) according to the respective importance of capillary and gravity forces. In natural environments, all the microsystems are interconnected. In a granite for instance, the dissolution-recrystallization processes in the biotite microsystems influences the formation of the secondary phases in the K-feldspars: Mg and Fe ions are found in the feldspar secondary products. Summarizing, if experiments remain a pertinent approach for the study of the dissolution mechanisms, the rates and phases produced are not comparable with those of natural processes.

**The role of crystal defects on the dissolution rate.** Crystal defects distort the chemical bonds in the lattice. For each, the crystal presents a local excess of energy which favors the ponctual chemical attack by aqueous solutions. Etch pits form and develop

as negative crystals (Eggleton and Buseck 1980). The dissolution is controlled by the crystal microtexture during the early alteration stage, (Martin and Parsons 1995; Martin et al. 1998). Then, etch pits coalesce and form corrosion voids which are filled by a microporous material composed of fine feldspar debris and newly formed minerals, i.e. the primary plasma.

Among the numerous experimental studies which have been published on the alteration of K-feldspar, only a few concern the secondary products of the reaction. Most deal with the calculation of the dissolution rate. Analysing the results of these studies, Wilson (2004 and references therein) discussed the interdependence of crystalline defect density and dissolution rates in conditions far intermediate- and near-equilibrium. He concluded that conditions far from equilibrium are so aggressive that the K-feldspar is chemically attacked even on defect-free surfaces. On the contrary, in near-equilibrium conditions, there is no etch pit formation, the feldspar surfaces being dissolved by steps. At intermediate conditions, dissolution takes place primarily at emerging defects and steps. The dissolution rate is related to defect density. Despite their fundamental interest, alteration experiments at far and near-equilibrium conditions are not directly applicable to natural weathering processes because in most microsystems, the corrosion does not produce empty voids but a polyphased microcrystalline primary plasma (fine debris of the hosting K-feldspar mixed kaolinite, smectite, Al-rich vermiculite and Fe-oxyhydroxides). The solutions which impregnate the microporosity of this microcrystalline material are those which interact with the remains of the host K-feldspar crystal. Their composition is buffered by the newly formed phases. Therefore, natural alteration processes would be better reproduced by intermediate- than far or near-equilibrium experiments. Unfortunately, this pure chemical point of view is not totally realistic. Indeed, the secondary products not only buffer the solutions but they also reduce the accessible surface of the primary crystals. In natural conditions, this physical effect becomes quickly dominant and controls the weathering rate.

**The amorphous or protocrystalline material problem.** Wilson (2004) summarized clearly the long (and still active) debate on the formation of a more or less amorphous leached layer at the very surface of the feldspar body. The amorphous layer (gel) is a by-product of incongruent dissolution. According to the way that the dissolution has been studied using chemical and physical methods, the results are apparently contradictory. However, it seems that an agreement can be found in the fact that, if any leached layer does exist, it cannot be more than a few nanometer thick. The classical nano-petrological studies are most often incomplete. Indeed, to be a “petrological object”, an amorphous or protocrystalline material must be observed in its context using transmission electron microscope observations. The absence of long range crystalline organization must be confirmed by selected area electron diffraction (SAED). Contrary to any crystal even in a highly disordered state, SAED applied to an amorphous material does not give spots or rings. Only diffuse rings or arcs can be obtained.

Given these criteria, such proto-crystalline materials have been undoubtedly observed in altered K-feldspar and plagioclase (Banfield and Eggleton 1990). They were previously described using TEM observations but without SAED analyses (Eswaran and Bin 1978; Eggleton and Buseck 1980). In spite of the lack of spheroidal shapes and high amounts of Fe, the proto-crystalline material has an allophane composition be-

cause the Si/Al ratio varies from 1.3 to 2.0 (Banfield and Eggleton 1990). However, in spite of the fact that an amorphous or proto-crystalline material may form in certain circumstances, it cannot be considered as a necessary precursor of newly formed clay. Indeed, direct formation of halloysite has been documented by Sheets and Tettenhorst (1997) for instance. If not a precursor, then the amorphous material should be considered as a phase participating in the mineral assemblage produced by the solution-feldspar reaction at a given alteration stage. The classical concept of mineral reaction sequences from amorphous material to kaolinite or halloysite through 2:1 clay species must be reconsidered. Most often, the mineral assemblages produced during the early weathering steps are polyphased. This is coherent with thermodynamics of closed or partially open systems in which most of the chemical elements behave as inert components (Meunier and Velde 1986).

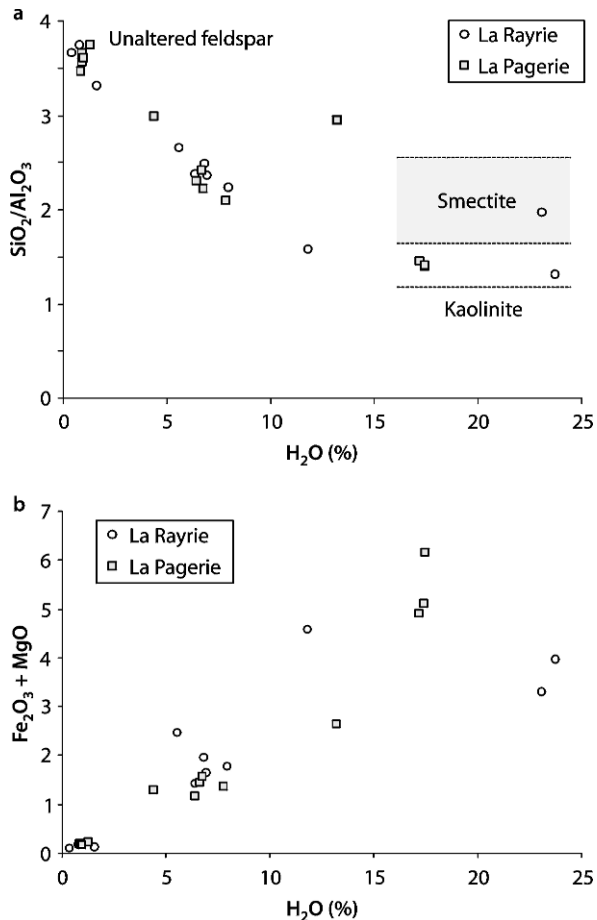
Summarizing, the presence of an amorphous or cryptocrystalline material (gel) has been frequently but not systematically observed in altered feldspars. Gel forms because of dissolution-precipitation kinetics. At the very surface of the dissolved crystals, the solutions are highly supersaturated with respect to different phases: smectite (Banfield and Eggleton 1990), kaolinite (Delvigne and Martin 1970), gibbsite (Delvigne 1998). Then, the nucleation rate is so important that the secondary crystals cannot grow. The gels are not precursors of the secondary minerals but rather a metastable state of these phases which are formed in the local chemical conditions imposed by the plasmic microsystem.

**The secondary minerals.** When corroded, the feldspars are replaced by the primary plasma. This microporous material is easily extractable by ultrasonic treatment. The coarsest fraction (5–10  $\mu\text{m}$ ) is mainly composed of feldspar debris while the less than 2  $\mu\text{m}$  portion concentrates the newly formed minerals, i.e. clays and oxyhydroxides (Fig. 4.23a). Concomitantly, the amounts of  $\text{Fe}_2\text{O}_3 + \text{MgO}$  increase from coarse to fine sized fractions (Fig. 4.23b). These elements, not contained in the parent feldspar in high amounts, with a concentration in the fine fraction indicate that they were provided by the altering solutions. This means that the microsystem in which the primary plasma formed (plasmic microsystem) was partially open.

According to the petrographical data published during the past three decades, it appears that the secondary minerals formed in the early weathering stage of feldspars are not always the same. Indeed, the following secondary assemblages have been described in K-feldspar and plagioclase alteration depending on the local physicochemical conditions imposed by climate, water circulation, topography or amount of microfractures (Table 4.3): (1) kaolinite-halloysite, (2) kaolinite + smectite, (3) kaolinite-halloysite + gibbsite. Feldspars do not always alter through the continuous sequence: gel  $\rightarrow$  smectite  $\rightarrow$  kaolinite-halloysite  $\rightarrow$  gibbsite. Data presented in Table 4.4 show that, whatever the secondary minerals formed, the chemical activity of silica and alkalis decreases. Thus, a question arises: why do the plasmic microsystems developed inside K-feldspar or plagioclase produce different clay mineral assemblages during the early stages of weathering?

The degree of opening of the microsystems under consideration varies according to the local geological situation. The major factor of variation is the physical state of the solutions which interact with the rock. The relative importance of pressure (gravity) and capillary forces respectively changes with topography, location of the water

**Fig. 4.23.** Composition of the primary plasma formed in K-feldspars (data from Meunier 1977); **a** a mixture of fine feldspar debris with newly formed clays (kaolinite + smectite); **b** the increasing amounts of  $\text{Fe}_2\text{O}_3 + \text{MgO}$  with  $\text{H}_2\text{O}$  % indicate that the alteration microsystem is partially open



table, density of the fracturation and climate. In other words, for a given rock type (granite for example), the difference of chemical potentials inside K-feldspar plasmic microsystems formed in the early weathering stage may not be identical in all the alteration profiles. The solution renewal rate in the largest passageways which are connected with the plasmic microsystems varies (see Sect. 2.2.1 and Fig. 2.13). If continuously diluted, the fluids in the large passageways behave as a permanent sink for the dissolved components and particularly for alkalis and silica. Thus, the chemical conditions imposed in the microsystem “jump” directly from that of the feldspar stability field to that of kaolinite or gibbsite without any intermediate stage in the illite or smectite fields (Fig. 4.24). On the contrary, if the renewing rate of the solutions in the largest passageways is slow, the differences are lowered. K-feldspar is transformed into illite or smectite and plagioclase into smectite.

How can one evaluate the degree of opening of the microsystem? This is of course a difficult task since direct measurement of the solution composition is not available. However, some indirect indications may be deduced from the amounts of some

**Table 4.3.** Petrographical data showing how secondary minerals have been formed in primary plasmic microsystems replacing K-feldspars and plagioclases during weathering

K-feldspar	Plagioclase	References
Gibbsite	Gel + kaolinite	Delvigne and Martin (1970) Lodding (1972)
	Gibbsite	Seddoh and Pedro (1975)
Smectite + kaolinite	Kaolinite	Meunier (1977)
	Kaolinite + smectite	
Allophane-like + halloysite + kaolinite	Beidellite + HIS	Proust and Velde (1978)
	Allophane-like + halloysite + kaolinite	Eswaran and Bin (1978)
Amorphous gel + 2:1 clay		Eggleton and Buseck (1980)
Halloysite + kaolinite + gibbsite	Halloysite + kaolinite + gibbsite	Anand et al. (1985)
Gibbsite + allophane Dissolution void + gel Kaolinite + halloysite Smectite		Okumura (1988)
Smectite + halloysite + protocrystalline material	Smectite + halloysite + protocrystalline material	Banfield and Eggleton (1990)
Smectite	Smectite	Banfield et al. (1991)
Halloysite	Halloysite	Sheets and Tettenhorst (1997)
Gibbsite	Gibbsite	Merino et al. (1993)
	Gibbsitic gel + gibbsite	Delvigne (1998)

allochthonous chemical components. Let us take an example: the step by step microprobe analyses of Delvigne and Martin (1970) of gel-bearing plagioclase alteration. They show that the amount of  $\text{Fe}_2\text{O}_3$  increases from <0.2% up to 8% in the unaltered plagioclase and the microcrystalline or amorphous material formed in the plasmic microsystems respectively. It is remarkable that the less  $\text{SiO}_2$  depleted areas are also the richest in Fe (Fig. 4.25). The composition points fit on the kaolinite-Fe oxyhydroxide mixing line indicating that the two mineral phases are the only ones produced by the alteration reaction: kaolinite deriving from plagioclase and Fe-oxyhydroxides being formed by precipitation from the solution. This suggests first that the composition of the altering solution is partly controlled by the mineral reactions operating outside the feldspar plasmic microsystem (origin of the Fe ions) and second that the gel (or cryptocrystalline material) is not an intermediate phase because it has the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of kaolinite. Consequently, the silica potential difference has been maintained at the plagioclase to kaolinite difference level in the solution through all the alteration process. Okumura (1988) detailed a complete alteration sequence of plagioclase crystals in a weathered gabbroic rock. He showed that according to the position of the plagioclase crystal inside the alteration profile, it is simply dissolved or transformed into

**Table 4.4.** Petrographical data showing how secondary minerals have been formed in primary plasmic microsystems replacing the pyroxenes during weathering

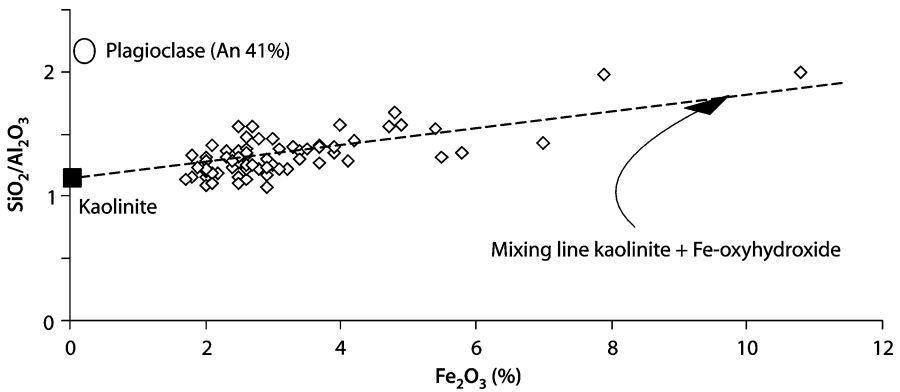
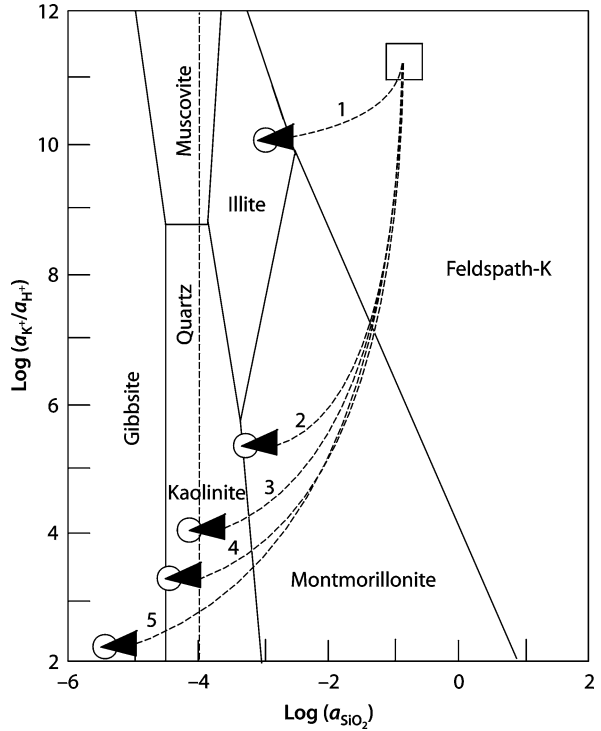
Orthopyroxene	Clinopyroxene	References
Vermiculite + Fe-oxyhydroxide	Vermiculite + Fe-oxyhydroxide	Basham (1974)
	Fe-montmorillonite	Eggleton (1975)
	Vermiculite + Fe-oxyhydroxide	Wackerman (1975)
Smectite + Fe-oxyhydroxide	Smectite + Fe-oxyhydroxide	Pion (1979)
Talc + tri-smectite		Eggleton and Boland (1982)
1 Gel		Nahon et al. (1982)
2 Fe-talc + saponite + nontronite		
3 Fe-oxyhydroxides		
1 Fe-Smectite + Fe-oxyhydroxide	1 Fe-Smectite + Fe-oxyhydroxide	Delvigne (1983)
2 Kaolinite + Fe-oxyhydroxide	2 Kaolinite + Fe-oxyhydroxide	
3 Fe-oxyhydroxide	3 Fe-oxyhydroxide	
1 Talc + saponite		Fontanaud and Meunier (1983)
2 Nontronite + gel		
1 Gel	1 Gel	Colin et al. (1985)
2 Ni-talc + Ni-saponite	2 Ni-talc + Ni-saponite	
3 Ni-stevensite (pimelite) + Ni-saponite	3 Ni-stevensite (pimelite) + Ni-saponite	
Nontronite	Saponite	Banfield et al. (1991)
Hematite		Merino et al. (1993)

gibbsite + allophane, kaolinite + halloysite or smectite. It should be observed that gibbsite + allophane which are classically considered as the ultimate alteration products are formed here in the initial stages of alteration.

### *Amphibole Microsystems*

**Nearly closed plasmic microsystems.** Trioctahedral smectites are systematically found as earliest alteration products along crystal defects or inside microfractures whatever the composition of the parent amphibole: hornblende, glaucophane, actinote (Proust 1983) or anthophyllite, gedrite (Banfield and Barker 1994). In all cases, the connected voids are narrow and form a highly tortuous network in the rock (nearly closed microsystems). The primary plasma (trioctahedral smectite + Fe-oxyhydroxides + amphibole debris) fills up these tortuous zones. The amphibole dissolution surfaces exhibit a sawtooth morphology (Fig. 4.26a). According to Banfield and Barker (1994), the chemical composition of the trioctahedral smectites is strongly dependent on that of the hosting amphibole crystal. In spite of large losses of Mg, Fe, Si and Al from the reaction sites, the 2:1 layers are directly inherited from the polymerized silica chains of the amphibole (so-called I-beams). The authors concluded that two 2:1 smectite layers are formed for

**Fig. 4.24.** Schematical representation of the chemical conditions prevailing in plasmic microsystems formed inside K-feldspar crystals in a granite during the early stage of weathering. The degree of opening of the microsystems increases from 1 (contact microsystem, almost closed) to 5 (plasmic microsystems in tropical countries)

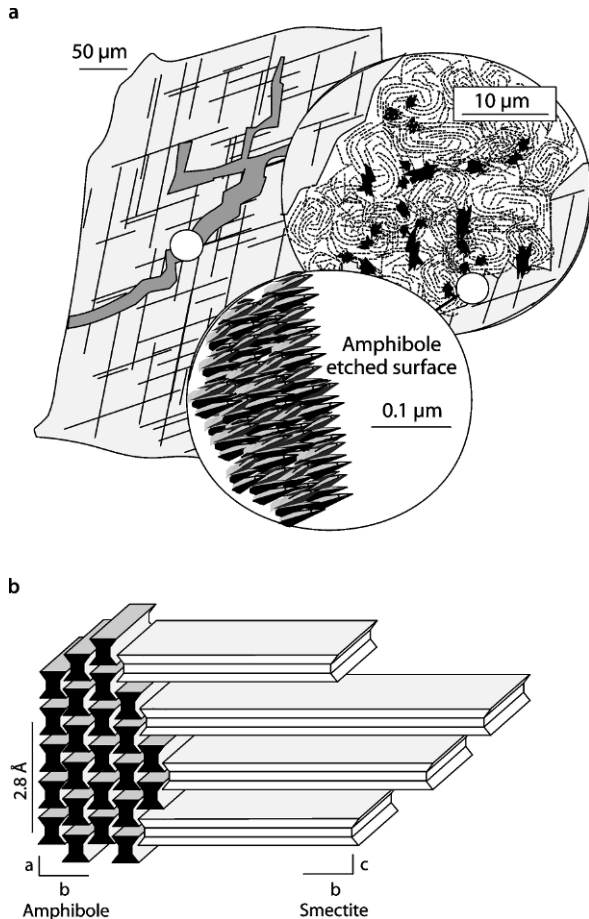


**Fig. 4.25.** Composition of the gel (or cryptocrystalline material) formed in plagioclase plasmic microsystems (data from Delvigne and Martin 1970)

3 I-beams (Fig. 4.26b). Such a chemical dependence has been observed in different amphibolite weathering profiles (Proust 1976, 1985). The early secondary products of hornblende (Fig. 4.27a), glaucophane (Fig. 4.27b) and actinolite (Fig. 4.27c) have different crystallochemical properties. Even if hornblende and actinolite are Ca and Mg



**Fig. 4.26.** Simplified representation of amphibole alteration; **a** the primary plasma is formed along the tortuous connected porosity within the amphibole crystal body; it is composed of trioctahedral smectite + Fe-oxyhydroxides + tiny amphibole debris; the dissolution amphibole surfaces are sawtooth shaped; **b** the 2:1 smectite layers are formed from the polymerized silica chains (I-beams) of amphibole during the early weathering stage (after Banfield and Barker 1994)



rich amphiboles, their secondary products are different: saponite + trioctahedral vermiculite and talc + hectorite-like smectite respectively. Talc and hectorite are characterized by the lack of Al for Si substitutions in the tetrahedral layers. They plot near the actinolite composition (Fig. 4.27c). However, it seems that such genetic chemical similarities between the hosting crystal and its secondary products are observed only in the most closed microsystems, i.e. inside nanometer sized microfractures. Banfield and Barker (1994) showed that, even at these early weathering stages, small amphibole debris are detached from the crystal body and are scattered inside in the clay matrix.

The smectites formed inside micrometer sized microfractures are also trioctahedral but their composition is different. They are all saponites (tetrahedral charge) and the chemical characteristics of the 2:1 layer are more or less similar whatever the composition of the parent amphibole (see the gray areas in Fig. 4.27). This shows that the primary plasmic microsystems formed in micrometer sized fractures are partly open even if no void is observed under the optical microscope. The secondary products fill up the microfracture volume. The microfracture walls are corroded giving the typical

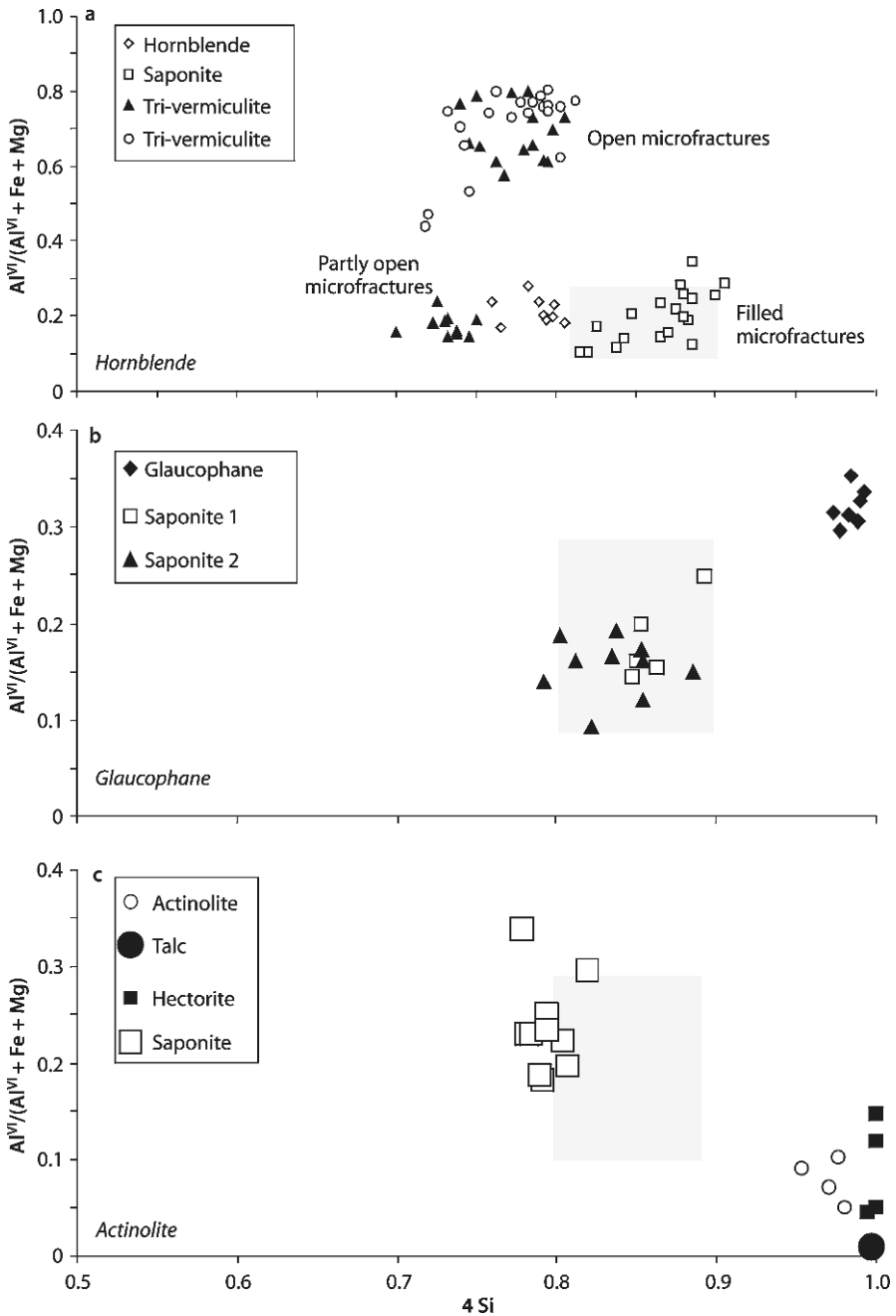


Fig. 4.27. Microprobe analyses of different amphiboles and their secondary products in nearly closed microsystems (data from Proust 1983); **a** hornblende in an orthoamphibolite from Limousin, France; **b,c** glaucophane and actinolite in a glaucophanite from the island of Groix, France. The *gray areas* represent the common composition field for saponites

saw tooth surfaces which result from the coalescence of etch pits. These features argue for a congruent dissolution of the amphibole.

When more directly connected to larger water passageways (partially open microfractures), the plasmic microsystems inside the amphiboles do not produce saponites anymore but tri-vermiculites (Proust 1983). The main difference is the amount of Al for Si substitutions in the tetrahedral sheets. It is highly probable that part of the  $\text{Al}^{3+}$  ions consumed in the vermiculite crystallization comes from the neighboring altered plagioclases.

**Partly open and open plasmic microsystems.** Most of the Al-rich clay minerals formed from altered amphiboles have been observed in the primary plasmic microsystems close to totally open microfractures inside the saprock or the saprolite. Here, the trioctahedral phases are no longer stable. Consequently, not only the trioctahedral clays cannot form but, if previously existing, they are dissolved. They are replaced by Al- $\text{Fe}^{3+}$  dioctahedral vermiculite or beidellite (Fig. 4.27a). A direct transformation of hornblende to a halloysite-kaolinite + Fe-oxyhydroxide mineral assemblage has been observed in the well drained saprolites developed from meta-dolerite or amphibolite rocks (Anand and Gilkes 1984; Velbel 1989). In those cases, the amphibole primary plasmic microsystems are more directly connected to large water passageways (open microsystems) than those described above.

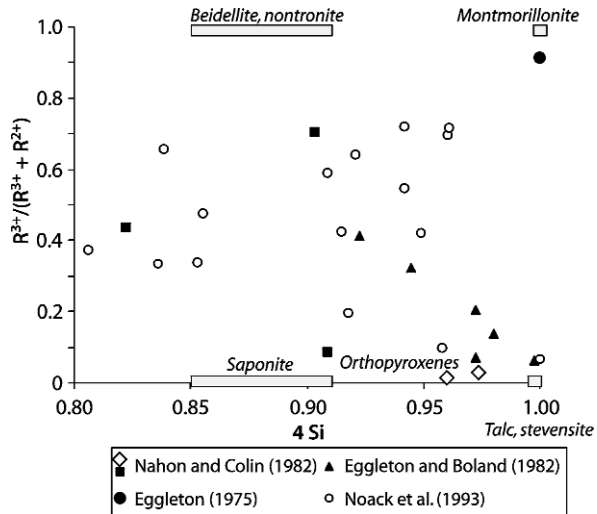
The dissolution of the amphibole crystals is obviously congruent in the open microsystems. Scanning microscope observations confirm the congruent dissolution because the amphibole surfaces are constantly sawtooth shaped. This particular habit results from the side-by-side coalescence of etch pits, each originating from a chemical attack on a crystal defect (Berner et al. 1980; Berner and Schott 1982). In the most open microsystems, some of the dissolved components are totally (Mg) or partially (Si) leached out. The less mobile ions (Al and Fe) oversaturate the resident solution with respect to kaolinite, gibbsite and Fe-oxyhydroxides (Velbel 1989).

### **Pyroxene Microsystems**

Numerous papers describe the secondary minerals which form inside the microfractures of pyroxene crystals during the so-called *early weathering* stages. Among them, those presenting micro- and nano-petrographical data (Table 4.4) show that these secondary minerals can be quite different: vermiculite, saponite, nontronite, talc, kaolinite or hematite. However, all have been formed directly and exhibit interfaces with the parent orthopyroxene (OPX) or clinopyroxene (CPX). This means that the most "evolved" secondary products (hematite) may be formed concomitantly with the less evolved ones (talc or smectite). As for all the other primary minerals described above, the large variety of secondary minerals is due to the way that the primary plasmic microsystems in which they form were connected to the large water avenues crosscutting the weathered rocks (Noack et al. 1993).

The crystallochemical characteristics of the smectites derived from pyroxenes vary from the tri- to the dioctahedral end-members (Fig. 4.28). Nahon and Colin (1982) observed that both species coexist inside minute aggregates in the samples they studied. However, when the pyroxene is totally replaced (pseudomorphs), the smectite is

**Fig. 4.28.** Variability of the chemical composition of the smectites formed in the primary plasmic microsystems within pyroxenes

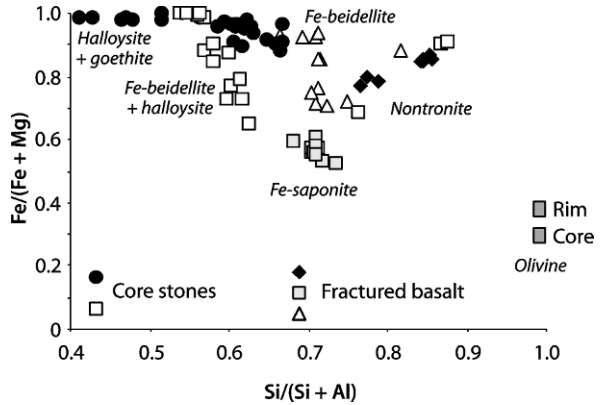


dioctahedral. If aluminum is lacking in the microsystem, the smectite is Fe-rich (Fe-montmorillonite rather than nontronite) as was shown for weathered skarn hedenbergites (Eggleton 1975). The compositional variability of the 2:1 layers is induced by the crystallization process. When formed by topotactic growth (see Fig. 1.38), the composition is largely inherited from that of the pyroxene I-beams. On the contrary, when forming honeycombed structures on the walls of dissolution pores, the 2:1 layers incorporate more Al and Fe<sup>3+</sup> ions in their structure. The smectites tend to be more dioctahedral.

### Olivine Microsystems

**Microsystems in the weathering profile.** The replacement of olivine crystals by secondary products has been classically considered to result from the following sequence of mineral reactions: olivine → trioctahedral Mg-smectites → beidellite-nontronite → halloysite + Fe-oxyhydroxydes (Wilson 2004). In fact, all the olivine crystals in a given sample of altered mafic or ultramafic rocks are not in the same state of recrystallization. Ildefonse (1987) described a basalt weathering profile exhibiting “unaltered” fractured parts and core rock elements (see Fig. 4.3). He showed that the compositions of the secondary products are highly variable. However, when plotted in the Fe/(Fe + Mg) versus Si/(Si + Al) coordinates (Fig. 4.29), these compositions determine a chemical trend: Fe and Al are concomitantly enriched while Mg and Si are totally or partially leached out respectively. It is remarkable that the compositions of the secondary olivine products formed in the fractured basalt are more variable than their equivalent in the core rock. This demonstrates that the first are controlled by local conditions (nearly closed microsystems) while the second are controlled by the solutions which flow through the connected porosity (nearly open microsystems). The number of olivine crystals which are totally replaced by goethite ±halloysite increases with increasing alteration intensity.

**Fig. 4.29.** Olivine: Chemical composition of the secondary products formed from olivine in a basalt weathering profile at Belbex, Massif Central, France (data from Ildefonse 1987). The mineral species are indicated for the fractured basalt and the core-stones



**Alteration process at the microsystem scale.** Olivine crystals have been shown to weather preferentially along “pseudo-layers” which alternate with more resistant blades (Smith et al. 1987; Banfield et al. 1990). The resistant blades are composed of laihunite, a mineral which resembles a distorted  $Fe^{3+}$ -bearing olivine. Excepting serpentine, most of the other secondary phyllosilicates formed by deuteritic or hydrothermal alterations of olivine are similar to those crystallizing through weathering processes, i.e. saponite, nontronite and talc. Consequently, a simple mineralogical analysis cannot decisively determine their origin (Wilson 2004). Unfortunately, at least for the early weathering stages, the petrographic features are not more indicative. This is why, whatever their origin, the secondary products of olivine have been assigned to the same term: iddingsite or bowlingite.

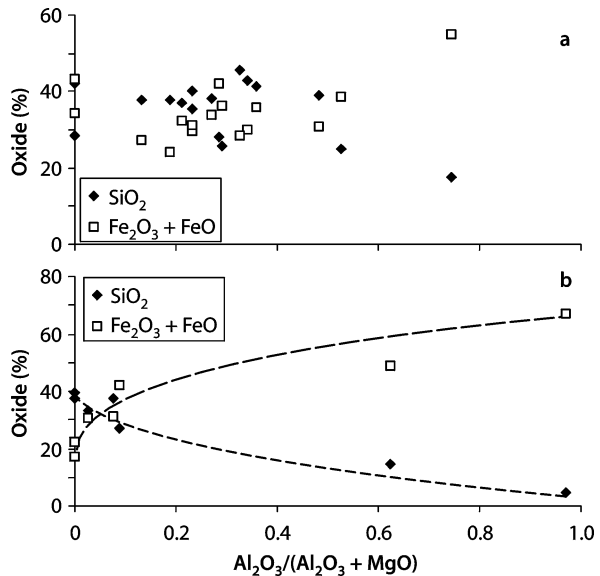
Iddingsite and bowlingite form in oxidizing and non-oxidizing conditions respectively. Both are mixtures of poorly crystallized minerals. This explains why their chemical composition is so variable (Table 4.5). However, they have a point in common: their composition is always Mg-depleted and Al-enriched compared to that of the parent olivine. Iddingsite or bowlingite are formed in plasmic microsystems which are partially open. Al ions and water molecules are provided from the solutions while Mg ions originating from the dissolution of olivine are progressively leached out. Al ions come from the plagioclase primary plasmic microsystems which are connected to the olivine ones. Ultramafic rocks do not contain plagioclase. Consequently, no Al ions are furnished to the olivine microsystem leading to the formation of talc in place of smectites (Noack and Duplay 1983).

As olivine does not contain aluminum, the  $Al_2O_3/(Al_2O_3 + MgO)$  ratio can be used as an indicator of the alteration progress. Theoretically, it may vary from 0 to 1 for unaltered to totally altered stages respectively. The  $SiO_2$  and  $Fe_2O_3 + FeO$  amounts remain roughly constant whatever the alteration intensity (Fig. 4.30a). New phases are produced by a mineral reaction which proceeds at constant silica and iron concentrations. In spite of their cryptocrystalline state, these secondary phases have been identified as Fe-Mg smectites (nontronite or Fe-saponite) associated with fine-grained goethite. Both species grow (epitaxy or topotaxy) on the dissolution surfaces of olivine. Those phases can be formed either in hydrothermal or weathering conditions until the microsystem remains partially open. In other words, the controlling parameter is

**Table 4.5.** Chemical composition of iddingsite. *1 to 5:* Ross and Shannon (1926), *6 to 8:* Gay and Lemaitre (1961), *9:* Sun (1957), *10:* Smith (1959), *11:* Tomkeiff (1934), *12:* Delvigne et al. (1979), *13:* Wilshire (1958), *14 to 15:* Walters and Ineson (1983), *16:* Eggleton (1984)

N°	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
1	36.83	1.78	0.24	32.49	0	6.64	2.79	0	0
2	42.12	0	0	34.16	0	6.4	1.72	0	0
3	40.28	3.16	0.12	29.76	0	10.36	3	0	0
4	35.6	3.6	0	31.24	0	11.92	1.64	0	0
5	38.94	4.62	0	29.78	0.96	4.96	2.26	0	0
6	37.9	5.6	0.7	20.7	3.3	24	3.6	0	0
7	25.59	6.53	0.61	31.44	4.64	15.83	1.3	0.31	0.28
8	17.52	8	0.42	55.09	0	2.73	1.29	0.18	0.31
9	28	4	0.64	42	0	10	1	0	0
10	24.77	14.77	0	34.09	4.5	13.27	0.73	0	0
11	38.1	2.53	0.08	33.75	0.2	6.87	2.23	0	0
12	28.3	0	0	43.3	0	6.6	0.5	0.1	0.1
13	41.2	3.81	0.14	35.42	0.38	6.85	2.35	0.12	0.1
14	42.8	4.1	0	0	29.9	7.9	2	0.1	0
15	45.7	4	0	0	28.3	8.3	1.9	0.1	0
16	37.96	3.28	0	0	27.41	21.29	0.93	0	0

**Fig. 4.30.** Chemical composition of iddingsite; **a** compositions from Ross and Shannon (1926), Gay and Lemaitre (1961), Sun (1957), Smith (1959), Tomkeiff (1934), Delvigne et al. (1979), Wilshire (1958), Walters and Ineson (1983), Eggleton (1984); **b** iddingsite formation (data from Smith et al. 1987)



not temperature but the local difference of magnesium chemical potential. According to the duration of the process, the olivine crystals may be partially or totally replaced by the secondary Fe-Mg phyllosilicates.

With increasing alteration intensity, the amplitude of the difference of the Mg chemical potential at a given place increases with time (amplitude: difference of Mg activity between the very surface of olivine and the pore solution). Consequently, the Fe-Mg secondary phyllosilicates previously formed in nearly closed microsystem conditions are no longer stable. They dissolve. The secondary porosity increases and a new mineral assemblage is formed: halloysite and goethite (Fig. 4.30b). Silica and magnesium are leached out. It seems paradoxical that an Al-rich phase is the remaining product of a parent crystal which originally did not contain aluminum. In fact, halloysite is forming in place of the smectites. Its crystal growth is undoubtedly fed by the dissolution of the other mineral components of the rock in adjacent microsystems (volcanic glass and feldspars). In these high amplitude conditions, the olivine remnants are congruently dissolved. Summarizing, smectite, halloysite and goethite can be formed concomitantly during the early weathering stages explaining why the chemical composition of the iddingsite varies continuously from unaltered olivine to goethite (Fig. 4.30b). Smith et al. (1987) have shown that several if not all that mineral reactions may be observed in a single crystal of olivine according to the relative location of the dissolution surfaces and the largest fractures (Fig. 4.31).

### *Serpentine Microsystems*

Serpentinite rocks are characterized by the mesh microstructure where fine grained chrysotile needles and antigorite plates are intimately mixed. This typical microstructure is conserved in the early weathering stages even if the parent minerals are totally replaced by secondary ones. Two different alteration mineral assemblages have been observed:

1. saponite  $\pm$  talc + Fe-oxyhydroxydes in the thin saprock layer on a serpentinized lherzolite in Pyrénées, France (Fontanaud 1982),
2. Fe-rich dioctahedral smectites (Fe-montmorillonite or nontronite) + Fe-oxyhydroxides in a thick reddish saprock on serpentinite rocks in Australia (Gaudin et al. 2004) or Limousin, France (Caillaud et al. 2004).

The presence of supergene talc in weathered serpentine minerals has been discussed by Noack and Duplay (1983). They found that supergene talc is characterized by a tetrahedral charge due to Fe<sup>3+</sup> for Si substitutions. The charge deficit is compensated by the positive charge of the octahedral sheet. The amount of Fe<sup>3+</sup> is higher in supergene than hypogene talcs.

The microsystems which first form inside the thin altered bedrock zone of the lherzolite are nearly closed because the rock is massive and the original porosity limited to small-size voids. On the contrary, the microsystems are partially open in the thick reddish saprocks which develop in well drained topographical sites (Limousin) or in lateritic conditions (Australia). The compositions of the Mg- and Fe-rich smectites do not fit exactly with the corresponding end-members. They are scattered in a broad domain (Fig. 4.32). In most cases, their octahedral sheet exhibits clusters of di- and





the three profiles all give Fe-rich smectites. However, these smectites are more nontronitic (tetrahedral charge) than those formed in the primary plasmic microsystems (Fe-montmorillonite). This is due to the lower silica chemical activity in open microsystems.

### *Volcanic Glass Microsystems*

Most studies relative to the weathering of volcanic glass concern soils developed on ash deposits because of their high agricultural potential. These soft rocks are frequently but not systematically formed from silica-rich magmas during the eruptions of rhyolitic, dacitic or andesitic volcanoes. They are more rarely formed from basaltic magmas (Hawaii). The ash deposits are rapidly settled by plants and altered because of their high porosity and the reactivity of glass with respect to meteoric water or soil solutions. The main secondary minerals produced by the destabilization of the glass are imogolite/allophane and halloysite (Wada 1989). This will be considered in later chapters.

We will focus here on the alteration processes of glassy microzones because they react as a mineral component inside massive rocks. They are encountered in basalts which are the most widespread volcanic rocks over the world. Basalts may cover large areas forming geological provinces such as the Parana and Deccan traps in Brazil and India respectively. The most detailed description of the alteration features of the glassy zones in basalts is found in Ildefonse (1987). The weathering profile at Belbex (Massif Central, France) is composed of a fractured black basalt overlain by a reddish saprock forming core stones (see Fig. 4.3). Unaltered glassy zones are isotropic, brownish and 80 to 200  $\mu\text{m}$  wide. They become progressively yellow but remain isotropic. In the most altered outer zones of the core stones, they form yellow but birefringent areas. As indicated by the poor definition of XRD patterns, the secondary products formed in the glassy zone are microcrystalline. However, halloysite was identified with traces of an expandable phase in the birefringent yellow glassy zones. This is confirmed by the chemical composition of the altered glass which varies toward the halloysite pole (Fig. 4.33a). Obviously, each glassy zone forms an open microsystem in which Si, Mg and alkali ions are leached out while Al is concentrated. Smectite can be formed as showed by Banfield et al. (1991), but it is a transitory step before the crystallization of halloysite.

The basalt rocks contain vesicles which were formed by magma degassing during the cooling stage. All the vesicles in the Belbex profile are rimed by green to colorless microcrystalline products whose composition approaches that of celadonite (proto-celadonite). Compared to proto-celadonite, the weathered products are silica-poor and Al-enriched. Their compositions converge progressively toward the halloysite pole in the core-stones (Fig. 4.33b).

### *Summary*

Alteration proceeds through microsystems. The most important property of the early rock alteration stage is HETEROGENITY: heterogeneity between and within crystals. All microsystems are open but with different degree of opening. The more open they are, the more the solutions influence the phased formed. Each microsystem transforms the parent crystals into a porous fine grained material: *the primary plasma*.

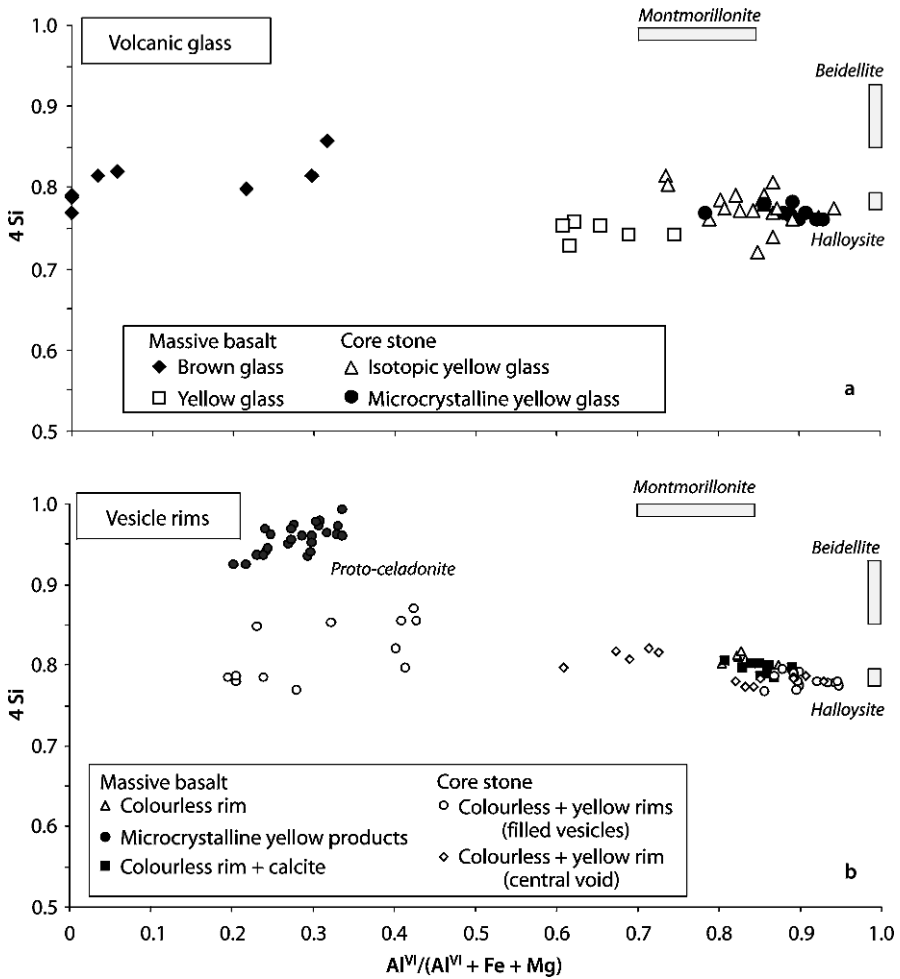


Fig. 4.33. Chemical composition of the alteration products from volcanic glass in a weathered basalt at Belbex, Massif Central, France (data from Ildefonse 1987); a alteration products of massive glassy zones; b alteration products of the vesicle rims. The halloysite end-member has been calculated on a  $\text{Si}_4\text{O}_{10}$  basis

### 4.3 Mineral Reactions in the Secondary Plasmic Microsystems

The earliest weathering reactions are controlled by the dissolution of the primary minerals when in contact with unsaturated solutions. Different secondary mineral assemblages are formed while the porosity increases. Weathering reactions occur in a mosaic of microsystems. At this stage, the initial structure of the parent rock is conserved (saprock). Each primary mineral is altered separately even if foreign elements are provided by the solutions (connection between different primary plasmic microsystems). The composition of the mineral assemblages is controlled by the local

chemical potential differences. Then, with increasing alteration, the rock structure collapses giving a new material whose macroscopic aspect is intermediate between the original magmatic rock and that of an unconsolidated sediment (saprolite). The physical mixing of primary mineral debris with their secondary alteration products changes the chemical conditions and induces the formation of a new type of microsystems: *the secondary plasmic microsystems*.

#### 4.3.1

##### Petrography of the Secondary Plasmic Microsystems

###### *Primary and Secondary Plasmic Microsystem: The Chemical and Mineralogical Differences*

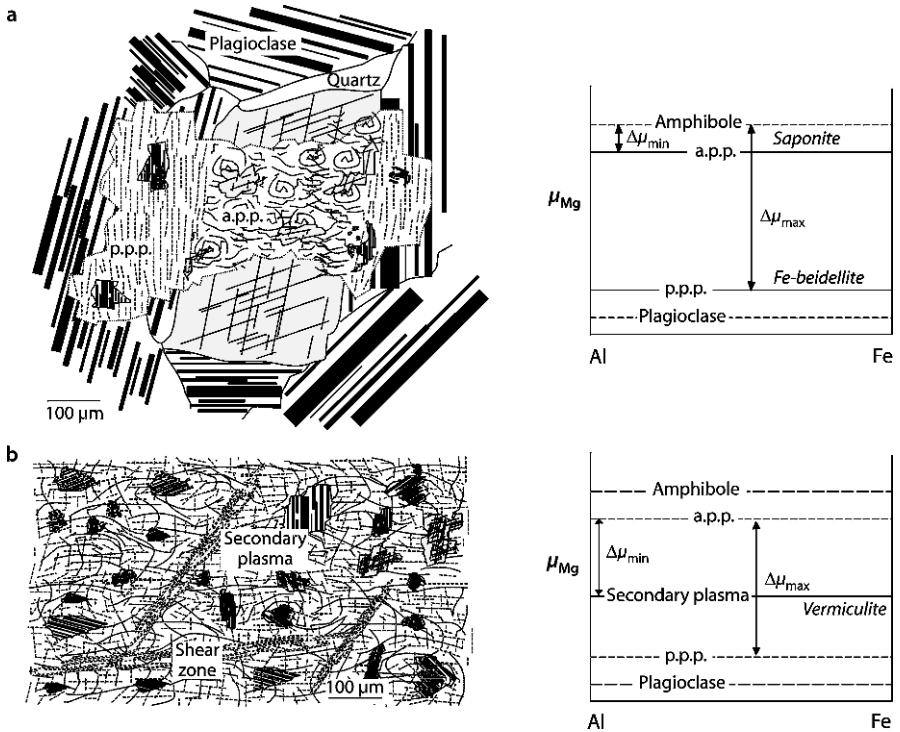
The original rock fabric is conserved as long as the volume of the altered zones in each primary crystal does not reach a yield value beyond which the mechanical resistance of the rock abruptly collapses. A new fine-grained porous material forms locally in one place of parent crystals, i.e. the secondary plasma. The secondary plasma is observed first as isolated patches inside the saprock (volume conservative alteration). Conversely, remains of saprock can be found in saprolite even in soil. Whatever their size, the secondary plasma zones are always enriched in clays compared to primary ones. The increase of clay fraction changes drastically the macroscopic aspect of the saprolite at the scale of the alteration profile. This effect is particularly important for mafic or ultramafic rocks (gabbro, amphibolite or serpentinite) which give clay-rich saprolites. A typical prismatic zone is formed due to the smectite expansion-retraction induced by the wetting-drying cycles. The main petrophysical characteristics of the primary and secondary plasma are presented in Table 4.6.

The different primary plasmas are formed during the internal destabilization of the rock parent minerals. Consequently, the mineral reactions occur in contrasted chemical conditions. Consider for instance the weathering of an amphibolite. The amphiboles are the unique sources of Mg ions. A low difference of Mg chemical potential is established between the dissolving amphibole surfaces and the secondary products in the primary plasmic microsystem ( $\Delta\mu_{\min}$ ). On the contrary, the difference is high with the neighboring plagioclase microsystem ( $\Delta\mu_{\max}$ ). This triggers the chemical diffusion of Mg ions from amphibole to plagioclase microsystems respectively. Consequently, the secondary clay minerals produced in the microsystems are different but their compositions are less contrasted than were the parent minerals. Saponite and Fe-beidellite crystallize in the place of amphibole and plagioclase respectively (Fig. 4.34a).

Summarizing, the mineral reactions which are activated in the primary plasmic microsystems partly reduce the chemical contrasts inside the parent rock. The controlling process is the chemical diffusion of Mg, Fe and Al ions toward plagioclase and amphibole primary plasmas respectively. The formation of the primary plasmic microsystems is the first step of a general process of homogeneization. The second step is triggered by the collapse of the rock microstructure. This happens in saprolitic zones. The chemical contrasts are reduced once more by the formation of the secondary plasmic microsystems. Then, a higher degree of homogeneization is attained for two reasons:

**Table 4.6.** Principal petrophysical characteristics of the primary and secondary plasmas in weathered rocks

	Primary plasma	Secondary plasma
Original rock structure	Conserved	Totally or locally destroyed
Porosity	Microfractures (intergranular joints, cleavages, ...) Parent crystal micropores	Microporosity (diffuse)
Mineral-solution interfaces	1 Primary mineral species (internal microsystem) 2 Primary mineral species (contact microsystem)	Several mineral species including primary mineral debris and their secondary products (clay minerals + oxyhydroxides)
Chemical composition of the newly formed mineral species	Derived from that of the parent primary mineral	Derived from that of a mixture of clays and parent mineral debris



**Fig. 4.34.** Schematic representation of the alteration petrographic features in a weathered amphibolite; **a** formation of the primary plasma inside plagioclases (*p.p.p.*) and amphibole (*a.p.p.*) in a structure conservative altered zone (saprocks); **b** formation of the secondary plasma and the shear zones in the saprolite

- the transformation of a coarse grained rock into a fine-grained one (fragmentation of parent crystals, formation of small-sized clay minerals),
- the physical mixing of the secondary products and the fine parent mineral debris.

Consider for instance the amphibolite saprolite. The new chemical conditions imposed by the mixing of saponite, Fe-beidellite and tiny debris of amphibole and plagioclase crystals induce the crystallization of new clay minerals whose composition is intermediate: vermiculite (Fig. 4.34b). The mixing process is engendered by the stress exerted by the swelling properties of the clay-rich new material which exhibits typical shear features. Physical forces (gravity and stress) contribute to the homogenization by mechanical reworking of the rock.

### *Mechanical Resistance of Altered Rock*

We saw that, whatever the chemical composition of the parent rock, the density decreases in the saprock (Figs. 4.6b and 4.8). Because of the conservation of the rock structure, the density decreases through increasing porosity. This is no longer valid when the initial rock structure is completely modified. The density decreases until a porosity threshold is attained beyond which a new rock structure is formed. The threshold is about 10% or 12–15% in gabbro and granite weathering profiles respectively. The volume proportions of primary plasma formed in place of parent crystals when the porosity threshold is attained vary from 40 to 50%. Obviously, at these values, the parent crystal framework of the rock is dramatically weakened and can no longer resist to the external forces. In natural environments, an uniaxial constraint is imposed by the weight of the rock itself. As soon as the porosity threshold is attained, the initial rock structure collapses producing a new material which is still porous but more fine-grained.

The resistance of a weathered granite to uniaxial constraint and the Young modulus are strongly lowered in the early stages of weathering (Baudracco et al. 1982). The decrease of the Young modulus indicates that the rock progressively changes from brittle to ductile material (Fig. 4.35). Such a physical state change induces the collapse of the parent rock structure and triggers downslope displacements by hill creep. Shear features appear at the boundary between the immobile and mobile bodies. Additionally, they form in smectite-rich saprolite by the drying-wetting cycles which induce local stress. Shear induces anisotropic properties in the newly structured material by preferential orientation of clay particles. These features are ordinarily thought to be pedological ones but, here, they are observed far below the soil level.

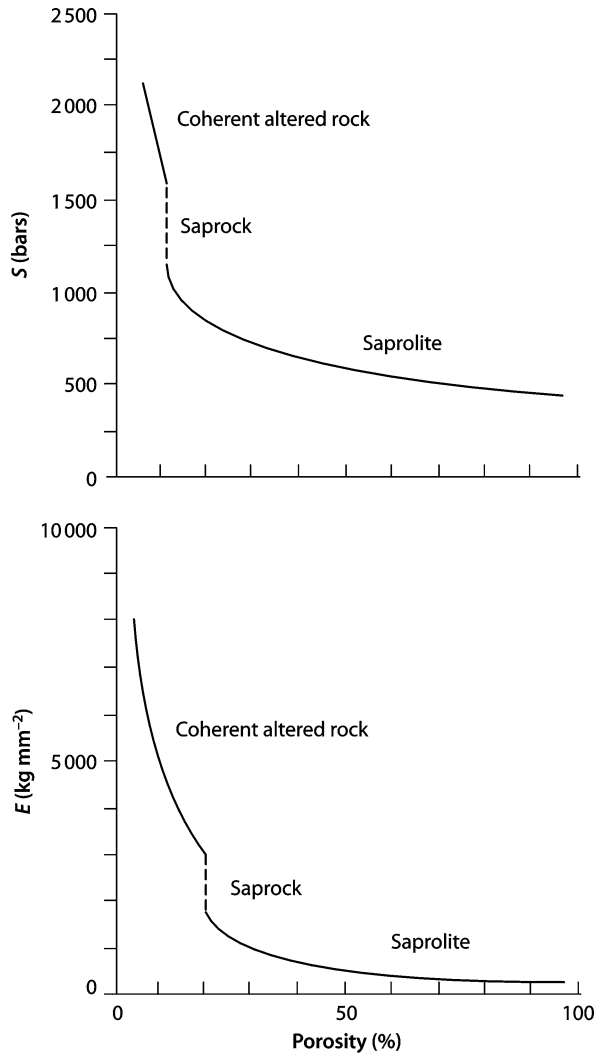
#### 4.3.2

#### Clays Forming in Secondary Plasmic Microsystems

##### *Illite in Granite Saprolite*

The secondary plasmic microsystems appear inside the newly structured zones (saprolitic) whatever their size. Indeed, small sized saprolitic zones can be observed in the saprock itself as scattered patches of a few millimeters in diameter. They, of

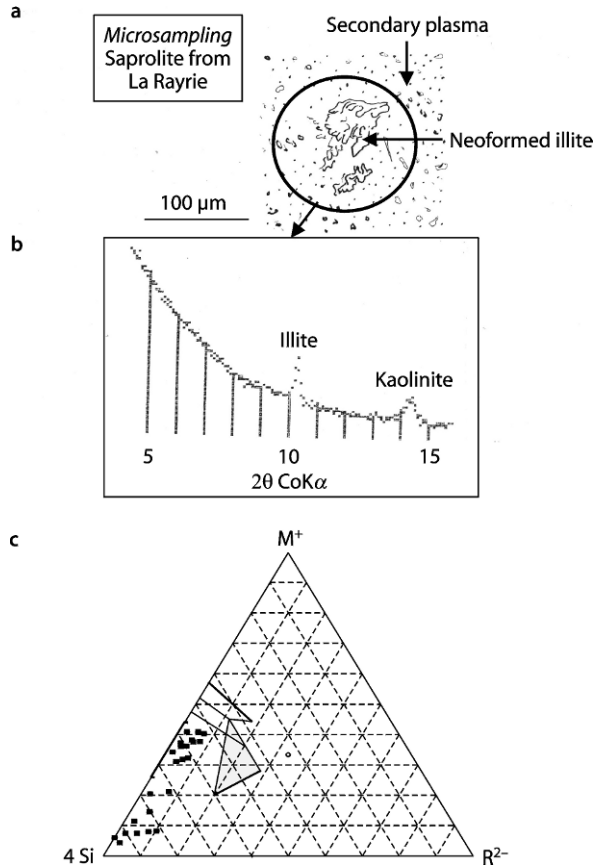
**Fig. 4.35.** Relation between physical properties and porosity of an altered granite from Sidobre, France (data from Baudracco et al. 1982); **a** variation of the uniaxial stress ( $S$ ); **b** variation of the Young modulus ( $E$ )



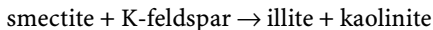
course, largely predominate in the saprolite. They are typically formed by a fine-grained plasma embedding debris of the most resistant parent minerals: quartz, orthoclase, white mica. From place to place, one can observe small incomplete spherulites or veil-shaped crystals (Fig. 4.36a). Using the micropicking technique (Beaufort 1987), it was shown that the fan-shaped minerals are composed of a mixture of illite and kaolinite (Fig. 4.36b,c). New mineral reactions have been activated in the secondary plasmic microsystems.

The local chemical conditions prevailing in the secondary plasma microsystems are obviously different from those which were established in the primary plasma ones

**Fig. 4.36.** Illite formed in granitic saprolites; **a** drawing from a micrograph of a secondary plasmic microsystem in a granitic saprolite from La Rayrie, France (from Dudoignon 1983); **b** X-ray diffraction pattern realized on the materials extracted by microsampling (*inside the circle of a*); **c** microprobe analyses of the veil-shaped crystals in different microsystems



which led to the internal destabilization of the parent minerals inside the saprock. The chemical conditions have changed because the higher porosity increases the fluid/rock ratio on one hand and the small size of the clays and the primary mineral debris increases the surface reactivity of the solids on the other hand. Under these new conditions, the orthoclase debris is dissolved creating locally high  $K^+$  chemical differences. A second generation of illite is formed in equilibrium with the dominating clay species which is kaolinite:



Microprobe analyses show that the illite formed in equilibrium with kaolinite is more Al-rich than that formed in the early mica-orthoclase contact microsystems (Fig. 4.37). Indeed, the secondary plasma no longer contains Mg-bearing primary minerals. They have been dissolved in the primary plasmic microsystems and most of the Mg ions have been leached out the rock before secondary plasmic microsystems form.

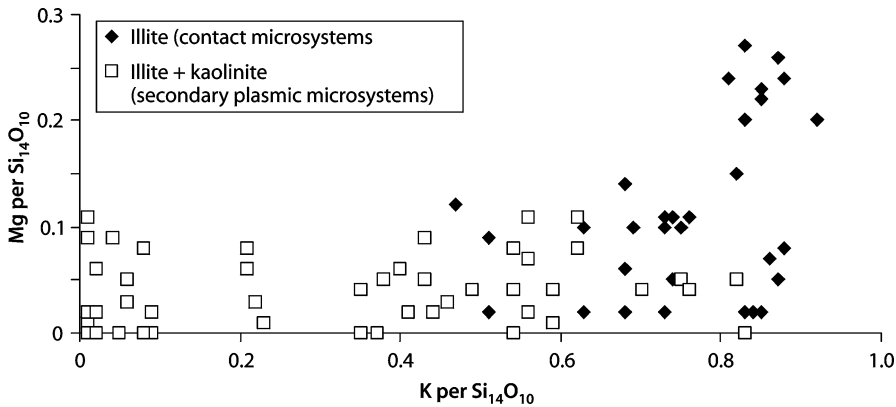


Fig. 4.37. Impact of the chemical conditions imposed by the primary and secondary plasmic microsystems respectively on the composition of illite in the La Rayrie granite weathering profile (data from Dudoignon 1983)

#### *Vermiculite in a Gabbro Saprolite*

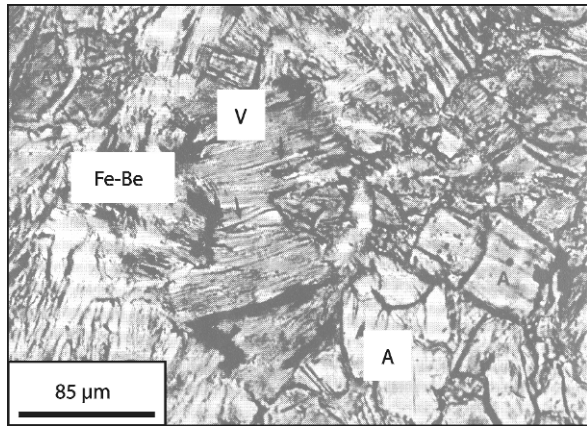
The saprolite of the gabbro weathering profile studied by Ildefonse (1980) is clay-rich (15–35%). It exhibits a prismatic structure which becomes polyhedral in the upper part (see Fig. 4.4). The transition to saprock underneath progressively forms a 20 cm thick irregular zone. The size and number of rock pieces in the saprolite decreases upwards. The dominating petrographical feature is the secondary plasma which is composed of detrital grains (mostly amphibole debris) embedded in a mixture of clay minerals and Fe-oxyhydroxides. Clay minerals and Fe-oxyhydroxides which were previously formed during the internal destabilization of plagioclase and hornblende crystals react in the secondary plasmic microsystems. The trioctahedral smectites have disappeared. The chemical composition of the dioctahedral minerals changes: it varies from that of Fe-Al beidellite to that of nontronite. Large phyllosilicate crystals (50 to 200  $\mu\text{m}$ ) are frequently observed in the vicinity of amphibole debris (Fig. 4.38). They exhibit perfectly planar (001) cleavages. They are pleochroic from yellow-orange (Ng) to colorless-pale yellow (Np). Their birefringence is high:  $1.57 < N < 1.67$  (third order reds and greens). Extinction in crossed nicols is parallel to the cleavage with a positive elongation. These crystals are nearly uniaxial and euhedral. XRD patterns are typical of vermiculite (Ildefonse et al. 1979):

- $-14.5 \text{ \AA}$  at 25 °C in the Mg- and Ca-saturated states respectively,
- irreversible collapse to  $10.2 \text{ \AA}$  in the K-saturated state.

The chemical compositions of the vermiculites formed in the prismatic zone are relatively homogeneous. Analysed after K-saturation in order to avoid artifacts due to amphibole contamination, they all exhibit a high negative tetrahedral charge:  $-0.75$  to  $-0.92$  per  $\text{Si}_4\text{O}_{10}$  (Table 4.7). This negative charge is partly compensated by a positive one originating in the octahedral sheet. The octahedral occupation is about 2.50.



**Fig. 4.38.** Vermiculite crystals formed in the secondary plasmic microsystems of a gabbro saprolite (from Ildefonse 1978). V: vermiculite; A: amphibole; Fe-Be: Fe-beidellite + Fe-oxyhydroxides



**Table 4.7.** Structural formulae per  $\text{Si}_4\text{O}_{10}$  of vermiculites after K-saturation and leucoxene (Ca-Ti) correction (from Ildefonse et al. 1979). *nd*: not determined

Vermiculites (gabbro)				
Si	3.15	3.13	3.08	3.15
Al <sup>IV</sup>	0.85	0.87	0.92	0.75
Al <sup>VI</sup>	0.63	0.55	0.50	0.69
Fe <sup>3+</sup>	0.63	0.69	0.62	0.64
Fe <sup>2+</sup>	nd	nd	0.10	nd
Mg	1.21	1.22	1.36	1.08
Mn	0.01	0.01	0.01	0.02
Ca	0.08	0.06	0.03	0.02
Na	0.08	0.06	0.06	0.09
K	0.38	0.43	0.47	0.40
Σoct	2.47	2.47	2.59	2.43
Oct. charge	+0.20	+0.18	+0.30	+0.19
Layer charge	-0.65	-0.69	-0.62	-0.56

Consequently, the number of octahedral vacancies is sufficiently high (0.50) to make the Hoffmann-Klemen test efficient. The  $d_{001}$  value irreversibly collapses to 9.81 Å after Li-saturation and 12 h heating to 300 °C. The interlayer region does not contain any “brucitic islands” as commonly observed in soils. The expansion with polar molecules and the stacking structure are similar to that of vermiculites formed by hydrothermal alteration of biotite in spite of the fact that they do not derive from a pre-existing phyllosilicate phase in the amphibolitized gabbro. These large sized vermiculite crystals are formed in response to a specific set of chemical conditions imposed in the secondary plasmic microsystems. These conditions are modified in the upper part of

the saprolite because the prismatic structure becomes polyhedral. There, the large vermiculite crystals are no longer stable. They transform into a nontronite-like smectite.

### *Nontronite and Mg-rich Gel in a Lherzolite Saprolite*

The weathered lherzolite profile studied by Fontanaud and Meunier (1983) presents a saprolite zone (see Fig. 4.5). The serpentinized olivine and pyroxene crystals are replaced inside the primary plasmic microsystems by microcrystalline talc and saponite. These mineral reactions are typical of the structure conservative alteration processes in the saprock. In their turn, the secondary products are destabilized in the secondary plasmic microsystems which form in the saprolite. They are replaced by an isotropic green gel and nontronite crystallites. The gel fills up cracks. Its chemical composition is close to that of chrysotile (Table 4.8). Large nontronite crystallites (30–50  $\mu\text{m}$ ) develop in areas limited by the microcracks filled up by the green gel. Their chemical composition constantly exhibits the following characteristics (Table 4.9):

- most of the substituted tetrahedral sites are occupied by  $\text{Fe}^{3+}$  ions rather than  $\text{Al}^{3+}$  ions,
- a part of the layer charge originates in the octahedral sheet (45% maximum),
- the layer charge is high (0.44 up to 0.83 per  $\text{Si}_4\text{O}_{10}$ ),
- Mg ions dominate in the interlayer zone.

**Table 4.8.** Chemical composition (per  $\text{Si}_4\text{O}_{10}$ ) of the nontronite platelets (20 to 50  $\mu\text{m}$  size) formed in the secondary plasmic microsystems of the prismatic level, lherzolite saprolite (from Fontanaud and Meunier 1983)

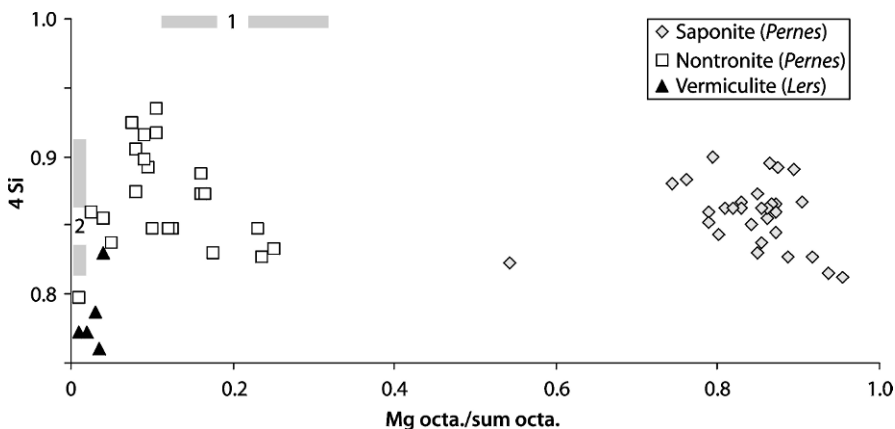
Nontronite (lherzolite)								
Si	Al <sup>IV</sup>	Fe <sup>3+IV</sup>	Fe <sup>3+VI</sup>	Mg	Mg <sub>exch.</sub>	Ca	Na	K
3.57	0.18	0.25	1.81	0.19	0.18	0.04	0.08	0.11
3.35	0.19	0.46	1.89	0.11	0.22	0.05	0.13	0.07
3.66	0.18	0.16	1.82	0.18	0.10	0.04	0.09	0.15
3.62	0.22	0.16	1.84	0.16	0.14	0.04	0.12	0.08
3.70	0.05	0.25	1.85	0.15	0.10	0.06	0.03	0.01
3.44	0.15	0.41	1.94	0.05	0.17	0.04	0.09	0.08
3.74	0.22	0.04	1.79	0.21	0.14	0.04	0.03	0.10
3.67	0.21	0.12	1.79	0.21	0.11	0.04	0.13	0.11
3.59	0.19	0.22	1.82	0.18	0.11	0.04	0.16	0.12
3.42	0.29	0.29	1.92	0.08	0.15	0.06	0.13	0.09
3.19	0.34	0.47	1.98	0.02	0.19	0.06	0.21	0.08
3.50	0.23	0.27	1.84	0.16	0.15	0.05	0.13	0.13

The Hoffmann-Klemen test shows that these crystallites are mixed-layers formed of collapsed and expandable layers. Figure 4.39 shows that the chemical compositions plot into two separate fields between Fe-montmorillonite and nontronite on one hand and nontronite to saponite on the other hand. Consequently, one may consider that the tetrahedral charge is inhomogeneously distributed in some crystallites. Chemical compositions in field 1 correspond to mixed layers of Fe-montmorillonite (collapsed layers) and nontronite (expandable layers). Chemical compositions in field 2 are composite nontronitic clays in which the octahedral charge is significant. However, these clays have a sufficiently high tetrahedral charge to conserve their expandability.

Summarizing, talc and saponite which are formed in the primary plasmic microsystems are destabilized in their turn in the saprolite. The mineral reactions produce two secondary phases dominated either by Fe or Mg ions: a 2:1 species form-

**Table 4.9.** Chemical composition (per  $\text{Si}_2\text{O}_5$ ) of the green gel formed in the secondary plasmic

Green gel (Iherzolite)				
Si	Al <sup>IV</sup>	Fe <sup>3+IV</sup>	Fe <sup>2+VI</sup>	Mg
1.92	0.04	0.04	0.42	2.63
1.85	0.08	0.07	0.52	2.59
1.94	0.05	0.01	0.51	2.58
1.92	0.07	0.01	0.48	2.57
1.88	0.10	0.02	0.50	2.58
1.88	0.08	0.04	0.49	2.58
1.87	0.09	0.04	0.49	2.59
1.76	0.10	0.14	0.31	2.84



**Fig. 4.39.** Chemical compositions of the primary phyllosilicate (chrysotile) and the secondary ones (saponite and nontronite) in the alteration profile of a Iherzolite (from Fontanaud and Meunier 1983). 1: domain of Fe-montmorillonite-nontronite mixed layers; 2: domain of nontronite

ing large nontronite crystallites and a 1:1 species forming a cryptocrystalline material. The contrast of crystalline state is to be related to the competition between nucleation and growth for the two species. The competition is in favor of crystal growth for the Fe-rich phase because the amount of Fe in solution is relatively low in an oxidizing environment. Consequently, the solution oversaturation with respect to nontronite is very limited. On the contrary, magnesium ions being highly soluble, the solutions are quickly oversaturated by the dissolution of talc and saponite. Small changes in physical state (evaporation during summer time for instance) may trigger an explosive nucleation of a chrysotile-like phase which cannot grow easily under surface conditions.

### *Kaolinite from Lateritic Profiles*

Large kaolinite booklets up to 100  $\mu\text{m}$  have been described in the saprolite zone of lateritic iron crust profiles formed from metabasic rocks (Ambrosi and Nahon 1986). They are scattered inside a secondary plasma which is composed of microcrystalline kaolinite (95%) and hematite (5%). The Hinckley test (1963) performed on the booklets which were microsampled indicates that they are well-crystallized kaolinite in spite of some  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  substitution in the octahedral sheet. These large-sized crystals disappear in the upper hematite-goethite rich horizons. They are replaced by a second generation of small-sized poorly-crystallized ones showing a greater  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  substitution ratio. The  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  substitution increases the  $b$  dimension of the kaolinite layers. If non-periodically distributed, it leads to the formation of crystal defects and the degree of disorder measured by the Hinckley index increases (Mestdagh et al. 1980; Petit and Decarreau 1990). It has been shown in lateritic profiles that the higher the amount of substitution, the lower the size of the kaolinite crystals (Giral-Kacmarcik et al. 1998). In other words,  $\text{Fe}^{3+}$  ions are a poison for kaolinite crystal growth.

The consequence is that, even if a phase is globally in equilibrium with the chemical conditions imposed at the scale of a profile or even of a country, its crystalline state constantly changes as the profile deepens. Successive generations of the same species are forming having different crystal size and habit. This has been shown for kaolinite whose  $\delta^{18}\text{O}$  varies in lateritic profiles developed on detrital sands and clays in the central Amazon basin (Giral-Kacmarcik et al. 1998). In order to be formed, large kaolinite booklets need a Fe-poor microenvironment or specific chemical conditions in which Fe ions are consumed by another phase.

## 4.4 The Ultimate Weathering Stages

### 4.4.1 The Fissural Microsystems: Cutans

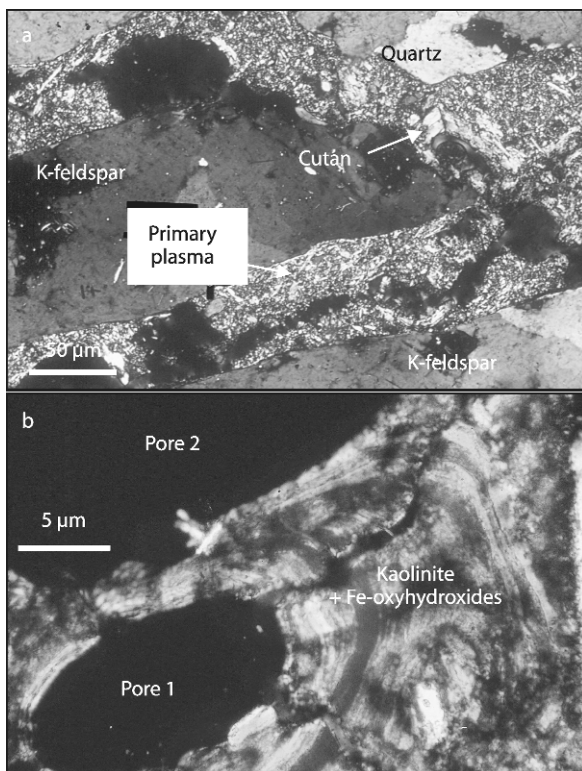
The most important parameter for weathering and soil formation is the rainfall regime. This regime varies over the world with the climate type (more or less the latitude). It is seasonally controlled with significant contrast between the humid and dry seasons in most places. During high rainfall periods, the amount of water circulating in the connected voids of the altered rocks increases. Fine clay particles produced in

the primary and secondary plasmas are partly displaced in stable suspensions. The proportion of clay moved by convection out of the system may be important (see Sect. 7.3). During the dry periods, these suspensions become unstable. They cannot flow anymore and the capillary forces entrain the clay particles to sediment on the walls of the fractures, microfractures and pores. These micro-sedimentary features are assigned as *illuviation cutans*. The term “*cutan*” designates any modification of the soil texture at the grain surface (Brewer 1964).

#### *Microstructural Characteristics of the Illuviation and Crystallization Cutans*

The cutans described here coat the pore or fracture walls and exhibit microsedimentary features. They are observed in every alteration facies of the weathered profiles from the unaltered rock to the saprolite. Figure 4.40a shows the petrographic relation between the primary plasma formed in an orthoclase and the cutans coating the pores. Cutans constantly exhibit a black cross under crossed nicols which is typical of an oriented fine-grained material. Cutans in weathered profiles are composed of alternating clay and Fe- or Mn-oxyhydroxides deposits (Fig. 4.40b). Considering these facts, one can deduce that cutans result from the deposition of the fine-grained solid par-

**Fig. 4.40.** Microphotograph cutans in the La Rayrie granite weathered profile; **a** cutan coating a micropore inside an orthoclase primary plasmic microsystem; **b** detail of a thick stratified cutan in the saprolite



ticles transported as suspensions through the porous network of the weathered rock, i.e. *illuviation cutan*. The deposit covers the walls of the micropores whatever their orientation in the 3D space.

The formation of a clay suspension is a two-step process which begins by the extraction of the fine clay or oxyhydroxide particles formed in the plasmic microsystems. Then, these particles are dispersed in the solutions where they form stable suspensions thanks to brownian motion and electrical repulsion. The suspensions are no more stable as soon as the dispersive forces are annihilated or overcome by physical or chemical ones which trigger the sedimentation. In large pores, gravity certainly predominates. In small ones, gravity is not the principal force at work. The meniscus tension is very powerful and may explain why the small pores are so homogeneously coated whatever the orientation of their walls. Besides, as the activity of water decreases with the pore size, the chemical properties of the solution change and modify their interactions with clay particles.

If illuviation cutans are frequently observed in altered rocks and soils, they are not the unique pore coating feature. Indeed, some cutans do not result from sedimentation but rather from a crystallization process (crystallization cutans). The growth of secondary crystal phases on detrital grain surfaces is ordinarily typical of diagenetic formations but it can also be observed in deeply altered saprolites from lateritic or bauxitic profiles (Eswaran et al. 1977). According to the dissolved ion relative movement, Tardy (1993) distinguished three types of crystallization cutans: incrustation, excretion, secretion. Whatever the process, these cutans exhibit euhedral crystals of gibbsite or goethite coating detrital grains, fine-grained matrix or the clay deposits of illuviation cutans.

#### ***Cutan Mineralogical Composition***

Whatever their type, illuviation or crystallization, all the cutans exhibit a specific mineralogical composition compared to that of the saprock or saprolite microsystems. Most often, the clay assemblages involved in the coatings are monophased (Table 4.10). They are associated with Fe-Mn oxyhydroxides. In the case of illuviation-type cutans, clays do not crystallize but are sedimented from suspensions. These suspensions are originally polyphased because they remove clays previously formed in plasmic microsystems. The clay assemblage becomes monophased if all the other phyllosilicates except one are dissolved. This is a consequence of the chemical properties of the solutions that flow inside the porous network of the rock. These solutions are diluted because they are constantly renewed by meteoric water input. They are drained to the larger fractures or springs. Compared to the rock, the solutions are enriched in mobile components and depleted in inert ones. They represent the compositions far from equilibrium with respect to the parent mineral phases submitted to dissolution.

Summarizing, in spite of the fact that clays forming the illuviation cutans are only deposited and not precipitated from the solutions, their crystallochemical properties are determined by the chemical composition of the solutions which flow through the fractures in the weathered profile. Feth et al. (1964) have shown that the chemical composition of most of the Sierra Nevada spring waters plot in the kaolinite stability field of the  $a_{K^+}/a_{H^+}$  versus  $a_{H_4SiO_4}$  diagrams ( $SiO_2-Al_2O_3-K_2O-H_2O$  system at 20 °C, 1 bar).

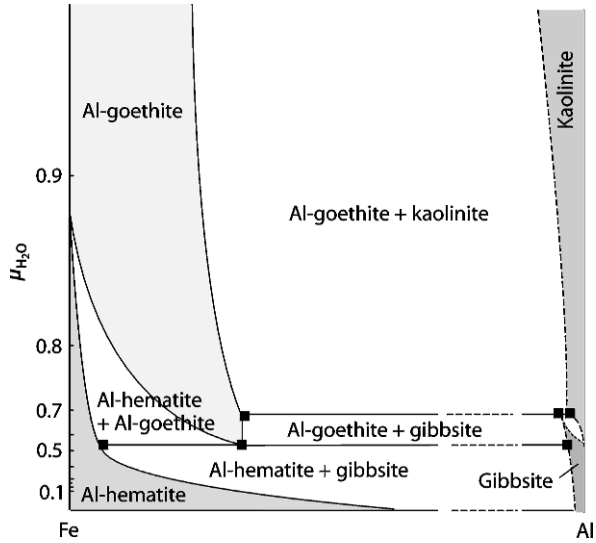
**Table 4.10.** Mineralogical composition of the clay fraction in illuviation cutans from different parent rocks and climates. Clay minerals are constantly associated with Fe-Mn oxyhydroxides

Rock type	Climate	Altered rock	Cutan clay component	References
Granite	Temperate	Saprock + saprolite	Kaolinite	Meunier and Velde (1979a)
Amphibolite		Saprock	Fe-beidellite	Proust (1983)
		Saprolite	Al-beidellite	
Glaucophanite		Saprolite	Fe-beidellite	
Meta-gabbro		Saprock + saprolite	Fe-beidellite	Ildefonse (1980)
Lherzolite		Saprolite	Nontronite	Fontanaud and Meunier (1983)
Basalt		Saprock + saprolite	Halloysite + Fe-beidellite	Ildefonse (1987)
	Saprolite			
Hawaïte	Equatorial	Saprolite	Halloysite + gibbsite	

However, using the same data set, Garrels and Mackenzie (1967) showed a difference between ephemeral and perennial spring waters. The first ones do not contain enough silica and alkalis to be in equilibrium with 2:1 phyllosilicates. On the contrary, the second ones contain enough silica and alkalis to be stable with a kaolinite + smectite assemblage. The duration of the water-plagioclase interaction is brief or prolonged for ephemeral or perennial springs respectively. In granitic areas, the large water passageways in weathered granites are covered by cutans composed of kaolinite + Fe-oxyhydroxides. This indicates that the fine smectite or illite particles which have been extracted from the plasmic microsystems along with kaolinite are dissolved before deposition on the pore walls. The kaolinite crystallites are the only ones which can “survive” the chemical aggression during the translocation process. In other words, the illuviation cutans result from a mineralogical sorting process.

The crystallization cutans are, by definition, formed from phases which precipitate from the solutions. It is to be noticed that they are never composed of silicates and specially of phyllosilicates but rather of oxyhydroxides. The most commonly encountered phases are goethite and gibbsite which form in lateritic profiles (Eswaran et al. 1977). The crystallization cutans are strictly monophased because the solutions are oversaturated with respect to one phase in these deeply weathered profiles. The oversaturation degree necessary to trigger the nucleation of the phase and, then, to engender the crystal growth is locally attained because of the dependence of the water chemical activity with pore diameter. Trolard and Tardy (1989) showed that Al goethite forms in higher water activity conditions than Al-hematite (Fig. 4.41). Tardy (1993) summarized the relation between the geometry of the surfaces (convex on grains, concave in pores) and the phase which crystallizes in the coatings.

**Fig. 4.41.** Potential-composition phase diagram for the  $\mu_{\text{H}_2\text{O}}\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$  system. Pressure, temperature and  $\mu_{\text{SiO}_2}$  are fixed (after Trolard and Tardy 1989)



#### 4.4.2

#### Accumulations (Absolute and Residual)

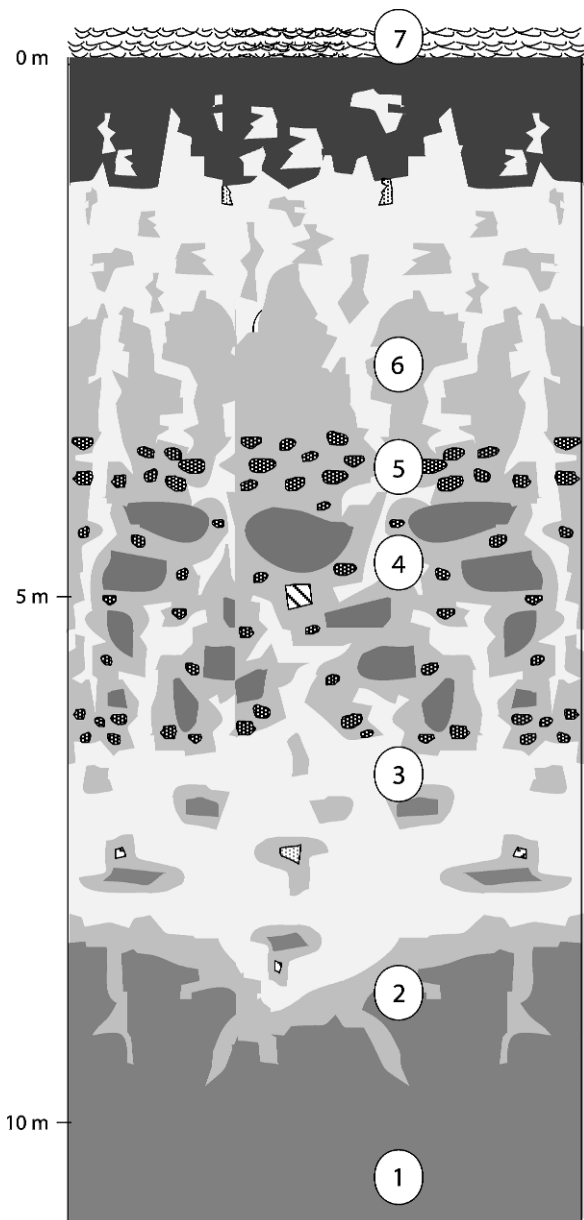
##### *Laterite, Ferricrete and Bauxite*

Today, ferricretes and bauxites are considered to be typical of the “laterite” intertropical zone. Laterites are deeply weathered mantles developed on sedimentary, metamorphic or igneous Si-Al rocks. Their origin is still debated. It seems that they are dismantled now everywhere in the world. They do not form today because they necessitate stable climatic conditions for hundred or millions of years (see Sect. 6.1.2). However, even if they represent a paleo-evolution, their mechanism of formation are rather well known. With time, the residual components accumulate in the weathering profiles producing nearly monomineralic materials which concentrate Fe- or Al-oxyhydroxides. A laterite profile is ordinarily composed of three parts: saprock, saprolite and accumulation zone (McFarlane 1976; Tardy 1993; Taylor and Eggleton 2001). The upper part of the profile is frequently degraded by the development of an organic soil or dismantled by physical erosive processes.

A typical laterite profile is presented in Fig. 4.42 from the observations of Muller and Bocquier (1986). The lower zone (1) is a saprock in which the primary minerals are replaced by primary plasmas formed of highly crystallized kaolinite, hematite and goethite. This zone is friable and porous. It gradually transforms into a saprolite in which the weathered rock remains are embedded in a red fine-grained matrix. The red matrix is composed of poorly-crystallized kaolinite and Fe-oxyhydroxides. Hematite accumulates forming a compact red zone at the top, (2). The saprolite above the hematite-rich level becomes friable and yellow. The yellow color indicates the predomi-



**Fig. 4.42.** Schematic representation of a laterite profile (from Muller and Bocquier 1986).  
 1: saprolite, 2: compact red matrix, 3: friable yellow matrix, 4: ferruginous lithorelict, 5: clay-rich ferruginous nodules, 6: compact yellow matrix, 7: organic matter accumulation zone



nance of goethite. The hematite is conserved in compact red zones (3). The saprolite is overlain by a nodular zone (4) where large- and small-sized nodules, 20–80 mm and <20 mm respectively, are scattered in a red hematite matrix. The largest nodules dominate in the center of zone 4. They are formed of hematite deposits centered on saprock relicts. The nodule-matrix contact is not sharp but progressive. The small-sized nod-

ules are round-shaped and composed of microcrystalline kaolinite associated with hematite; they do not contain any saprock remains. They are the dominant feature of zone 5.

The upper part of the laterite profiles above the nodule concentration (5) is a re-structured saprolite in which induration and degradation processes have triggered new dissolution and precipitation events controlled by local environmental conditions. Degradation is observable in the profile studied by Muller and Bocquier (1987). The upper part is composed of a yellow, goethite-rich and friable material which is more or less compacted (6). The nodules are scarce and totally disappear one meter from the surface. The progressive destruction of the nodules is due to a chemical dissolution related to the development of the organic soil. This degraded zone is itself overlain by a thick organic horizon which is constantly fed by vegetal debris (7). Degradation is particularly active under equatorial forests. On the contrary, the profiles formed in zones of contrasted wet and dry seasons exhibit indurated formations (cuirasses). The accumulation of Fe-oxyhydroxides reduces the porosity. The nodules are cemented forming a hard hematite-rich rock which is, in its turn, degraded or dismantled by biological or physical processes. From that description, it seems that the upper part of the profile presented in Fig. 4.42 is the one active today. The old soil is beneath the nodule horizon (5).

According to Taylor and Eggleton (2001), bauxite or laterite can form in any topographic position. However, Tardy (1993) showed that gibbsite accumulates preferentially in steep slope hills where kaolinite is destabilized in high drainage conditions. Gibbsite may be micro- or macrocrystalline when replacing the porous kaolinitic plasma or precipitating into open voids respectively. Boehmite is formed by dehydration of pre-existing gibbsite.

The climatic signification of ferricrete and bauxite is not as simple as it sounds. It has been debated in many papers. Because ferricretes are most frequently observed in contrasted season countries today, they are thought to be typical of such climates. However, as all weathering processes, the ferricrete formation is kinetically controlled. In other words, the main parameter is not temperature alone but *time × temperature*. Consequently, there is no reason to relate ferricretes exclusively to hot climates (Taylor and Eggleton 2001, p. 256). Even if the climatic signification of ferricretes is not the problem under consideration here, it is important to keep in mind that time in geological process is an important parameter.

### ***The Petrographical Analysis of Accumulation Zones***

The ultimate weathering stage is dominated by the accumulation of the most insoluble chemical components, i.e. iron and aluminum (Chesworth 1973). The question is: how does accumulation proceed? Two ways are theoretically possible: relative or absolute accumulation which are respectively due to the loss of the more soluble chemical elements or to the input of the less soluble ones. To determine which is correct one needs to do mass balance calculations. Unfortunately, whatever the chosen invariant parameter, i.e. volume for structure conservative alteration or inert chemical component for all alteration facies in the profile, the experimental error may be too high to make conclusions unequivocal. Besides, most often, the accumulation results from several processes which have been simultaneously or successively active (Beauvais 1999). Con-

sequently, it is necessary to reconstruct the history of the chemical element transfers using petrographical analysis of the dissolution and deposition features before to calculate a mass balance of indurated rocks.

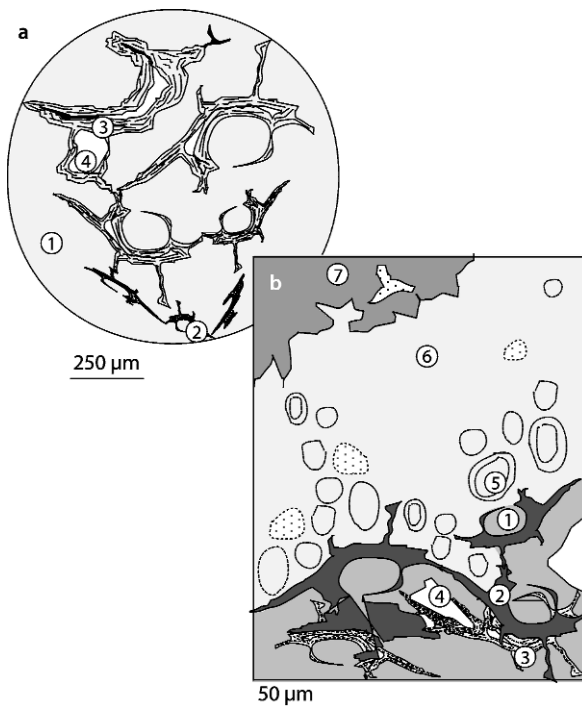
At a given time, the saprock or the saprolite may experience dissolution and/or deposition. Considering that the structure of the altered rock did not change at that time, a residual accumulation is simply triggered by a loss of soluble elements through fluids impregnating and flowing inside a rigid framework. The loss of mobile elements and/or the translocation of fine particles increase the global porosity. New voids are formed while the size of the pre-existing ones increases. On the contrary, an absolute accumulation necessitates chemical input from outside. The porosity decreases by deposition or crystallization of minerals on the pore walls. This induration process has been described in the transition between the soft nodular iron crust and the indurated layer of a laterite profile from Burkina Faso (Ambrosi and Nahon 1986; Fig. 4.43).

The accumulation of the most insoluble components results from two different processes according to the conservation or non-conservation of the parent rock structure. The conservation process is represented in Fig. 4.44. The rock structure is preserved if the replacement of the pre-existing minerals by secondary ones is pseudomorphic (conservation of the shape and size of the pre-existing crystals). This implies that the dissolution of the pre-existing crystals and the growth of the replacing minerals take place simultaneously and at the same instantaneous rate (Merino et al. 1993). The replacement occurs first along the intergranular and intracrystalline microfractures giving a specific saprock feature (saprock 1). This level is systematically overlain by a

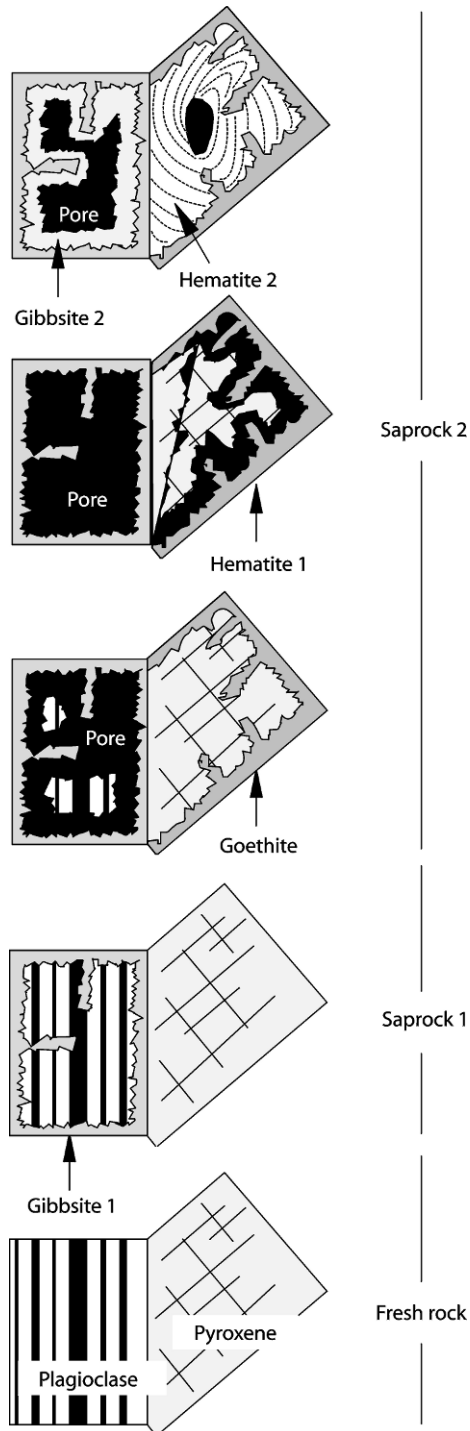
**Fig. 4.43.** Petrographic features of accumulation zones in a laterite profile (from Ambrosi and Nahon 1986);

**a** soft nodular iron crust layer (kaolinite + goethite); 1: non-oriented plasma, 2: oriented plasma, 3: cracks in oriented plasma, 4: tubular void;

**b** purple-red indurated layer above the soft nodular one; 1: micronodule of kaolinite + goethite plasma, 2: oriented plasma, 3: argilliferan, 4: alveolar void, 5: ghost of micronodular structure, 6: ferruginous plasma, 7: hematitic purple-red nodule



**Fig. 4.44.** Schematical representation of the pseudomorphic replacement of primary or secondary crystals in a lateritic profile by gibbsite and hematite (from Merino et al. 1993); *saprock 1*: pseudomorphic replacement of primary minerals (plagioclase and pyroxene) along intergranular or intracrystalline microfractures; *saprock 2*: pseudomorphic replacement of primary minerals with formation of a secondary porosity



highly porous saprock (saprock 2) in which the core of the parent crystal is totally dissolved. According to Merino et al. (1993), the pseudomorphic mineral reactions in saprock 1 are fed by the congruent dissolution of the parent crystals in saprock 2. If not, the replacement of minerals in saprock 1 by Al-Fe oxyhydroxide would increase the porosity. This is not the case since gibbsite 1 and goethite pseudomorphically replace the plagioclase and pyroxene respectively. The dissolution in the saprock 2 is triggered by proton input from rainwater. Concomitantly, goethite is replaced by hematite 1. In its turn, the secondary porosity is partly filled by new gibbsite (2) and hematite (2), crystallizations which are fed from the upper levels in the weathering profile. The porosity decreases in saprock 3. Al and Fe ions released in the aqueous solutions even in very low concentrations travel downwards for short distances and entertain the pseudomorphic replacement of primary or secondary crystals by gibbsite or hematite.

In some cases, the structure of the saprock or the saprolite is not conserved during the accumulation process because of hill slope creep or other gravity controlled movements. This implies that both fluids and solids are involved concomitantly. Therefore, the accumulation results from a mineral selection operated during the formation of the new structure. In other words, the most unstable minerals disappear during the topographic reworking of laterite or bauxite (Tardy 1993). In spite of the fact that hematite and goethite phases are always present, it is possible to identify the remains of the old deposits reworked in a new matrix using their Al for Fe substitution ratio. The ferricretes of hillslopes are composed of inherited Al-poor hematite formed during dry periods embedded within an Al-rich goethite matrix formed during a humid period (Beauvais 1999).

### ***Epigenesis: The Ultimate Stage of Non-Residual Accumulation***

From the above, we saw that Fe- or Al-oxyhydroxides concentrate in deeply altered rocks. This is typically a residual accumulation of the less soluble chemical elements. Most often in the same intertropical countries, another process of accumulation is observed. It concerns, on the contrary, the soluble components and particularly those which are incorporated in the most widespread minerals at Earth's surface: the different silica phases and the carbonates. This process leads to the formation of indurated rocks resulting from cementation and epigeny of pre-existing ones. They are assigned as silcretes or calcretes if formed by silica or carbonate accumulation respectively. These indurated rocks exhibit different facies according to local geological situations (see reviews in Thiry 1997; Taylor and Eggleton 2001).

Silcretes and calcretes result from a double process which reduces the porosity by cementation and leads to a volume-conservative replacement of the pre-existing minerals (epigeny). If the cementation process is quite well known (it has important effects on oil prospection for instance), epigeny which gives spectacular replacements when fossils are silicified, is less commonly studied. Epigeny was shown to be controlled by the "*force of crystallization*" which is the pressure that a crystal is able to bear when growing against others (Maliva and Siever 1988; Dewers and Ortoleva 1990). It is equivalent to the non-hydrostatic stress exerted by the growing crystal on its constraint. The presence of a solution film at the interface is necessary to make the chemical diffusion efficient at low temperature conditions. In order to grow a crystal requires

supersaturation of the solution. The level of supersaturation ( $\Omega$ ) is pressure dependent (Dewers and Ortoleva 1990):

$$\Omega = \exp\left(\frac{\Delta V(P-p)}{RT}\right) \quad (4.1)$$

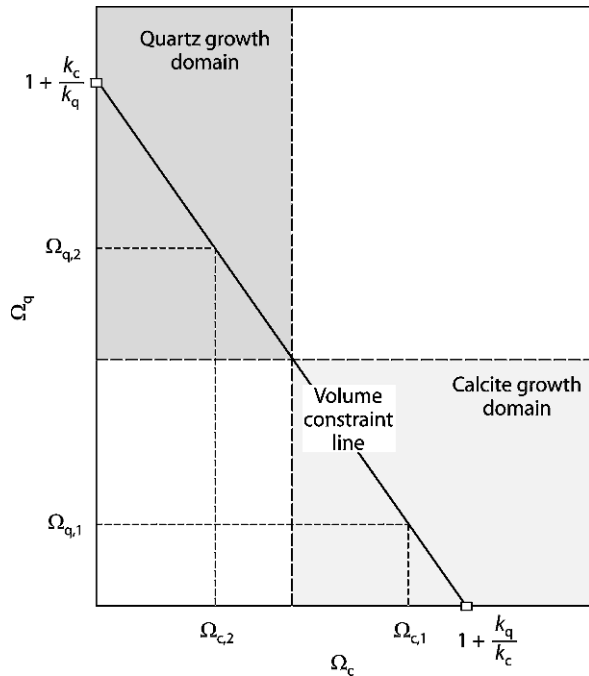
where

- $P, p$ : non-hydrostatic and hydrostatic pressures respectively,
- $\Delta V$ : partial molal volume difference between the solid and solutes,
- $R$ : gas constant,
- $T$ : absolute temperature.

From Eq. 4.1, one can deduce that for a perfect isovolumetric replacement of calcite by quartz, the system continuously adjusts the levels of supersaturation of the solution with respect to quartz ( $\Omega_q$ ) and undersaturation with respect to calcite ( $\Omega_c$ ). The adjustment function is represented by a negative slope line in Fig. 4.45. Negative or positive values mean that the crystal dissolves or grows respectively.

The formation mechanism of silcretes in surficial weathering environments (pedogenetic silicification according to Thiry 1997) is still controversial. However, common sense indicates that dissolved silica which is leached out of the altered zones can be locally supersaturated with respect to opal-CT by evaporation during the dry season or by an increase of the salinity of natural waters or both. Then, the process by

**Fig. 4.45.** Schematic representation of the chemical and physical constraints imposed during a volume conservative replacement of silica by carbonate or carbonate by silica, i.e. epigeny (from Dewers and Ortoleva 1990).  $\Omega_q$  and  $\Omega_c$ : levels of supersaturation with respect to quartz and calcite respectively; 1 and 2: supersaturation states with respect to quartz and calcite respectively;  $k_q$  and  $k_c$ : dissolution rate for quartz and calcite respectively



which silica replaces all the other silicates or minerals whatever their composition is a matter of ion diffusion and force of crystallization. With time, even if the rate of the process is very slow, the indurated levels may represent significant thicknesses in geological formations at the Earth's surface. Calcretes are commonly observed in soils (see review of Taylor and Eggleton 2001). Yaalon (1988) estimates about 13% of the continental surface to be covered by them. Most often, Ca- or Ca-Mg carbonates cement the porosity of the soil of the weathered rocks. However, they can also epigenetically replace pre-existing silicates in granite or silico-clastic rocks (Millot et al. 1977; Paquet and Ruellan 1997).

## 4.5

### The Weathering of Porous Sedimentary Rocks

From the above, we have seen that the alteration processes of granite or other crystalline rocks are first controlled by the fluids invading a fracture network. These processes are volume-conservative. They make the rock friable (saprock). Then with increasing intensity, (increasing time), the structure of the parent crystalline rock collapses forming a new one (saprolite). Saprolite is essentially a porous matrix embedding mineral or rock debris with few fractures. It looks like a sedimentary rock (arkose). The transition from crystalline to sedimentary-like rocks leads one to consider how weathering processes could change in typically sedimentary microstructures. Do any sedimentary rocks behave as a "saprolite"? We saw (Sect. 4.1.2) that the weathering reactions do not proceed in the same way for a marl and a glauconitic sandstone in spite of the fact that they are both phyllosilicate-bearing rocks. The marl is microcrystalline and microporous. It is a highly homogeneous fine-grained rock. On the contrary, the glauconitic sandstone is heterogeneous at the millimeter scale. The chemical composition of the grains (glauconite, quartz, carbonates) is contrasted. In other words, the chemical variations are as important in the glauconitic sandstone as in a granite but the porosity is much higher. This section presents the petrographical and mineralogical characteristics of the weathered zones formed on a marl and glauconitic sandstones in order to determine if the weathering of sedimentary rocks proceed or not through similar microsystem types than in crystalline ones.

#### 4.5.1

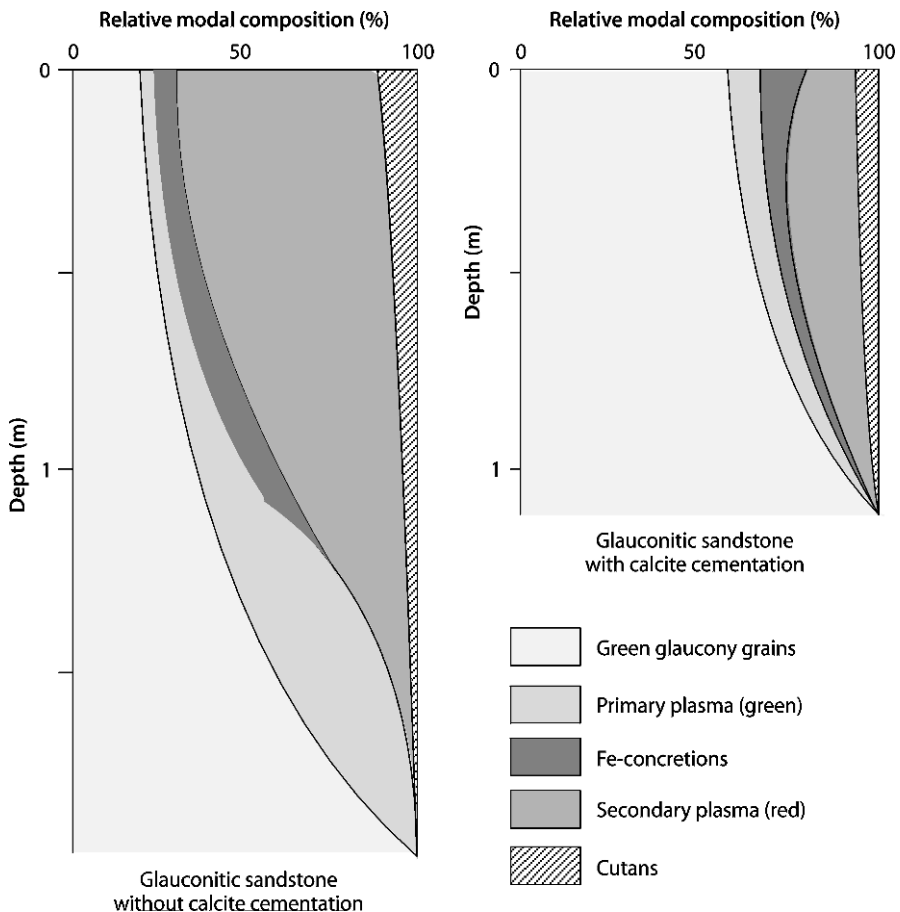
##### Glauconitic Sandstones

Two weathering profiles of glauconitic sandstones have been studied by Courbe et al. (1981) in Chacé (Maine et Loire, France):

- profile 1: 2 m deep, formed on a highly porous quartz-rich sandstone which does not contain carbonates,
- profile 2: 1.20 m deep, formed on a calcite cemented sandstone with lower porosity.

Both are fine grained green sandstones in which the amount of glauconite reaches 30% and 15% respectively. The two sandstones remain green in the first alteration stage. Some of the glauconite grains lose their rounded shape and are replaced by a green

plasma. Concomitantly, thin reddish cutans coat the pores. When present, the calcitic cement is partly dissolved. Above the green altered level, the rock becomes reddish and the clay amount increases upwards. The upper part of profile 1 exhibits the prismatic structure typical of clay-rich materials. The clay fraction increases up to 40% and 25% for profiles 1 and 2 respectively (Courbe 1980). In both rocks, the clay minerals and Fe-oxyhydroxides are formed exclusively by alteration of the glauconite grains. If all the non-phyllsilicate primary components (quartz and calcite) and the voids are ignored, a simple modal composition can be used to study the variation of the relative proportions of clay mineral with depth. (Fig. 4.46). Unaltered glauconite grains are conserved even in the topmost parts of the two profiles. However, they are less abundant in the highly porous non-cemented sandstone. The green primary plasma



**Fig. 4.46.** Relative modal composition of the clay bearing petrographical features in the two profiles studied by Courbe (1980). The non-phyllsilicate primary components (quartz and calcite) and the voids are ignored



is also observed at all depths but it is increasingly replaced by a red secondary plasma associated with Fe-oxyhydroxide concretions toward the top of the profile. Cutans are thicker and more numerous upwards.

The mineralogical characterization of the secondary products based on XRD and micro-analyses are summarized in a  $\mu_K$ -Al-Fe diagram (Fig. 4.47). The amount of K decreases regularly from the unaltered glauconite grains to the red secondary plasma. Glauconites are progressively transformed into a kaolinite + Fe-oxyhydroxide assemblage through Fe-rich illite/smectite mixed-layered minerals and smectite. This has also been observed by Loveland (1981). During weathering, glauconite releases K and Fe ions into the altering solution inducing the formation of a series of new minerals. Iron-rich mixed-layers ( $I/S_{Fe}$ ) form first. Then, with increasing alteration, the  $I/S_{Fe}$  be-

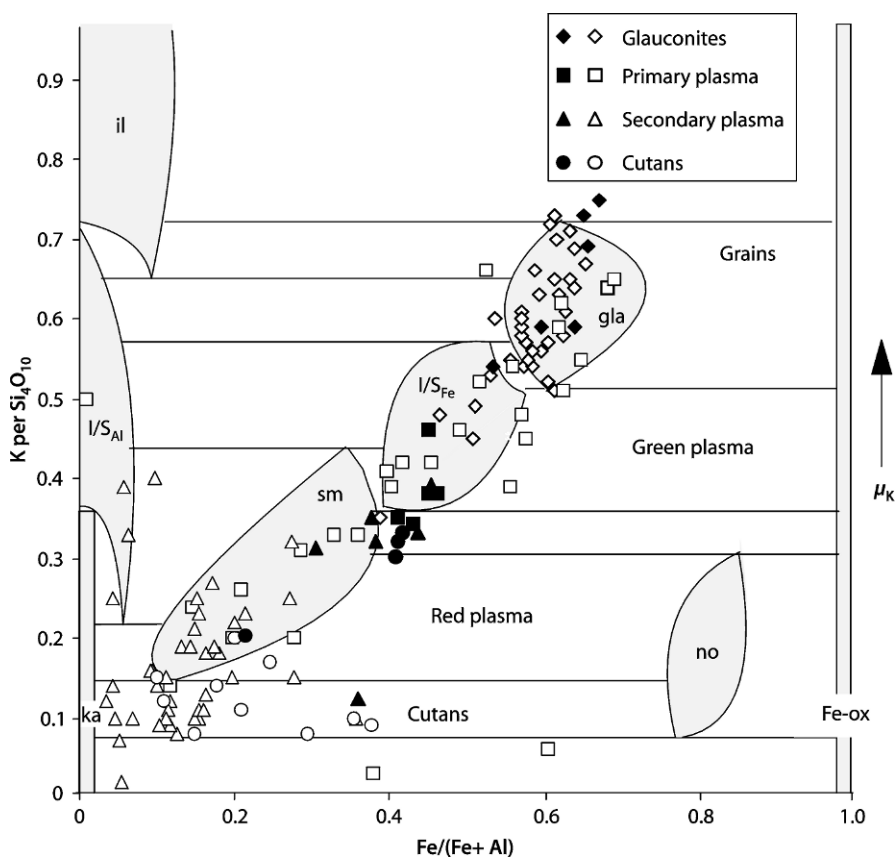


Fig. 4.47. Microchemical analyses per  $Si_4O_{10}$  of glauconite grains, primary and secondary plasma and cutans in the non-cemented (*open symbols*) and cemented (*full symbols*) glauconitic sandstones of Chacé, France (data from Courbe et al. 1981). The composition fields of the primary and secondary phases are represented by the *gray areas*; *gla*: glauconite, *il*: illite,  $I/S_{Fe}$  and  $I/S_{Al}$ : Fe- and Al-rich illite-smectite mixed layer minerals respectively, *sm*: smectite, *ka*: kaolinite, *no*: nontronite, *Fe-ox*: Fe-oxyhydroxides. The *horizontal lines* indicate the value of the potassium chemical potential ( $\mu_K$ ) corresponding to the stability of three phased assemblages

come more aluminous and the smectite content increases. The green plasma is the equivalent of the primary plasmic microsystems described above in altered crystalline rocks.

New mineral reactions occur in the reddish plasma (equivalent of the secondary plasmic microsystems). A fully expandable Al-Fe smectite crystallizes in the green to red transition zones. The red plasma in the vicinity of Fe-concretions is the most altered stage. It is composed of kaolinite + Fe-oxyhydroxide. The cutans are formed of Fe-oxyhydroxides associated with Al-Fe smectites or kaolinite in profiles 1 and 2 respectively.

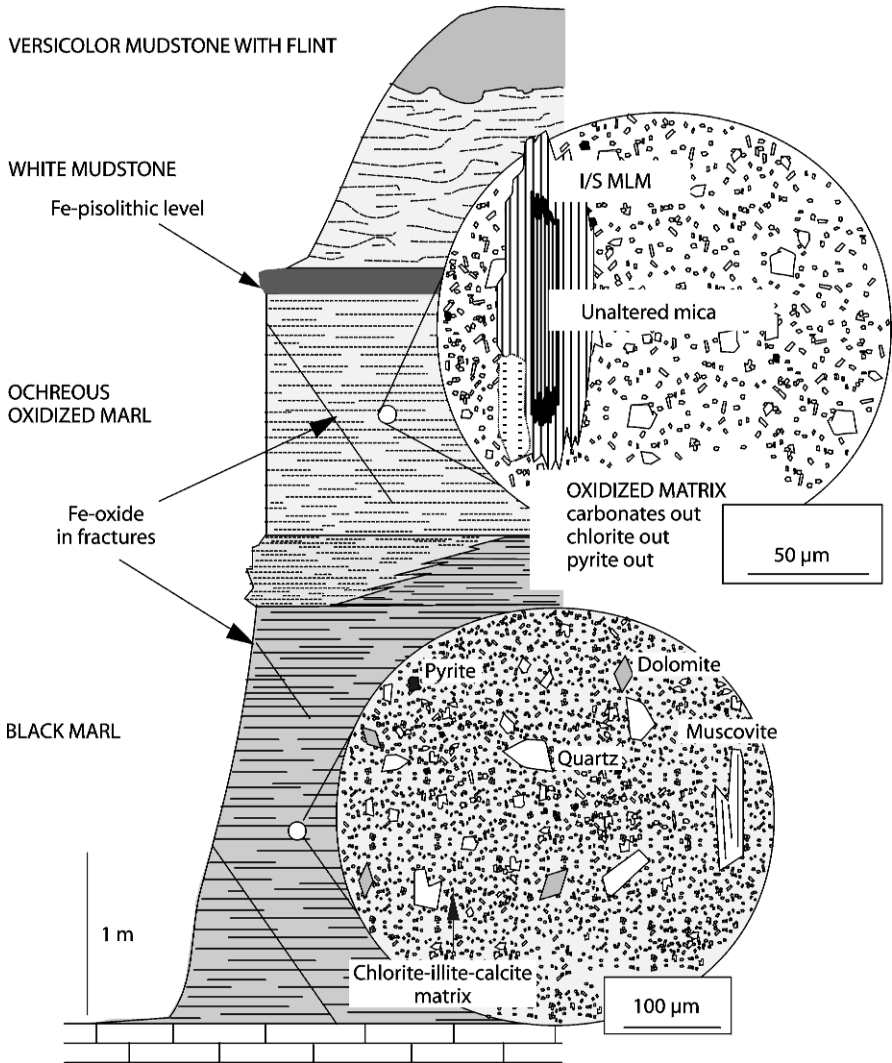
Summarizing, the weathering of glauconite sandstones or crystalline rocks proceeds through comparable microsystem types: internal microsystems (green primary plasma); secondary plasma and fissural microsystems. Only contact microsystems are lacking because inter-crystalline microfractures do not exist in the sandstones. It is remarkable that the mineral sequence observed in the two profiles is the reverse of glauconitization one which operates at the interface sea water/sediments (see review of Meunier and El Albani 2007). This suggests that glauconitization should be considered as a reversible process under Earth's surface conditions.

#### 4.5.2

##### Weathering of Marls

Marls are sedimentary rocks commonly composed of clay minerals intimately mixed with carbonates and sometimes pyrite. Their permeability is very low. They are candidates as geological barriers for waste storage. Their alteration induces a color change from black to ochreous in the unaltered and altered levels respectively. The Roumazières profile (Charente, France) used here as an example is developed on a Toarcian marl which is composed of detrital mica, quartz, pyrite, dolomite, illite and chlorite (Laffon and Meunier 1982). No modification of the rock structure is observed in the ochreous weathered areas (Fig. 4.48) but significant mineralogical changes are observed: the pyrite crystals are oxidized and the dolomite and calcite grains are dissolved. The large white mica flakes (about 100  $\mu\text{m}$ ) are almost unaltered. The fine-grained matrix is severely recrystallized: the initial illite + chlorite assemblage is partly replaced by a kaolinite + illite/smectite mixed layer + Fe-oxyhydroxide.

Because of the oxidation of the pyrite crystals, the solutions become more acidic. The Mg-rich trioctahedral phyllosilicates (chlorite) and the carbonates dissolve. Consequently, the solutions were locally strongly enriched in Ca, Mg, Si and Al. These new chemical conditions favored the formation of Si-Mg rich dioctahedral clay minerals at the expense of illite. Illite was replaced by illite-montmorillonite (I/S) mixed layer minerals. The excess Al ions were incorporated into kaolinite. The change of the initial illite + chlorite clay assemblage to the I/S + kaolinite in the weathered zones is represented in Fig. 4.49. The total loss of dissolved components in such a low porosity rock is quite small and can be neglected. Thus, the major effect of the weathering process is the oxidation of  $\text{Fe}^{2+}$  ions. When plotted in the  $\text{MR}^3\text{-}2\text{R}^3\text{-}3\text{R}^2$  coordinates, the bulk rock composition (large dot) moves from the right to the left side of the triangle, i.e. from the di- + trioctahedral domain to the di-dioctahedral one. In summary, the weathering of the fine-grained marl does not proceed through microsystems similar to that of a crystalline rock or a glauconitic sandstone. Contact and primary plas-



**Fig. 4.48.** Weathering profile of the Toarcian marl at Roumazières, France (from Laffon and Meunier 1982). The black unaltered marl is a diagenetic formation containing illite + chlorite + pyrite + Ca-Mg carbonates. It is overlain by an ochreous oxidized level formed of I/S MLM + kaolinite + Fe-oxhydroxides

mic microsystems do not exist. The rock reacts rather homogeneously to the chemical attack of the oxidative solutions which impregnate the micropores. In other words, the degree of homogeneity is sufficiently high for the marl to behave as the saprolite of crystalline rocks. It is to be noticed that, identically to glauconitic sandstones, the weathering of the marl is the reverse process of mineralogical change in diagenesis (Velde 1985).

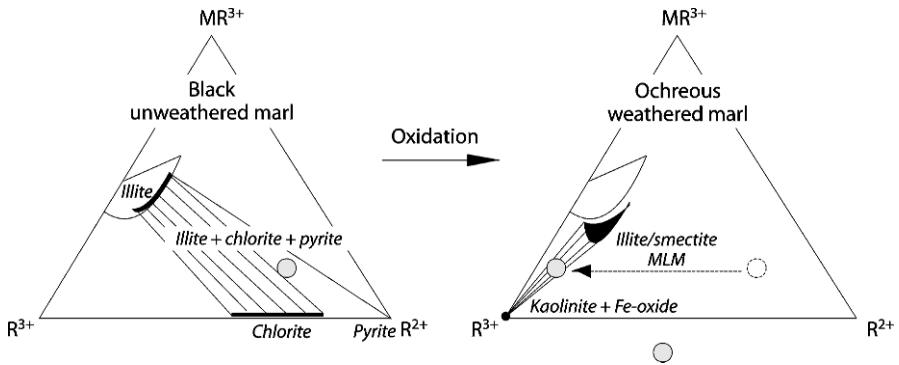


Fig. 4.49. Change of mineral assemblage in the porous fine-grained matrix during weathering reactions in the  $MR^{3+}-2R^{3+}-3R^{2+}$  system

### Summary

1. Fine-grained sedimentary rocks are sufficiently homogeneous to alter directly in conditions similar to that prevailing in the secondary plasma microsystems formed in crystalline rocks.
2. It is remarkable that the weathering of sedimentary rocks, i.e. glauconitic sandstone and marl, follows the reverse step-wise pathway of glauconitization and diagenesis respectively. This could indicate that reactions involving formation of clay minerals in low temperature conditions are stable or at least reversible metastable reactions.

## 4.6 Possible Models for Weathering Processes

### 4.6.1 From Heterogeneity to Homogeneity

Why does a rock weather when at the Earth/atmosphere interface? The fate of any rock, whatever its origin or composition, is to reduce the chemical disequilibrium with respect to the meteoric water which constantly flows inside it. The general trend for alteration processes is to transform any rock into a chemically homogeneous material in order to be in equilibrium with the solutions in every part. To gain homogeneity, a rock must suffer physical, chemical and mineralogical transformations:

- reduction of the average crystal size by fragmentation of primary minerals and crystallization of clay minerals which are always small (see Sect. 1.7).
- reduction of the number of mineral species as alteration continuously impoverishes the rock composition. The trend is to reach an ideally monomineralic composition in order to reduce the intercrystalline chemical differences.

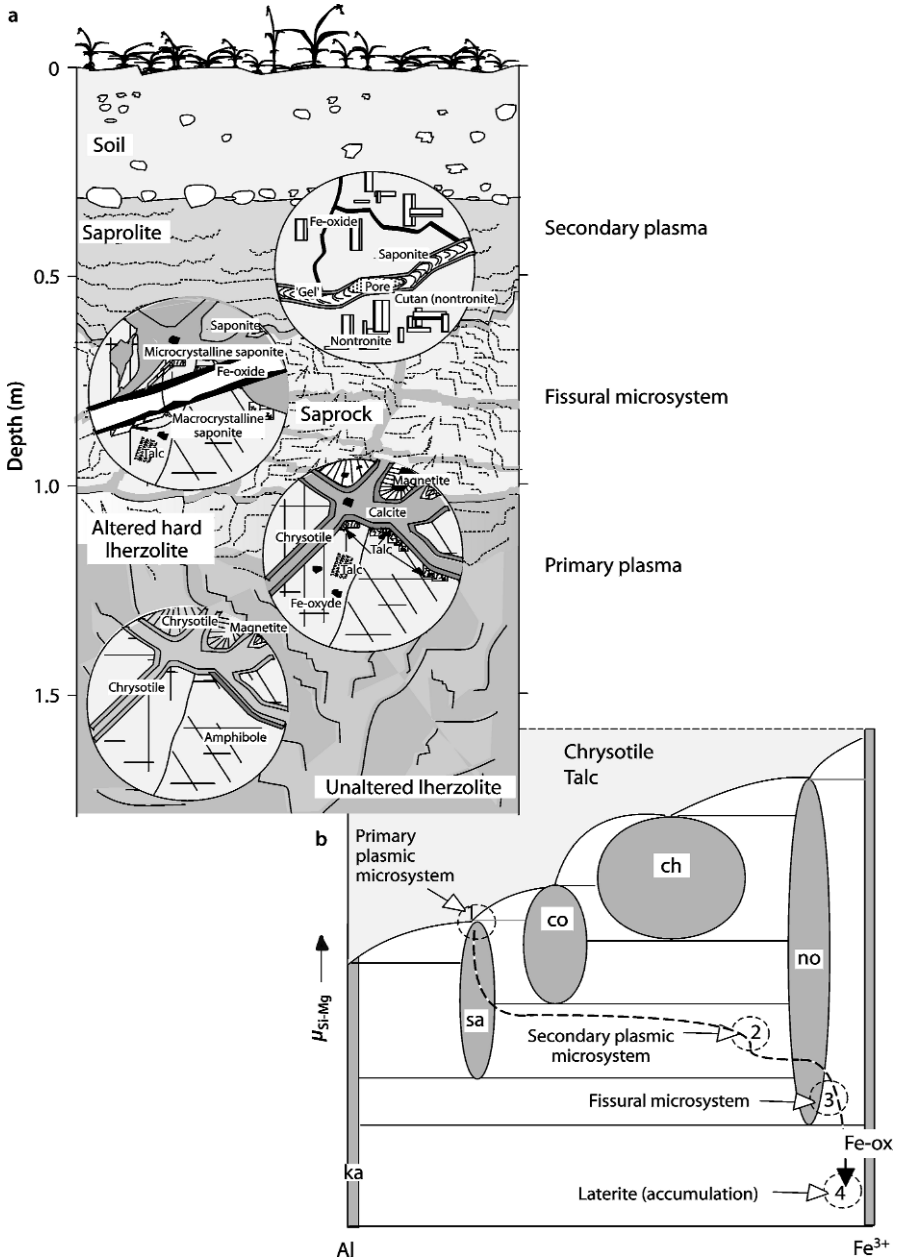
The progression toward the ultimate monomineral stage is classically described by a four step sequence of reactions. The first step is the formation of secondary

phyllosilicates whose chemical composition is close to that of their parent minerals. They form through nucleation and crystal growth processes if their parent minerals are not phyllosilicates. Specific mechanisms transform the primary phyllosilicate minerals into secondary ones (see biotite, muscovite or chlorite microsystems in Sect. 4.2.3). The second step is the recrystallization of all of the secondary phyllosilicates into more dioctahedral ones through the oxidation of  $\text{Fe}^{2+}$  ions and loss of the other bivalent cations ( $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$  or  $\text{Mn}^{2+}$ ). Most often, a part of Fe ions is expelled from the silicate lattice to form distinct oxyhydroxide minerals. The third step is the formation of a homogeneous rock composed of kaolinite/halloysite + Fe-Mn oxyhydroxides whatever the parent rock composition. The fourth step is the total dissolution of silicates leading to an accumulation rock formed of Al- and Fe-oxyhydroxides. It is clear that the sequence concept can be applied to the description of any sufficiently old weathering profile. For instance, the lherzolite weathering profile studied by Fontanaud (1982) shows a sequence of mineral reactions from the unaltered rock to the saprolite (Fig. 4.50a): (1) talc + saponite; (2) saponite + nontronite; (3) nontronite + Fe-oxyhydroxides; (4) kaolinite + Fe-oxyhydroxides. Plotted in the  $\mu_{\text{Si-Mg-Al-Fe}^{3+}}$  phase diagram, the sequence can be represented by a thermodynamical trajectory from the unweathered mineral assemblage to the ultimate accumulation one (Fig. 4.50b).

The concept of alteration sequence implicitly integrates time (successive steps) in the description of the weathering process. Time is a parameter which can be determined through the calculation of the alteration rate (see Sect. 3.1.2). The expected result is the estimation of the duration of the weathering process. For instance, bauxite deposits need million years to be formed. However, the calculation of the alteration rate in natural conditions is far from easy for two major reasons (White and Brantley 2003):

1. it is several orders of magnitude slower than alteration rates measured through experiments,
2. its rate decreases with time.

We must keep in mind that several reactions transform concomitantly each primary mineral in a given rock according to the properties of the different microsystems. For instance, gibbsite is not automatically the ultimate weathering products of granitic rocks. It may crystallize directly in the saprock of weathered profile developed under temperate climates but in specific topographic conditions such as mountains with sharp slopes which favor an intense leaching. During weathering, a rock experiences first a multi-equilibrium state through a great number of microsystem types, each of them imposing specific chemical conditions according to the local chemical differences. With increasing alteration, the number of different microsystem types decreases. However, as saprock remnants still persist in saprolites, some residual microsystems are temporarily active. They progressively disappear. Finally, only one type of microsystem remains active in the ultimate alteration stages which form ferricrete or bauxites. The progressive reduction of the different microsystem types leads typically to the final homogenization of the most altered rock (Fig. 4.51).



**Fig. 4.50.** Schematical representation of the mineral reactions in a lherzolite weathering profile; **a** petrographical and mineralogical characteristics of the different zones; **b** representation of the stability fields of the secondary minerals (*gray areas*) and the reaction sequence (*dashed line*) in the  $\mu_{Si-Mg}-Al-Fe^{3+}$  system

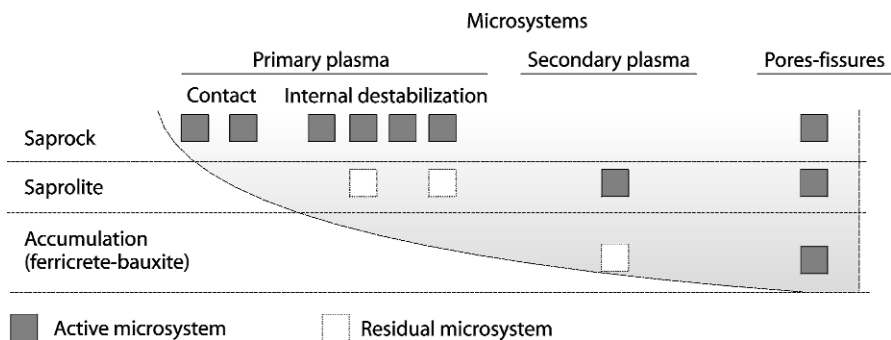


Fig. 4.51. Schematic representation of the homogenization process through the reduction of the number of different microsystem types. The initial number of microsystems in the saprock depends on the mineralogical composition and the microstructure of the parent rock. Residual saprock microsystems may locally and temporarily survive in the saprolite

#### 4.6.2

##### Mass Balance and Weathering Rates

Mass balance calculations can be performed at different scales from a continent (evaluation of the denudation or erosion rates) to the local profile (loss of chemical components, mass of secondary minerals). All give complementary views of the Earth surface evolution which theoretically should be related one to the others. However, fitting the different scales of study remains highly difficult until now. The recent progress in weathering rate knowledge is a tribute to Art White and his co-workers. They presented the fundamental basics of weathering rates in volume 31 of *Reviews in Mineralogy* devoted to “*Chemical weathering rates of silicates minerals*”. Many developments of these basics have been published in a series of papers since 1995. Our goal here is to summarize the lesson we can extract from these references in order to link what has been petrographically described in this chapter with the rate calculation procedures. We shall propose an alternative way to model the weathering processes.

##### *From Mass Balance to Weathering Rate Calculation*

One of the first attempts to calculate the chemical mass balance of weathered rocks is certainly that published by M. Ebelmen in the “*Annales des Mines*” in 1847: “*Recherches sur la décomposition des roches*”. From that pioneer work up to now, a huge number of papers have been published on that topic. A mass balance is calculated by comparison of altered with unaltered samples assuming that physical (volume) or chemical (inert components) properties do not vary. Because the invariant parameter is critical for the calculation of the mass balance, it is of greatest importance to check the validity of the chosen assumption. Petrographic evidence of volume preservation or chemical evidence of residual concentration of a perfectly inert component are not as easy to establish as its sounds. White et al. (2001) used a suite of inert components (Ti, Zr and Nb) to establish the extent of the volumetric changes. Considering one of the inert conservative chemical species ( $i$ ), the volume change is given by:

$$\varepsilon_i = \frac{\rho_p C_{i,p}}{\rho_w C_{i,w}} - 1 \quad (4.2)$$

where  $\rho_p$  and  $\rho_w$ : densities of the protolith and weathered samples respectively ( $\text{g cm}^{-3}$ ) and  $C_{i,p}$  and  $C_{i,w}$ : concentrations of species  $i$  in the protolith and weathered samples respectively ( $\text{mol l}^{-1}$ ).

If  $\varepsilon_i$  is equal to zero, the weathering process is volume conservative. If  $\varepsilon_i$  is higher or lower than zero, the weathering induces expansion or collapse respectively. White et al. (2001) showed that the granite alteration is almost entirely isovolumetric except in limited zones in the saprolite where it is squeezed.

Using a mass balance calculation in the Panola granite, profile White et al. (2001) have shown that weathering proceeded through four successive alteration stages. From stage one to four, the progress of the weathering reactions is controlled by a continuous increase of the hydraulic conductivity. The authors successfully demonstrated that the relative rates of plagioclase and K-feldspar weathering vary in the different rock facies of the profile (Table 4.11). These results were an encouraging progress which opened the possibility to determine an overall weathering rate for the Panola granite. However, discrepancies in published alteration rates of minerals in experimental and natural conditions necessitated a re-examination of what were the actual weathering processes.

#### Why Does Alteration Rate Decrease with Time?

White and Brantley (2003) show that the correlation between the decreasing reaction rates of silicate minerals with increasing alteration duration is observed both in experimental and natural conditions. However, even the lowest values obtained in experiments are several order of magnitude faster than natural ones. The authors suggested that the BET specific surface ordinarily used in the rate equations must be corrected by an additional parameter: *the surface roughness*. The surface roughness is defined as being the ratio of the BET specific surface area to the geometric surface area. The surface roughness increases with time due to increasing surface pitting and internal porosity. Using the relationship between surface roughness and time, the authors calculated a normalized BET specific surface area equivalent which is introduced

**Table 4.11.** Summary of the four alteration stage characteristics of the Panola granite weathering profile (from White et al. 2001)

Stage	Rock facies	Permeability	Dissolution rate control	
			K-feldspar	Plagioclase
1	Pristine granite	Low primary, no secondary	Unweathered	Unweathered
2	Weathered bedrock	Low primary + low secondary	Fluid transport	Fluid transport
3	Saprolite	Moderate permeability	Fluid transport	Kinetics
4	Soil	High permeability	Kinetics	Kinetics



in the rate equation. Doing that, they obtained a power function describing the decrease of the weathering rate of the Panola granite with time:

$$R = 3.1 \times 10^{-13} t^{-0.61} \text{ (mol m}^{-2} \text{ s}^{-1}\text{)} \quad (4.3)$$

Because weathering rates are normalized to surface area, White and Brantley (2003) explained that the time-dependency of silicate weathering accounts for one third of the increase of that factor. However, the result of these studies suffers from large uncertainties because several parameters are not taken into account. The BET method does not distinguish the surfaces of the dissolving minerals from those of their secondary products (Brantley and Melott 2000). Consequently, the roughness factor is certainly overestimated. The difficulty of measuring the dissolution surface area for each primary mineral in a weathered rock leads to reconsideration of what are the “reactive” surfaces. White and Brantley (2003) argued that the dissolution rate decreases with time because the energetically reactive surfaces are depleted by the elimination of the most defective areas and most soluble zones in the minerals. Additionally, the development of leached layers and mineral or organic coatings reduces the diffusion rate of solubilized elements (Banfield and Barker 1994; Nugent et al. 1998). Pacheco and Alencão (2006) consider that the gap between laboratory and field weathering rates is reduced if the rates are normalized by the fracture area which is calculated through the measured hydraulic conductivity and the effective porosity of the rocks. It is remarkable that the reason why the weathering rate decreases according to a power function can be sought either at the atomic scale (dissolution surface of the minerals) as well as at that of the rock bodies.

Summarizing, the reactive surfaces cannot be directly measured. This is confirmed by Gautier et al. (2001) who showed that the most part of the surface area of experimentally altered quartz measured using the BET method is unreactive to etch pit walls. The dissolution rate does not increase proportionally with etch pit development. This means that the major effect of etch pit development is not chemical but physical because it changes the transport parameters. The increase of the fluid passageway length and tortuosity can slow the diffusion-limited transport of reactants. White and Brantley (2003) claimed that “*For natural weathering, large increase in time continue to increase weathering intensities and further decrease permeabilities and reaction affinities, leading to further declines in natural weathering rates with time*”. This is not totally coherent with observations since the permeability increases (or at least, does not decrease) with alteration intensity. In fact, the connectivity of the secondary porosity increases with the dissolution of the parent crystals as shown by the autoradiographs of  $^{14}\text{C}$ -PMMA impregnated samples. The continuous formation of pores increases the tortuosity which should lower the permeability. However, this effect is compensated by the widening of microfractures and pores. Therefore, the permeability and the length of the diffusion paths concomitantly increase with time.

The weathering rate decrease with time could be compared to non-zero order kinetics which are dependent on the proportion of reactant left in the system after a period of reaction time. Here there are fewer non-reacted grains present as reaction progresses and the pathways to them are longer. As in reaction kinetics, the fewer the reacting molecules left in a system, the lower the probability that they can react.

## 4.6.3

## From Qualitative to Quantitative Models

*The Theoretical Basis*

The basic Fick equation which describes the solute flux controlled by chemical diffusion has been established by Holchella and Banfield (1995):

$$f = \frac{dq}{dt} = \frac{\beta c_q T (C_i - C_e) A}{\eta l} \quad (4.4)$$

- $dq/dt$ : flux ( $f$ ) of species  $q$  per time  $t$  (quantity per time  $\text{mol s}^{-1}$ ). By definition a flux is normalized to a unit surface area. It is expressed in  $\text{mol s}^{-1} \text{m}^{-2}$ . Doing that, the  $A$  factor disappears from the right side of Eq. 4.1.
- $\beta$ : geometric constant taking into account the porosity or tortuosity (adimensional)
- $c_q$ : constant that scales the radius of species  $q$ . To be coherent with the Stokes-Einstein equation,  $c_q$  must be equal to  $k_B/6\pi r$  where  $k_B$  is the Boltzman constant and  $r$  the radius of the particle.
- $T$ : absolute temperature (K);
- $C_i$  and  $C_e$ : concentration of species  $q$  in the internal and external parts of the system respectively ( $\text{mol l}^{-1}$ );
- $A$ : effective pore area ( $\text{m}^2$ );
- $\eta$ : viscosity (Pa s);
- $l$ : average length of diffusion paths (m).

Equation 4.4 is based on a simplifying assumption: at the very surface of dissolving minerals, the effect of the electrical double layer is reduced to the increase of the water viscosity. This is not totally true since other electrical phenomena are involved in the complex ion-solute interactions which occur in the double layer (Revil 1999). However, we can ignore these nanometer scaled effects here and consider that the increase of water viscosity with decreasing pore size is negligible.

In a first approximation, several terms in this equation can be considered to be roughly constant in the weathering reactions. The first is average temperature at a given latitude even if it can change with time as argued by White et al. (2001). However, temperature averages are nonsense if not calculated on the basis of the days that are ice-free. Indeed, temperature is an active parameter only when water is in the liquid state and can react with the rocks. Consequently, the proposed approximation is valid for temperate or tropical conditions where the number of frost days are negligible or null.

The second parameter is the  $C_i - C_e$  difference. In weathering conditions, for a given microsystem, it represents the difference between the concentration of species  $q$  at equilibrium with the dissolving mineral ( $C_{eq}$ ) with that corresponding to the equilibrium with the ultimate secondary product observed to form in that microsystem ( $C_{\min}$ ). For instance, considering the weathering of plagioclases under temperate conditions,

$C_{eq} = C_{plag}$  which is the concentration of Si or Ca or Na ions at equilibrium, the ultimate secondary product formed in the largest fractures is kaolinite. Thus, the lowest concentration level ( $C_{min}$ ) is the concentration of ion species  $q$  (Si, Ca or Na ions) at kaolinite equilibrium ( $C_{kaol}$ ). Consequently, the concentration range ( $C_{eq} - C_{min}$ ) in the set of microsystems considered is given by  $C_{plag} - C_{kaol}$ . In tropical countries, the ultimate product being gibbsite, the concentration range  $C_{eq} - C_{min}$  is given by  $C_{plag} - C_{gibb}$ . It is greater than in temperate conditions.

Summarizing, the  $C_{eq} - C_{min}$  parameter represents the near to far equilibrium concentration range in a given set of microsystems inside a weathering profile. The corresponding chemical potentials  $\mu_{near}$  and  $\mu_{far}$  define the limits of the chemical potential difference of the mobile components, namely Si and Ca for weathered plagioclases. At a given time the energetic state of a set of microsystems formed along some connected microfractures can be simply represented by the variation of the chemical potential difference with the length of the diffusion path, i.e. *the chemical potential gradient*  $d\mu_i/dl$ .

### From Petrography to Chemical Model

The simplified representation of the microsystem-porosity relationships is based on the autoradiograph analysis (see Sect. 4.2.1, Fig. 4.13). This representation leads to a qualitative model of the alteration processes. At a given time ( $t_0$ ), a difference of chemical potential is established between microsystems controlled by surface (3) and transport (1) kinetics. These microsystems form in narrow pores or microfractures or near large water passageways respectively (Fig. 4.52) giving the maximum difference. As micropores, microfractures and large passageways are connected, a set of intermediate microsystems may appear in which the potential difference varies between 0 and the maximum value. The difference can be great or small depending on the length of the diffusion path. However, whatever its slope (chemical potential gradient  $d\mu_i/dl$ ), the curve crosses the conditions of formation of different secondary products in near, intermediate (one or several) or far equilibrium microsystems. For instance, K-feldspar alteration gives illite or smectite + kaolinite or kaolinite in near, intermediate and far equilibrium microsystems respectively. In tropical countries, the far equilibrium conditions are encountered in gibbsite forming microsystems. The limit for the far equilibrium conditions is given by the congruent dissolution of the feldspar. These extreme conditions were frequently used in dissolution rate experiments.

The set of microsystems at the initial time  $t_0$  is schematically represented in Fig. 4.52. The connected microfractures and the primary porosity ( $\Phi_1$ ) are symbolized by the wide and narrow parts of the diffusion path, the length of which integrates the cumulated lengths of all the pathways connecting the pores with the microfractures. The fluids are resident, capillary or gravity flowing according to microsystem type. The variation of the chemical potential difference is represented by a single curve whose limits are given by  $C_{eq}$  and  $C_{min}$ , the near- and far from-equilibrium concentrations respectively. A secondary porosity is formed by dissolution of the primary minerals in every microsystem along the connected microfractures. At  $t_0$ , the dissolution rate of the parent crystals in each microsystem is controlled by the local chemical conditions. The dissolution rate varies from high to low values in the far, intermediate or near equilibrium conditions respectively.

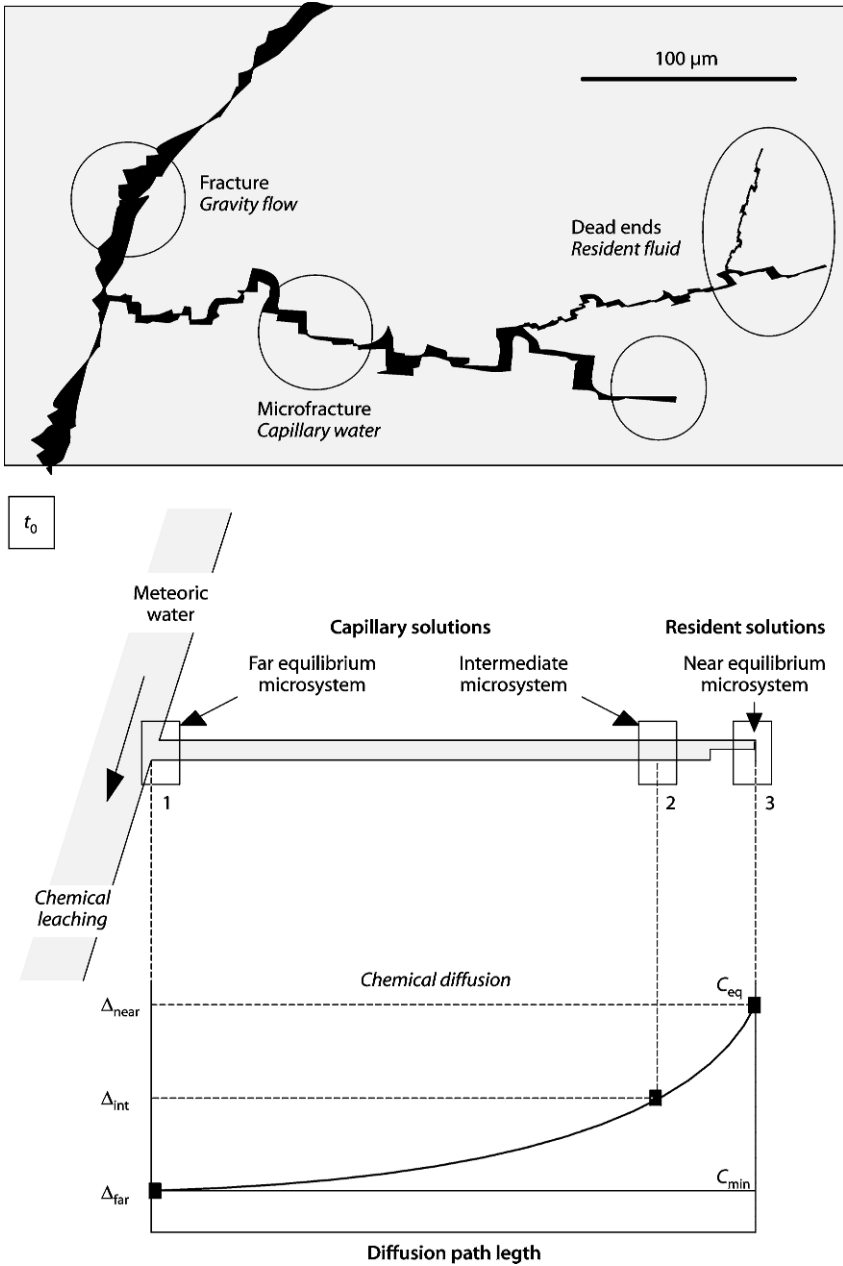


Fig. 4.52. Simplified model representing the petrographical relations between the microsystems and the chemical potential difference of a given element  $i$  ( $\Delta\mu_i$ ) at the beginning of alteration processes (time  $t_0$ ). The limits of  $\Delta\mu_i$  variation are the end-member chemical potentials established in near ( $\mu_{i,near}$ ) and far ( $\mu_{i,far}$ ) equilibrium conditions for concentrations at equilibrium with the dissolving mineral ( $C_{i,eq}$ ) and in the water passageways ( $C_{i,min}$ ). Secondary phases are considered to precipitate at intermediate chemical potential ( $\mu_{i,int}$ ) conditions

The primary mineral dissolution creates new voids that are totally open or partly filled by the clay mineral and oxyhydroxide crystals or amorphous material. The secondary porosity ( $\Phi_{II}$ ) is given by:

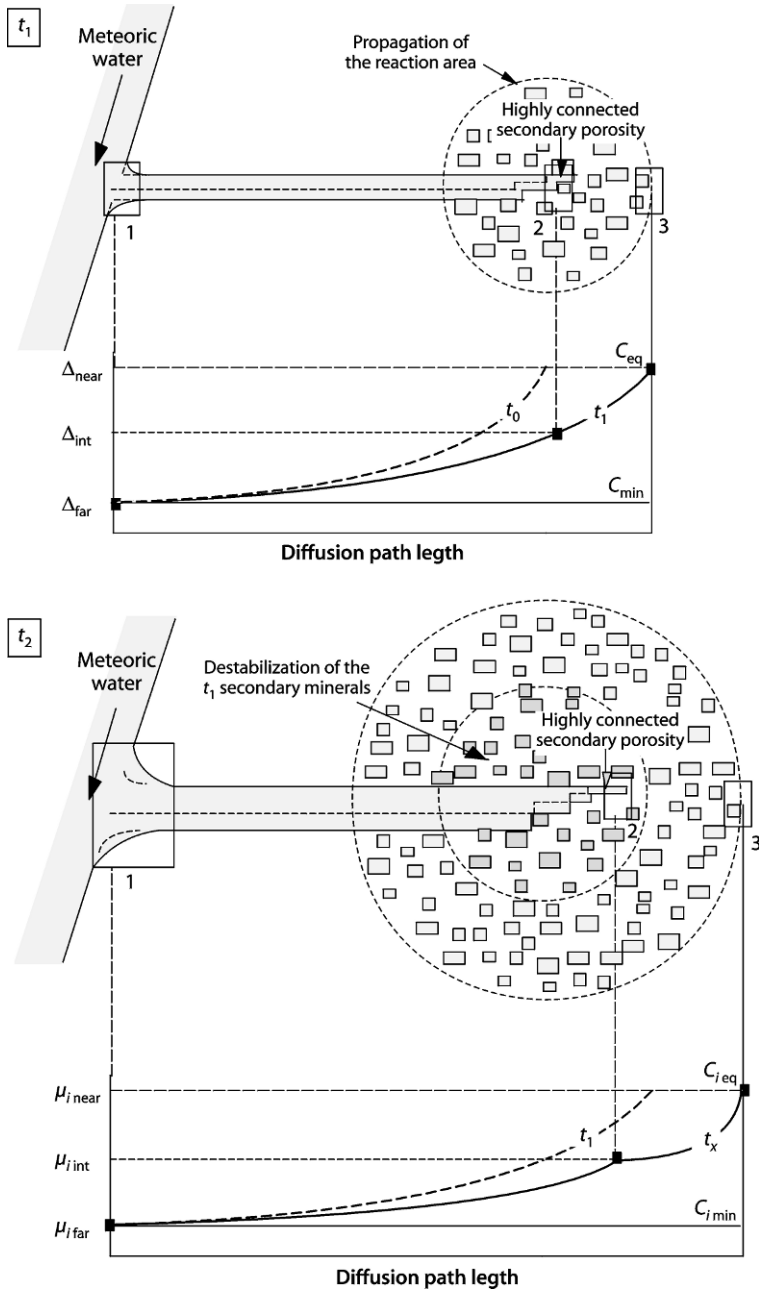
$$\Phi_{II} = (V_v - V_m) / V_r \times 100 \quad (4.5)$$

where  $V_v$ ,  $V_m$  and  $V_r$  are the volumes of dissolution voids, secondary minerals and rock respectively. Whatever the quantities of the new phases formed, the secondary porosity globally increases because the alteration products never totally fill the dissolved volume even in the case of pseudomorphic replacement of the primary crystals. Figure 4.53 schematically represents an integration of the contribution of all the microsystems which were active from  $t_0$  to  $t_1$ .

Geometrical parameters of the total connected porosity ( $\Phi_I + \Phi_{II}$ ) in a rock change during alteration (Sardini et al. 2001b; Sausse et al. 2001). As alteration reactions progress, the access of solutions to the reactive sites increases. Because dissolution is maintained by the chemical potential difference, the fluid passageways and the pores widen. This increases the connections between them. The fluids which were originally stagnant in a given place (resident) begin to move (capillary) after alteration reaction because the passageways have been enlarged. Figure 4.53 schematically shows how the chemical potential differences may change with time from  $t_1$  to  $t_2$ . As dissolution progresses, the number and the maximum size of the pores continuously increase. The secondary porosity is more and more connected because it transforms the dead ends into water passageways. Even if the limits of the chemical potential difference remain those established in near and far equilibrium conditions, the length of the diffusion paths globally increases. Consequently, the chemical potential gradient decreases. The local chemical conditions at a given place change with time. The secondary minerals formed in a given place at  $t_1$  can be destabilized at  $t_2$ .

The alteration progresses with time inducing several modifications of the local alteration microsystems. First, the continuous dissolution of the primary minerals increases the porosity and the length of the diffusion paths (arrow 1 in Fig. 4.54). Second, the major fluid passageways which impose the lowest chemical concentrations are progressively coated by clay minerals and Fe-oxyhydroxides. In other words, the fluids “do not see” the parent rock anymore (a granite for instance), but rather a new rock offering a composite reactive surface formed of clay minerals and primary crystals. Coatings influence the dissolution rate of the coated mineral (Nugent et al. 1998; Hodson 2003; Ganor et al. 2005). The predominance of the secondary clay minerals on the fluid composition is particularly obvious in the large passageways which are most often coated by monophased assemblages, i.e. kaolinite, Fe-beidellite or nontronite in granite, gabbro or lherzolite respectively. The solutions which are rapidly renewed in these passageways are in equilibrium with these phases. The fluid-cutaneous clay equilibrium represents the new far from equilibrium condition imposed on the system at time  $t_x$ . The difference of chemical potential for the most part of the diffusion path is reduced to the  $\mu_{int} - \mu_{cut}$  value (arrow 2 in Fig. 4.54). Consequently, the chemical potential gradient decreases for two reasons:

- increase of the diffusion path length (arrow 1),
- lowering of the potential difference for increasing proportions of the diffusion path (arrow 2).



**Fig. 4.53.** Simplified model for the evolution of the rock properties with increasing alteration from  $t_1$  to  $t_2$ . The chemical potential difference changes because of the formation of a secondary porosity which is increasingly connected. The length of the diffusion paths increases. The limits of the difference are always the end-member chemical potentials established in near and far equilibrium conditions ( $\mu_{i\text{ near}}$  and  $\mu_{i\text{ far}}$ )

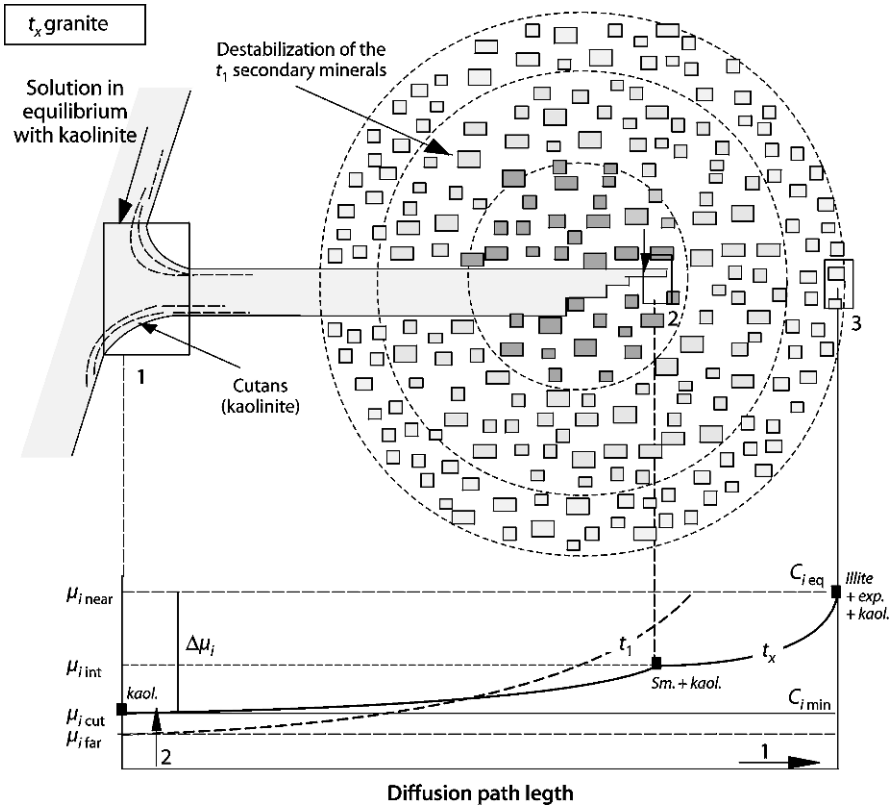


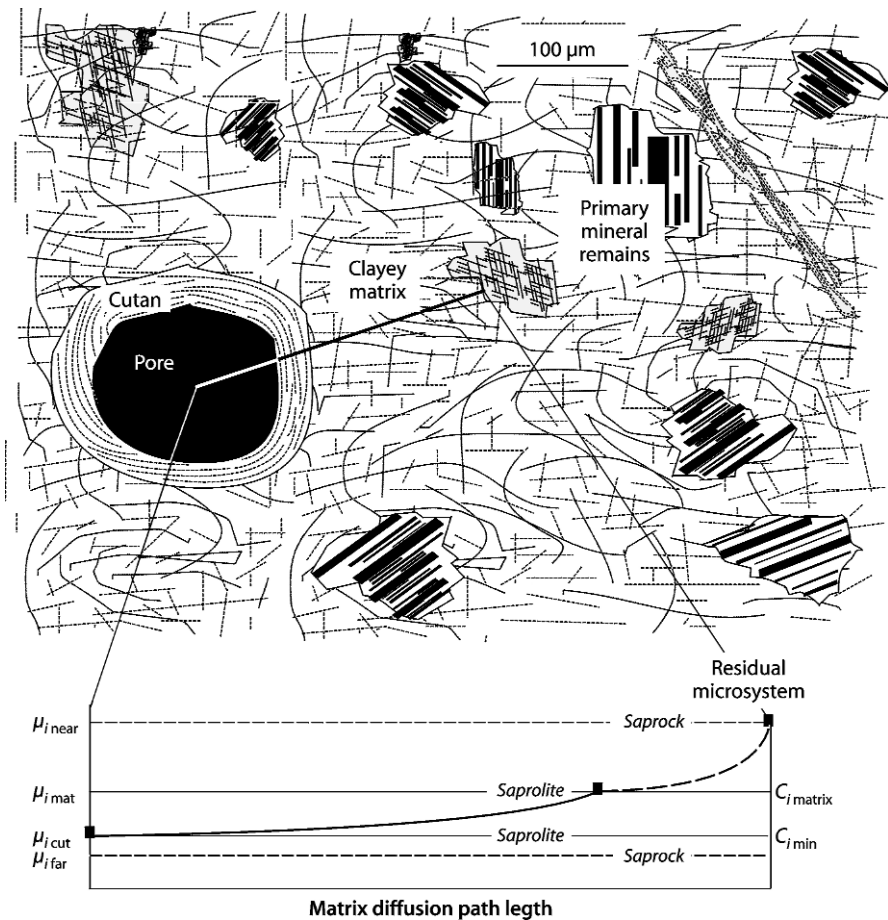
Fig. 4.54. State of the weathering system at  $t_x$  for a granite rock. The length of diffusion paths continuously increases (arrow 1). The difference of chemical potential ( $\Delta\mu_i$ ) is reduced by the equilibration of meteoric waters with the clay species forming the cutans (arrow 2). Increasing portions of the diffusion path experience a reduced potential difference ( $\mu_{\text{int}} - \mu_{\text{cut}}$ )

Summarizing, two reasons may explain why the reaction rate decreases with time during weathering:

1. the length of the diffusion paths increases continuously. Consequently, according to Eq. 4.4, the flux decreases.
2. as fluids continuously invade the same passageways, they are permanently in contact with the products of primary mineral alteration reactions. Namely, they are in contact with clays, oxyhydroxides and free primary mineral surfaces. In other words, even if the granite weathering produces less than 10% clay minerals under temperate climate conditions, the fluids which flow in the altered rock “see” a clay-rich rock in their passageways. Consequently, the difference in chemical potential is reduced with time.

### Application to Saprolite or Fine-Grained Sedimentary Rocks

We saw that the mechanical resistance of the rock dramatically decreases with alteration (see Sect. 4.3.1). The rock structure collapses under gravity giving a new material: the saprolite. The saprolite is formed by fragments of rock or parent crystals scattered in a clayey matrix. The clayey matrix is itself a fine-grained mixture of tiny parent crystal debris with clay minerals formed in the primary plasma microsystems. Consequently, new differences of chemical potentials are established between the large-size connected pores and the microporous matrix (Fig. 4.55). These differences are



**Fig. 4.55.** Schematical representation of the relation between the saprolite microstructure and the differences of chemical potential between the solution passageways (pores) and the clayey matrix. The parent rock or remains of primary crystals form residual microsystems in which the secondary phases are similar to that formed in the saprock



lower than that established in the saprock because the chemical compositions of the clay matrix and the cutan are less contrasted than that of the parent rock and the cutan. Concomitantly, parent rock and large primary crystal debris are altered inside residual microsystems which produce a primary plasma.

### *The Choice of the Most Appropriate Parameter for Alteration Progress Measurement*

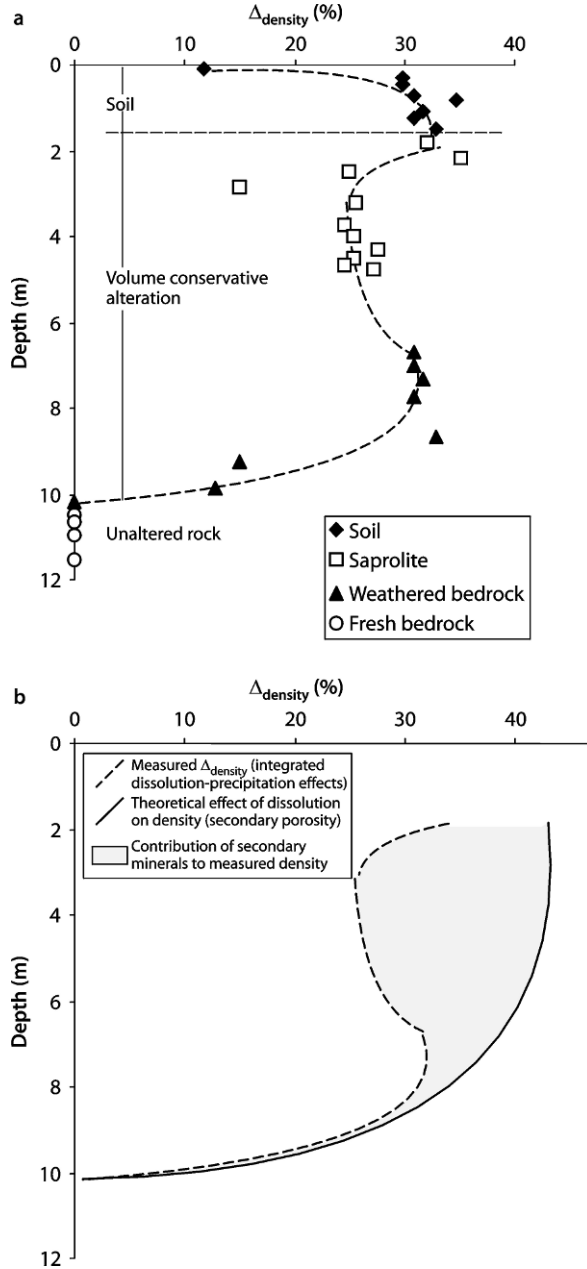
Coming back to basic observations, the weathering reactions can be simply regarded as coupled dissolution and crystallization processes. Dissolution creates a secondary porosity while crystallization creates new solids. The first decreases the rock density while the second increases it. The apparent density of weathered samples from volume conservative altered zones (weathered bedrock and saprock) integrates the effects of the two processes: it varies with the difference between the dissolution and crystallization rates. These rates depend on the local chemical conditions which change from place to place in the weathering profile. The difference of density between the unaltered rock and the altered samples ( $\Delta_{\text{density}} = 100 \times (\text{density}_{\text{unweathered}} - \text{density}_{\text{weathered}}) / \text{density}_{\text{unweathered}}$ ) is an average parameter which can picture the alteration intensity. Applied to the Panola weathered profile studied by White et al. (2001), the  $\Delta_{\text{density}}$  variation reaches 30% in the weathered bedrock at the bottom of the profile and decreases to about 25% in the saprock (Fig. 4.56a).

We know that the dissolution rate slows because of the increasing length of the diffusion paths and the progressive invasion of the reactive surfaces by the secondary products. Transitory fluid-secondary phase equilibria are imposed along the diffusion paths. Nevertheless, the dissolution does not stop until the chemical potential differences are reduced to zero. Thus, dissolution voids continuously form in primary minerals but at a decreasing rate. The density variation ( $\Delta_{\text{density}}$ ) induced by the dissolution voids is important at the beginning of the alteration but it decreases in the saprock. The theoretical and measured  $\Delta_{\text{density}}$  curves are represented by the full and dashed lines respectively in Fig. 4.56b. The difference (*gray area*) is due to the formation of the secondary minerals which partly compensate the decrease of the rock density. Summarizing, the volume of the secondary voids ( $V_v$ ) can be used as a criterion for reaction progress because the mass of dissolved components ( $M_d$ ) is a function of  $V_d$ :

$$M_d = f(V_d) \quad (4.6)$$

How can one measure the volume of the dissolution voids ( $V_v$ )? The gas adsorption methods are not appropriate (see Sect. 4.6.2). The geometrical porosity measurement methods are more convenient if the scaling problem is resolved. Indeed, at the SEM scale of investigation, the dissolution void measurement is accurate but concerns very small volumes of minerals or rocks. Any extrapolation to volume several orders of magnitude higher is questionable. This drawback is avoided if SEM measurements are associated with image analyses of autoradiographs obtained from samples which have been impregnated with the  $^{14}\text{C}$ -PMMA (Hellmuth et al. 1993). The impregnation proceeds even if secondary products are present in the voids. This method provides 2D pictures of the connected porosity at the scale of micrometer in several cubic centimeter sized samples. In order to be impregnated, the voids must be connected to the

**Fig. 4.56.** Variation of the  $\Delta_{\text{density}}$  ( $100 \times (\text{density}_{\text{unweathered}} - \text{density}_{\text{weathered}}) / \text{density}_{\text{unweathered}}$ ) with depth in a weathering profile of the Panola granodiorite (data from White et al. 2001); **a** measured variation (the major altered zones in the profile are indicated by different symbols). A simplified variation curve is given by the *dashed line*; **b** theoretical interpretation of the respective effects of the increasing volumes of the dissolution voids (*full line*) and secondary phases (*gray zone*) on  $\Delta_{\text{density}}$



surface of the sample and second to be accessible to the MMA monomer. Deuteric pores in feldspar have been shown to be inaccessible because of the extreme constriction of the connection pathways. Therefore, the impregnation method underestimates the

porosity of the unweathered samples. The deuteritic voids have to be measured using an SEM study (Sardini et al. 2006). The impregnated porosity integrates the black and gray areas in the autoradiographs (see Fig. 4.12) which correspond to voids and microporous clayey matrix respectively. These areas picture the dissolution voids in a 2D space (dissolved area  $A_d$ ). A statistical study allows one to determine the 3D properties from 2D analysis. Then  $V_d$  can be calculated from  $A_d$ . Knowing the mineral density ( $\rho_x$ ) the dissolved mass ( $M_{dx}$ ) is easy to calculate for each primary mineral species:  $M_{dx} = V_{dx} \times \rho_x$ .

The porosity distribution for each primary mineral is obtained using a combined image analysis of mineralogical maps and autoradiographs (Oila et al. 2005). This allows one to measure the increase of the dissolution void volume ( $V_{dx}$ ) with progressing alteration for each primary mineral from the fresh to the deeply altered samples. Therefore, the quantities of dissolved primary minerals ( $M_{dx}$ ) can be determined in each level of a weathering profile.

### *The Concept of Residence Time for Diffusing Ions*

One of the goals of a quantitative model is to determine the duration of the water/rock alteration process. A possible approximation would be to consider the duration of alteration as equivalent to the time needed by the dissolved mass ( $M_{dx}$ ) to be lost by the rock. To calculate this time necessitates a knowledge of the rate at which the dissolved components are leached out of the profile. Coming back to basic definitions, the flux  $J_i$  of a chemical component  $i$  ( $\text{mol s}^{-1} \text{m}^{-2}$ ) is related to the diffusion coefficient  $D_i$  and the chemical potential gradient ( $d\mu_i/dl$ ) according to:

$$J_i = -D_i \frac{d\mu_i}{dl} \quad (4.7)$$

We know that the weathering rate decreases with time for two reasons: (1) an increase of the secondary porosity which increases the length of the diffusion paths; (2) the progressive decrease of the primary mineral surface area in contact with solutions to the benefit of the secondary minerals. The effect of increasing porosity leads one to reconsider Eq. 4.4 which is based on the assumption that the diffusion coefficient  $D_i$  is constant. This is obviously an oversimplification since that coefficient should change with the geometry of the diffusion paths. Coming back to the basics of chemical diffusion, the "apparent diffusion coefficient"  $D_{a(i)}$  of a solute in a porous medium varies with porosity:

$$D_{a(i)} = \frac{D_{0(i)}G}{R} \quad (4.8)$$

$D_{0(i)}$ : diffusion coefficient in free water ( $\text{m}^2 \text{s}^{-1}$ ),  
 $G$ : geometrical factor (adimensional),  
 $R$ : retardation factor (adimensional).

The geometric factor  $G$  is considered to be dependent on the constrictivity ( $\delta$ ) and tortuosity ( $\tau$ ) according to:

$$G = \delta / \tau^2 \quad (4.9)$$

Both the constrictivity and tortuosity have been empirically related to porosity ( $\Phi$ ) by Archie (1942) using electrical conductivity of rocks:

$$G = \alpha \Phi^{-m} \quad (4.10)$$

The experimental values of the  $m$  and  $\alpha$  constants are 1 and 2, 0.71 and 0.58 for clayey materials (Archie 1942) and crystalline rocks (Parkhomenko 1967) respectively. The retardation factor is determined according to the following relation:

$$R = 1 - \frac{\rho K_{d(i)}}{\Phi} \quad (4.11)$$

$\rho$ : dry rock density ( $\text{kg m}^{-3}$ ),

$K_{d(i)}$ : sorption coefficient of chemical species  $i$  ( $\text{m}^3 \text{kg}^{-1}$ ),

$\Phi$ : rock porosity

Some experimentally measured  $K_d$  values for cations diffusing through different crystalline rocks are presented in Table 4.12 (Byegård et al. 2001). The  $K_d$  may vary by several orders of magnitude depending on the chemical characteristics of the ion species.

The variable to be determined is the residence time of the dissolved components in their diffusion path. The rate of any alteration process depends on the determination of that variable. Because of the presence of different microsystem types, the calculation of the alteration rate depends on the statistical analysis of the residence time of the dissolved components before they are leached out of the rock. During the transfer from the internal source to the outside of the system, these components can be retarded by three principal phenomena:

- the diffusion in the matrix (Neretnieks 1980; Carrera et al. 1998),
- the precipitation of secondary mineral phases containing the element,
- the absorption on inner and outer surfaces of other secondary mineral.

**Table 4.12.** Values of the sorption coefficient for different ionic species diffusing through a granite rock (through-diffusion experimental data from Byegård et al. 2001)

Ionic species	$K_d (\text{m}^3 \text{kg}^{-1})$
$\text{Na}^+$	$4.5 \times 10^{-6}$
$\text{Cs}^+$	$4.7 \times 10^{-4}$
$\text{Sr}^{2+}$	$8.2 \times 10^{-7}$
$\text{Ca}^{2+}$	$5.2 \times 10^{-6}$

The effect of matrix diffusion has been measured through diffusion experiments of iodine or fluoresceine in granites or shales (Hadermann and Heer 1996). These components are almost “chemically inert”. They are little adsorbed by the mineral surfaces. The residence time depends only on the trajectory of their molecules or ions in the fluid. In other words, their residence time depends on the geometrical characteristics of the porous network (constrictivity, tortuosity, ...). This is not the case of course for most of the chemical components involved in the alteration processes. Some (Si, Al,  $\text{Fe}^{3+}$ ) are trapped in the crystal lattices of the secondary phases. Others are adsorbed on the inner and outer surfaces of clay minerals (Ca, Na) or oxyhydroxides (metallic trace elements). At least, some components have a double fate: they are incorporated in the crystal lattices of the secondary phases or, sometimes, adsorbed on exchangeable sites (K, Mg). For the former, the retardation effect is very high because, to be liberated again in solutions, these components require the dissolution of the secondary phases previously formed. Their residence time depends on the duration of these secondary phases in the weathering profile. Components of the second category are more easily liberated in the solutions than those forming the crystal lattices because the secondary phases do not need to be destroyed to liberate them. These components are only exchanged from the solids to the fluids. The chemical behavior of the third ion category is more complex. However, they can be used as indicators of weathering intensity in some particular cases (Mg for mafic or ultramafic rocks).

Any alteration system can be represented in a simplified way by the variation of the chemical potential gradient versus residence time (Fig. 4.57). The transfer of a given cation from its source (dissolving primary mineral) to the water passageways can be retarded once or several times by incorporation in or adsorption on secondary phases. This means that the best markers of the alteration rate would be the components or elements for which the retardation effects are as low as possible. In temperate climate conditions, this discards the inert components such as Al and Fe but also the mobile ones such as Si, K or Mg ions which are commonly incorporated in secondary clay minerals. The best candidates would be Na and Ca which are simply adsorbed as exchangeable cations in the interlayer zone of expandable clay minerals. Their  $K_d$  is rather

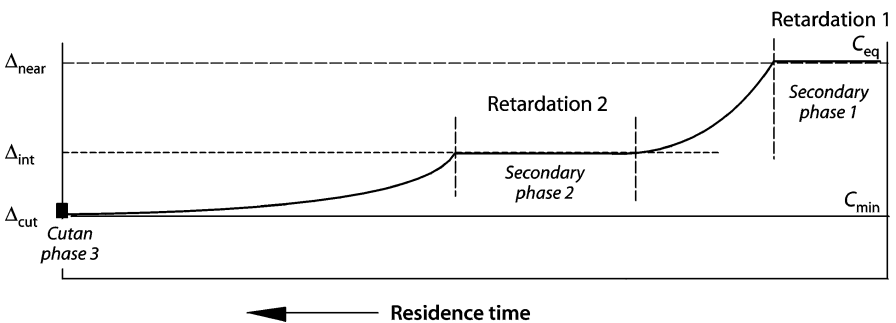


Fig. 4.57. Schematic representation of the relation between the residence time of a given element and its chemical potential in a weathered rock

similar (Table 4.12). In tropical countries, where the accumulation levels of the laterite profiles are dismantled, the markers should be the Al and Fe ions.

### *Toward a Quantitative Model: A Possible Experimental Approach*

The exit-diffusion experiments on crystalline rocks could be used as analogs of the weathering process, at least under temperate conditions, if the Na and Ca ions are considered to be the markers of the alteration progress. Using image analysis of autoradiographs, Sardini et al. (2003) determined first the geometrical parameters of the connected porosity of a granite. These parameters have been introduced in the time domain diffusion (TDD) equations to fit the experimental diffusion curve of  $^{14}\text{C}$ -MMA molecules through the porosity network to outside of the sample. This method seems to be, today, a promising one which could help to model the alteration processes. New alteration experiments are needed to determine the actual diffusion rate of Na and Ca ions in a granite matrix with different values of the chemical potential difference.

Even if the development of quantitative studies is beyond the scope of this book, one can easily see how much the weathering rate can slow with time. According to Eqs. 4.3 and 4.4, to calculate the flux of a chemical component  $i$  one needs to know its apparent diffusion coefficient ( $D_{a(i)}$ ) and the chemical potential gradient ( $d\mu_i/dl$ ). Because of its high importance for nuclear waste safety, the  $D_{a(i)}$  has been experimentally determined for various elements diffusing into different rocks. It has been shown to decrease of one order of magnitude with alteration in a granodiorite:  $4.3 \pm 3.7 \times 10^{-11}$  and  $9.7 \pm 2.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for fresh and altered samples respectively (Sato 1999). Concomitantly, the difference of chemical potential for soluble cations such as  $\text{Na}^+$  decreases of several order of magnitude when the near and far equilibrium conditions are controlled by the congruent dissolution of plagioclase and by the formation of gibbsite, kaolinite or smectite. Consequently, the chemical potential gradient  $d\mu_i/dl$  decreases also of several order of magnitude.

## 4.7

### Summary of the Water/Rock Interaction Clay-Forming Processes

Weathered rock mineralogy appears to be so complicated that weathering phenomenon could seem to be ruled by chaos. In fact, even if the petrological analysis of heterogeneous clay-rich materials is more difficult than that of high temperature crystalline ones, the mineral reactions are controlled by the same laws. At Earth surface conditions, the pressure variation is negligible. The temperature variations are too weak to change the mineral species; they only have an effect on the reaction rate. Then, the unique source of energy is of a chemical nature: the gradient of chemical potential. To summarize, weathering can be simply described by the following statements.

#### *Major Principles*

- High temperature minerals are unstable at the Earth's surface. Among the silicates, clay minerals are the stable phases under these conditions.

- The structure and texture of the rocks formed at depth are unstable at the Earth's surface. Weathering triggers the collapse of the original crystal framework. Unavoidably, the reduction of the crystal size makes the rock more homogeneous. The scale of heterogeneity decreases from millimeter to micrometer. Weathering is a homogeneization process.
- An alteration profile is composed of two major parts: one in which the original texture and structure are conserved and one where they are erased, i.e. saprock and saprolite respectively.

### *Microsystems*

- Weathering proceeds through microsystems in which dissolution-recrystallization reactions are ruled by local equilibrium conditions. A similar process was described by Korzhinskii (1959) in a pioneer work devoted to metasomatism.
- In structure-conservative zones, weathered rocks exhibit different kinds of microsystems. They are made concomitantly reactive according to the accessibility of water. At a given time ( $t_0$ ), all are open systems but with a variable degree of opening. All produce a primary plasma.
- In saprolite zones, because of the collapse of the original rock structure, new microsystems are formed in a fine-grained matrix, i.e. secondary plasmic microsystems. Primary plasmic microsystems may persist in rock debris.

### *Homogeneization*

- The number of microsystem categories decreases with increasing alteration,
- The parent rock is progressively converted to a fine grained material in which the scale of chemical contrast decreases from millimeter to micrometer (secondary plasma),
- The number of secondary mineral species decreases. The ultimate weathering stage is attained when silicates have disappeared and Fe,Al-oxyhydroxides accumulate.

### *Transport of Clays*

- Fine clay particles are extracted from primary and secondary plasma by flowing solutions which invade the alterite during the rainy season. They are exported out of the profile or sedimented on the walls of fractures, microfractures and pores during the dry season,
- During the rainy season, the solutions are quickly renewed. They are constantly diluted. Most of the clay particles in suspension are not stable and dissolve. The cutans are generally monophased.

### *Weathering Progress with Time*

- With increasing alteration (increasing time from  $t_0$  to  $t_x$ ), a given microsystem becomes more and more open. A succession of phases formed as microsystems becomes less isolated and less variable. All successive reactions lead to a convergence toward

monophased clay mineral assemblages (kaolinite or gibbsite in granitic rocks for instance).

- The weathering rate decreases with time because the chemical potential gradients lower in every part of the profile. This is essentially due to the increase of the diffusion path length and the reduction of the difference between the chemical potentials in the near and far conditions.
- Globally, weathering mimics non-zero order kinetics reactions.

### *Calculation of the Weathering Rate*

- To relate the mineral reactions at the microsystem scale to a mass balance at the scale of a profile (super system) one needs to choose some adequate markers. The best would be chemical components which are the most weakly adsorbed in microsystems.
- The weathering rate could be estimated through the calculation of the residence time of these markers.
- The alteration rate is on a geologic time scale ( $10^5$  to  $10^6$  years).

### **Suggested Reading**

- Colman SM, Dethier DP (1986) Rates of chemical weathering of rocks and minerals. Academic Press, Orlando, 603 pp.
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- White AF, Brantley SL (1995) Chemical weathering rates of silicate minerals: an overview. Rev Mineral Geochem 31:1–22



# Plants and Soil Clay Minerals

## Introduction

A brief review of clay mineral assemblages in weathering profiles indicates that the upper-most zones (A horizons for the most part) contain species that are not present or less represented in the layers below, the alterite or C horizon. This is indicated in Chap. 3. If there is a difference in the A horizon mineralogy, it must be either due to a higher intensity of weathering due to rainwater and clay interaction, or to the influence of the chemistry engendered by plants on clay minerals. Since there is rarely an indication of more highly weathered minerals in the A horizon, such as gibbsite, one might suspect that the influence of plants can account for the differences in clay assemblages between A and C (alterite) horizons. We would like to investigate this possibility using studies based upon time which demonstrate the dynamics of plant-clay interaction. The next step is to identify the general occurrence of soil clay minerals as a function of their occurrence in alteration profiles. The last step is to identify clay mineral assemblages by plant associations or ecological types. The concept of the interaction of clays and plants in a mutual interaction is little explored at present and merits more consideration.

### 5.1

## Dynamics of Clay Reactions in the Soil (Plant/Clay Interaction) Zone of the A Horizon

### 5.1.1

#### Disequilibrium in Plant/Soil Zone Clays

The general descriptions of clay occurrence given in Chap. 3 indicate that the surface materials react to chemical change much faster than do deeper zones. Such a schema has been evoked by Jenny (1994) and Birkeland (1984, p. 224). We would like to go into this aspect of surface clay mineralogy in a little more detail.

To summarize, the origin of clay minerals under weathering conditions is hence two fold, one of water/rock interaction where essentially anhydrous or low hydration state minerals are transformed into new, hydrous (OH) forms and a second and very important origin and/or transformation of clays which occurs in the soil zone where plants interact with their clay-rich silicate substrate. This dual origin schema is the key to understanding the resources and their potentials which are the soils of the Earth.

One of the fundamental causes of change at the surface is the interaction of plants with the silicates which is effected by changing the chemical constraints of the sur-

face system. Figure 5.1 shows, in a schematic manner, the effects of plants, especially grasses or prairie plants, on an alteration profile. At the surface one finds the root zone, where interaction of plants and clays is greatest. Plant roots produce a complex array of exudates which are most often transformed by soil bacteria into other organic compounds. The root zone is one characterized by oxidation. Most plant roots need oxygen to survive. The root zone is one where air, solids and water coexist. At times the air zone is reduced, as in the case of aquatic plants, but in general plants need oxygen from air to grow well. The soil porosity, for the most part of the time occupied by air, is where oxidation can occur. Soil porosity is typically closed to a large extent under conditions of rainfall, where clays capture water on their surfaces and within the interlayer layers and hence swell to decrease the porosity. Normal cycles of little or no rainfall allow the surface layer of the soil to dry partially and open porosity. Depending upon the amount of organic matter present and its state of chemical activity, one can expect more or less reducing conditions in the overall chemistry of the solids of the soil. However, there is a continual re-equilibration between air (oxidizing) and organic matter (reducing) where there is loss of organic carbon through oxidation, and production of  $\text{CO}_2$ . The overall, long term, trend is for the silicates to be oxidized in non anoxic soils. This promotes the de-stabilization of iron-bearing minerals where the iron is in the divalent state. Thus one tends to find that high temperature trioctahedral phyllosilicates, such as chlorite and biotite, are unstable in soils (the plant/silicate interaction zone). This instability of rock-forming phyllosilicates engenders the formation of soil clays minerals initially of the HI or soil vermiculite type. Such changes occur of course in water/rock interaction zones as described in Chap. 4.

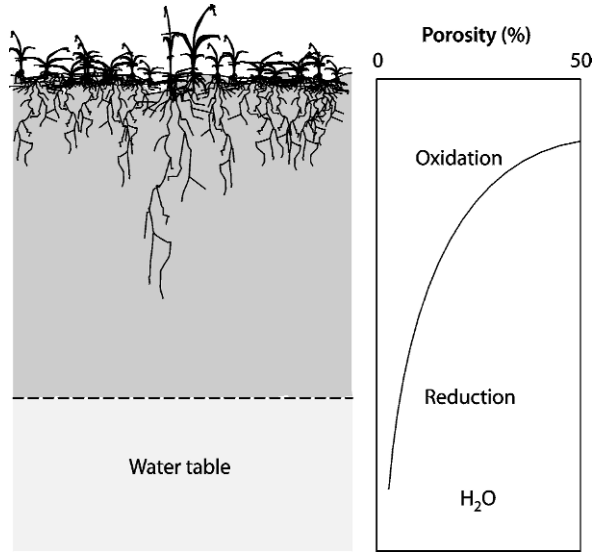
### 5.1.2

#### Dynamics of Clay Reactions in the Soils

Following the conclusions of Dethier (1986) the alterations involving water-rock reaction are those responsible for chemical dissolution, below the soil-organic interaction zone. Clay minerals are produced from the less soluble elements in the high temperature silicates, notably alumina and silica. This process takes hundreds of thousands of years. Once clay minerals are formed they are approximately chemically stable under temperate climate conditions. The rate of formation of new minerals in the upper, soil horizon (plant/silicate interaction zone) shows a strong tendency towards stabilization after hundreds to a thousand years. One can probably think of the A and upper B horizon of alteration sequences as being those of mineral chemical re-organization which are generally matter-conservative, i.e. one where mineral transformation is dominant more than dissolution-recrystallization. Loss of material comes largely from physical transport of clay particles in the soil column and under strong conditions of erosion where clays and larger particles are transported physically out of the system. The alterite, C horizon is one of chemical interaction and the A-B horizon one more characterized by mineral interaction. This is true for temperate climates but under tropical conditions, the 2:1 minerals become unstable and chemical alteration is the rule throughout the alteration profile.

One should then consider these differences in rate of mineral change as a function of distance from equilibrium and the type of transformation necessary to attain a final steady state. In the case of rock water interaction, the initial material is of high

Fig. 5.1. Illustration of the impact of plants on the solution chemistry through the increased porosity towards the surface of a weathering profile



temperature origin, igneous, metamorphic or diagenetic (sedimentary rocks) origin. These reactions are relatively easy to envision but perhaps not all that easy to accomplish at low temperatures. If one considers metamorphic rocks, often the minerals present in a rock are zoned showing chemical disequilibrium despite reactions producing stable minerals which occur over millions of years at temperatures of hundreds of degrees. The distances of chemical diffusion necessary to attain an equilibrium state are on the order of less than a millimeter. Velde et al. (1991) indicate the relations of time and temperature necessary to form a homogeneous chlorite composition in diagenetically altered rocks. Here the rates of change within the mineral structure are in fact rather slow. Alteration of rock silicate minerals is in general much more complicated, necessitating complete mineral transformation and crystal growth. Hence one should not be surprised at the million years or so necessary to transform a rock into a new clay assemblage.

However, in the soil zone, one finds mineral changes which occur over much smaller intervals of time. In fact the observation period for most surface horizons cannot be much greater than tens of thousands of years due to erosion and climatic changes which have occurred and are still occurring. Thus the upper part of a soil profile must represent the most recent events in mineral change. In order to appreciate the importance of reaction rates we can observe two similar situations of clay mineral adjustment to environmental (chemical) change. We will consider two situations where grasses affect minerals which are incorporated into soil zones by surface deposition/salt marsh sedimentation:

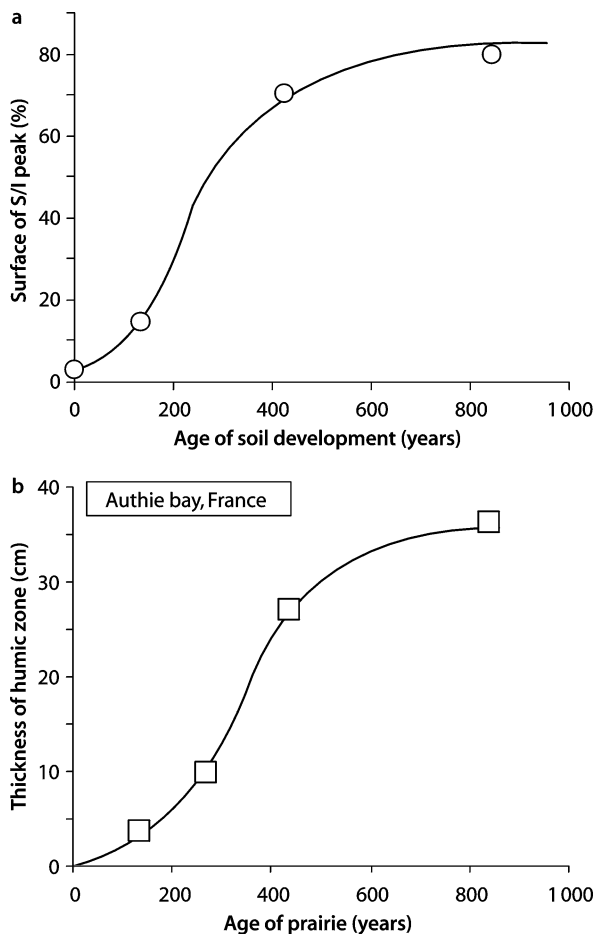
**Baie d'Authie.** Velde et al. (2003) used cores in poldered sediments from a northern French river bay flowing into the Channel, to show clay mineral change developed over 850 years under prairie developed from initial channel sediments. As sedimentation increased along the banks of the Authie river, sections were successively poldered

(i.e. protected from further sediment influx) and allowed to develop a natural prairie growth which was grazed.

The initial sediments were dominated by clays coming from continental erosion, essentially those from farmed or prairie lands. They should be considered to be in near equilibrium with the prairie grasses which develop on the sediments. The upper humic portion of soils developed on these sediments under grazed prairie are slightly basic, pH 7.5. The thickness of the humic A horizon layer developed as a function of time forming a plateau value after about 500 years (Fig. 5.2b).

The clays maintained the initial sediment illite-smectite mineralogy (both S/I and I/S). However below the A horizon zone they gradually were transformed into a very smectite-rich S/I mineral (pH 8.5). The illitic clay assemblage was maintained in the grass root (humic) zone. The development of the clay portion into a smectitic S/I mineral is shown as change in area percent of the I/S peak compared to the other clays present (Fig. 5.2a). Here also the change in proportion of the S/I phase reaches a pla-

**Fig. 5.2.** Data from Velde et al. (2003) for samples of poldered sediments, Authie Bay, north of the Somme estuary on the Channel. Age of soil development indicates poldering event when sediments were turned into grazing land. Parallel development can be observed in the development of the smectite-rich interlayered mineral (S/I) indicated by the relative area of the diffraction peak at depth below the soil, organic interaction zone (a) and the thickness of the upper, humic zone (b). Here it is apparent that change in clays, development of the S/I phase and the thickness of the humic zone and organic development are closely related. This suggests that the different parts of the alteration profile formed on sediments develop at about the same rate



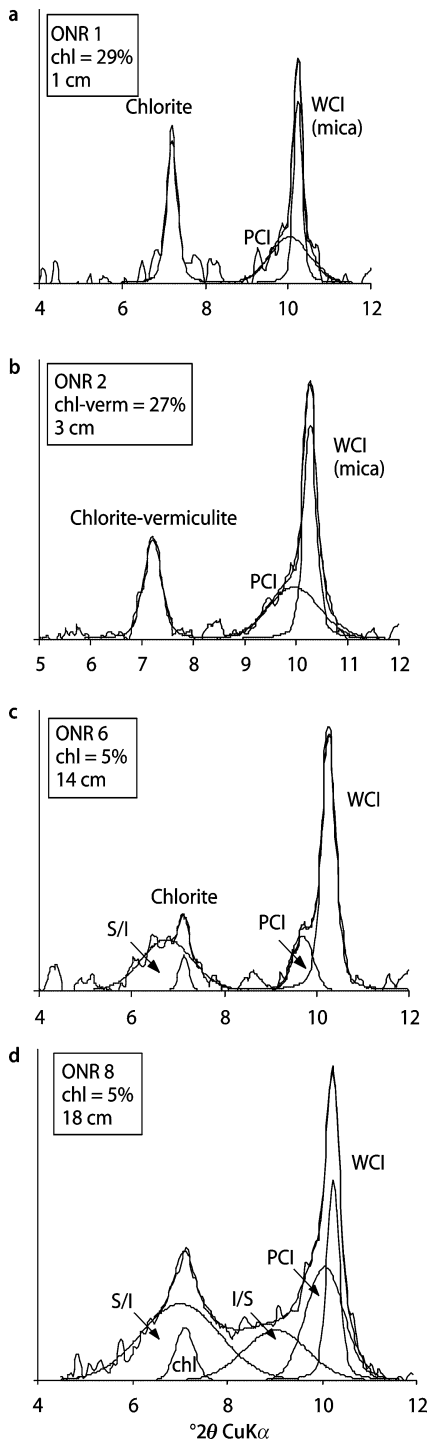
teau value after about 500 years similar to the development of the humic zone. In the A horizon of the developed prairie soil the illite and I/S minerals were maintained with only slight change in mineralogy. The initial clay material here was of soil origin and its illitic, potassic mineralogy was maintained by the development of prairie on the sediments. Thus one finds a change in the initial sedimentary material which forms two parts of the profile, the A horizon and the lower, "C horizon". The reaction takes roughly 500 years to establish an equilibrium value. In this example the clays in their initial state (where soil development begins) are near to a soil chemical equilibrium in that they are derived from the soils of the French countryside, largely in prairie or grain farming form most of the period considered. In this example it is quite clear that there are two portions of the upper alteration profile developed by prairie forming on sediments. The upper, root-humic zone favors or stabilizes different illite-smectite minerals whereas the lower, plant-free zone favors smectitic S/I.

The initial material is a soil clay assemblage which should be near to equilibrium with plants from the same temperate climate such as that of northern France and southern England. Hence the rate of adaptation to new chemical constraints is relatively rapid, on the order of hundreds of years. However the chemical potential of change is not great, and the reaction rate would be relatively slow.

**Delaware Bay area.** An example of an entirely different nature but occurring in a similar setting is given by Velde and Church (1999). Here a natural salt marsh sedimentation was observed in the southern Delaware Bay area. The effect observed is that of plants growing on deposited continental shelf sediments coming in on storm events. These sediments are composed of essentially high temperature mica and chlorite (glacial flour from the Canadian Shield). This sediment deposit in the salt marsh prairie shows that mica and chlorite were transformed into an illite and illite-smectite mineral assemblage in the root zone (pH 5–7 depending upon the season). The zone of mineral transformation is thin (several centimeters) and sedimentation rate sufficiently great so that one can deduce the average time necessary for the mineral transition to be about 4 years, at 5 cm depth. Subsequent burial by further sedimentation stabilizes the clay mineral assemblage developed by the spartina grasses. In this case unstable, high temperature detrital minerals are transformed directly into the illite-smectite (I/S and S/I) mineral assemblage in the prairie root zone (Fig. 5.3). There seems to be little or no soil vermiculite formed in the process. One sees the loss of chlorite, the 14 Å mineral in the upper zone (1–2 cm).

We see in these two examples of similar plant regimes, (salt marsh and near shore prairie) under very similar climatic conditions (temperature and rainfall), that the mineral assemblage developed by salt marsh and normal prairie grasses is one dominated by mixed layered illite-smectite minerals. However the rate of reaction is quite different depending upon the initial materials subjected to the effects of plant/silicate interaction. The rate of reaction depends on the disequilibrium between surface conditions and plant regimes compared to those that the silicate materials have experienced in the past. In the case of Delaware Bay sediments, high temperature chlorite and mica are subjected to plant interaction whereas in the case of the Baie d'Authie the input material is already soil-equilibrated. The difference in reaction rates here is on the order of  $10^2$ .

**Fig. 5.3 a–d.** Sequence of clay mineral changes in a salt marsh depositional soil as a function of depth. The illite-chlorite input material is quickly changed to a new assemblage containing a mixed layered smectites/illite mineral. The burial rate is such that the reaction can be estimated to occur in about 4 years time. *S/I* = smectites-rich interlayered mineral, *I/S* = illite-rich mixed layer mineral, *PCI* = poorly crystallized illite, *WCI* = well crystallized illite. Data from samples reported by Velde and Church (1999)



Thus within the same soil interaction zone, under the same climatic conditions and with very similar vegetation, reaction rates forming soil clays can be very different depending upon the types of material present. However the reaction rate in forming clays (mixed layer illite/smectites) from high temperature minerals (muscovite and chlorite) is nevertheless much faster than the hundreds of thousands of years to millions necessary to transform rock into clay under the water/rock regime. One can attribute this to an input of supplemental energy through plants. Biological processes are often more efficient than solely mineral ones; one can cite the formation of aragonite which is a very high pressure and temperature mineral form of calcite effected by common shell animals in the sea. Energy input by living organisms controlling chemistry can be very important.

Nevertheless, the hierarchy of reaction rates will be respected according to the difference in potential energy between the reacting phases under the action of plants. The further from equilibrium a reacting phase, the faster it will transform. A corollary to this observation is that when soil material is taken from its state of equilibrium into another situation where new chemical or physical parameters prevail, it will react at a rate according to the difference in energy from its preceding state and the new one. For example, one would expect that soil clays produced in a high mountain zone will react more rapidly to new conditions of soil interaction at sea level than those coming from low lying prairies for example. The parameters of temperature, rainfall and plant type will combine to affect the clay materials.

## 5.2 Clay Mineral Types in the Plant/Soil Interaction Zone

### 5.2.1 Illite

Illite is sufficiently common in soil clay mineral assemblages as to be entered into soil taxonomic criteria (Harris and Zelazny 1985). This being the case what are its origins?

#### *Formation of Illite in Soils*

Classical studies by Jackson (1964b) and more recently a summary by Righi and Meunier (1995) and Ellis and Mellor (1992) indicate that soil illites have their origin in high temperature micas, usually muscovite, which are inherited in the soil sequence from the source materials on which the soil is formed. Such a situation is due to the preponderance of farmed soils which are largely formed from sedimentary and low grade metamorphic pelitic rocks. This origin supposes that soil illite forms only from mica-containing source materials. Most of the general studies describing illite genesis in this manner indicate that large mica flakes break into smaller particles essentially by physical processes until they become clay sized. The aluminous dioctahedral muscovite changes composition becoming an illite, a potassium-poor, silica-rich slightly more hydrous mica. Generally there is no mention in these studies as to how the mica composition changes to that of illite (with less potassium and more silica in the tetrahedral sites) except by leaching of potassium. The extensive review by Reichenbach and Rich (1975) indicates that the consensus at that time was that potas-

sium leaching in small micas created soil illite. However in at least one observation Meunier (1980) has shown that illite (low potassium, high silica) can form by growth in potassium feldspar by pseudomorph processes during early stages of rock/water interaction during granite weathering. Such an occurrence indicates clearly that illite can be formed from a non-phylosilicate mineral under surface conditions.

### *Stability of Illite in Soils*

The illites occurring in soils are often considered to be unstable in their turn in studies of soil genesis, where they are assumed to be transformed into vermiculites (Wilson et al. 1984; Wilke et al. 1984; Koch et al. 1992) or interstratified illite/smectites (Hughes et al. 1994; Dabkowska-Naskret and Dlugosz 1996; McDaniel and Nielson 1985; Böhmann and Schoeman 1995). Illites transformed into smectites or I/S minerals are reported by Ross et al. (1987)

However, the illite or the illite content of I/S minerals is seen to increase in the upper, organic soil horizon layer compared to assemblages from greater depth as has been reported in a number of instances suggesting that it is in fact stable in the upper soil horizons. An example is given by Kuzila and Lewis (1993) where loessal soils in Nebraska were studied. Here we see a smectite-rich interlayered mineral (S/I) of loessal parent material origin transformed to a more illitic I/S mineral in the upper B horizon of a prairie soil. Spiers et al. (1984) show data which indicate the strong shift in illite content of mixed layered minerals and the formation of vermiculite in the A horizon of Solonetz soils in Alberta (Canada). Boettinger and Southard (1995) present data which indicate a change of smectitic I/S minerals into more illitic I/S minerals in the upper horizons of sage and grass desert soils derived from granitic materials.

Illite content related to plant regime has been reported by Tributh et al. (1987) and Singh and Goulding (1997) who indicate, using controlled field experiments and XRD spectra, that potassium loss is accompanied by loss of illite in soil clay assemblages. However, Tice et al. (1996) give data which indicate the formation of illite in the A horizon of a sandy loam under oak based upon diorite rock in the San Gabriel mountains, California. The effect is not seen under pine trees. Madsen and Nornberg (1995) also demonstrate that the type of vegetal cover can influence the clay mineralogy of the A horizon in soils derived from glacio-fluvial material in Denmark. Grass cover favors the formation of illite while spruce shows a strong tendency to produce vermiculite (HI minerals). The lower portions of the soil profiles show I/S (illite-rich illite-smectite mixed layer mineral) and S/I (smectite-rich illite-smectite mixed layer mineral) plus illite as the major clay minerals.

It is clear that illite and illite/smectite mixed layer minerals are intimately associated with the plant cover in the soil interaction zone.

### 5.2.2

#### **Kaolinite**

This mineral is almost omnipresent in soil clay assemblages. Its relative importance is usually related to rainfall or age of alteration. The higher the rainfall, the more kaolinite one finds. Millot (1964, chapter 12) outlines the long term trends of chemical alteration and the types of clays one finds under different conditions of alteration.



There is a general relation between soil fertility and kaolinite content because kaolinite has neither a significant cation exchange capacity, where useful cations can be attracted and desorbed by plants. Further it is devoid of potassium, and hence not a reservoir for this precious element. Thus kaolinite is often more of a hindrance to agricultural soil use than anything else.

### 5.2.3

#### Oxides and Oxyhydroxides

These minerals occur frequently in soils in minor amounts, showing their presence by a typical color, red to brown, which indicates a general state of iron oxidation state (see Table 1.6). However, much material is also present which does not color the soil material. It is in fact a complex of hydrated and hydroxyl alumina and minor amounts of other elements. This is allophane, a material without specific composition nor atomic order. Hence it is difficult to call it a mineral but one would more likely indicate it as a substance in soils. Oxyhydroxide forms of alumina and iron, are present in large amounts under two situations in soils: one when glassy materials alter to form soil materials under conditions of high rainfall, andosols, and the other in laterite deposits (see Chap. 6). Andosols are relatively transformed material, where much of the Si, Al, and Fe are preserved and the alkali and alkaline earth elements are lost through weathering. Al and Fe often are present in the same materials. Laterites are highly transformed materials, under conditions of high rainfall and high temperatures. Here most of the initial silica content of the parent material is lost under the weathering conditions. Alumina and iron are usually separated into specific, crystalline phases.

Gibbsite is a somewhat special case of aluminum hydroxide formation, found as a specific mineral. It occurs in the early stages of weathering, in the water/rock interaction zone, and can be found in very altered soils of the laterite type. Although hydroxyl-oxides can have a very high cation exchange capacity, their presence in soils does not usually signify high fertility.

### 5.2.4

#### Mixed Layer Minerals

##### *Formation of Mixed Layered Minerals (MLM) in Soils*

Soil clay minerals are basically of two sorts: 1:1 and 2:1 structure minerals. These minerals are found to form in the water/rock interaction zone also. However, the 2:1 minerals are most often mixed layered, i.e. showing alternance of two or more types of clay types. These structures are typical of soil clay minerals. Mixed layering indicates heterogeneity between individual 2:1 layers in either charge or charge site origin. In diagenesis such mixed layer minerals occur currently where they can often be considered as intermediate stages in a mineral reaction from smectite to illite for example (Velde 1985, chapter 3.5). However in soil clays such a transition type is not all that clear in many instances. Some types of mixed layer minerals such as kaolinite/smectites can appear to be transitional in type (Herbillon et al. 1981, for example). Often smectite is interlayered with either vermiculite (either HIV or HIS) with increasing abundance as one approaches the soil organic horizon (Fichter et al. 1998; Righi and Lorphelin

1987; Olsson and Melkerud 1989, for example). Most often smectite/HIS or smectite/HIV minerals are considered to be the indication of gradual mineral change towards a smectite mineralogy. Other interlayered minerals such as vermiculite (HIV) and illite have been described as representing gradual change from illite to vermiculite in soils towards the surface horizons (Bain et al. 1990).

Initial stages of weathering show the presence of biotite/vermiculite minerals which are normally regularly interstratified. This is a special and obvious case of mineral weathering via a transitional mineralogy.

By contrast, illite/smectite mixed layer minerals are not often considered as transition state minerals. Usually they are not considered much at all. However these minerals which are of two sorts in soils both being randomly interstratified, are very often present in soil mineral assemblages. Probably the I/S and S/I minerals are the most abundant clay minerals in fertile agricultural soils. The reason is obvious, they contain the major part of potassium resources in soil clay minerals along with illite. Potassium is found in all plant parts and is known to contribute to plant growth, the underlying physiological reasons are not clearly known at present (Treshow 1970, p. 182). It is a major factor in plant growth and fertility. It is found in abundance in 2:1 minerals. The importance of illite and illite/smectite mixed layer minerals is great. Let us consider it in more detail.

#### *Mixed Layered Minerals (MLM) as Alteration Products*

It is striking that in the descriptions of rock alteration where minerals are of high temperature origin, the so-called crystalline rocks, almost no identification of mixed layered minerals is reported in the descriptions of Chap. 4. For the most part, the transformation of feldspars, pyroxenes, olivine and various metamorphic minerals such as garnet, amphibole, and so forth form either kaolinite (1:1 mineral) or illite, smectite or vermiculites (2:1 minerals). The major cases of the presence of mixed layer minerals are during the de-stabilization of the trioctahedral mineral biotite and chlorite (Righi et al. 1999; Egli et al. 2002; Buurman et al. 1976; Kretzschmar et al. 1997; April et al. 2004). The initial clay material is vermiculite-mica or smectite-mica. These phases are destabilized in the A horizon for the most part after several hundreds of years.

One can propose the following changes in clay layers in such minerals:

Mica, chlorite → expandable high charge 2:1 layer → expandable low charge 2:1 layer

Righi et al. (1999) and Gillot et al. (2000) indicate with detailed chemical analysis of individual mineral grains that the changes are internal and chemical, i.e. the substitution of Al for Mg and Fe in the structures forming eventually a dioctahedral mineral from initially trioctahedral minerals. As the layer charge and composition changes, the materials become more smectitic. The change from mica or chlorite to high charge mineral usually results in a mixed layer mineral with a strong combined "superstructure" X-ray diffraction peak indicating regular interlayering.

These alterations are effected in the plant/silicate interaction zone for the most part. The changes occur when a pre-existing phyllosilicate of high temperature origin is destabilized under surface alteration conditions. The reports are for young soils where most of the rock material is as yet untransformed and the relatively thin soils are af-

ected by organic materials for most of their depth. Otherwise, the numerous references to mixed layer minerals and their transformations cited in Sect. 3.3.4 for example are largely confined to the upper portions of alteration sequences. A special case is loess-derived soil material which is treated further on in Chap. 7.

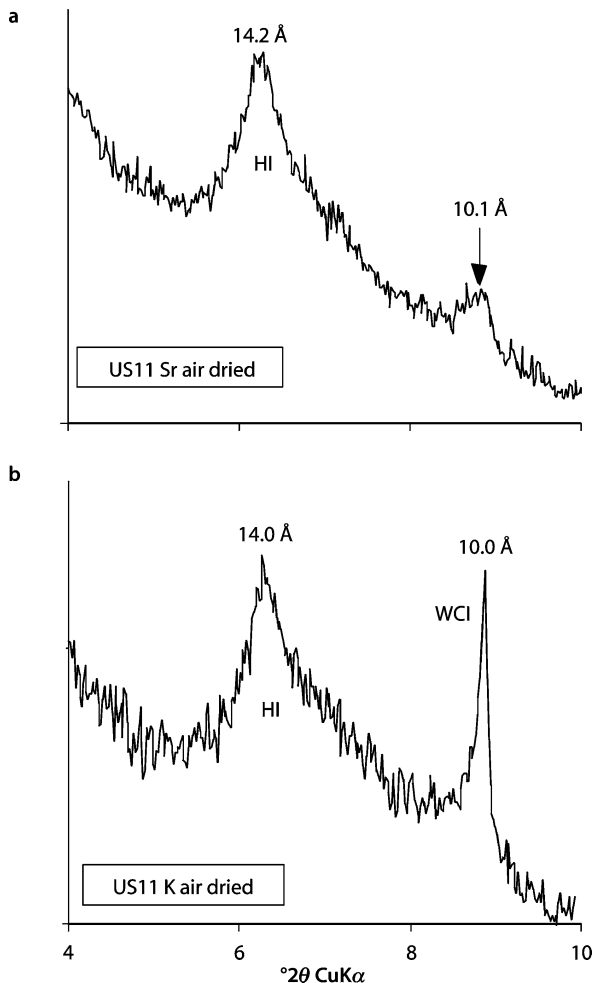
### *Soil Mixed Layer Minerals*

**HI mixed layer minerals.** HI-mica or HI-illite minerals occur when high charge layers are present, most likely of different charges which creates alternating behavior of the layers as far as interlayer ions are concerned. Millot (1964) and Millot and Camez (1963) have indicated that this mineral type is very common in coniferous forest soils in eastern France. As a basis for discussion we have defined the interlayer ions as being of two types, hydroxyl Al where the aluminum forms a more or less continuous Al-OH network and Al exchangeable where the Al is in an ionic form, associated with some OH units. The distribution of these two types of layers determines the mixed layer type, by X-ray diffraction identification (see Sect. 1.8.4 and Annex 4).

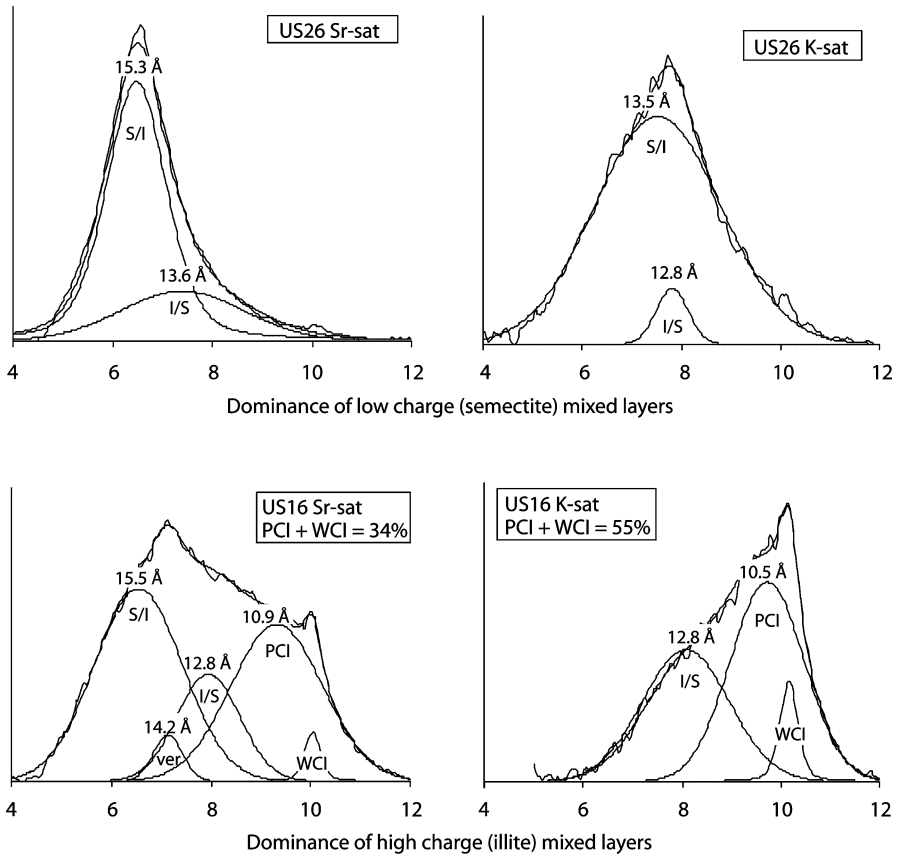
A typical behavior of HI minerals can be seen in Fig. 5.4, where forest soil minerals have been subjected to potassium treatment (0.05 M KCl). An operational definition of HI (hydroxy-interlayering) is that the basal spacing does not change on potassium treatment at 25 °C (Chap 1.8.4). Aluminum exchangeable HI minerals can in many instances by contrast change their interlayer spacing to 10 Å upon potassium treatment at 25 °C. As one could expect, the natural cases are complex, where some layers respond while others do not. Thus HI mixed layer means an Al-OH interlayer phase where the proportion of hydrated exchangeable aluminum ions is variable compared to the hydroxyl-interlayer of Al-(OH) material which is not exchangeable. Figure 5.4 shows a typical case of response to potassium exchange where a portion of the layers are exchangeable while others are not. This is an interlayer of hydroxyl-interlayers with high charge exchangeable Al ion layers.

**Smectite/illite mixed layered phases.** Smectite/illite is probably the most common mixed layer type of soil clay mineral. It is present under prairie and deciduous forest conditions on a variety of parent rock type soils. A brief study by Velde (2001) indicates that various types of sedimentary rock, glacial till or loess give rise to similar clay assemblages dominated by illite/smectite minerals under prairie grass conditions. Similar mixed layer clay mineral assemblages have been reported by Righi et al. (1995) for clays developed on salt marsh sediments put into culture. These marsh materials are an average of deposition of clays coming from the Loire and Gironde rivers, draining much of center and western France and also indicate a clay assemblage developed upon marsh sediments coming from the Channel (Seine river and Thames river input) and deposited in northern France. In these sediments (based upon soils of course) and soils one finds two illite-smectite mixed layer minerals, one of high illite content and the other of high smectite content. Both are disordered in stacking type. It is important to insist on the frequent presence of both types of interlayered minerals in soil clay assemblages. The smectite-rich mixed layer mineral with a disordered stacking sequence is well known in series of diagenetic sedimentary rocks. However, the disordered I/S mineral is not found in buried sediments and rocks. It is particular to the soil clay environment.

**Fig. 5.4.** XRD spectra of an agricultural soil sample from Pochahantas, AK, USA (Velde 2001); **a** Sr-saturation state; **b** K-saturation state. Low concentration KCl solutions (0.01 M) effect a collapse of a part of the 14.2 Å (*HI* or hydroxyl interlayer) material giving a sharp (*WCI*) illite peak (10 Å) under air dried conditions without heat treatment



An interesting aspect of these clay mineral assemblages is that they seem to represent overall differences in layer charge, for each of several phases. In initial samples, saturated with Sr ions, with almost no illite present (Fig. 5.5) one finds a dominance of low charge *S/I* mixed layer minerals. Potassium saturation (saturation at the very low concentration of 0.05 M KCl) closes a few layers in the *S/I* structure, at times forming an *I/S* phase, and/or illite-rich mixed layered mineral. In samples with more abundant illite layers in the mixed layer minerals, and significant illite (*PCI* and *WCI*) present, the *I/S* phase is in variable quantities. Upon potassium saturation of these samples, one finds that there is a strong tendency to form more illite as an independent phase (*PCI* and *WCI*) as well as more illite layers in both *S/I* and *I/S* as seen by shifts to lower *d*-spacings for the major peaks (Fig. 5.5). This indicates that the more illitic mixed layer clay assemblages contain more high charge expanding layers in both *S/I* and *I/S* phases as well as the presence of illite itself. Bouabid et al. (1991) indicate



**Fig. 5.5.** Examples of the effect of strontium and potassium treatment (0.01 M chloride solutions, unheated, air dried samples) on different types of soil clay assemblages (data from samples reported in Velde 2001). The more of the smectitic interlayered mineral (*S/I*) present the less change with K-saturation. The more illite layers present (either in the mixed layer minerals, *I/S* or illite phases, *PCI* and *WCI*) the more layers are closed with the low intensity potassium saturation process. Both *WCI* and *PCI* increase upon treatment. *S/I* = smectites-rich interlayered mineral, *I/S* = illite-rich mixed layer mineral, *PCI* = poorly crystallized illite, *WCI* = well crystallized illite

that the potassium fixation properties are due to charge in the tetrahedral site of the 2:1 layers.

Here we see that a very light treatment with KCl increases the number of closed layers, either to 12.5 or 10 Å and increases the amount of illite material. It does not close all layers to attain the normal mono-hydrate state of 12.5 Å typical of potassium under moderate humidity conditions. The major peak of the *S/I* minerals is most often of a higher spacing than the 12.5 Å spacing for a monohydrated cation. This effect of double hydrated potassium ions is especially evident when the initial material is *S/I*.

In many cases a large number of initially expandable interlayers are high charge, taking up potassium to form either illite layers in the mixed layer mineral or forming

independent diffracting domains of pure soil illite. It is clear in these examples that illite is not necessarily a stable, closed layer structure in soils. This is all the more evident in that the samples shown and others investigated were taken from agricultural soils, at the end of a growing season. If potassium fertilizer was added, as in the case of the laboratory treatments, the clays would become illitic. Virtually all agricultural practice today involves the addition of potassium to soils. Since the clay minerals have a capacity to close layers and fix potassium after a growing season where plants would have extracted potassium, it is evident that the absorbed potassium forming independent illite minerals, had been extracted by plants during their growth cycle. Thus it appears that exchangeable potassium is not only absorbed onto clay surfaces, but also within the clay structure.

**Kaolinite/smectite mixed layer minerals.** Kaolinite/smectite (K/S) minerals have been known for some time (Sudo and Hagashi 1956 for example) and have been identified in soils clay assemblages since the 1960s and 1970s (Altschuler et al. 1963; Wilson and Cradwick 1972; Watanabe et al. 1992; Kodama et al. 1976). Thus they are well recognized, and have been studied for quite some time. Unfortunately this is about all that one can say today. These minerals can be a minor or major part of the soil clay mineral assemblage, they can be formed in soils with quite varied parent material; acid volcanic rocks (Yerima et al. 1985; Takahachi et al. 1993; Quantin et al. 1988), basalts (Wada et al. 1990; Vingiani et al. 2004), young sediments (Mohindra and Parkash 1990). Climates range from Ganges plain monsoon to arid climates and from Scottish cool to Hawaiian warmth.

Mixed layered minerals of 1:1 and 2:1 structures are rather rare in soils and alteration assemblages but they do occur in certain specific situations. They have been reported by Takahashi et al. (1993), Wada et al. (1990), Yerima et al. (1993) Schultz et al. (1971), Wilson and Cradwick (1972) in soils based upon volcanic materials of basaltic to acidic composition. These occurrences are related to andosols and the soils have andic properties.

One characteristic of K/S occurrence is that the smectite content of the soils or the smectite portion of the smectite-kaolinite mixed layer mineral generally decreases upward in a soil profile. This is generally taken to indicate increasingly severe weathering conditions or chemical effect in the profile (Yerima et al. 1985). The reaction of smectite to kaolinite is generally assumed to be observed in such sequences.

Bühmann and Grubb (1991), Herbillon et al. (1981) and Vingiani et al. (2004) report the occurrence of kaolinite/smectite minerals in soils based upon basalt flows. These occur in rather dry grassland landscapes and seem to be related to topography (see Chap. 7 for a more complete discussion).

However, Mohindra and Parkash (1990) indicate the presence of kaolinite/smectite minerals in alteration profiles of the monsoon climate Gangetic plain in India. Old and young alteration profiles show this mineral developing from a variety of detrital minerals. Churchman et al. (1994) summarized the occurrence of kaolinite/smectite minerals in Australian soils as far as the mineralogy is concerned but little information concerning their place in soil genesis is given in their brief account. According to these authors one can find all stages or compositions of interlayering between the pole minerals.

Karathanasis and Hajek (1983) review several possibilities which have been proposed for such a transition by various mechanisms and propose in their turn a dissolution-precipitation model based upon thermodynamic considerations. These combined with mineral chemical formulae from a series of clays from four pedons indicate in fact a more complex change of smectite from a montmorillonite type to beidellite which would then transform to kaolinite. The beidellite would first become a soil vermiculite mineral, and eventually the adjacent silica tetrahedral layer next to the interlayer hydroxyl-alumina sheet would invert its structure to form a bonded tetrahedra/octahedra sequence forming kaolinite.

It is generally felt that K/S minerals are transitions between smectite and kaolinite in soil profiles. In many cases, the smectite is iron-rich and the stability of the kaolinite/smectite depends upon the oxidation state of this element (Bühmann and Grubb 1991).

**Chlorite/mica mixed layered phases.** Li et al. (2003) report the presence of a disordered mica-chlorite mineral in Chinese red soils. It seems to be rather common also in loessic soils and fluvial deposits, at least in the Shanghai area (observations of BV). This mineral is an illite/magnesium chlorite phase which is non-expandable. Its origin is unclear in that it appears in recent loess as well as red soil deposits developed from Tertiary sedimentary rocks. However, the high amount of loess materials in central China might indicate that this mixed layer mineral is related to a desert soil or desert alteration process. It is a potential source of potassium, more stable than illite at least under flood rice cultivation environments.

### **Summary**

It appears that most mixed layer clay minerals originating from surface alteration processes are found in the soil horizons (A and B) of alteration profiles. These are the zones of plant-soil interaction. For the most part, the mixed layer clay types are between 2:1 structural types, involving HI, vermiculite, smectites and illite. As outlined in Chap. 1, these minerals are in fact strongly inter-related in that the basic structural unit is the same with differences in charge site and charge intensity. The major difference, seen by laboratory identification methods is the interlayer site occupancy. If potassium is present as the major or exclusive cation it is not hydrated and the mineral is an illite with a 10 Å structure. If the charge is neutralized by a hydrated cation it is identified as a smectite. If the charge is neutralized by Al ions, or hydroxyl ions it is an HI exchangeable mineral and if the aluminum is in a hydroxyl structure (AlOH<sub>3</sub>) it is a HI non-exchangeable mineral or a soil chlorite. It is clear that if the 2:1 structures are not homogeneous in charge site and charge intensity, some layers of a crystallite will behave as one type of mineral and the others as another. This gives the mixed layer mineral in the 2:1 family. Further, it is clear that the type of interlayer ion population will change depending upon the geochemical situation in which it is found.

## **5.3**

### **Soil Clay Mineral Assemblages by Ecological Type**

It has been known for some time (Jenny 1994; Birkeland 1984; Birkeland et al. 2003 for example) that the great groups of plant ecosystems under temperate climates, prairie

and deciduous forest, can influence the clay content and chemistry of the soil zone. It has also been recognized that these ecosystems favor certain clay mineral assemblages. In general one can consider the prairie, deciduous forest and conifer forests function as ecological plant-soil units for temperate to cool climates soil units. These types of ecological regime appear to develop, in a general way, typical clay mineral assemblages in the upper portions of the alteration profiles. We will investigate these plant regime types as they form the soil clay minerals present in the plant-silicate interaction zone. It is useful to look at the general differences in profiles seen to represent forest and prairie types. In general (see Birkeland 1984, chapter 10 for example) the main difference between these two vegetal types as they affect soils is the appearance of the E soil horizon in forest soils, one where soil clays are less abundant, acidity is higher and Fe-Al content lower. The extension of the organic-rich horizon is more limited in forest soils. Below the E horizon, one typically has a stronger concentration of clay minerals and oxy-hydroxides. Root masses are of course different, that of prairies soils being more extensive forming the thicker, more clay-rich organic plant/soil interaction zone. It is clear from such a description that the plant type has an enormous influence of the structure of the soils and therefore should have an influence on the clays formed and stabilized in the soil horizons. Figure 5.6 indicates these relations.

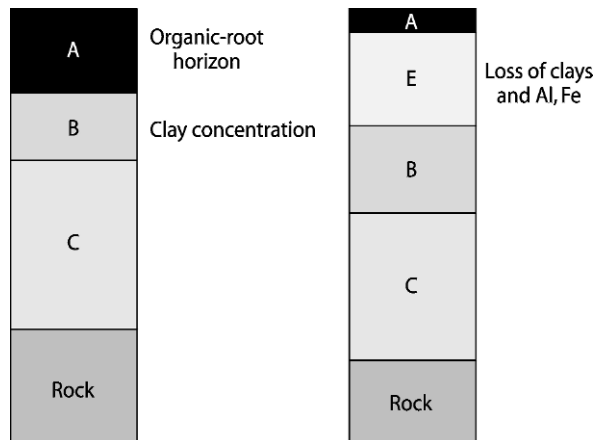
### 5.3.1

#### Prairie Soils

This category of plant type regime is dominated, usually, by grasses. They can occur under steppe or savannah climates, i.e. under cool, arid conditions or warm, dry climates. Also one finds grass dominated soils in the near tundra regimes of cold climates. The soil clays are similar under these varied climates. One can expect then that the plants are largely responsible for the clay species present.

The most important mineral types are the smectite-smectite/illite mixed layered-illite series. These are the 2:1 potassic minerals and expandable mineral types. They

**Fig. 5.6.** Comparison of theoretical forest and prairie soil profiles where one sees the development of a low clay content E horizon in the forest soils and a thicker B horizon of transported clays. The organic-rich zone is usually much thicker in prairie profiles than in forest profiles resulting in a dark gray color whereas forest soils tend to be brown





have high cation exchange capacities, and high potassium content. Below we follow the evolution of illitic soil clay minerals.

### *Formation of Illite/Smectite in Young Prairie Soils at High Altitude*

In order to answer the question of what are the parameters which form the soil clay minerals in prairies, we will look at some published work and new data on soils and their clay minerals coming from several different ecological contexts in order to try to understand the origin of their clay species. As it turns out prairie soils are only infrequently the subject of detailed pedological investigation including mineral analysis in that they have most often been farmed and hence disturbed in their spatial and mineral distributions. Such disruption is considered to make most observations of mineral sequence and origin invalid because the upper portions of the profile are mixed through agricultural practices. However several examples of undisturbed samples have been observed which can be used to our ends.

The data presented by Egli et al. (2002, 2004) and Righi et al. (1995, 1999) for chemically treated soil samples, indicate that soils under prairie or shrub growth in the French or Swiss Alps and Himalaya develop S/I minerals in their upper most levels (A or E horizon of root growth). The pH in the upper parts of these soils was between 3.5 and 5. The underlying rocks producing the soils are greenschist facies for Egli et al. (2002) where the phyllosilicates would be muscovite and chlorite and muscovite; biotite and chlorite-bearing high temperature metamorphic rocks for Righi et al. (1999) and chlorite schist for the samples considered in Righi et al. (1995). The initial clay minerals formed by rock water interaction with the substrate are chlorite or mica-smectite regular interlayered minerals or soil vermiculite types (HIV or HIS). Significant concentration of smectite-rich illite-smectite minerals is found in the clay assemblages of the upper, humic or plant root horizon occurs as a function of time, (several thousand years) as is demonstrated in these studies. The rock starting material which reacts with altering aqueous solutions in the lower portions of the soil profile involves the destabilization of a high temperature mineral assemblage which is gradually changed into one compatible with surface conditions. This clay mineral material then interacts in the humic soil horizon where a change to illite-smectite mineralogy can be observed. Egli et al. (2002) give data which indicate that the time necessary to establish a stable soil clay mineral assemblage (expressed as total smectite content of the clay assemblage) is on the order of 3 000 to 4 000 years under alpine conditions. It appears that at high altitude, prairies favor illite-smectite mixed layer minerals in the humic, root interaction layers of soils. All of these soils are acid having a pH of near 5 or less. The soil clay mineral sequence is rock-vermiculite (HIS, HIV)-smectite/illite.

Buurman et al. (1976) report on soil clay minerals developed on calcareous metamorphic rocks from alpine meadow and lightly forested areas at 2 000 m altitude. The observations are similar to those cited above, with smectite-rich I/S formed in the uppermost horizons (A<sub>1</sub> and A<sub>2</sub>). Illite is present in about constant quantities. Although no pH values are given, the presence of calcareous rock fragments would indicate values near neutral in the silicate soil matter.

Bain et al. (1990) find that muscovite is transformed into HI minerals in the B horizons of grassland soils on granite in Scotland. However, the E horizon shows significant I/S mineral presence suggesting the stabilization of this mineral in the soil zone.

### *Low Mountain Carbonate Soils*

Bottner (1972, p. 95) gives data which indicates similar relations (prairie/forest) on soils formed on carbonate substrate in low mountain regions in the south of France. Basically the prairie soils form expanding interlayer mineral soils at the surface with illite/chlorite and kaolinite at depth. In several sequences there is a contrast between prairie and forest soil clay mineralogy, especially at the surface in the upper A horizons. The mineralogy is somewhat affected by the type of calcareous rock forming the substrate but in general, the ecosystem can be considered determinant as far as the upper horizon mineralogy is concerned. Prairie favors expanding mixed layer minerals.

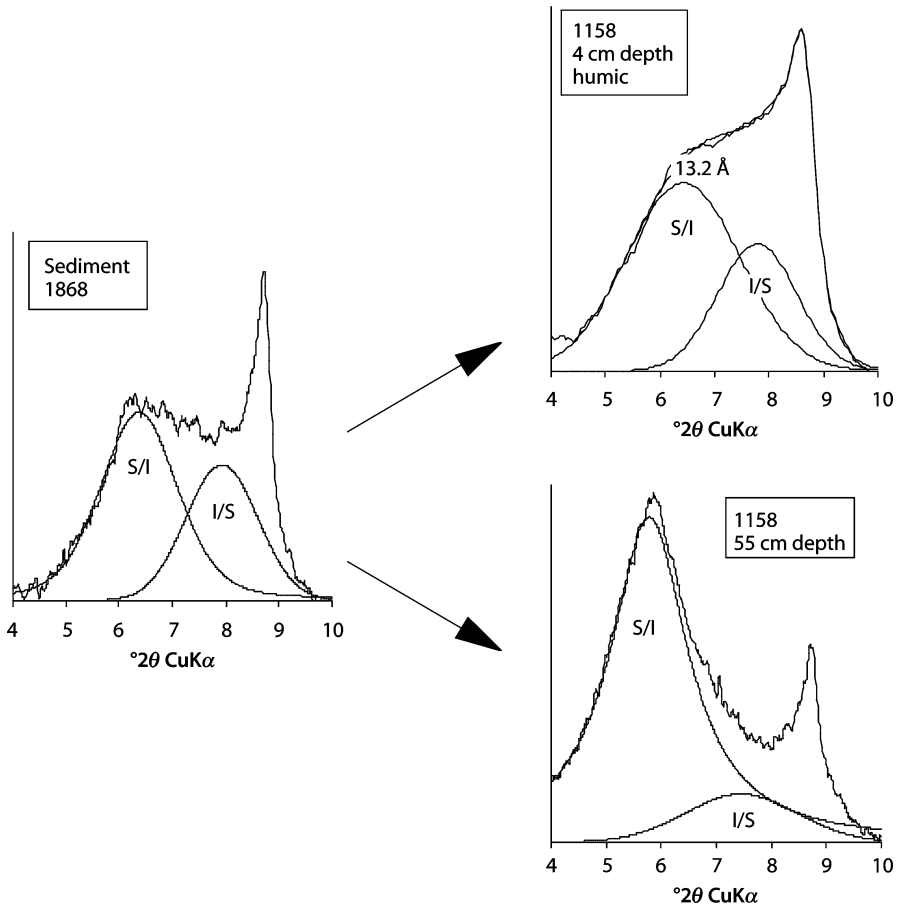
### *Studies on Poldered Sediments*

A very different situation of grass colonization and prairie soil development is that of poldered mica-chlorite sediments. In Delaware Bay salt marsh sedimentation an initial input of clay rich sediment is affected by the establishment of a prairie. Velde and Church (1999) observed the clay mineral suits produced by *Spartina* grass prairie which affect continental shelf sediments composed of essentially high temperature mica and chlorite (glacial flour from the Canadian shield). This sediment was deposited in the salt marsh prairie and the mica and chlorite were transformed into an illite and illite-smectite mineral assemblage in the root zone (pH 5–7 depending upon the season). The average time necessary for the mineral transition was about 4 years. Subsequent burial by further sedimentation stabilized the clay mineral assemblage developed by the *spartina* grasses. In this case unstable, high temperature detrital minerals are transformed directly into the illite-smectite (I/S and S/I) mineral assemblage in the prairie root zone. There seems to be little or no soil vermiculite formed in the process.

In another study, Velde et al. (2003) used cores in poldered sediments from a northern French river bay flowing into the Channel, to show clay mineral change developed during 850 years under prairie. The initial sediments were dominated by clays coming from continental erosion, essentially those from farmed or prairie lands. Here the clay assemblages were essentially those of top soils, those in equilibrium with plant regime alteration. In the upper humic portion of soils developed on these sediments under grazed prairie (pH 7.5), the clays maintained the initial illite-smectite mineralogy (both S/I and I/S) with an increase in the I/S mineral abundance but below this zone the clays were gradually transformed into a very smectite-rich S/I mineral (pH 8.5). Here the prairie maintained the illite-smectite I/S mineralogy (Fig. 5.7).

### *Continental Plains*

Kuzila and Lewis (1993) present data indicating that illite-smectite (I/S) minerals formed in the upper, humic horizons of prairie soils developed on a smectitic (S/I) loess substrate in Kansas, USA. Here a soil clay mineral of low temperature origin, smectite, is transformed into the illite-smectite I/S mineral. Spiers et al. (1984) give X-ray diffraction data which can be taken to indicate that the initial, deep smectite-rich (S/I) till clays become more illitic in the upper horizons of prairie soils from Alberta. These two studies show that prairie interaction tends to enrich the clay assemblage in an illitic (K-rich) component.



**Fig. 5.7.** Evolution of the initial clay assemblage in the Authie Bay sediments poldered for 850 years and used as grazing prairie. *S/I* (smectitic mixed layer mineral) minerals are favored at the bottom of the profile whereas illitic mixed layer minerals (*I/S*) are maintained in the upper, soil horizon. *S/I* = smectites-rich interlayered mineral, *I/S* = illite-rich mixed layer mineral, *PCI* = poorly crystallized illite, *WCI* = well crystallized illite. Samples reported by Velde et al. (2003)

A very general study of clay mineralogy across the mid United States plains area (Velde 2001) indicates that in fact the dominant clay mineralogy of these old short and tall grass zones, now under cultivation, show a dominant illite-smectite clay mineralogy with frequent occurrence of illite and kaolinite. The surface area of the illite XRD peaks (*WCI* + *PCI*) can vary from 70 to 0% of the clay mineral assemblages. Examples of the types of clay assemblages are shown in Fig. 5.8.

It should be noted that the increase in importance of the illite peaks (*PCI* + *WCI*) is accompanied by a greater surface area for peaks of the *I/S* type. This indicates that the higher illite mineral is accompanied by more illitic mixed layer minerals. The fact that a higher illite mineral content is accompanied by a higher illite layer content in

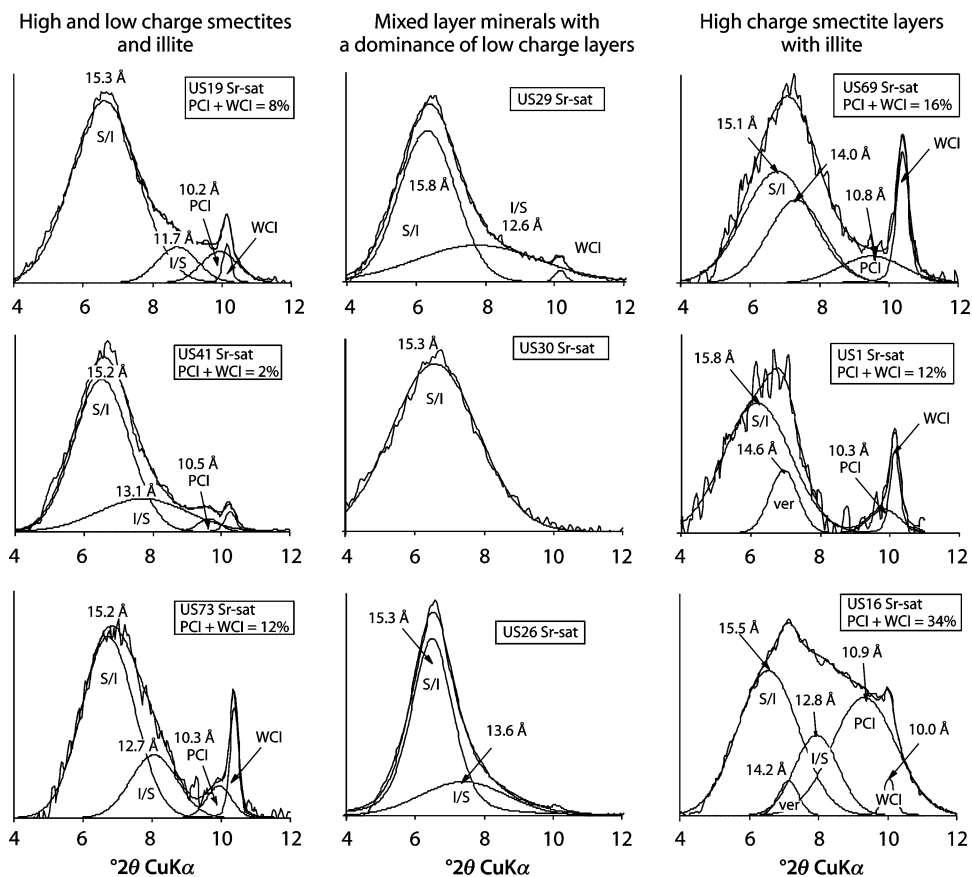


Fig. 5.8. Representation of different types of clay associations from prairie soils in Central USA. As more illite is present, the proportion of I/S, illite-rich mixed layer minerals is greater. Sr-saturation was effected by a 0.01 M SrCl solution and the spectra were run in the air-dried state. S/I = smectites-rich interlayered mineral, I/S = illite-rich mixed layer mineral, PCI = poorly crystallized illite, WCI = well crystallized illite. Samples reported by Velde (2001)

illite-smectite minerals is important in interpreting the chemical forces in the upper portion of prairie soils. This suggests a higher amount of potassium available in the soil materials. All phases react to this potassium availability.

### Aridisols

Delhoume (1996, p. 70) gives spectra showing an increase of S/I and I/S minerals in the upper horizons of desert soils (sparse grass and shrubs) in northern Mexico which replace soil vermiculite found at depth. Illite also becomes more abundant. Boettinger and Southard (1995) give data which indicates the increase in illitic illite-smectite mixed layer minerals in the upper portions of Mojave desert soils populated by brush and grasses.

### *Summary*

It appears then that prairie soils, those dominated by grasses occurring under different climatic conditions, show illite-smectite mixed layer mineralogy with varying amounts of illite and mixed layer phases in the upper portions of the alteration profile, that where plant/silicate interaction is important. Vermiculites are rare in mature prairie soils whereas they can be present in significant amounts in young mountain soils. These clay mineral facies occur in young, acidic soils in mountain terrains as well as steppe areas or arid desertic areas.

#### 5.3.2

#### **Forest Soils**

We will consider two broad categories of forest types; conifer and deciduous. In general, the deciduous leaves are relatively easily decomposed by bacterial action while needle from conifers tend to produce a thick mat of organic litter on the soil surface.

#### *Conifer Forest*

Graham et al. (1990) and Millot and Camez (1963) indicate that HI is the A horizon mineral in various soils, based upon serpentine rocks, sandstones or granites. Ezzâim et al. (1999), Olsson and Mekerud (1989) and Egli et al. (2004) find HI minerals dominant in the A horizon in conifer forest soils from low massifs or alpine terrains. However, Teveldal et al. (1990) and Gillot et al. (1999) show the formation of smectite in sandy pine forest soils of nordic countries.

In general it is considered that conifer forest soils contain soil vermiculite (HI mineral) in the upper levels (A, E, B horizons) but it is clear from the few examples cited here that this is not always the case. Some of these soils can form smectites.

#### *Deciduous Forests*

Data from Carnicelli et al. (1997) and Egli et al. (2002) indicate the formation of I/S minerals and smectite in the upper horizons of deciduous forest soils found at high altitudes. April et al. (2004) indicate the formation of smectites from vermiculite in Adirondack forests in the A horizons. Harris et al. (1987) found that HI minerals were replaced by smectitic phases under woodland conditions in Florida. Bottner (1972, p. 95) indicates that deciduous forest (beech) forest soils on carbonate rock formed on low mountains in the south of France form HI mineral assemblages at the surface horizons (upper A zones). Thus it seems that deciduous forest top soils would tend to contain illite-smectite mineralogies. However on calcareous substrates there is a preponderance of HI minerals.

An experimental study of the reaction of vermiculite (pure expanding mineral, high charge smectite) to exposure in different forest soils shows the formation of HI minerals depending upon the type of tree present, conifer (spruce) or deciduous (beech), and to a larger extent, the type of soil and parent material (Augusto et al. 2001). In this study it appears that granite favors smectite forms (high charge, vermiculite) while sandstone parent soils produce HI minerals.

### Comparative Studies

Several studies have been performed in order to compare the effect of different types of vegetation on clay minerals in soils. Madsen and Nornberg (1995) demonstrate that the type of vegetal cover can influence the clay mineralogy of the A horizon in soils derived from glacio-fluvial material in Denmark. Grass cover favors the formation of illite while spruce shows a strong tendency to produce vermiculite (HI minerals). The lower portions of the soil profiles show I/S and S/I plus illite as the major clay minerals.

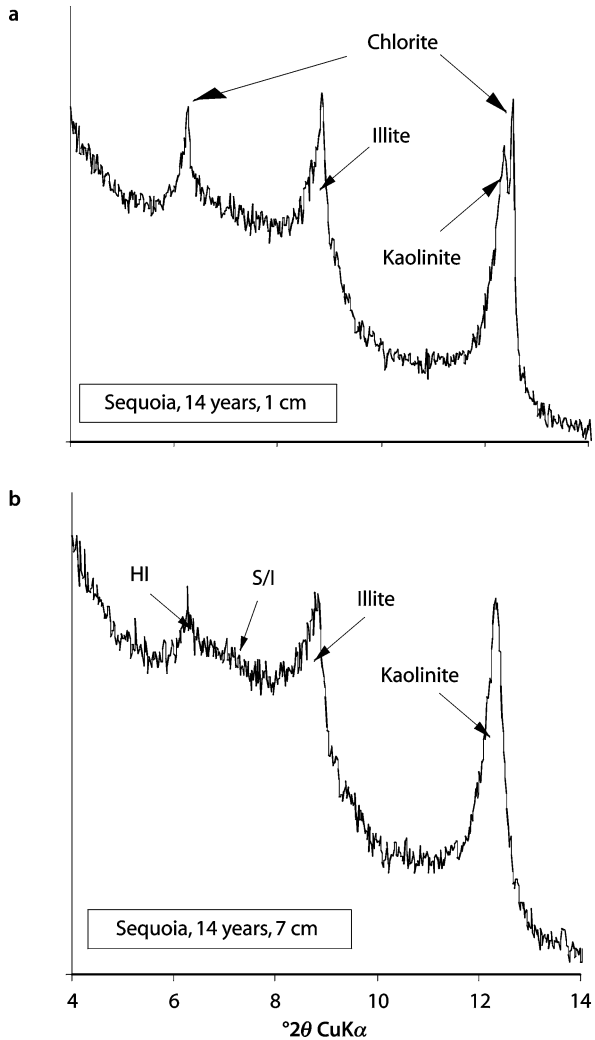
Tice et al. (1996) give data which indicate the formation of illite in the A horizon of a sandy loam based upon diorite rock in the San Gabriel mountains, California. The study reports results on a comparative study of the effect of either oak or pine forest planted on essentially scrub soils. In the A horizon of the oak forest, 41 years after planting, one finds a strong illite peak along with the initial vermiculite (HI minerals) found in the original soil as well as in the lower portions of the profile. The pine forest showed no change in clay mineralogy between the initial state or at different points at depth.

An example found in the garden of the author (BV) indicates that sequoia tree needles can produce a well crystallized chlorite (dioctahedral) after fourteen years of growth in west central France (Fig. 5.9a,b). The surface soil shows the chlorite while at depth (7 cm) this phase is not present and in samples taken from one meter from the edge of the tree cover, the clays are essentially those of the 7 cm samples beneath the tree. Here the very local chemical composition (upper 6 cm or so) seems to be sufficiently different as to form a well ordered chlorite (a very sharp and intense 7 Å peak is present) in a rather short period of time (14 years).

Unpublished data gathered by Velde, indicate that in mountain soils based upon granite (Bighorn mountains, Sheridan Wyoming) and rhyolite (Hebegen Lake, western Montana), the type of vegetation can be relatively important. Three series of samples were taken from zones near the natural prairie/forest interface. Soils below isolated trees or in small groups of 2–5 individuals surrounded by prairie or soils from natural prairie were sampled in triplicate. Sampling was within 20 meters one from the other at each of the sites. The soils were young, with a maximum of 30 cm depth to bedrock. No significant structure was observed, i.e. A, B and C horizons. Strong organic content was found throughout the soil zone. In general, the prairie soils showed strong illite content and much less interlayered illite-smectite material. Soils under both aspen (deciduous) and spruce (conifer) trees showed significantly more S/I and I/S minerals in the XRD diagrams (Fig. 5.10).

If we assume that the conifer and aspen trees are replacing prairie vegetation in these boundary zones, it is apparent that the first soil clay mineral formed from the underlying rocks by interaction with prairie plants in abundance is illite. Since both the granite and rhyolite contain much fine-grained muscovite, this is not surprising. A small but definitely HI mineral peak is present. One should note that there is a significant amount of PCI present, indicating the possible presence of soil illite. Illite remains a major component of the soils under conifer and deciduous trees but very much interlayered illite/smectite is present as well as a persistent HI mineral. It appears that in these cases the initial stages of tree colonization engender the formation of smectitic minerals.

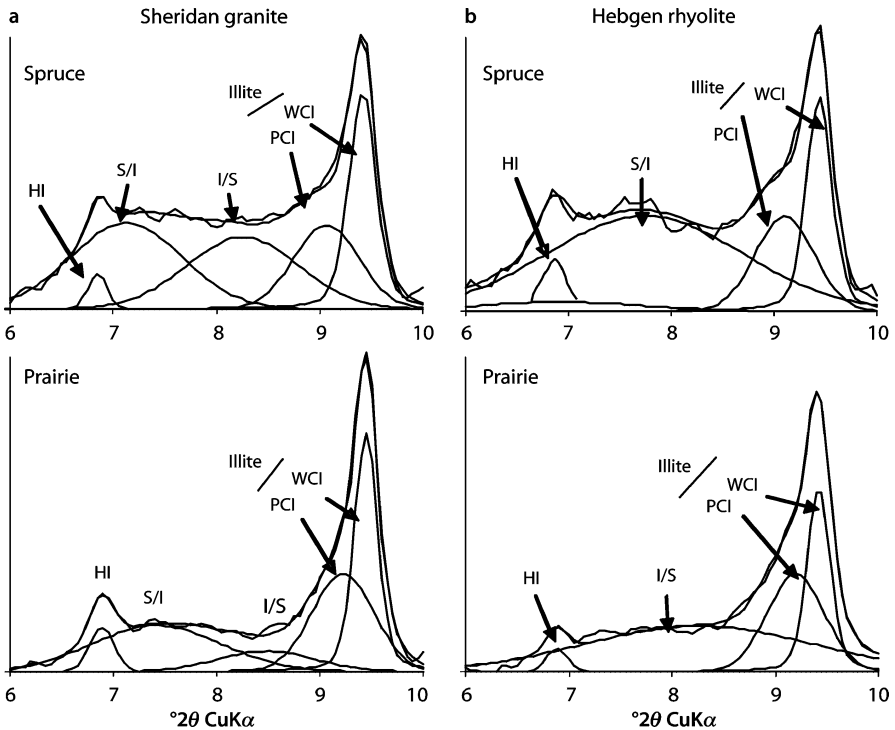
**Fig. 5.9.** Formation of chlorite, most likely aluminous and dioctahedral, under conditions of sequoia tree growth. Well crystallized chlorite (with a strong 002 peak) occurs at the expense of mixed layered illite: smectites minerals found lower in the soil profile under the tree. Grass soils outside the range of tree needles shows essentially the same XRD patterns as that of the deeper part of the sequoia soil profile at the surface and at depth



In general one can surmise from the above that forest soils tend to favor the formation of HI and smectite-illite minerals in the upper horizons. This seems to be more the case for conifer forests but not exclusively so. Deciduous forests seem to favor illitic materials in the upper layers of the alteration profile, in the soil horizon. Thus the conditions which favor HI minerals are most often present in conifer forests but not always.

### Summary

In a very general way, one can feel that prairie soils will form illite or illite-smectite mineral assemblages in their A horizons. Forests more often form HI minerals. Since



**Fig. 5.10.** Soil clays under different vegetation in high country areas in the Western United States; **a** Sheridan granite from the tundra–forest border near Sheridan Wyoming; **b** Hebgen rhyolite near Yellowstone Park west entrance, Hebgen Lake. Both sequences show that the prairie soils have a high illite content while the tree growth soils, aspen or spruce, tend to have more mixed layer minerals present. *S/I* = smectites-rich interstratified illite/smectites, *I/S* = illite rich mixed layer minerals, *HI*, present in small quantities in all samples = hydroxyl interlayered mineral

these observations are not systematic one can conclude that conditions other than the plant type can intervene in the formation of the typical soil clay mineral types.

Let us consider the mineralogy of the clay phases present. The difference between illite, smectite and HI minerals is two fold; one a factor of layer charge and charge site which determines the force with which potassium or hydroxy-aluminum ions are fixed between the 2:1 layers of the mineral structure. The second difference between the minerals is the cation in the interlayer site. Smectites can generally contain a wide variety of cations, and most often multiple species. HI minerals appear to contain almost exclusively aluminum ions. Illite contains almost exclusively potassium. Since both illite and soil vermiculites (HI minerals) are reputed to be high charge types, the only major difference in their genesis would be the availability of potassium and hydrous aluminum ions. One can then surmise that, in general but not exclusively, prairie plants favor the fixation of aluminum on material other than clays, most likely organic matter. This produces illite, which is also associated with some deciduous trees soils. Conifer soils seem not to fix aluminum on organic matter but on clays. The aluminum is present in higher amounts due to the almost systematic highly acid soil



humic materials. Acidity is not the only factor in that mountain, Ranker soils, of pH below 4 form smectites.

In general, forest soils tend to form high charge 2:1 structures. These are either in equilibrium with solutions rich in hydrous aluminum cation complexes ( $\text{Al}(\text{OH})_2^+$ ) or  $\text{K}^+$  ions. The high charge structures produce non-expandable minerals, either potassic or aluminous. The extent of formation of HI minerals will depend probably upon the forest tree type (conifer or deciduous) and also on the base soil mineralogy which depends upon the parent material.

A practical consequence of this situation influences agriculture. Given that prairie and deciduous forest seem to favor the formation of illitic clay assemblages (illite and illitic illite-smectite mixed layer minerals) it is not surprising that archaeologists have found a strict limit in earliest farming in Norway between conifer-birch forest areas and deciduous forests (Clarke 1955). It appears that the initial slash and burn techniques could not produce viable agricultural land under spruce forest conditions. This is most likely due to the presence of HI minerals in the conifer forest soils which are difficult to farm. The smectite/illite assemblages of the deciduous forests were more fertile for the plants grown by early agricultural man in northern Europe.

#### 5.4

### Chemical Control in Soil Horzion by Plant Action

Weathering (interaction of rainwater with continental rocks which are essentially silicate mineral assemblages) is an age old process which has been investigated for quite some time (Ebelmen 1847 for example). The overall trends have been noted to be an initial loss of alkali and alkaline-earth cations and then silica, with a resultant concentration of hydrated alumina and iron oxides. A typical chemical weathering sequence on several rock types along the Appalachian front is illustrated by the data of Oh and Richter (2005) where potassium loss in the upper parts of the weathering profile is on the order of 50% with the transformation of the 30–40% of initial rock into clay minerals. More intense weathering shows loss of both alkalis and silica with a clear change in clay mineralogy from temperate to tropical to laterite soil types (Pedro 1966). The sequence can be indicated by the clay mineral relations:

mica → illite → smectite → kaolinite → gibbsite

Alteration of rocks is typified by the loss of alkalis and alkaline earths. This is due to the replacement of these elements by hydrogen ions during the water/rock interaction. The end result is the enrichment of Si, Al and Fe as oxides or hydroxides in the altered materials. Typical compositions of altered materials, from the A to C horizons show for example potassium loss. However, it has been noted (Lucas 2001; Jobaggy and Jackson 2004) that plants seem to enrich certain elements in the upper portion of soil profiles, especially in the A horizon. Bardossy and Aleva (1990, p. 171) summarize papers which indicate that possibly the origin of bauxite can be attributed to extraction of silica by tropical forest vegetation. Control of silica in soils water and streams has been considered to be often controlled by plants (Alexandre et al. 1997). The overall observations of the effects of weathering lead one to deduce that normal alteration reduces alkalis in weathering. However, there is some evidence that soil materials af-

ected by plants concentrate some of the elements lost in the water/rock interaction process. Let us look more closely at these effects.

#### 5.4.1 Silica

If plants can have an overall effect on the chemical composition of the soil horizon several elements are critical to clay mineral stability. The presence of phytoliths in plants (silica) is of course well known but perhaps not often considered as having a major effect on soil horizon chemistry (Alexandre et al. 1997). A numerical demonstration of this effect has recently been made for soils on basalt (Derry et al. 2005) using minor element analysis methods where the transfer of silica from deep soil to streams waters via plant transport is demonstrated. Two aspects of this study are important, one of course is the transport via plants of silica from root zone to the superficial biomass zone. More important from a standpoint of clay mineralogy is that the silica thus moved upward in the soil changes physical and mineralogical state. In most rocks and in soils developed from them silica is largely found as quartz. Quartz is notoriously insoluble, metastably, but it nevertheless can control the silica activity in soil solutions to the lower end of activity or chemical potential. Low silica activity in aqueous solutions favors the formation of low silica clays such as kaolinite. However, the silica transported by plants, when deposited in surface litter, is usually amorphous or eventually in the form of cristobalite. The silica activity engendered in aqueous solutions in contact with these unstable silica minerals will be higher than that of quartz, and thus will favor the presence of more silica-rich 2:1 minerals such as smectites and illite. In plant systems with a high phytolith content, such as grasses, smectite would be favored over kaolinite for example. 2:1 minerals are favored by higher silica activity.

Data presented by Dahlgren et al. (1991) for grass and oak forest soil solutions in Japan formed from basic volcanic rocks indicate that silica concentrations in the organic horizon are significantly higher than in the lower horizons, by a factor of five, and potassium content is ten times higher than in pore water below the surface zone. The clays at the surface in these soils are 2:1 hydroxy-vermiculites which disappear below the upper horizon. If one considers the reports of Norfleet and Smith (1989) and Bryant and Dixon (1964) for example, mature soils formed under the humid, warm conditions of the South eastern United States show kaolinite and gibbsite at depth and throughout the alteration profile in the clay size fraction but there is a strong presence of 2:1 minerals (siliceous) in the form of HI minerals in the A horizons. Hajek and Zelazny (1985) summarize published data indicating that in old, strongly weathered largely forest soils in the Southeastern United States, the silica-rich minerals HI vermiculite and illite typically occur in the soil zone (plant/silicate interaction horizon) while kaolinite and gibbsite are found below this zone indicating that severe weathering occurs at depth. Here the upper horizon shows an increase in silica-rich clay minerals most likely engendered by the mixed forest growth where the samples were taken.

The presence of siliceous clays in the upper part of strongly altered materials suggests some outside intervention to promote their stability. One can invoke silica transfer due to plant activity.

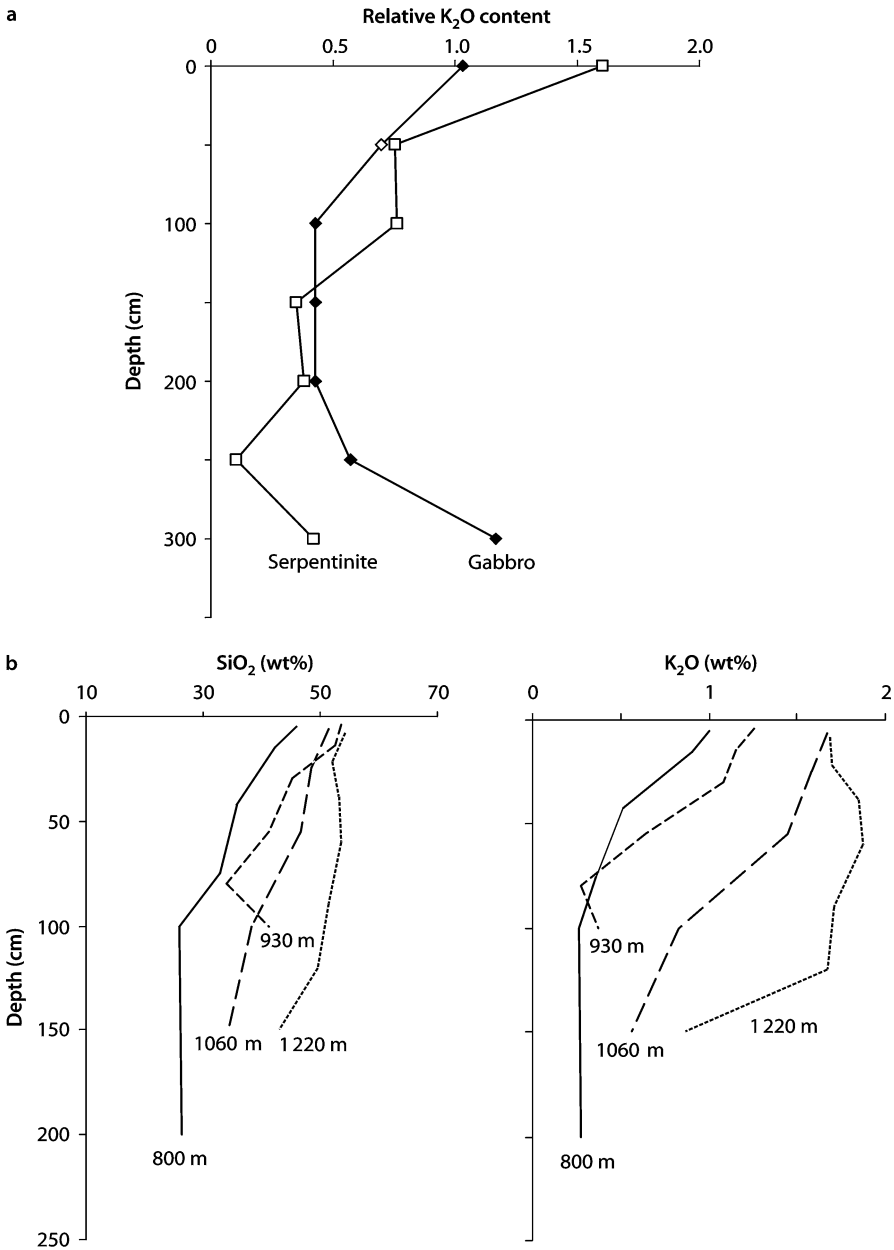
## 5.4.2 Potassium

### *Potassium in Soils*

Our old friend potassium is found in increased quantities in the exchange cation population soil layers in unfarmed profiles in the United States, compared to lower parts of an alteration profile (Jobaggy and Jackson 2004). Potassium nevertheless remains at a low level in a relative manner, representing only about 10–15% of exchangeable ions throughout most soil profiles, as seen systematically in most soil studies. In general there is a strong relationship between depth and exchangeable ions, and one can find that exchangeable potassium for example is strongly reinforced in the A horizon (Mariotti 1982, data on p. 232–236) in soil types where potassium is lost from the overall bulk soil (Egli et al. 2004). Also, typically, pH increases in the A horizon where organic material decays, root activity is intense and organic acids are present. Increase in exchangeable ions is due to the cation exchangers in the form of organic material and clay minerals. The importance of the exchange capacity of one or the other is of course variable, values for organic materials vary but are on the order of 6 to 12 milli-equivalents per gram (Sposito 1989; Foth 1990; Black 1968) where soils commonly contain between 0.5 to 4 percent organic carbon whereas clays are present at levels of 5 to 30 percent with a CEC varying from 5 to 125 milli-equivalents per hundred grams or at levels of 1 to 40 milli-equivalents. Thus clays tend to have exchangeable potassium in increased quantities towards the surface of alteration soil profiles but potassium is none the less a minor component of exchangeable bases.

However, the absolute amount of potassium increases in the soil exchange population. The higher amount of exchange ions present indicates a higher potassium content in the soil materials, silicate clays and organic matter exchangers. This increase has a strong influence on the presence of illitic clay minerals. The increase in potassium seems to be dependent on a return of plant material to the soil profile, either from leaf litter or upper level root masses. In fact most plant ash is relatively potassium-rich. (Gain 1895; Dahlgren et al. 1991; Mussa 1887) Hence plants typically enrich the surface layers of soils with potassium, among other elements. The impact is rather strong when replacement occurs each year by plant litter. Grasses for example enrich soils greatly in potassium while trees do less so. Trees on the contrary keep a significant part of the nutrient material (potassium and silica) in their woody parts which remain above ground. Such a prolonged subtraction of alkalis as well as calcium, changes the balance of cations and favors acid soils where  $K^+$  and  $Ca^{2+}$  are replaced by hydrogen ions. This is one of the major reasons why forest soils are acidic. Burning of trees and return of ash material into the forest soil can increase the pH by two units or so (Duchauffour 1979).

Bonifacio et al. (1997) and Pion (1979) give chemical data for soils formed on serpentines, and basic intrusive and metamorphic rocks which are potassium-poor where there is an increase in potassium in the uppermost levels of the alteration profile (Fig. 5.11). The potassium translocation effect can also be seen for weathering profiles on basic eruptive vitreous materials forming andosols and extrusive basic vitric materials (Meijer and Buurman 2003; Lorenzoni et al. 1995). Thus in the extraction and



**Fig. 5.11.** Composition of horizons in profiles developed on; **a** ultrabasic (serpentine) and basic rocks (gabbro) (Bonifacio et al. 1997 and Pion 1979); **b** andosols developed on basalts in a catena sequence (Meijer and Buurman 2003). For ultrabasic rocks, serpentine and gabbro, the K<sub>2</sub>O content increases strongly in the upper most part of the profile. For andosols on basalts formed on a volcanic slope under tropical forest conditions, both potash and silica are seen to increase at the top of the profile. This is attributed here as being the effect of translocation of these elements by the tropical forest plants on the volcano slope

transfer of potassium from lower portions of an alteration profile to the soil horizons (essentially A horizon) there is an enrichment in potassium for most plant regimes but also a decrease in pH due to cation extraction.

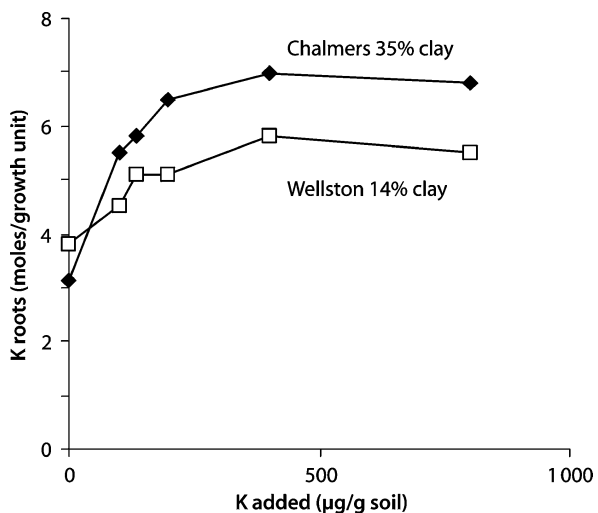
### Stocking Potassium in Clays

If plants are responsible for potassium translocation, what effect can this have on the solids present, i.e. the clay minerals? In the translocation and potassium use processes it appears that plant roots tend to reach a maximum in potassium uptake from solutions of increasing potassium content (Herrman 1979). This effect is shown in Fig. 5.12. This suggests that a plant ecosystem will absorb a limited amount of potassium from a given soil substrate. However plant roots appear to absorb potassium according to local availability, root by root, and not overall plant access through all of the roots according to split root experiments by Herrman (1979).

In parts of a root system of low availability they will absorb as much as possible but if there is a local over supply at another horizon, they will reach a limit of absorption. In other words, roots at depth will continue to transport potassium from dissolving minerals while those at the surface may be saturated with available potassium. If plants use less than they bring to the surface they will induce an excess of potassium in the soil chemical environment. Is this seen in clays?

In order to assess the possibility of the stocking effect in a natural system we can observe the illite (most potassic clay mineral) in a series of soil profiles developed over different periods of time. The example comes from a sequence of poldered soils (Baie d'Authie, Département de la Somme France) put into pasture at intervals since 1058 (reported by Velde et al. 2003). Initial sediments (recent sedimentation in poldered soils from an 1868 diking event) are compared to polders put into prairie from the time of diking at various dates. Treatment of X-ray diffraction data of the clay fraction is presented using peak area computations of decomposed spectra (see Lanson 1997) in a

**Fig. 5.12.** Relations of corn (*Zea mays*) shoot uptake compared to concentration of KCl in nutrient solution in hydroponic growth experiments. Uptake reaches a plateau value indicating a maximum capacity of uptake by the plant (data from Herrman 1979). *Chalmers* and *Wellston* are two different soil types from Indiana, USA



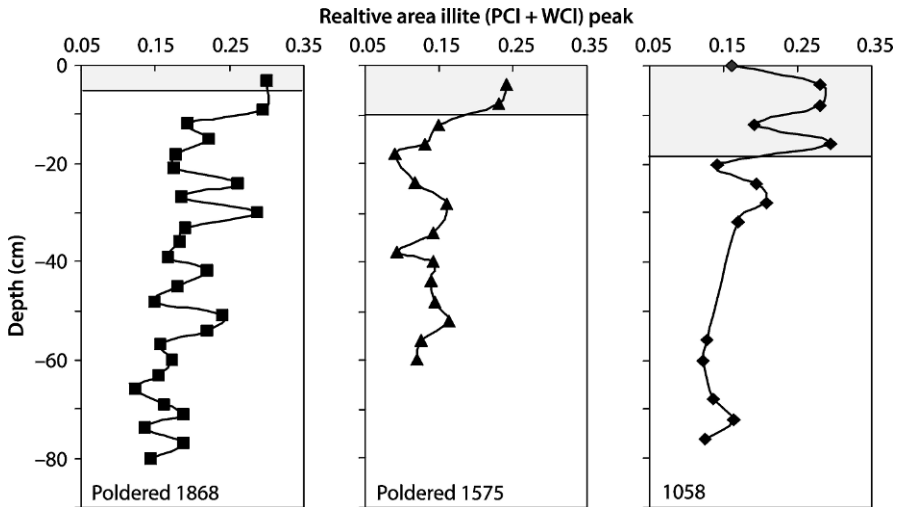


Fig. 5.13. Relative peak area of the illite minerals (*PCI* and *WCI*) in the Authie Bay samples showing the conservation of illite closely associated with the humic layer (*gray zone*) in the profile and loss of the potassic phase at depth

comparative manner (Fig. 5.13). This shows that there is a segregation of clay types in the profiles as they become older. At depth the clays become potassium poor (shown by a decrease in illite mineral content) due to weathering whereas at the surface they are slightly enriched in the potassic mineral illite. It appears that under the prairie in sandy poldered soils of the Baie d'Authie, the tendency for the grazed prairie ecosystem is to accumulate potassium-rich minerals in the clays. This substantiates the general conclusions on prairie clay mineralogy cited above. However, in the lower portion of the profiles, normal weathering takes over and there is a loss of potassium to percolating solutions.

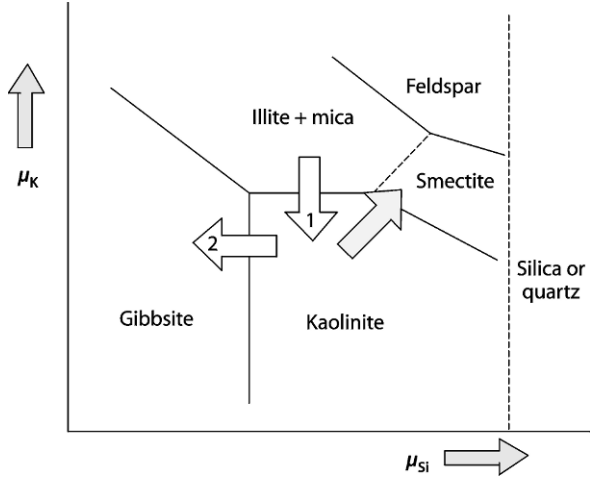
### 5.4.3

#### Element Loss and Element Gain

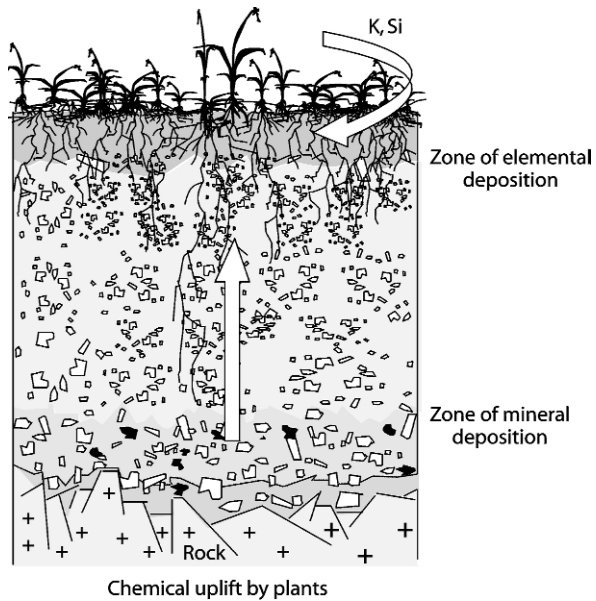
Figure 5.14 indicates the major relations for the elements Si and K in a system where alumina is present in constant quantities. Weathering is usually assumed to effect the change from potassic minerals to less potassic ones or eventually potassium-free clay minerals (Pedro 1966). Arrow 1 indicates the step from potassic minerals to kaolinite. Further loss due to weathering will cause the destabilization of kaolinite in favor of gibbsite. Here silica is lost. However, several studies cited above indicate that more silica-rich minerals are found in the upper portions of alteration profiles and even 2:1 minerals such as smectites, illite or HI minerals. The shaded arrow in Fig. 5.14 shows such a trajectory. This "reverse" weathering is due to translocation of elements by plants through root action. Figure 5.15 summarizes these ideas.

In the deep root zone, where water/rock interaction is the major chemical action occurring, roots will capture or absorb silica and potassium, among other elements,

**Fig. 5.14.** Schematic phase relations of potassic and aluminous minerals as a function of the relative chemical potential of Si and K in solutions which are in equilibrium with the silicates indicated. *Numbered arrows* show the path taken under the influence of water-rock reactions. Alkali loss and silica loss are the major effects of water-rock interaction. The importance of hydrogen activity (pH) is not taken into account. The *gray arrow* indicates the path taken under the influence of elemental translocation effected by plants which stabilizes the 2:1 mineral smectites which is the fundamental clay mineral in soils



**Fig. 5.15.** Schematic representation of the action of plant roots in absorbing and translocating K and Si to the plants growing at the surface. Restoration of these elements is made to the soil by leaf and stem deposition on the soil surface



necessary for the physiology of the plant. These elements are deposited as leaf litter, shoot and stem matter at the surface. These elements are then used by the more dense root mass at the surface and incorporated into the plants. However, the increased silica and potassium favor the presence of silica-rich 2:1 clay minerals. These minerals can stock potassium needed for plant growth. If the plants translocate more silica and potassium than needed they form illite-rich clays in the soil zone as appears to be the case for prairies. If the soil is more acid, such as is often the case for forests, the interlayer sites of the 2:1 minerals become saturated with aluminum ions, if the or-

ganic matter and compounds in the humic zone does not fix the aluminum ions first. This produces HI minerals.

It is highly probable then that plants control the clay mineralogy in the soil (plant/silicate) interaction horizon by translocation of silica and potassium plus other base cations. Thus the presence of these minerals is to a large extent dependent upon the presence of plants and they can be destabilized if the plant regime is changed.

## 5.5 Agricultural Influences

Agriculture is synonymous with disequilibrium in soils. The act of farming is such that the natural equilibrium of plants and soil will be changed. The farmer wishes to extract elements out of the soil and export them out of the system as quickly as possible in the form of vegetal matter whereas natural plant/soil systems are based upon steady state, gradual elemental loss through dissolution and evacuation from the bottom of the profile in dissolved form. Plants attempt to stabilize the nutrients necessary to growth by accumulation of elements as leaf and lignitic litter in the upper parts of a soil profile where they are readily available to the dense root mass present.

Depending upon the crop, the intensity of extraction and the climate, different effects of agriculture have been noted in certain instances. The impact is of course variable and dependent upon the soil clay mineralogy, the plants grown and the climate under which the plants are grown. Prairies have been seen as an important part of agricultural practice. The use of grazed prairies as a natural enhancing agent for soil fertility under classical farming practices producing grain crops has been outlined for some time (de Serres 1600, p. 169). The frequency of different plant species in natural prairies varies with soil and climate in France for example (Garola 1918, p. 6–26). In the 18th and 19th centuries it was observed (Patullo 1758; Mathieu de Dombasle 1830, p. 369) that certain plants were more beneficial than others for soil fertility (different perennials) and these were eventually selected to enter into a regular cycle of crop rotation. Garola (1918, p. 17) states that alternative grazing and haying increases the proportion of legume plants in prairies. Prairie plants such as clover and luzern among others became a part of crop rotation in 19th century in Europe. Such artificial prairies were either grazed or harvested as hay. These practices were continued there and in the United States (Getman and Ladd 1925; Cox 1925) until the advent of the tractor.

Black (1968) summarizes the effect of plants on available potassium under various agricultural practices. It is clear that so called non-exchangeable potassium, that probably within interlayer sites, can be extracted by plants. This suggests that the apparent clay mineralogy will be affected. What are then some of the effects and how can we assess their impact on clay minerals?

### 5.5.1 Prairie Soil Clay Mineralogy in Agriculture

#### *Impact of Grazing on Prairie Soil Mineralogy*

Unpublished data of Barré and Louault (INRA Clermont Ferrand) indicate an effect of decreasing illite content of the clay mineral assemblage where soil vermiculite and



I/S minerals replaced illite under conditions of heavy grazing by sheep. Samples were taken from adjacent plots, one heavily grazed (five times per year) and the other low intensity grazing (one time per year). After 15 years, the heavily grazed soils showed a strong decrease in illite content (PCI + WCI) with 45% for the plot grazed five times per year and 74% for the low grazing intensity plot (average values of four replicate samples in each plot). From the shift in peak intensities, it appears that the I/S minerals replace illite and there is some increase of HI minerals (Fig. 5.16a,b).

It appears from these results that the prairie soils which contain illite-smectite mixed layered minerals with large amounts of illite under normal grazing conditions become less illitic with intense grazing. This suggests that the export of grasses and other plants impoverishes the soil mineral assemblages in their potassic component.

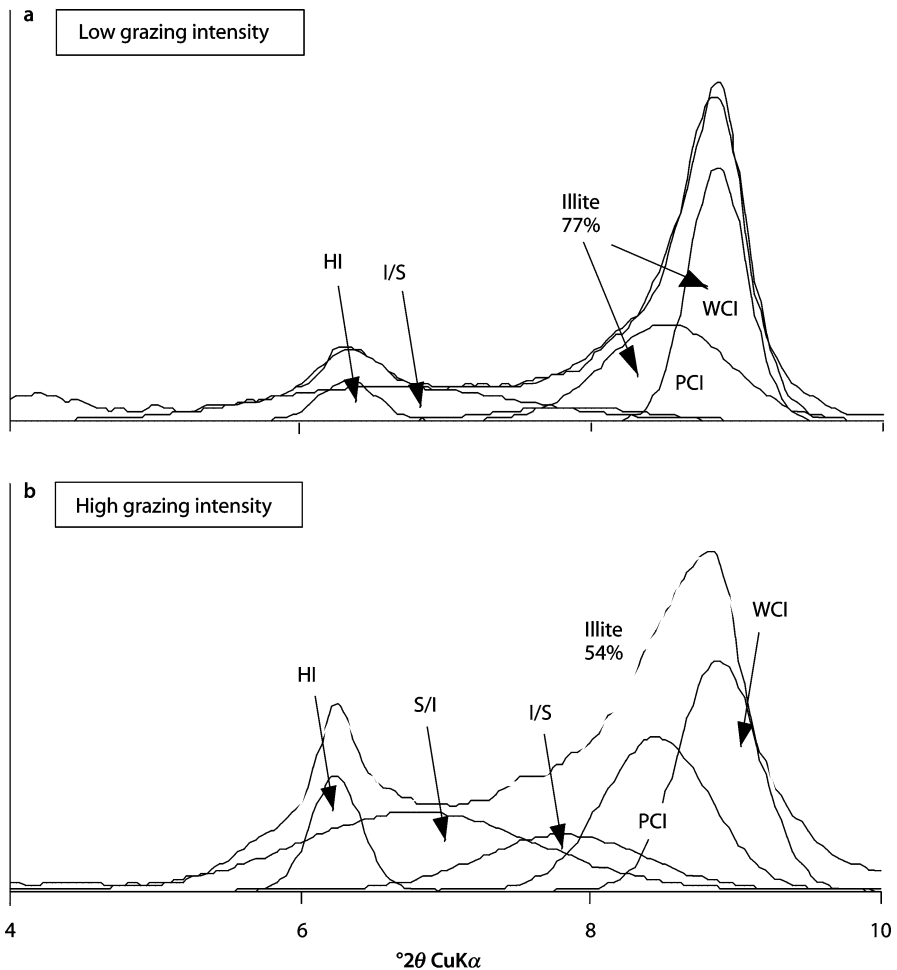


Fig. 5.16. Relative peak areas for clay assemblages in low and heavily grazed prairie plots after 15 year regimes. Spectra are averages of four samples (unpublished thesis data by P. Barré)

A study which supports the hypothesis of illite formation over long periods even in a situation of low or normal potassium activity, can be found in Righi et al. (1995) where poldered sediments were farmed for varying periods going back to 1665. No information is available concerning the chemical regime due to farming methods, but for the longest portion of the period of cultivation traditional manure fertilization was practiced and chemical fertilizer applied since the 1950s. The initial crops, until the latter 20th century, were based upon wheat and barley (Riou 1983). XRD investigations show that in the fine clay fraction ( $<1\ \mu\text{m}$ ) in the clay minerals present, S/I, I/S contained more illite layers as a function of the time of cultivation. PCI appears to have increased in diffracting domain size as shown by a shift in peak position and a narrowing of the diffraction band. However total PCI + WCI peak area remains roughly constant over the time period of cultivation.

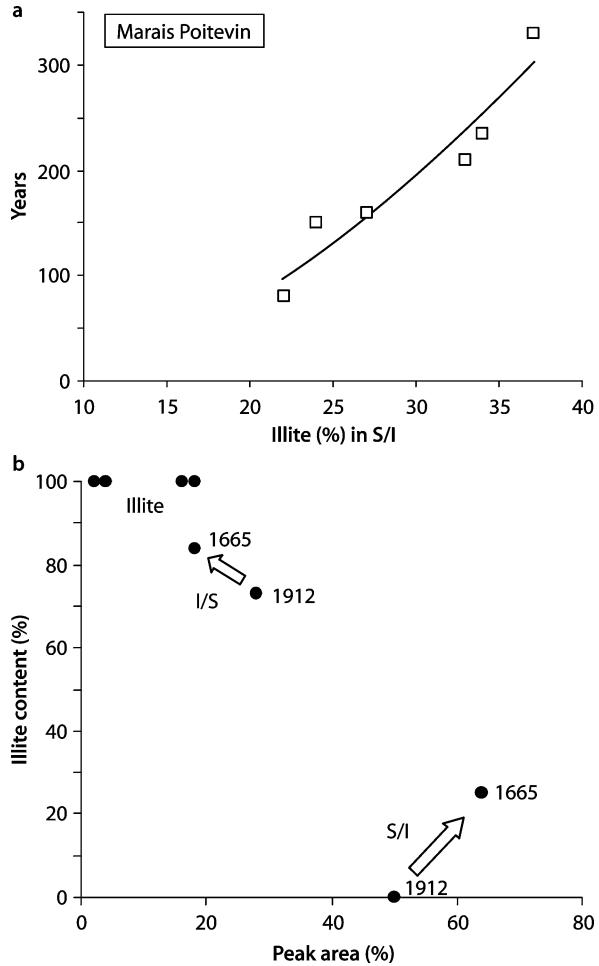
The chemical data reported in this paper, show that in fact the potassium content of the fine clay fraction appears to decrease slightly over the cultivation period, going from 2.42 to 2.28%  $\text{K}_2\text{O}$ . When calculating peak areas and illite content of the mixed layer minerals there seems to be an equilibrium between the older more recent poldered areas. Illite content appears to remain the same. The increase in illite content of both mixed layer phases is compensated by an increase in the less illitic (S/I) mineral compared to the I/S mineral. Figure 5.17 indicates the shift in illite content and peak area for the recently poldered sample compared to the 1665 poldering soils. Thus it appears that illite content can increase in the phases but the proportions of the phases respect the total potassium content of the clay fraction. This indicates that the illite content of minerals must be considered in relation to the relative proportions of the phases.

### *Clay Mineral Changes under Intense Farming Practices*

**Corn cropping.** Velde and Peck (2002) give X-ray diffraction data for clays in soils having been cultivated in a continuous corn cropping system without chemical fertilizer. The soils were cropped for 70 years where previous traditional farming had already occurred for 50 years or so. The soil is a mollisol on the University of Illinois experimental farm. In the experimental plot study other cropping methods were used and it was demonstrated that crop rotation of corn, wheat, oats and meadow did not affect the diffraction patterns of the clay assemblage to any large extent. After 40 years of non-fertilizing regimes for continuous corn cropping, use of NKP fertilizer for 30 years resulted in the restoration of the original clay mineral assemblage.

Considering the soil illite phases (PCI and WCI) in the clay assemblages there is a notable decrease in the relative intensity of the WCI peak and a significant widening of the PCI peak as a result of continuous corn cropping for 80 years (Fig. 5.18). The peak area of PCI + WCI in the initial stages of the experiment is near 30% while at the end only WCI remains at 4% peak area. Illite content, as a specific phase decreases dramatically. In the first part of the experiment WCI decreases and apparently in the second illite layers are lost from the PCI, forming an illitic I/S mineral. Overall there is a decrease of 12% illite layers in going from PCI to I/S. Also a significant shift is seen for the peak position of the smectitic S/I mineral to higher d-spacings indicating loss of illite layers in the disordered mixed layer mineral going from 55% to 45% illite component. Measured potassium content of the clay fraction indicates a decrease from 1.67 to 1.49 weight percent  $\text{K}_2\text{O}$  over the sequence.

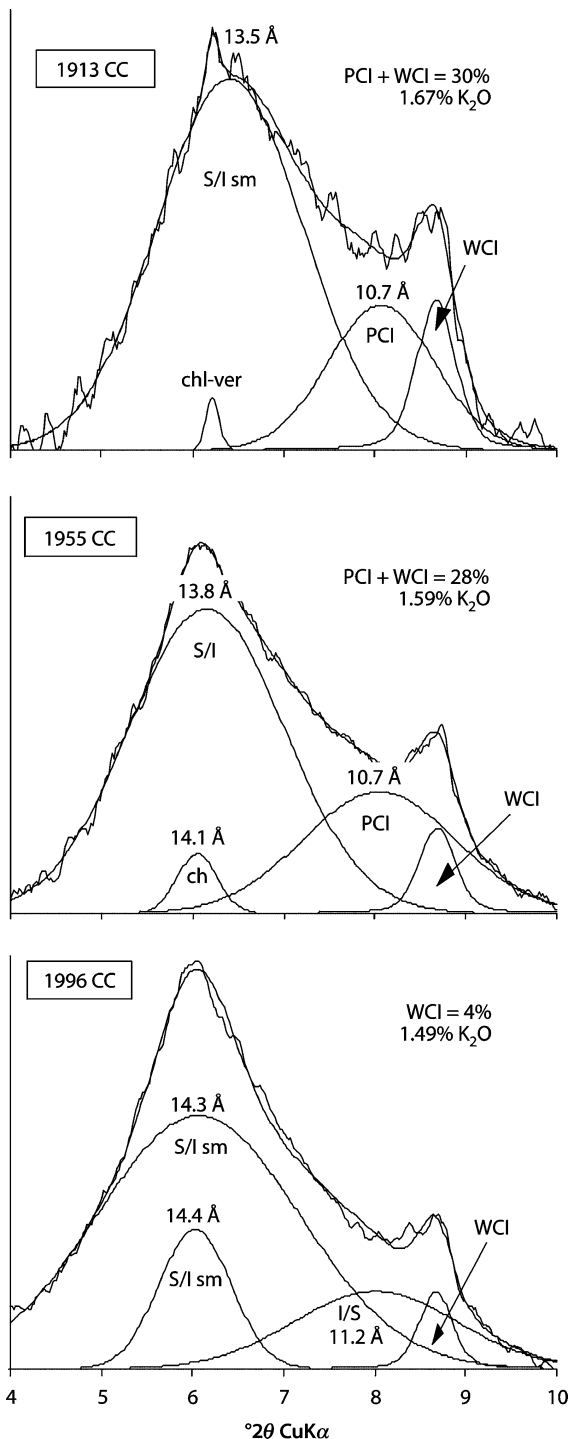
**Fig. 5.17.** Relations of mineral composition as a function of time in the poldered Atlantic salt marsh example at the Bay of Aiguillon, Vendée, France. The soil was cultivated in grain crops for the most part. Increase in illite content in the S/I mixed layer mineral is seen as a function of time (a). It was noted that the overall potassium content of the soils remained constant. Thus there is a re-equilibration between the different clay minerals which contain illite so that although they all increase in illite content, there is a difference in abundance of the phases to maintain a constant overall illite content, shown by arrows for youngest material (1912) to oldest (1665) (b). Data reworked from Righi et al. (1995)



However, possibly more importantly, a close examination of the published results shows that in the initial stages of the experiment, corn production decreased, and in fact the illite content of *all* of the peaks showed an increase. When corn production increased dramatically, due to the introduction of hybrids in the 1950s, illite was lost. This suggests that illite layers in the mixed layer minerals were re-generated under conditions of lower stress, i.e. lower production of corn. From this study it appears that potassium fixation in closed (non-expandable) layers can be a reversible process in short periods of time.

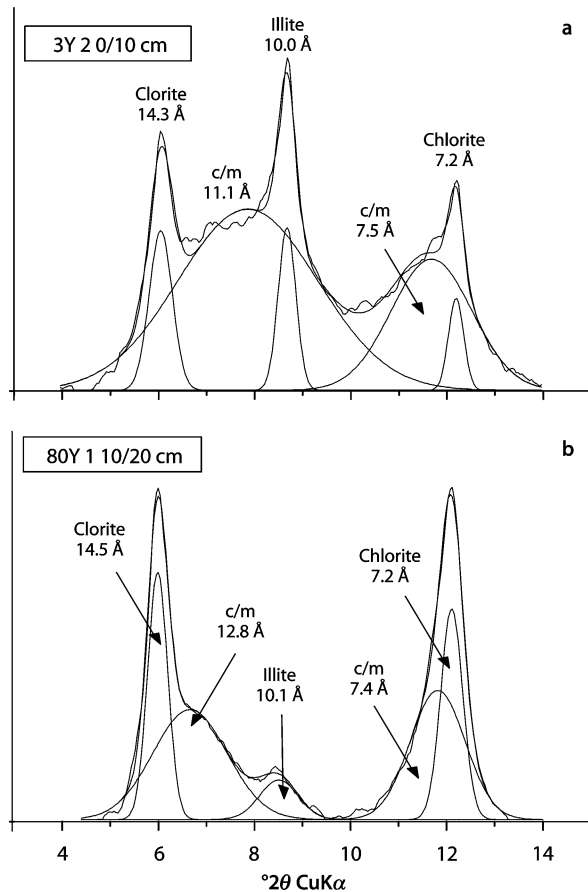
**Flood-irrigated rice paddy development.** A case of clear loss of illite due to cultivation practice is reported by Li et al. (2003). This study presents data from a sequence of flood irrigation rice paddies in China developed on red soils which show a dramatic change in the clay mineralogy of the soils as a function of the length of cultivation time.

**Fig. 5.18.** Shift in the abundance of illite, indicated by relative peak area, for soil clays under conditions of continuous corn cropping without fertilizer in an experimental farm plot sequence (Morrow Plots, University of Illinois). Overall potassium content is reduced for the clay fraction as illite is lost and illite layer content of the smectites-rich *S/I* mineral is reduced. It is notable that both *PCI* and *WCI* minerals are lost in the process (Velde and Peck 2002)

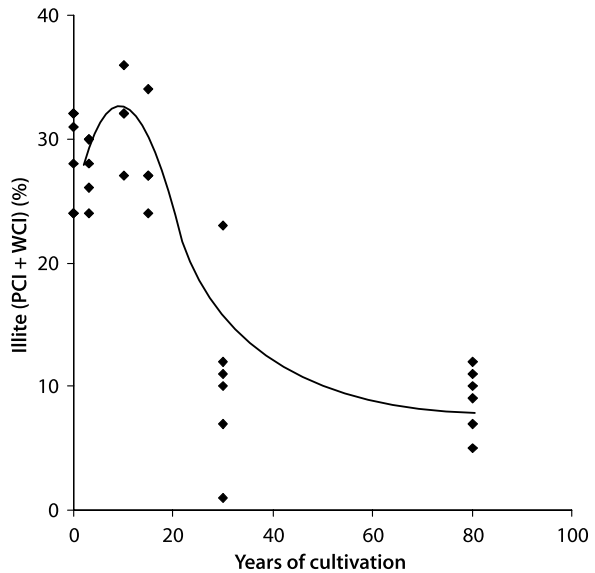


The most important change is in the illite-mica (PCI plus WCI) content which is shown in Fig. 5.19 Initial clay mineralogy is an illite, a chlorite and a mica-chlorite mixed layer mineral (indicated by the shoulders at 7.4 and 12.6 Å). Iron oxide is very prominent in the soil, giving it a strong red pigment coloring. Clay content is strongly reduced in the samples with time as is the iron oxide content rendering the soils a dark gray color. The proportion of illite in the clay fraction, determined by peak ratio compared to the other clay minerals present, decreases dramatically with rice culture, from above 30% to less than 10% (Fig. 5.20). Within 30 years most of the potassium-bearing clays are largely lost from the cultivated horizon and potassium content of the soil clay fraction, despite addition of chemical fertilizer (NKP). It is interesting to note that there is a slight initial increase in illite content in the initial stages of cultivation, probably due to the initial input of potassium fertilizer to a naturally potassium depleted soil clay mineralogy. Potassium content of the total soils decreases as does illite content (Fig. 5.20) most dramatically in the older samples. The end result is that in rice cultivation on these soils, 2 to 3 times the normal amount of potassium fertilizer is needed to maintain an average rice production. Here it is clear that there is a relation between cropping practice,

**Fig. 5.19.** Indication of illite loss from clay assemblage or red soils under flood irrigation rice culture reported by Li et al. (2003). Cultivation times of (a) 3 and (b) 80 years are shown. *Chlorite* = magnesian chlorite, *c/m* = mixed layer chlorite/illite mineral



**Fig. 5.20.** Relative proportion of illite peaks in the XRD patterns is shown for soils from an experimental farm plot site in China at the Red Soil agricultural station (Li et al. 2003). Initial periods indicate increase in illite due to potassium fertilizer but subsequent mineral change decreases illite content despite increased fertilizer treatment



potassium content of the soil clay fraction and the presence of illite despite use of potassium fertilizer.

A probable reason for the dramatic loss of potassium-bearing clays is the strong change in oxido-reduction of the system due to flood irrigation and the formation of magnesian chlorite as suggested by Li et al. (2003). Thus even though potassium is added as fertilizer, there is strong loss of soil illite.

### 5.5.2

#### Effect of Fertilizer on Clay Minerals

##### *Uncultivated Plots*

A novel experiment is reported by Pernes-Debuyser et al. (2003) which shows the importance of fertilizer type on uncultivated soils. These authors give data concerning a 70 year experiment where the effects of fertilizer on soils were studied. The initial starting material was a cultivated forest soil in the Paris area of France. The total period of cultivation is unknown but probably it is in the range of thousands of years, perhaps not in continuity. Different mineral fertilizers were used in the 70 year experiment and plant life eliminated by plowing, and weeding throughout the year. No significant effects on clay mineralogy as observed by X-ray diffraction were noticed under the different chemical fertilizers (pH ranging from 3.5 to 8.5) except in two, the use of KCl and manure. In these samples there is an observable increase in the PCI and WCI content of the clay assemblage. In the KCl and manure samples, the total illite content is quite similar, 9 and 7%, with a slightly higher WCI content in the KCl treated sample. However the S/I peak shifts in the manure treated sample to 14.7 Å indicating an increase of about 20% illite content. Here the KCl increases the discrete

illite mineral content but the manure increases not only the soil illite but also illite layer content of the I/S minerals. Manure is thus a powerful potential source for potassium incorporation in 2:1 clay minerals. In this case one must also consider the possibility of ammonium incorporation into illite layers in the S/I mineral which might take the place of potassium. Larbaletrier (1891) indicates that among pig, sheep and cow manure (i.e. feces mixed and matured with straw) potassium is the major inorganic element present. One can believe that this abundance of potassium could explain the effect on the clay minerals present.

### *Effect of Fertilizer in Cultivated Plots*

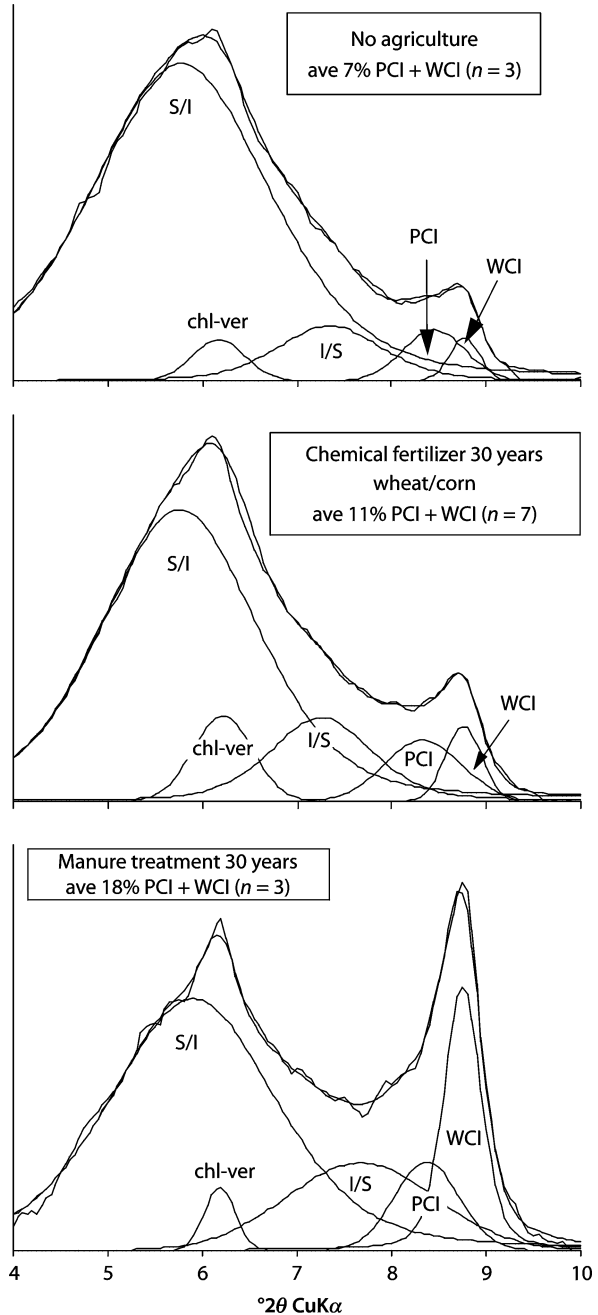
Huang and Velde (unpublished, "Effect of fertilizer management on agricultural vertisols in Anhui Province", Institute of Soil Science, Chinese Academy of Science, Nanjing) investigated the clay assemblages from the top soil horizon (agricultural) of experimental plots developed on vertisol sequences in Anhui Province China. Sampling was done on plots which had been dry land farmed in a classical manner (crop rotation of wheat, etc). After 40 years of no culture, chemical fertilizer (NKP) use and barn yard manure fertilizing one sees significant differences in illite content of the clay mineral assemblages. The unfarmed soil clays are dominated by smectitic I/S minerals as would be expected in a vertisol. Illite (PCI and WCI) is a minor component, 7% peak area. Chemical fertilizer treatment under agriculture increases the proportion of the illitic I/S mineral component and there is a slight increase in the illite component. Total PCI + WCI = 11% peak area. The most striking change seen in the experiment (Fig. 5.21) is in the barn yard manure-treated plots, where the WCI illite component is significantly greater than that in the unmanaged or NKP fertilized plots (18% PCI + WCI compared to 7 and 11% respectively). Since manure can contain a significant amount of potassium, up to 20 to 60% dry weight (Larbaletrier 1891, p. 169) but probably less than the normal NKP additions, one could suspect that the illite formed under manure treatment in these experiments is due to the clay interaction with bacterial-reacted organic matter. This effect is very similar in nature to that seen in the Versailles experimental plots but where no agriculture was performed. Both soils contain a large amount of S/I minerals initially. In this study the WCI component is potassic, since ammonium illite has a peak at 10.3 Å. However, changes in illite content of illite-smectite mixed layer minerals could contain ammonium illite.

It is clear that intensive culture tends to exhaust the potassium reserves in the form of illite layers in soil clay mineral assemblages. The abandoning of prairies as an alternation of cropping leads to the necessity of potassium amendment, a practice begun in the 1860s in France for example (Larbaletrier 1891). This method of treatment leads to a higher crop yield and can enhance crop production under different types of crop rotation.

One can consider the formation of illite as a type of reservoir of potassium, exhausted gradually by crops over a period of years, traditionally three. The formation of illite appears to be favored in grazed prairie soils over 7 year periods. These relations suggest a specific eco-system (*senso lato*) which should be considered in future attempts to establish sustainable agriculture based upon natural, ecological principles.

The observations on clays minerals in the various agricultural regimes reported here indicates that prairies tend to produce or conserve illite either as an indepen-

**Fig. 5.21.** Indication of the effects of different fertilizer treatment on vertisol from Anhui Province (Huang, unpublished). A strong increase in *WCI* peak area is seen in the manure treated plot soils. *S/I* = smectites-rich interlayered mineral, *I/S* = illite-rich mixed layer mineral, *PCI* = poorly crystallized illite, *WCI* = well crystallized illite



dent phase or in illite-smectite mixed layered minerals. It appears that the action of intense grazing can decrease the illite concentration phenomenon. Thus the impor-



tant place of prairies in the classical crop rotation schemes was in fact an action of increasing the potassium stock in the 2:1 minerals through the production of illite as individual layers or as an independent mineral in the soil. Prairie plants tend to produce more potassic material than they consume which builds up in the surface soil layer. Intensive exploitation of the soils leads to a net export of potassium.

### 5.5.3

#### Plants and Soil Clay Minerals: Some Thoughts for Further Consideration

From the discussion in this chapter, it would appear that plants have a very strong role in determining the clay mineralogy in the upper, A horizon of alteration profiles. Their action is through the translocation of key elements which govern the stability of clay types, first through the accumulation of active silica which favors the presence of 2:1 minerals. Further, for certain types of biotopes a sufficient abundance of potassium is brought to the surface and re-cycled to stabilize illite layers, either in mixed layer minerals or in the PCI/WCI illite forms. If the chemistry of the organic materials present allows sufficient aluminum in solution, HI minerals will form. Mixed layer minerals of various types represent intermediate steps in the formation of one or the other of the major 2:1 "minerals" HI, smectites or illite. Plants then determine to a large extent the presence of 2:1 minerals in the soil zone and they condition the chemistry of soil solutions which determines the interlayer ions be they hydrated cations (Na, Ca, Mg, K), dehydrated cations (K) or hydroxyl ion complexes. The clay minerals identified as illite (anhydrous K), HI or soil vermiculite (hydroxyl Al) or smectites (hydrated cations) can be present in a single phase state or interlayered in different proportions in the 2:1 mineral structure. Interlayered minerals reflect the inhomogeneity in the layer charges from one 2:1 unit to the next in a clay edifice.

Climate will dictate the types of plant regime present, and this related to rainfall will determine the balance between translocation and loss through water/clay interaction. Hence it is extremely important to observe the type of plant regime when describing soil (A horizon) mineralogy and hence the type of reaction possible when changing from one plant regime to another.

### Suggested Reading

- Black C (1968) Soil-plant relationships. John Wiley, 789 pp  
Duchaufour P (1964) Pédologie. Sol, végétation, environnement. Masson, Paris, 289 pp  
Ellis S, Mellor A (1992) Soils and environment. Routledge, London, 364 pp  
Treshow M (1970) Environment and plant response. McGraw Hill, New York, 423 pp  
Velde B (ed) (1995) Origin and mineralogy of clays: clays and the environment. Springer-Verlag, Heidelberg, 334 pp

# Clays and Climate – Clay Assemblages Formed under Extreme Humidity Conditions

## Introduction

Generally when one considers alteration sequences one thinks of climates and conditions common to one's environment; i.e. inhabited, agricultural areas. However some climatic conditions create special chemical systems where specific minerals form due to the climate, i.e. variations of total rainfall and rainfall distribution throughout a yearly cycle. Of course one can consider glacial conditions as a climate. But given that very little of the yearly interaction with rock and atmosphere occurs under conditions of liquid water/rock interaction, this climatic possibility is ignored here. Very cold, tundra, climates tend to be more assimilable to those of temperate climate systems but these systems operate only part of the year and biological activity is weak. The alteration rate is thus hindered but the quality of the minerals present and their specificity is not significantly modified compared to those of more clement temperate climate soils.

Climate extremes can create special mineral assemblages through very abundant, constant rainfall in tropical forest conditions or very sparse and concentrated rainfall experienced under desert conditions. We will consider here the cases of too much rainfall (tropical and near tropical conditions) and too little rainfall, concentrated in short periods (desert conditions). The two extremes show very different clay mineral formation patterns.

### 6.1 Impact of High Rainfall on Clay Mineralogy

#### 6.1.1 Soil Development as a Function of Rainfall

One of the major factors in alteration (water/rock interaction) is that of rainfall and hence the ionic concentrations in solutions in alteration profiles. The lower the rainfall, the more influence a rock and its chemistry will have on the clays formed. The chemical potential of ionic species will tend to be controlled by the rock and the silicates present. Under such circumstances one tends to have multi-mineral clay assemblages forming at the expense of unstable high temperature minerals. The more water present in an alteration system, the more dilute the solutions will be throughout and the more the initial chemistry of the aqueous solutions will weigh on the clays stable. An infinite amount of water will cause the total disappearance of a rock. It will dissolve entirely. As the ratio of water to rock or silicates tends to one or less, the less soluble elements will tend to form solid phases. Iron and alumina are the least soluble

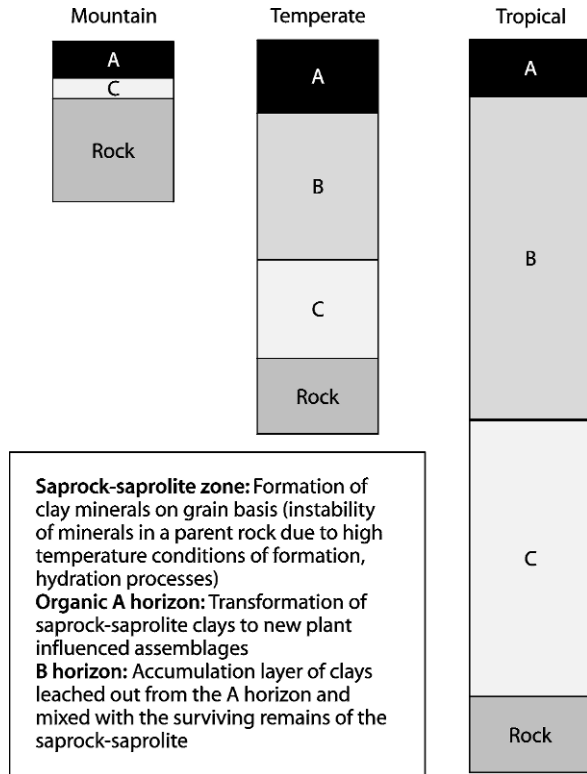
elements in major abundance in surface rocks. Next silica will combine with the insoluble elements to form clays and eventually incorporate potassium, calcium and some magnesium into these phases. Basically clay minerals and stable minerals in alteration zones are formed for the most part of iron, alumina and silica.

The overall tendency in alteration sequences (water/rock interaction) is then to lose silica content compared to alumina in soil clay assemblages (Pedro 1966). The strong loss of silica relative to alumina marks the difference between temperate climate soils and humid tropical alteration. This change in overall chemistry is applicable to the clay minerals, phyllosilicates and oxyhydroxides. It does not include quartz. In fact Lelong (1969) demonstrates that in tropical rain forest soils based upon granite, the chemically inert quartz (and hence silica) content increases in many cases towards the surface while kaolinite content decreases in favor of oxides and oxyhydroxides. On basalts, the clays show a decrease in aluminum hydroxides in favor of iron oxyhydroxides. As a result humid tropical soils do not show much smectite content which is the most silica-rich clay mineral in soils. Most commonly one finds kaolinite as the clay mineral present for several to tens of meters depth in such soils (Schultz and Ruhiyat 1998). In general, it is apparent that soils formed under conditions of high rainfall tend to contain kaolinite at the expense of 2:1 minerals. Kaolinite and muscovite have the same Si/Al ratios (one) whereas smectite has a higher relative silica content than kaolinite. In fact if one considers the phyllosilicate transformations from micas and chlorite (high temperature minerals) to soil clays under temperate climate conditions, the initial equilibrium is towards a more silica-rich phase, smectite in most cases. One can contrast then the clay assemblages in temperate climate to humic tropical soils as being more silica-rich than those formed under high rainfall.

The major chemical difference between tropical humid soil situations and those typical of temperate climates is one of rainfall. The throughput of water is much higher and constant in humid tropical climates than in temperate ones. Therefore the altering fluids contain much less dissolved material than do those in temperate climate soils and alteration profiles. The importance of climate can be seen in the thickness of different portions of an alteration profile. This is outlined in Fig. 6.1. The differences in thickness of the different zones is essentially one of water availability.

In very cold or very dry climates, water is not active for the largest portion of the year with the effect that plant growth is very minimal and the rate of rock alteration is small also. Ice sequesters water from both plants and silicates and lack of water slows alteration processes as well. Temperate climates have a balanced situation where there is an interaction between plant growth and alteration reaction times for rock/water interaction. The plant-alteration portion of the profile, soil horizon, is usually well developed, being several tens of centimeters thick. A lower horizon of clay accumulation (along with some of the soil horizon organic matter) is often developed below the soil horizon. This zone contains soil derived clay minerals and water/rock interaction clay minerals. Below the B-C horizons and the saprolite lies the zone of altered rock or saprock horizon which is again reasonably well developed under temperate conditions. In all horizons one finds a rather high rate of water flow in cracks and open pores while more chemically bonded water is found in capillary zones. The capillary water comes towards chemical equilibrium with the minerals present whereas the pore and crack water is not in equilibrium but under saturated with respect to the component elements in the clays of the profile.

Fig. 6.1. Schematic representation of soil profiles according to climate



Therefore one can look for strong differences in profile segments as a function of rainfall. However, the availability of under-saturated aqueous solutions also has a strong effect on the clay minerals present in the alteration and soils. We return to our initial definition of soils – surface environments affected by plant activity – which keeps us from considerations of abiotic situations such as barren rocks in glacial areas or entirely dry desert areas. Even though such situations can have materials present in the fine size fraction, they are normally not affected, or little affected by water/silicate or plant/silicate interactions. Hence they are unlikely to contain soil clay minerals. They are based upon the internal constraints of a rock induced by differential thermal expansion.

We consider below two major environments – those of abundant, and continuous rainfall and those of low rainfall where sudden storms bring large amounts of water at rare intervals.

### 6.1.2

#### Very High Rainfall

The tropics are areas of abundant, almost constant water saturation of surface materials. A glance at daily world weather maps shows that each day it rains in the equatorial zones and adjacent areas. The situation where there is no dry season is one of con-

stant water input and high alteration by silicate/water interaction. The normal geographic definitions of tropical rain forest areas include the Amazon River basin, the Congo River basin and the southeast Asian island arc of Indonesia and other islands. In the first two areas the tropical rain forest is bounded by a savanna of high rainfall but contrasted seasons. These two climatic zones produce specific weathering facies and soil clays which characterize their climates.

### *Tropical Rain Forests*

When water is in excess of plant/rock interaction, as in the case of tropical (wet) climates where there is an excess due to high rainfall one finds a great amount of alteration in the rock/water interaction zone where alkali and alkaline earth ions as well as magnesium enter into rainwater solution due to the high undersaturation of these fluids. There is little conservation of elements other than some silica, alumina and iron. In such alteration profiles, the alterite is highly developed. The clay minerals present are in general equilibrium with water of low alkali, alkaline earth and magnesium ion content. As these elements are in low abundance, one finds a predominance of kaolinite (or its hydrated form halloysite) and oxyhydroxides of aluminum and iron. The presence of low silica clays indicates that not only is there a lack of alkalis but also silica is of low abundance. The 2:1 soil clay minerals are of a higher silica content than is kaolinite.

The soil horizon, zone where organic matter accumulates, is very thin owing to the lack of 2:1 clay minerals and low K, Na, Ca and Mg ion concentrations. One must be careful in assessing tropical climate alteration profiles. Those that are the deepest are the product of not only high rainfall inputs but also long periods of formation in that they are found in flat, tectonically inactive areas. Not only are these soils highly weathered due to high water input but also they have experienced weathering for longer times than other soils.

In the initial approach of this book, we have considered temperate climate conditions where one tends to find clay mineral assemblages developed from high temperature minerals which give a majority of 2:1 minerals accompanied by kaolinite (1:1 mineral) in the clay fraction. These clay minerals are due to water/rock interactions at the rock/altered rock interface which continue until all of the unstable, high temperature minerals are consumed (some 1 Ma or so). However, under conditions of higher water activity due to continuous rainfall which is evacuated from the alteration zones i.e. not in lakes or ponds, one has a situation where eventually the dissolution of clays becomes a factor in their stability. For the most part under temperate conditions, the major mineral-forming reactions occur under conditions where the silicate clays determine the silica and alumina content of the pore solutions. There is a re-adjustment of the 2:1 clay mineralogy to chemical conditions of the soil and alteration solutions which tends to favor the presence of 2:1 minerals.

Under conditions of high influx of rainwater, one finds that the 2:1 minerals are no longer stable with the result as a decrease in the silica content of the clays (see Pedro 1996). In humid tropical alteration profiles one finds that kaolinite becomes dominant towards the bottom of the profile where granitic or pelitic rocks are the parent material. When basic rocks are present, gibbsite and goethite dominate (Lelong 1969). Towards the surface one finds more quartz for pelitic rocks parent materials and more

goethite for basalts. Compared to temperate climate alteration of similar materials (see Chap. 4) there is a strong tendency to go beyond the initial rock/water microsystem mineral transformations.

In humid tropical alteration profiles there is clearly a new chemical equilibrium which produces more silica-poor clays under water/silicate alteration conditions. Given the low chemical activity of tropical surface clays, kaolinite, gibbsite and oxides, one can expect that the plant/soil clay mineral interaction will be reduced. In fact the humic horizon in humid tropical soils, typically forests, is particularly thin and apparently there is little plant soil interaction as far as one can gather from the rare studies of soil clay mineralogy. Plants must reach very deeply, up to tens of meters, to find unaltered alkali and alkaline earth ion material.

The general schema presented by Lelong (1969, p. 81) indicates that as a function of rock type, granite or basic, the sequence of clays is different. Granite weathers to kaolinite at the rock/water interaction interface with some goethite and gibbsite. Quartz is strongly present. By contrast basic rocks transform primarily to gibbsite and form increasing quantities of goethite towards the surface. The lack of kaolinite in basic rock alteration is most likely due to the relatively low content of silica in the rock material which leads to a direct formation of gibbsite instead of kaolinite as is the case in granitic rocks alteration.

### *Laterites and Red Soils*

A special case of alteration under tropical conditions is the formation of laterites. These alterations are found in the savanna areas bounding the tropical rain forests of Africa and South America. The difference in the two alteration types is climatic, in the savannas the season is contrasted, with high rainfall during one season and a contrasting dry season. The vegetation is of course different, rain forests are tree dominated and the savannas are grass dominated. However, Ségalen (1995) believes that true laterites (crusts of iron oxide above gibbsite layers) are relict soils having formed under climates no longer existing where the laterites are now found.

Intense weathering can lead to the formation of concentrations of aluminum in the form of gibbsite or boehmite, hydrous and anhydrous alumina, and iron in the form of oxyhydroxides. Such soil concentrations are called laterites. Much work has been done on these soils or soil residua due to their economic importance as resources of aluminum. Their striking feature is a zone of accumulation of oxides and hydroxides below the soil zone. This accumulation zone is considered to be one due to intense leaching and transport of fine grained material (Aleva 1994). Laterites are complex, showing the formation of concretions and nodules which indicate local, intense migration of ions to form specific mineral concentrations (Boulangé 1984, p. 136–149). In certain, typical or ideal, cases the alumina is separated from the iron oxides into two layers, the iron forming a top crust or duricrust (Millot 1964, Lelong 1969). These cases are due to formation in tropical contrasted season climates under savanna vegetal cover (see review by Temgoua 2002, p. 4–6). These soil sequences were formed under conditions of intense rainfall for a part of the year and a more dry regime for the other part of the year. This is the contrasted season climate of the tropics.

Since such intense concentration and segregation of elements in a soil context is likely to be a lengthy process, one can assume that laterites are the products of long

periods of alteration which must have persisted over at least tens of thousands of years to millions (Aleva 1994, p. 73). Thus one can assume that the formation of laterites necessitates a stable climate or at least one that has not changed drastically as did those in the northern hemisphere. Most places where they are now found the oxide crusts appear to be unstable and can be seen to be breaking up.

The saprock zone (recent water/rock interaction) usually has kaolinite and smectite along with iron oxides (goethite). Gibbsite and goethite-hematite become important in the bauxitic and duricrust zones. Quartz is present in most horizons indicating its low reactivity to chemical constraints.

Temgoua (2002, p. 7) indicates that the laterite structures formed in contrasted season tropical conditions are not stable under tropical forest conditions, where the concentration zones tend to be ruptured by climatic change. Thus the formation of mono-elemental zone concentrations of Al and Fe depends upon wet and dry seasons, not those of a humid tropical forest.

According to Boulangé (1984) the initial stages of alteration or mineral transformation in the rock/water interaction zone produces kaolinite and gibbsite and biotite-HI phases in granites. Quartz and goethite are present as are white micas. As one moves up the alteration profile, gibbsite is more abundant at the expense of kaolinite. More basic rocks (amphibolite) produce gibbsite and goethite with less kaolinite. Hence the major change is a decrease in the silica content of the clay assemblages. This shows the impact of the high input of the unsaturated rainwater on the mineral stabilities.

Pion (1979, p. 190) gives a general scheme for the occurrence of different clay minerals formed from basic rocks under climates of relatively low rainfall (400–1 100 mm yr<sup>-1</sup>) to moderate (850–1 400 mm yr<sup>-1</sup>) to high rainfall (1 200–2 200 mm yr<sup>-1</sup>). Under high rainfall one can find vermiculite type minerals at the rock/alterite interface whereas above this zone gibbsite and kaolinite (plus iron hydroxides) are dominant. The alteration minerals in profiles formed under less rainfall show the strong presence of more siliceous 2:1 soil clay minerals.

One can consider red oxisols to be the product of contrasted season alterations. Here strong dissolution occurs during the rainy season and strong evaporative movement and dehydration of oxyhydroxides occurs during the dry season. This process is slow to occur and hence much of what one sees today as laterite material is frequently being degraded by forces of new climatic actions.

## 6.2

### Rainfall and Vitreous Rocks (Andosols)

#### 6.2.1

##### Andosol Characteristics

Andosols represent a combination of two specific variables which produces very characteristic, and unusual soils. Andosols are noted for their high water content, high content of organic matter in the A horizon (15–30%), high capacity to fix phosphorous, and moderate to low CEC often related to the amount of amorphous or extractable alumina present (Shoji et al. 1993, p. 2; Garcia-Rodeja et al. 2004). Although fresh or immature andosols usually select Ca over K in cation exchange reactions, it has been noted in several instances that slightly more mature andosols (containing 1:1 miner-

als) can strongly select potassium (Ndayiragije and Delvaux 2004). In general andosols are very fertile. This fertility is most likely due to a continued high weathering rate of glassy materials which furnishes plant nutrients such as K and P (Shoji et al. 1993, p. 210). As an example, the volcanic context of central and southern Italy and the development of andosols undoubtedly attracted populations from regions with less fertile soils, such as the limestone Aegean area, and as a result the Italian peninsula became an area of constant population movement from the early times of human agricultural practice.

Andosols occur under various latitudes from tropical Africa and Oceanic Pacific regions to mid continent areas such as Italy, Germany (Kleber et al. 2004) or France (Quantin 2004) to northern climates such as Iceland (Arnalds 2004). Temperature is obviously not a significant variable in the formation of andosols (see *Catena*, vol. 56, 2004).

Several principal factors then are necessary to produce these special soils. Regular rainfall is necessary, equal to or less than the tropics but above what is normally considered to be necessary for temperate climates. The soils should be well drained. The second factor is a source rock which contains significant amounts of glassy material, usually volcanics. It appears that there is not much difference between basic, basaltic material and more acidic types as they form andosols except that the transformation or alteration rate for basalt is significantly higher than for acidic glass up to two times greater (Shoji et al. 1993, p. 38). The essential material for the formation of andosols appears to be a glassy, or highly alterable substrate.

A distinct problem in the study of the properties and the development of andosols is that they are normally found in active volcanic areas and hence subject to renewed accumulation of fresh material on the top of the profile. Andosol alteration profiles are frequently interrupted by paleosols, indicating renewal of material by ash flow or lava flows which buries and fixes the soil zone with a renewed starting material upon which soils are formed.

Major phases characteristic of andosols are (see summary by Shoji et al. 1993, p. 113–123):

- *Allophane* which contains a hydrated network of Si-Al-O atoms. Both H<sub>2</sub>O and OH units are present. The stoichiometry is slightly variable but usually is between 1:1 to 1:2 Al/Si atoms,
- *Imogolite* a hydrated network of Si-Al-O atoms with a rather well organized tubular structure which is not detectable by XRD methods. The ratio of Si to Al is near 1,
- *Gibbsite* the hydroxyl form of aluminum,
- *Opaline silica*,
- *Halloysite*, the hydrated form of kaolinite,
- *Kaolinite/smectite* mixed layered minerals often occur in soils materials associated with andosols,
- *Iron hydroxy-oxides* are of course present in andosol materials,
- *Humic material* is extremely important for the stability of the hydrated phases as is of course a ready supply of rainwater.

Clay minerals which are not typical of andosols are:

- *Kaolinite* usually not in a true andosol material,
- *Vermiculite-smectites* also usually not found in andosol soils.



It is clear from this resume of the phases present in andosols that the initial rock materials have lost their alkalis and alkaline earths. Andosol minerals are dominated by Al, Si, Fe hydroxyl and oxide phases. Further, the ratio of silica to alumina and iron is much less than in the source rocks indicating a strong loss of silica. Such a loss is a key to the formation of the particular mineralogy of andosols. Elemental relations in andosols are clearly shown in the summary in Shoji et al. (1993, p. 148). Such material will not provide much transfer of nutrients by CEC or more tightly bound potassium as is the case for 2:1 minerals. Some data however suggest that the soil (plant/silicate interaction zone) can accumulate K and Si at the surface (Meijer and Buurman 2003). Cation exchange appears to come largely from the abundant organic material in the surface horizons.

Mohr and Van Baren (1959, p. 302) and Sifferman (1973, p. 150) indicate that there is a strong evolutionary trend in the development of andosol soils where an initial stage of “juvenile and virile” evolution produces a high vegetal cover which decreases strongly with time in the “senile” and lateritic stages of soil development on volcanic ash materials under tropical humid conditions. This indicates a natural exhaustion of the soils concerning plant activity. Thus the effects of high water influx and dissolution strongly affect the soils making them evolve rather rapidly towards concentrations of oxy-hydroxides.

The geographic situations in which andosols occur are very important as to their extension, longevity and relations with other soil types. In fact andosols depend upon the volcanic (glassy) substrate, high rainfall or constantly humid conditions and good drainage. If one is in the humid tropics, these conditions can be considered to be roughly general. However, the actual rainfall can depend upon geographic relief even there. In many instances where andosols occur, the volcanic material forms a mountain which affects the weather patterns, rainfall being higher on the summit. Ocean islands tend to accentuate this effect with rain shadow effects, such as the Hawaiian Islands, Azores, etc. Thus, on the same contiguous edifice, one can find soils developed under conditions of high rainfall and those under less humidity or one can see differences depending upon the climate of different islands (Bates 1962, p. 318). In these instances andosols will be present on one part of the edifice and other types around them (Delvaux et al. 2004; Fauzi and Stopes 2004; Sifferman 1973). This situation leads to the gradual change between andosol characteristics and those of other, more classical soil types. However, in some instances, other rock types can give rise to andosols such as is the case for a granite in Austria (Delvaux et al. 2004).

### 6.2.2

#### **Weathering Processes Affecting Vitreous Rocks under Constantly Humid Conditions**

Generally the high rainfall interacts rapidly with the highly unstable silicate glass to form an alkali and alkaline earth-depleted mass. Since there are few micro-sites (places where pre-existing minerals transform into new clays, see Chap. 4), there is little tendency to form new clay mineral phases, i.e. those with continuous layer structure edifices. Thus the more glass present, the more alteration will occur. One finds that there is also a loss of silica to the soil solutions which leads to the formation of the silica-poor phases, imogolite and allophane. These are the water/rock interaction minerals

found at the rock-alteration interface (Sifferman 1973, p. 149–151). As one moves upward in a profile, towards the surface one can find gibbsite (Al hydroxide) and some halloysite, depending upon the drainage, age and development of the profile. The presence of halloysite appears to be dependent upon a continuously humid environment. In soils which experience periods of drying, kaolinite is present. In more crystalline eruptive rocks one can find halloysite forming from feldspars in the early stages of alteration (Bates 1962).

In general, under conditions of highest water input one finds that silica and alkali-poor or unstructured phases have formed. As rainfall decreases over the year in adjacent areas, more structured minerals occur, halloysite and kaolinite with eventually smectite or HI phases. Using the comments of Sifferman (1973) one can construct the following weathering schema (Fig. 6.2)

The different variables of ground water flow, presence or not of primary crystals in the volcanic material, seasonality of rainfall and so forth can and do modify the mineral succession relationships in andosol sequences. The zones of contrasted seasonal humidity tend to destabilize the allophane and favor gibbsite-halloysite and eventually kaolinite mineral assemblages.

One can say in general that andosols and amorphous minerals are found as young soils developed from highly glassy materials. Even this is not universal in that kaolinite and smectite mineralogy was found in the surface horizons in soils formed on recent (Krakatoa 1883) ash fall material developed in a rain forest environment (Fauzi and Stoops 2004).

In a very general way, one can outline the relations of chemical activity and mineral destabilization in a simplified diagram such as that of Fig. 6.3. Feldspars and mica are destabilized in favor of kaolinite and eventually gibbsite. Loss of silica and alkalis are the causes of these changes. The higher the rainfall, the stronger tendency to reduce both silica and alkali (plus alkaline earth) elements. Both are essential for 2:1 clay minerals. The balance between allophane or the more mature form of hydrous alumina, gibbsite, is probably one of time.

**Fig. 6.2.** Relations of clays and humidity in various profiles on glassy materials after Sifferman (1973)

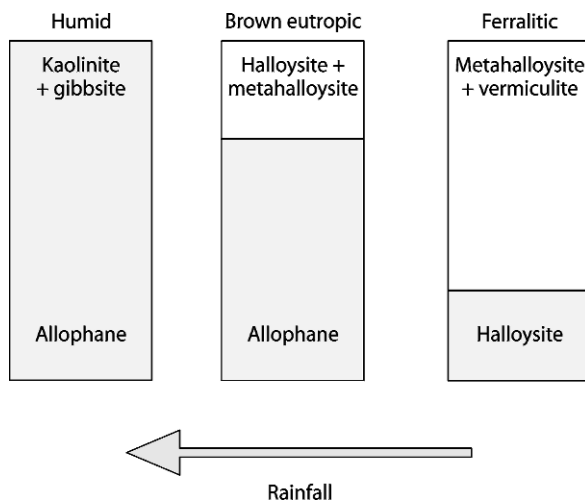
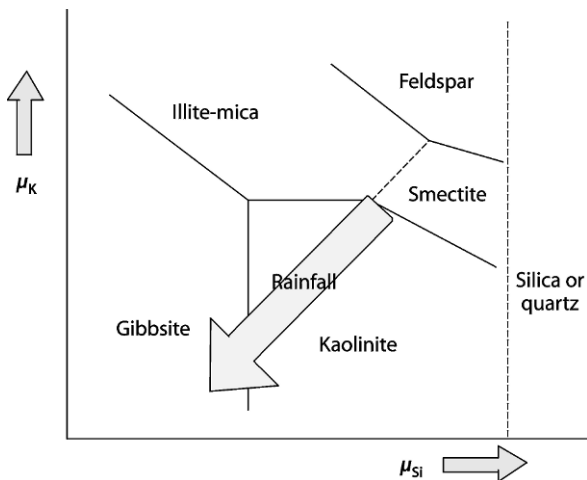


Fig. 6.3.  $\mu_{\text{Si}}-\mu_{\text{K}}$  diagram showing the normal water-rock interaction path of chemical change. Loss of potassium (lowering chemical potential) and decrease in silica (lower chemical potential of Si) change the clay mineralogy from 2:1 minerals, illite-mica and smectites to kaolinite and eventually gibbsite



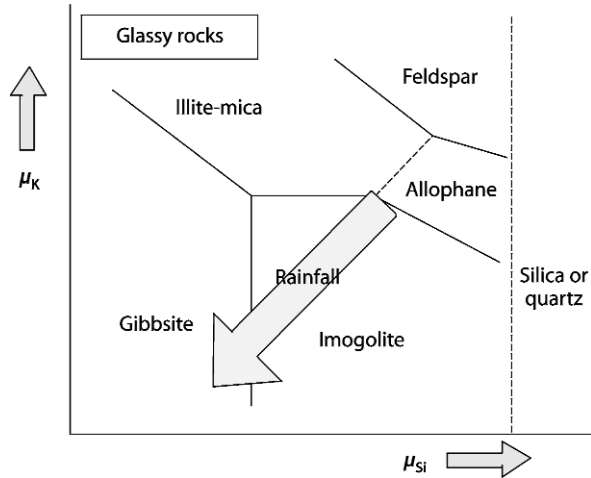
However, in the list of typical minerals in andosols, smectites and kaolinite are not frequently present. These minerals, are replaced by imogolite and allophane. Hence the glassy character of the initial rock materials determine another mineralogy in the initial stages of alteration. Sifferman (1973) reports allophane at the base of alteration profiles in the zone of most recent rock/water interaction and the presence of gibbsite in the upper portions of the profiles. These relations are indicated in Fig. 6.4.

Andic properties (due to the presence of amorphous and poorly crystallized materials) are found in soils forming on glassy materials under climates of lesser rainfall such as described by Takahashi et al. (1993) for xeric soils in California. In these cases allophane or imogolite are present with 1:1 clays and 2:1 clays in the soils. These should probably be considered as early stages of alteration which will eventually become 1:1 and 2:1 soil clay assemblages.

The effect of vegetation on andosols has been reported to be one of enhancement by grasses forming imogolite and allophane and destruction of andosol mineralogy to form more silica-rich podzols under forest growth (Shoji et al. 1993, p. 130) in Hawaiian soils. Meijer and Buurman (2003) give data for soils on an acidic volcanic edifice in Costa Rica where the plant regime varies from fern-grass at altitude, through deciduous forest, tropical forest to grazed land at low altitude. In the chemical data reported one frequently sees an increase in potassium in the uppermost samples of the profiles, the organic horizons ( $A_h$ ). This is especially true for the fern-grass soil at high altitude and tropical forest profiles. In the tropical forest profiles, one can note the presence of kaolinite, and vermiculite in these horizons whereas lower portions contain the less siliceous mineral assemblage gibbsite, goethite and halloysite. In these Costa Rican soils it is possible that the plants have an effect on the chemistry of the  $A_h$  organic horizon.

Typically, gibbsite is abundant at the rock/water interaction interface. Also one finds kaolinite or the hydrated form halloysite. Towards the plant/clay mineral interface one can find smectite in some abundance. It appears that the alteration intensity of silica loss is greatest at the base of the profile. This would seem to paradoxical in that the

**Fig. 6.4.**  $\mu_{\text{Si}}-\mu_{\text{K}}$  relations for imogolite and allophane weathering assemblages formed from glassy eruptive rocks. Loss of potassium and silica (shown as lower Si and K chemical potentials) forms allophane and imogolite in the fields where smectites and kaolinite would normally be present



water which reaches the rock interface should be the most highly charged in dissolved ions and hence at least a little silica. Conversely the rainwater falling on the soil surface should be the least saturated. However, if one considers that significant silica can reach the surface by plant action (phytoliths) one can imagine a source of silica beyond that of rainwater/kaolinite interaction (Derry et al. 2005; Farmer et al. 2005). This can be stretched to the existence of podzols in tropical forest areas (Lucas 2001, p. 138). Clearly the types of plants present can have a strong impact on soil clay mineralogy.

### 6.2.3

#### Mineralogy and Hydration State of Andosols

##### *Clay Mineral Origin in Andosols and Andic Soils*

In the brief description above, it appears that andosols, soils based upon the alteration of glassy silicate materials, will first produce unstructured materials which cannot be called minerals because they lack a determined composition and mineral structure (crystallographically identifiable). Allophane is one material and the hydroxyl-iron complexes are the other. Further there is a strong association between organic matter and these elements, Al and Fe. These materials are typical of the initial stages of rock/water alteration in andosols which are themselves due to high water input and constant humidification. Alkalies, alkaline earth elements and silica are evacuated by percolating solutions. Another important phase is imogolite, a much more stoichiometric phase of nearly equal portions of Al and Si. The diffuse organization of this material makes it essentially non-detectable by XRD methods, infrared is the major method of identification (see Farmer et al. 1983). In this phase one finds Si in roughly equal proportions with Al.

Under different conditions, either as replacement of crystalline phases such as feldspar or in zones nearer the surface of the alteration profiles, one can find halloysite (“hydrated” kaolinite) and gibbsite. It is not clear from the data in the literature if the presence of these minerals is due to a kinetic process, taking thousands of years, or

specific chemical conditions. One can imagine that gibbsite will replace allophane, which is largely of the same composition. However, the presence of halloysite indicates the conversion of imogolite, which has a similar Si/Al ratio. Thus both gibbsite and halloysite may be successors of allophane and imogolite, or perhaps form under slightly different chemical conditions that the first two phases. The minerals which give the physical and chemical characteristics of andosols (high water content, low density, high capacity to fix phosphorous) and perhaps not the stable end product of silicate equilibria.

One can outline the following classification based upon phases present:

- imogolite, allophane – *early andosol*
- gibbsite, halloysite (imogolite) – *mature andosol*
- kaolinite, smectite (imogolite) – *andic soil*

In any event, the phases typical of andosols are probably not stable under long term equilibria.

### ***Hydration State of Clays under Humid Conditions: Seasonal Effects***

The striking feature of clay minerals from tropical areas is their hydration state. Typically one finds allophane, a very highly hydrated alumina mineral. It is found basically at the rock/water alteration interface. However, when rainfall is unequally distributed over the seasons (contrasted seasonal climates) even though the rainfall is in total high, one can see that the highly hydrous minerals are replaced by less hydrated ones. Lowe (1986) has commented upon this effect, where he notes that contrasted season assemblages are less hydrous in tephra soils in New Zealand. Observations from many authors indicate that allophane is replaced by gibbsite in the upper portions of profiles those which are less permanently hydrated. Goethite is another highly hydrated mineral which is replaced by hematite in laterite deposits when the effects of contrasted seasons are felt in the upper portions of the alteration profiles. Halloysite, hydrated kaolinite, becomes kaolinite in the upper portions of soil profiles. Thus one finds that the existence of high and continuous hydration states in soils is reflected in hydrous minerals while under conditions of more contrasted humidity, the hydration state is reduced and hydroxyl clay minerals are found. We then have a direct reflection of chemical constraints on the clay minerals in profiles formed under conditions of high rainfall. The permanence of hydration promotes the amorphous or poorly crystalline minerals whereas contrasted seasons gives rise to more structured and less hydrous phases.

## **6.3**

### **Weathering Trends as a Function of Time**

#### **6.3.1**

##### **Weathering Trends as a Function of Time under Tropical Conditions**

###### ***General Trend***

Mohr and Van Baren (1959, p. 302) present a general scheme concerning the alteration of surface materials under tropical conditions as a function of time. If alteration is

based upon the exchange of hydrogen ions for other ions in silicates, the end product will be iron-aluminum deposits. Their arguments are based upon observations for volcanic deposits but should be valid for others in a general way. The evolution series is divided into juvenile, virile, senile, and laterite stages. The authors insist on the relation between plant activity and the stages of evolution or weathering. The vegetal cover diminishes over the senile stage to be almost absent during the formation of laterites. This is reflected in the overall color of the soils, being brown during the active stage and more red in color with decline in organic matter in the soils.

Thus one can take the tropical weathering scheme as a model for all other situations with adequate water. Alteration will inevitably produce a sterile oxide-dominated soils without silicates or phyllosilicates. However such a process takes about a million years or so, so that one must have stable climatic conditions and little change in topography, conditions which have not been fulfilled in the northern hemisphere until about the last 4 000 years or so.

The presence of high amounts of kaolinite, iron oxides and gibbsite will indicate past conditions of intense weathering under conditions of plentiful rainfall, continuing for long periods of time.

### *Climate, Vegetation and Host Rock*

Ségalen (1995) indicates the special distribution of soil types or alteration facies for tropical climates. His classification shows gradations of soils by color and hence oxidation state and iron content along with silica content as it affects clay mineral stability (smectites). Basically, and schematically, one finds yellow soil types with iron oxides and kaolin present in tropical forest zones, where the iron oxide is hydrated (goethite). On the edges of the forests under contrasted season climates one finds grasslands with red soils but where silica content is higher and smectites are present along with kaolinite. These relations are above all valid for soils formed on pelitic or aluminous rocks such as granites and sedimentary or meta-sedimentary rocks.

The Indian subcontinent is an exception having large surfaces covered with basalts, an iron-rich and alumina-poor rock. Even though the climate is equatorial and humid, though far from enough so as to form a rain forest, the soils are vertic, i.e. containing very much smectite. In this instance there is a tendency to maintain a siliceous mineral because the next alteration step is difficult to attain, the formation of kaolinite. However in some cases the stage of iron oxide laterite is attained.

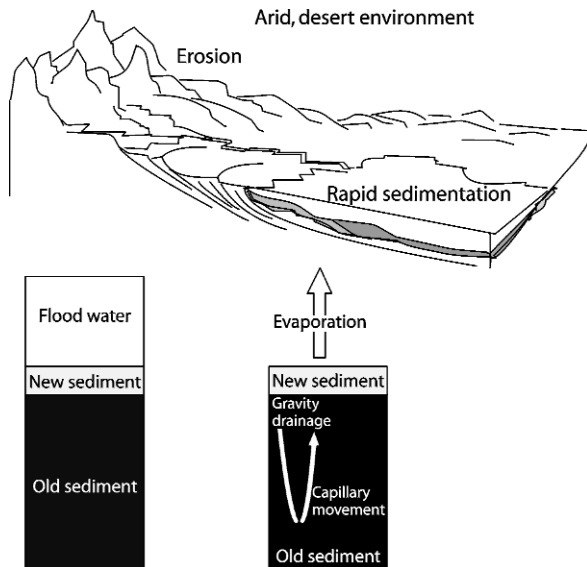
### 6.3.2

#### **Weathering Trends in Semi-Arid and Arid Climates**

##### *Desert Alteration Profiles: The Effect of Evaporation*

Desert soils are typified by high, episodic erosion rates and high sedimentation rates. The violent and highly episodic rainfall events cause this state. Figure 6.5 indicates a general relationship of this situation. The alteration profile, dominated by newly deposited materials, is one of episodic high water influx and subsequent evaporation of the waters found in the shallow profiles. Since the erosion zone on slopes is of high activity and usually occurs under conditions of sparse vegetation, few soil clay miner-

Fig. 6.5. Desert erosion and deposition. Diagram indicating the trajectories of water and sediment in a desert environment



als are found here. The major process is thermal expansion-contraction which breaks the rock into its individual mineral components and breaks the minerals themselves. The zones of deposition can support more stable plant/silicate contact, though this is variable and depends upon the rates of deposition.

### *Mineralogy of the Desert Soils: Sepiolite and Palygorskite*

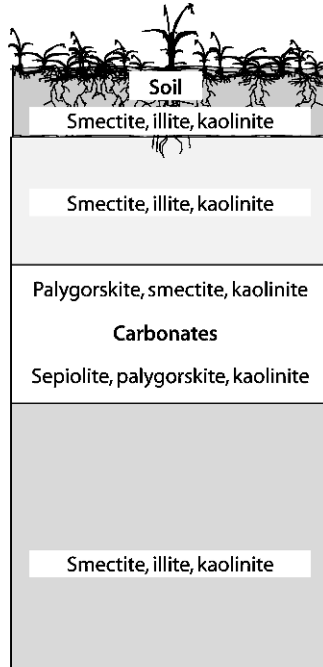
It has been observed for some time that desert or arid soil soils can at times produce a special mineralogy below the soil zone, i.e. the plant soil interaction zone. In these profiles, below the B horizon, one finds an accumulation of carbonate material and at times the presence of magnesium silicates, sepiolite and palygorskite (Singer and Galan 1984). Sepiolite is a magnesium silicate, trioctahedral in nature with a needle-like morphology. Palygorskite is a dioctahedral magnesium, aluminum silicate with the same morphology (see Velde 1985, p. 229 for a summary of the chemistry and chemiographic relations of these minerals,). Palygorskite is the more common of the two minerals in soil parageneses. These minerals are found occasionally in soils but their presence can be due to aerial input, at times over great distances (Bain and Tait 1977). The trajectories of Saharan, palygorskite-laden dust are varied and at times astonishing, ending up in Scotland, Florida and deep sea Atlantic sediments for example. In general sepiolite and palygorskite are not stable in the plant/silicate horizon, be it ever so thin. The formation of palygorskite is restricted to reasonably well drained alteration profile, being replaced by smectite in hydromorphic zones (Paquet 1977). These magnesium silicates are formed under specific hydrologic conditions.

We will use the careful description of Van den Heuvel (1966) as a model to explain the genesis of sepiolite and palygorskite in alteration profiles. In the surface A horizon (plant silicate interaction) and in the B horizons where soil minerals are displaced

downward, one finds 2:1 and kaolinite minerals. In the C horizon, developed in recent sediments, one finds strongly expressed deposits of secondary carbonate material. Here one finds palygorskite. Further down the profile palygorskite and sepiolite are found together. Below the carbonate zone only palygorskite is found along with the 2:1 and kaolinite mineral assemblage. The presence of secondary carbonate is the sign of solution saturation and precipitation of calcium reacting with solutions initially in equilibrium with air. Evaporation increases the concentrations of dissolved species until they precipitate as carbonate. The silicates palygorskite and sepiolite are then most likely reaction products of interaction between Recent sediment clay minerals and saturated aqueous solutions. If we consider that Mg is more soluble than Al and Si, the percolating aqueous soil solutions are most likely to be charged with this element as well as Ca. Little Mg is taken into the carbonate phase and it then is in overabundance relative to the equilibrium values with other silicates. The solutions must be alkaline in that sepiolite is stable between the pH values of 8 and 10 (Siffert 1962). The carbonate zone (the term caliche is used in the Western United States) is then one of palygorskite-sepiolite formation. These relations are outlined in Fig. 6.6.

In fact the limit of capillary movement upward during the normal dry periods is where the concentrated solutions (Ca, Mg, Si, OH) interact with the aluminous minerals kaolinite, smectite and illite. Illite is the mineral most affected by reaction and then kaolinite. Smectite appears to remain present in all zones of the profile. Here the dissolution of minerals at the surface (soil zone) are re-precipitated within the profile.

**Fig. 6.6.** Indication of the minerals present in a desert soil profile where solution concentration provokes the formation of palygorskite and sepiolite frequently in the presence of carbonates



Desert formation of sepiolite-palygorskite  
in soil sequences



Only alkali elements are lost as illite becomes unstable under conditions of high Si and Mg activity.

The typical desert water regime is one of extreme low activity for the largest portion of the year with intermittent high input (desert rainstorms). The heavy rains cause flooding and rapid saturation of the soils. Under high evaporation regimes the water tends to leave the system from the top with the result that the aqueous solution left behind becomes highly concentrated in dissolved salts. An extreme case is the formation of salt pans in flat, dry lake beds. In these cases the salts themselves are formed at the surface because little downward movement of the solutions can be effected. In better drained situations, the water can move downward by flow in macropores but the capillary movement still bring up much solution of high concentration of certain elements. When some downward movement occurs, the highly soluble chloride salts can be evacuated to a distant water table. The more insoluble silicates remain, sepiolite and palygorskite. It should be noted that the first magnesian mineral to form, palygorskite, is the most aluminous indicating that the initial reaction solutions are richer in alumina than those below where sepiolite (low alumina content) occurs.

An interesting case of palygorskite formation has been noted by Pharandre et al. (2000). In Indian soils, based upon basalt alteration of the Deccan plateau, intensive flood irrigation has produced palygorskite in smectitic soils. Farmers who use sprinkler irrigation, more expensive, do not have the problem of palygorskite formation in their agricultural soils. The palygorskite changes the physical properties of the soils making them less workable and it reduces the cation exchange properties. If we make the parallel of desert hydrology and that of flood irrigation, the same flux of water occurs and the same evaporative forces concentrate dissolved salts in the capillary water. It seems that the phyllosilicate to chain silicate (smectite to palygorskite) reaction occurs in the two instances. However in the Indian soils the smectite is iron-rich forming on basalt, whereas the palygorskite in alkaline desert soils is magnesian. In order for the reaction to occur in the Indian soils, it is unnecessary for the iron in the smectite, dominantly  $\text{Fe}^{3+}$  must be reduced to  $\text{Fe}^{2+}$ . This is possible in the flood irrigation situation where much organic matter is available at the surface which will aid in reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . In cases of sprinkler irrigation, the water does not stay within the soil, and instead of surface evaporation, most flows to the water table. There is little time for evaporation and iron reduction in such a situation and hence no palygorskite is formed.

Sepiolite-palygorskite bearing soil materials can be assumed to be due to high surface evaporation and concentration of OH, Si and Mg in the capillary solutions. These minerals represent a rather special set of physical and chemical conditions, High and rapid rainfall and low drainage but without standing water at the surface during the evaporation cycle.

### 6.3.3

#### Summary

Soils under climatic extremes, high rainfall or very low rainfall, show two inverse processes. Under conditions of high input of unsaturated water, most minerals are found to transform to low silica or non-silica forms. In these cases the alkali and alkaline

earth elements are lost and eventually silica also. Solutions are evacuated, and in any event they are of low concentration for the elements taken out.

Soils under desert conditions, where the small amount of water which arrives is strongly concentrated in time, show the effect of evaporation of surface waters upwards in the soil. The effect is seen below the soil zone where the evaporation/water table interface is present and water evaporates forming strong concentration of dissolved elements, the pre-evaporation zone of rising water. Here new minerals form which combine the dissolved elements into new phases. As the major dissolved elements are alkaline in nature, the pH is high in these evaporitic concentrates, and the minerals sepiolite and the more aluminous magnesian silicate palygorskite crystallize along with carbonates. These minerals are not stable in soil profiles under temperate climate conditions, probably due to their requirement of high pH conditions which are not favored by the decay of organic matter in the A horizon. Here the movement of water is upward, the elements become more and more concentrated and new minerals form by crystallization from solution.

Thus the tropical mineral regime is one of elemental loss while the desert, evaporitic soil regime is one of elemental concentration. The two are quite opposite but then the hydrologic regime is inversed also.

### Suggested Reading

- Fitzpatrick E (1983) *Soils*. Longman, London, 353 pp  
Jenny H (1994) *Factors of soil formation*. Dover, New York, 281 pp  
Millot G (1964) *Géologie des argiles*. Masson and Cie, Paris, 499 pp (English translation 1970: *Geology of clays*. Springer-Verlag, New York, 429 pp)

# Physical Disequilibrium and Transportation of Soil Material

## Introduction

Surface movement of geological materials is a very important factor in interpreting clays at the surface. Much of what we see today at the surface has been displaced from its initial position of contact with the atmosphere to the site where it is now. This is in fact one of the major problems of interpreting soils and soil clay relations and has been known and studied for many years by pedologists. Multi cycle surfaces are very often sites of human activity. For example, the initial great civilizations were produced on sites of fluvial transport. Ancient Egypt was renowned for the Nile River and its regular flooding and subsequent fertile renewal of surface soils. The Tigris and Euphrates flood plains were sites of soil renewal. The Ganges flood plain is continually fertile. Xian in the old cradle of Chinese civilization was at the same time subject to active loess deposition and river flooding. It seems that early city dwelling could be sustained for man if he lived and profited from surface clay renewal.

However not all displacement gives a happy ending and some movements of Earth materials can be considered to be catastrophic. Landslides and tsunamis are not all that welcomed. The interesting point in catastrophic events (flooding especially) is that they are periodic and the greater events are always on the time scales of hundreds of years (see Smith and Ward 1998 for example). Thus strong displacement is a rare but extremely important event whereas yearly river overflow or loessal deposition is more regular and can be handled more easily by farmers. It is interesting to consider that flooding for example has no geographic limits, flooding occurs in arctic climates, mountains, temperate zones, tropical forests and deserts. By contrast, massive land slides are more contained to regions of steep relief. However they can be a major part of surface displacement and geomorphological processes (see Evans and Van de Graff 2002).

In all of these displacements clays of surface origin are put into new chemical contexts where they will react with their silicate surroundings and the chemical forces imposed by plants. New alteration profiles are produced after transport events.

## 7.1 Slope Effects and Physical Disequilibrium

### 7.1.1 High Slopes in Mountains

In looking at topographic maps of the different parts of the world, it is clear that the exposed continental surfaces are rather flat. For example strong, high mountain relief

in the Western Hemisphere is relegated to about one third of North America and one fifth of South America. The African continent is rather flat for the most part as is Australia. One finds high mountains around the Mediterranean Sea the Middle East and along the giant Himalayan Tibetan massif. However, these massifs present a very special type of erosion and displacement of soils.

High mountains show rock faces which give them esthetic interest. However these cliffs basically indicate that the alteration mantle once developed has been displaced. One can look for it at lower altitudes. Again looking at high mountain topology, one can see that ice has been a major vector of transport in a classical glacial displacement system, with deposition at lower altitudes, and also one can see the results of deposition fans due to more recent landslide events (see Evans and Van de Graff 2002). It is probable that most present erosion (quantitatively) occurs through these catastrophic events. Small stream transportation is most likely of minor importance. The end result of landslide events is to mix altered material with rocks that are less in equilibrium with rainwater. One has a mixing of the different parts of an alteration profile into one more or less homogeneous structure which will gradually come back into chemical equilibrium with alteration processes. However, boulders are mixed with clays and gravel in a random manner which involves local chemical re-equilibration. Essentially landslides move large amounts of material and create new soil and alteration profile development. However some of the silicates in the fine fraction have already come into equilibrium with plant and alteration chemistry.

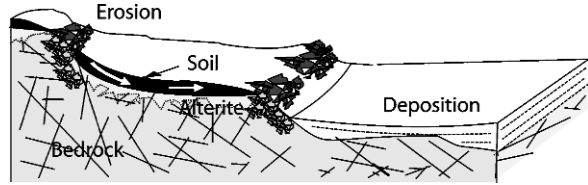
Lower mountain relief often indicates more regular events which move material in a slightly less catastrophic way. In such events, more akin to flooding events, one finds that the finer materials are sorted from the coarse and one develops depositional fans which grade out from the high relief as a function of grain size. This is especially true in drier mountain areas. One must remember that flooding can occur in any climate regime. In dry inter mountain basins the finer materials are spread and sorted by grain size and hence by chemical reaction zones corresponding to the amount of interaction with plants and water hydration alteration. Thus one finds a sort of banding of coarse grained (boulder and gravel) zone at mountain bases with more fine grained material found along river and sheet food surfaces grading into more arid zones. These distributions are still subject to movements through catastrophic events by flooding. However a non negligible amount of material in the flat intermountain areas can be moved by wind erosion if vegetation is sufficiently sparse; this is the loess transport mechanism.

### 7.1.2

#### Moderate Slopes

Geomorphological forces, slopes and water movement, create disequilibrium at the surface by displacing material from its equilibrium chemical environment. In cases of transport, clays which have come into equilibrium with water and chemical flux are abruptly put out of equilibrium through surface movement. Such change creates catena or sequences of soils and soil types depending upon the surface structure or their place in a landscape. In such situations where transportation of clays occurs due to water transport, new and unstable material is added to the soil surface and it interacts with the plants present (Fig. 7.1). In such situations there can develop a new set of chemical

**Fig. 7.1.** Major vectors of soil clay displacement on slopes in temperate climates. Alteration creates a plane of mechanical weakness between rock and alterite on slopes which fosters landslides and the displacement of altered, clay-rich material



constraints which develop new equilibrium between clays and plants. Movement of clays from the surface a given site in a profile contributes to its shortening and a disequilibrium. In general, profiles which are being eroded are thin and immature where the saprock zone is minimal. A significant portion of fine grained material can move within the soil profile down slope. This material can accumulate in the level, flat lying soils or be transported further to be deposited in flat basins.

Birkeland (1984, p. 246–257) indicates that movement of fine grained material is very frequent on sloped soil sequences (catena). At the base of slopes one finds thick layers of very clay-rich materials. In temperate climate landscapes one can often observe that flat inter hill zones are more clay rich and that the soils are decidedly deeper in color if not black. When one sees such a topographical sequence one should think of lateral clay migration and accumulation. Birkeland's analysis demonstrates the fact that soils showing clay accretion will have mixed mineral assemblages, i.e. those with clays from the alterite, portion of the alteration sequence where they are not in equilibrium with the surface. Alteration sequences (vertical) will show regular transitions of clay minerals from unaltered material to that reacting with plants in the soil zone. Zones of accumulation at the base of slopes will show mixtures of clays having come from different chemical systems.

### 7.1.3

#### Wind and Water

One can divide transport systems into perhaps three broad types:

1. slope movement and local deposition of clays at the foot of the incline.
2. water born deposition of material along the edge of a river or stream and deposition by tidal and storm action into marshes along a coastline
3. movement by wind

In the second and third situations, the input material is largely dominated by clay sized material usually of 40% or more  $<2 \mu\text{m}$  size material. Slope movement (case one) can give fines and more coarse material to a deposit depending upon the slope grade and the material present. Slumping will bring all material to the bottom of a slope in a chemically "disordered" state where new soil parameters must be established and new plant regimes formed. Gradual runoff will give a deposition of fine clays to the down slope catchment area. Deposition along rivers (case two) is the most variable where the energy of the flow in the river determines the size material which will be deposited. Wind deposition (case three) will transport the fine sized materials. The physical process of particle transportation are detailed in Allen (1997).

### *Movement Vectors*

Some of the effects of geomorphology on soil clay mineral sequences has been outlined by Birkeland (1984). He develops the concept of soil chains depending upon the catena in which they are found. Paquet (1977) has gone further in attempting to identify the clay mineral changes induced by topographical effect. This is of course dependent upon climate which dictates the types of vegetation and the development of clays in the soil horizons. However emphasis is placed upon lateral movement of clays and ions in solution.

What are in fact the specific consequences of such translocation of material from one soil profile to another, or the introduction of sediments into and onto a soil? Initially it is clear that the clay minerals stable in a previously established soil profile will become unstable when moved into a new, disturbed environment. First the soil chemical regime will be different due to the new plant regime which imposes new chemical equilibria. Second, the new environment can have different hydric constraints, some hydromorphic periods, for example. Changes in pH and oxidation potential can strongly affect clay mineral stabilities. Further, addition of new clay resources can stimulate or enhance plant growth, due to different potassium availability for example. It is well known that alluvial plains along rivers give high productivity due to a good availability of water and renewed clay-organic resources. Such places are typically where vegetable gardens are placed and have been for many thousands of years. In all situations, new chemical equilibria will effect changes in clay mineralogy.

Surface material becomes inherently unstable as alteration proceeds and it becomes more and more fine-grained. Such alterite absorbs large quantities of water, shrinks and expands with wetting and drying, and tends to desolidarize with the rock strata upon which it is formed. Such situations lead to land surface instability and massive movement of material down slopes. It is probable that most erosion removal in mountains is through such a mechanism. The surface soil is generally held in place by plants, roots are a good insurance against massive failure of surface materials. However despite the stabilization by plants there is nevertheless movement of the finer material within runoff water movement or within the soil itself. As water follows the down the general slope in the porous soil medium clay is moved also. Figure 7.2 indicates such a situation.

### *River to Sea Transportation*

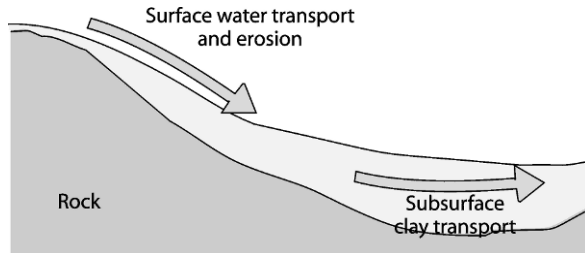
The ratio of fine-grained material in soil and surface erosion movement depends upon the slope and intensity of rainfall. When sufficient water is moving, sediments are carried to a river outlet and move along its course. Eventually they get deposited along the edges of the river in flood plains. Further movement brings the fine-grained material to the ocean and it can be re-deposited along the coast by re-deposition in salt marshes. In each of these transportation steps the material is of smaller grain size and the clay fraction increases in the deposited material. Thus the material deposited by water action is more and more concentrated with soil clays which were formed under surface alteration conditions. As the proportion of clay increases the materials should be more and more in equilibrium with the surface environment. Less old, unstable material such as mica, feldspar or pyroxene will be present. However the unstable, high

temperature mineral material will tend to alter more rapidly due to its small grain size and hence great surface area per mass. The large flood plains are traditionally areas of fertile soils. They are essentially zones of transported soil clay. Coastal areas frequently accumulate sediment through tidal action where the clay-rich material is flocculated and re-deposited in marsh zones. These areas are frequently ploughed and used for their relatively high fertility. (Fig. 7.3)

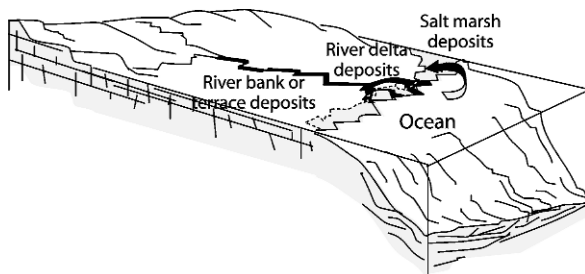
In each of these situations clay-rich material due to alteration processes is exposed to plant/clay interaction since the areas of deposition are normally in temperate climate zone where plant colonization can occur. New plant regimes can change the clays in these soil zones. However, in zones of continual deposition, the new materials are exposed to the new plant/soil regime for a relatively short period of time, being buried by the accumulation process in place. If the sedimentation is interrupted or slowed, one finds an accumulation of organic matter in a “static” situation forming a soil sequence (A, B and “C” horizon). When sedimentation resumes this static situation it is buried and is identified as a paleosol. In such situations of river and marsh accumulation, one should remember that the C horizon material has already passed through the plant/soil zone to be eventually buried. Hence it is not a representation of the initial stages of water/“rock” interaction as found in normal alteration profiles where the source material is reacting with aqueous solution when the upper material is reacting with plant regimes.

Another, very important but often neglected source of displacement of fine-grained material is wind transport creating loess deposits. This material is taken off of scarcely or un-vegetated areas during periods of dry weather by wind storms. Such events can now be followed and monitored by satellite imagery. We can determine with precision the direction, time of flight and deposition area of such material. At present most wind born material originates in desertic areas, especially the Sahara and Gobi-Asian pla-

**Fig. 7.2.** Movement of clay particles on soil profiles (erosion) and in soil profiles (elutriation) along slope planes with the result of deposition at the bottom of the slope on or within the soil profile at the base



**Fig. 7.3.** Displacement of fine sediment by river transport into oceans and resulting re-deposition in coastal salt marshes



teau areas. However in the past a great source of dust movement as air-born material occurred at the front of continental glacier masses. This was not necessarily in desert or dry climate areas but those which had a sufficiently high deposition rate from glacial deposit to prevent significant plant growth. Thus fine-grained material was present on glacial outwash plains which could be eroded by wind movement.

In each of these environments the fate of clays and unstable materials depends upon the existence or not of plants which can rapidly transform the fine grained material into clay minerals. We will investigate these different situations as a function of plant interaction.

#### 7.1.4

##### **Movement of Coarse Grained Material**

Displacement of surface clays is a very important feature of geomorphologic and geologic action. Any slope upon which soil is formed has a tendency to move fine particles laterally. Erosion is the general term for such movement. Usually the finer material is moved but at times landslides can occur moving all loose material, especially when the topographic relief is great. One could expect that a large part of erosional displacement in high mountain terrains is by landslide movement.

Landslides and desert wash formation suggest massive, rapid transportation of rock and altered material. Essentially all materials in different sites of equilibrium with water/rock interaction and soil plant/silicate interaction are mixed together and taken out of their chemical context. Here all is to be done again. The gradual implantation of plant communities will occur in a sequential manner and water-rock/rock alteration will begin again. However, these chemical forces will act on heterogeneous materials some of which have already come into equilibrium with surface chemical influences and others are untouched by such action. Hence resulting clays will be highly dependent on local conditions and the origin of the materials. In the case of landslides in humid environments, one can expect a change due to plant interaction as well as water interaction. However under dry conditions, the change of the material will occur much more slowly if at all. With low residence time of water, and low plant occupation of the surface chemical change will be difficult to attain. Deserts retain the imprint of the material moved into their basins.

Mountain landslide materials are much more active chemically due to higher rainfall and plant activity. In fact much mountain slope material is in constant re-equilibration as movement is frequent. The further one moves up onto the mountain, the younger the soils are, i.e. the less clay material present and they become less deep. Nevertheless, such young soils can come to a chemical equilibrium as seen by the change in soil clay and soil clay mineralogy (see Chap. 3).

## 7.2

### **Fine Grained Material**

Massive transport of fine grained material is effected by two main agents, wind and river transport.



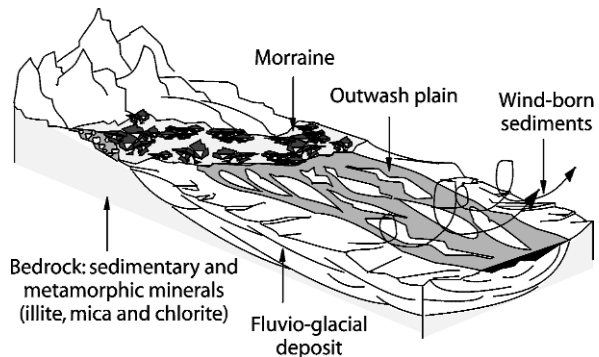
### 7.2.1 Wind Transport and Loess

#### *Loess Deposits*

However another category of fine grained geologic material, which is moved laterally is the result of the action of wind. This is loess. The origin of loess deposits is generally considered to be from wind ablation of relatively flat zones of sediment accumulation of fine materials. The North American continent and Europe are examples of what are considered to be peri-glacial accumulations of fine material moved by wind (see the review by Catt 1988). The fine grained material would have been deposited on outwash plains from peri-glacial torrents which dry periodically and wind action transports the fines to be deposited at greater distances, usually several hundreds of kilometers. Grain size studies show diameter/distance relations indicating air born transport. It is generally assumed that the outwash plains were not covered by vegetation. One then has the deposition of the fine fraction of glacial, moraine material at various distances from the retreating glacier front. In some areas the accumulation of loess is very thick, tens of meters. However, the possibility of secondary accumulation of loess material should be entertained. For example if one compares the loess thickness of the Peoria unit in Illinois to the old river channels, there is a strong thickening at their edges (Lineback 1979; Fehrenbacher et al. 1984, p. 68). One can suspect secondary accumulation by surface water effects after wind deposition. A Schematic description of this process is given in Fig. 7.4.

Loess deposits in China, active today, seem to be still accumulating from the large Gobi desert region (Zhang et al. 1991). In this situation it is clear that there is no plant/soil interaction at present on the loessal materials. It is logical that plants be almost absent otherwise wind action could not ablate large quantities of fine-grained material. Loess deposits in Central China appear to be dominated by detrital chlorite and high temperature (2M) muscovite micas (Li and Chen 1999).

**Fig. 7.4.** Situation of glacial deposit on outwash plains and subsequent air born transport of the fine fraction by wind. The major cause of this transport is the high sedimentation rate and consequent lack of vegetation which could stabilize the sediment



### *Clays in Glacial Loess and Related Deposits*

Loess has been derived from till materials in the large European and North American deposits. (Catt 1988). The clay sized material in till deposits as we see them now are typical of soils, i.e. interaction of plants and alteration products. They are composed mostly of vermiculite, S/I and I/S clays; and kaolinite. Silt sized fractions in loess contain illite and chlorite plus some kaolinite in French deposits (Hardy et al. 1999; Jamagne 1973) while tills in the American Mid-West show indications of weathering mineralogy although illite-chlorite is frequent (Willman et al. 1963, 1966; Hensel and White 1960). Most often these soil clay types are found to great depths, tens of meters just to the underlying rock substrate. The question is: why and how do soil clay minerals form these thick wind-transported deposits?

In general loess is found to be relatively homogeneous as far as grain size and clay mineralogy are concerned throughout its thickness except at the present day plant/soil interface where clay assemblages are found to change at the surface (Kuzila and Lewis 1993; Burras et al. 1996 for example). Loess clays are smectite-rich in North America and contain high amounts of soil vermiculite-S/I in Western Europe, at least France (conclusions based upon published XRD spectra by Jamagne 1973; and discussion by Hardy et al. 1999). Loessic soils on the Russian Steppes appear to contain I/S and S/I minerals (Reichenbach and Rich 1975). Kaolinite is present in most loess materials, especially in the upper portions of profiles (for example Frye et al. 1960, 1962, 1968). The S/I and I/S assemblages suggest plant/soil interactions in that these minerals are found in soils and not in the water/rock interaction alteration zones.

If we take the case of Illinois glacial deposits studied in detail in the period 1960–1975, in the tills one finds mainly illite and chlorite except for the oldest, Kansan till deposits where mixed layered clays, typical of weathering are found (Willman et al. 1966). Weathering produces the mixed layer minerals along with soil vermiculite. In the youngest till (Woodfordian) illite-chlorite content is highest. One can imagine that the tills represent the glacial material transported to the glacier front which is sifted by water transport and re-deposited on the outwash plains in front of the glaciers. It would be expected that the till material is mostly unweathered rock ground from the shield substrate by glacial action. Since much of the Canadian shield or basement is of greenschist facies rocks, illite (muscovite)-chlorite would be a major component of the fine-grained fraction of such actions. Such clay fraction minerals are in fact dominant in unweathered till in Illinois.

#### 7.2.2

#### Reaction Rates due to Plant/Loess Interaction

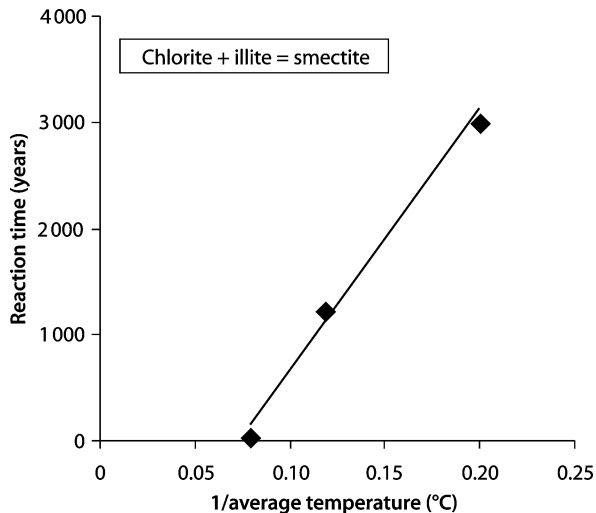
##### *Loss of Chlorite*

If illite-chlorite is transported into a climate where plants establish themselves quickly, how long does it take to alter them in the soil (plant/silicate) zone? In other words, could one expect plants to change clay mineralogy in depositing loess regimes? Transformation of illite-chlorite fine grained fractions to smectites is known in soils based on periglacial sediments in Denmark (Moberg 1990) Norway (Teveldal et al. 1990) and Finland (Gillot et al. 1999). The vegetation cover of the soils in these reports is conifer

forest for the most part. The weathering reactions, illite + chlorite to soil vermiculite and S/I take several thousands of years in northern climates when developed on tills but Gillot et al. (1999) indicate that soils based on sands show much more rapid development of smectite, on the order of 1 200 years. One should note that the soil/plant interaction zone is smectite-dominated in the soil clay fraction while deeper in the profile, below the soil plant interaction zone HIV, chlorite, and micas are more dominant. However, we know that illite-chlorite is highly unstable in salt marsh (*Spartina* grass) prairies (Velde and Church 1999) being transformed into S/I assemblages in several years time in the plant/soil interaction zone. From these observations it appears that climate (temperature and rainfall), and perhaps vegetation type, could influence the reaction rate of formation of the soil clay minerals.

If we consider the estimations of time necessary to form smectite from illite + chlorite in moraine materials to roughly 80% completion, Egli et al. (2002) indicate a 3 000 year period for high altitude mountain glacial moraine soils. Gillot et al. (1999) indicate 1 200 years for alteration of moraine materials in Finland and Velde and Church (1999) 4 years or so in Delaware Bay salt marsh sediments of glacial origin. If we consider that reaction progress is related to temperature as  $1/T$  (Ritchie 1966, p. 14), we can plot the time necessary to complete 80% reaction against the temperatures. In the case of high mountain climate, average temperature is not a very significant number in that all of the temperatures below zero are equivalent. Let us assume half of the year under ice and 10 °C average for the others which gives a value of near 5 °C. For Finland the temperature is certainly higher for non sub zero days, and one can estimate an average for all non-iced days to be near to 9 °C. The Delaware Bay, a very temperate climate probably has a 15 °C average value. Given these estimations and the determined values for reaction progress to completion by the different authors one can plot  $1/T$  against reaction time (Fig. 7.5). The values align very well, but given the probable errors in the estimated temperatures and times, the relations are probably less well aligned than in the figure. However, it is clear that the differences of 3 000 years reac-

**Fig. 7.5.** Relation of chlorite transformation into a mixed layer mineral as a function of temperature. The stage of 80% reduction of chlorite content was observed in three situations, Delaware salt marsh, Finland till deposits and high Alpine tundra sequences on till deposits. The linear relation of reaction time vs. temperature<sup>-1</sup> suggests a strong thermal relationship which would govern biological activity which enhances the reaction rate. Data from Egli et al. (2002), Gillot et al. (1999) and Velde and Church (1999)



tion times can largely be accounted for by differences in average temperature (climate). This analysis confirms that under temperate climates, one should see illite-smectite being transformed into smectites rather rapidly.

Given the possibility of a rather rapid rate of transformation under favorable conditions (repeated tidal flooding), one could expect that plant action at the surface of a soil could rapidly efface the initial illite-chlorite mineral of fine clay materials. However, if the burial rate is great enough, basically unaltered loess materials would be deposited and buried without mineral change. If this is the case, loess should be essentially illite-chlorite bearing. If it is not, at least as it seems in Illinois and France, soil clays dominate. Jamagne (1973) finds the typical soil clay mineralogy in French loess in all but one of his carefully studied profiles. At the Picardie ouest site, the deepest sample (4 m) is illite/chlorite-bearing. But in general, the loess soils under prairie or deciduous forest situations show a soil clay mineralogy to great depths, illite, S/I and soil vermiculite, kaolinite. Potassium exchange treatment closes significant portions of the smectite or soil vermiculite (14.2 Å spacing) materials suggesting smectite and HIS components of the clays.

### *Clay Mineral Formation in Loess Materials: Gain of Mixed Layered Minerals*

Let us look again at the dynamics of clay mineral transformation in the cases loess and till examples cited. In the soil clays of the Scandinavian forests (till and outwash materials), the top most layers contain smectites. As one goes downward the illite-chlorite mineralogy becomes rapidly dominant, especially in the youngest soil profiles. However, smectite mixed layer minerals are dominant in the top most part, where the plant/clay interaction is the most intense. In the till profile the material treated by plants is fixed in place and alteration proceeds from the top downwards. Now, considering the salt marsh example where the clays are transformed rapidly, they are changed in the upper most part of the profile, where sediment accumulation occurs. Each year fresh unstable illite-chlorite is deposited mainly in the winter and during the growing season, plants interact with it. The action is through a relatively thin layer of material (several centimeters). Below this interaction level the clays change but little. This is the reverse of a soil profile developed upon a static deposit of glacial material where the plant interaction must penetrate into the profile.

### *Clays and Loess Deposition Rate*

The case of loess accumulation and soil development is more similar to that of the salt marsh than it is to till weathering. In loess deposition, new material is layered onto the surface each year. If plants are present, probably prairies near the glacial interface, they will interact each year. Should burial be reasonably rapid, the typical characteristic of a soil (humic accumulation, clay mineral translation, etc.) will probably not be visible to any great extent in the burial sequence. In order for the deposition process to appear to be homogeneous, the upper layers of the deposit which have interacted with the plants need to be buried and new interaction take place in a new upper horizon upon further loess accumulation. If the loess transformations take place as rapidly as those in the salt marsh, 3–4 years are necessary to accomplish the formation of the typical S/I and I/S soil clay assemblage.

The reaction rates at 15 °C can be sufficiently high to produce such an effect. If the material is buried at a sufficient rate, there will be little development of typical soil features such as clay migration, development of a stable humic layer, etc. The buried clay mineralogy will represent that of the soil plant interaction. Lateral movement of surface horizons by water transport will concentrate the upper most portion of the clay profile. The deep loess horizons along major rivers in the United States are probably the result of such transport/deposition actions. This means that the soil materials in the sequences of one to several and tens of meters of loess in North America and northern Europe have been strongly affected by plant interaction.

A preliminary investigation by BV of soil clays in the Xian loess deposits and those in the Yangtze delta region showed that they are dominated by illite-chlorite with less important amounts of interlayered minerals. The interlayered mineral appears to be illite/chlorite most often. As the accumulation rate in Xian is very high (2 mm yr<sup>-1</sup>) the relatively unaltered mineralogy of the soil clays could reflect high burial rate where the interaction of plants is not rapid enough under the reigning climatic conditions.

Paleosols seen in loess sequences must then represent pauses in the sedimentation of the fine grained material. Under such conditions there is a tendency to form a strong humic layer and to allow clays to migrate downward in the soil sequence as stated by Catt (1988). Since burial occurs after a resumption of sedimentation the soil profile is preserved as a paleosol.

### *Present Day Plant/Clay Interactions in Loess*

Various investigations show that the soil clays are not greatly different in the different parts of the profile. Burras et al. (1996) find that the smectitic clays are quite similar in B and C horizons in soils based upon Peoria loess in western Ohio. Ransom et al. (1988) find that the highly smectitic clays in the B-C horizons are partially transformed into HI minerals (soil vermiculites with exchangeable aluminum in potassium solutions) in the A horizon of Peoria loess soils and Frye et al. (1968) show X-ray spectra indicating a strong increase in illite content of the S/I minerals in the upper soil horizons of an Illinoian Woodford loess. In these studies it is clear that the present day plant/soil interaction does not favor the S/I mineralogy that was produced in the loess materials upon their initial sedimentation.

Given that most of the clay minerals deposited from desert outwash plains, in China for example, have clay mineralogies representing the high temperature phases of the rocks from which they were derived, it seems logical to ascribe the typical soil clay mineralogy of European and North American loess deposits to soil clay interaction after deposition. Hence the soil clays found today are due to interaction between today's plants with minerals developed in old plant/soil interaction zones. In other words we see today the influence of new climatic and plant regimes on clays developed under other climates. Given the similarities between high plain grassland mineralogies in present soils (Birkeland et al. 2003 and Velde 2001) one would be tempted to attribute the clay mineral assemblages reported in deep loess as those formed on the dry steppe lands several tens of thousands of years ago (Fitzpatrick 1983, p. 52; Bridges 1978). Here the clay assemblages are dominated by the smectite, illite mixed layered and illite 2:1 clay minerals. The changes in present day non-deposition regimes are those of new plant regimes engendering formation of HI, and illite due to the installation of forest biotopes replacing the drier prairies.

If sedimentation of loessal material resumes, the present day soil profiles will become paleosols fixing indices of climate change in the clay mineral cortege present in the upper, humic zones.

### 7.2.3

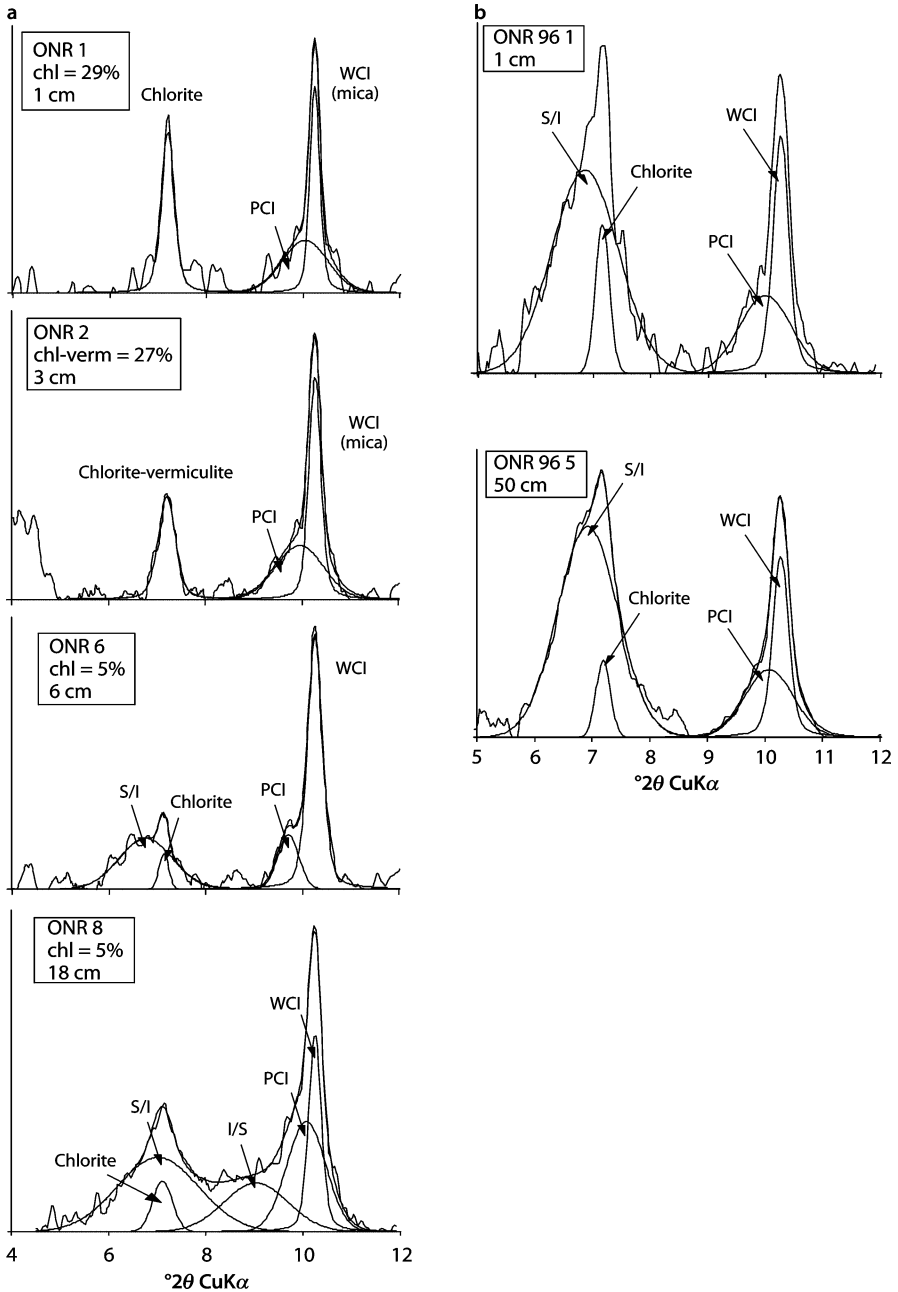
#### River Transport and Salt Marsh Sediments

Salt marsh sediments usually are fed by river transported materials which are deposited on shallow shelves of the Continental Plateau and remobilized during storm event. The material is usually in equilibrium with terrestrial plants, having come from soil environments. Salt marsh vegetation is frequently dominated by grasses, *Spartina*, and can contain some broad leaved types of plants and very low shrubs. Broadly one can describe salt marsh vegetation as a type of prairie.

An example of salt marsh interaction has been reported above (Velde and Church 1999). In this instance one finds that unstable glacial flour sediments composed of mica and chlorite react quickly to the plant regime in the soil zone. A period of 4 years is all that is necessary to transform the unstable high temperature minerals into a largely new clay assemblage. Sedimentation quickly buries these materials and they do not change significantly in their composition after they leave the soil zone. This is shown in Fig. 7.6a. In the upper centimeter the clay assemblage is illite-chlorite. Chlorite represents 27% of the peak surface areas. The illite WCI peak is very sharp ( $WHH = 0.3 \cdot 2\theta$ ). In going down the profile, one sees an initial appearance of highly smectitic S/I minerals and then the formation of a slightly more illitic mineral. Eventually an I/S mineral is present also. Chlorite content drops by 80%. In a core taken along a small river, tributary to the Bay, where no plants are present on the mud banks, one finds a sequence of S/I-rich clays of similar composition to different depths. The similarity of these clay assemblages with the initial stages of transformation (Figure 7.6b) suggests that the river edge sediments are in fact due to a re-working and transportation of the uppermost layer of the salt marsh clay assemblage. Local transportation produces a homogeneous clay assemblage buried rapidly and not subject to plant-soil interaction.

This analysis demonstrates a rapid interaction of plants with new highly unstable phyllosilicate materials which produces a new clay assemblage at a rate great enough to mask the initial sedimented material. We see that a transportation of the surface material and subsequent deposition without plant interaction leaves the new soil clays unchanged. The contrast in soil clay mineralogy is very great as is the difference below the root/clay interaction zone. Essentially the climate and vegetation is the same whereas the sedimented material is quite different, one much more reactive than the other is closer to the equilibrium imposed by the plants.

In salt marsh sediments one finds that transportation and deposition initiate an interaction between plants and sediment, as in the case of loess deposition. The initial stage is a chemical equilibration with plants at the air/water interface which determines the clay mineralogy. If reaction is rapid, the imprint of the plants will be very important. Burial essentially freezes the mineralogy determined at the surface interaction zone. If great chemical disequilibrium between plant and silicates exists, clay mineral change will be significant but if the sedimented clay material is not significantly out of equilibrium little change will be observed.



**Fig. 7.6.** Clay mineralogy of Delaware Bay sediments in a salt marsh core (a) and river bank sediment (b). These XRD patterns indicate that the re-mobilization of the salt marsh material through surface activity brings a relatively mature (altered) clay assemblage into re-deposition. However significant sediment is included, indicated by the presence of chlorite. This example can also be used as a model for loess transformation and re-deposition

### 7.3

## Catena Movement of Fine Grained Material on Slopes

### 7.3.1

#### Topographically Controlled Soil Sequences

Most treatises on soil formation deal with alteration profiles that are on flat land, i.e. where little or no movement of material occurs in a lateral direction. The movement of clays and dissolved matter is assumed to be vertical. However, in many areas of land surface there is a distinct slope which moves material, either on the surface or within the alteration profile towards a lower altitude. The importance of this concept has been emphasized by Millot (1964) and Birkeland (1984) who followed studies of soils as a function of their geomorphological situation. Two things happen under such circumstances: first, material is moved by water flow to the lowest local topography and second, the plant regime usually changes from high plateaus, down slopes to more hydromorphic sites. Combination of both strongly affects, in many cases, the clay minerals formed and forming in the alteration and soil zones. Some examples are given below.

### 7.3.2

#### Slope and Smectite Genesis (Catenas)

##### *Tropical Soils in Tchad*

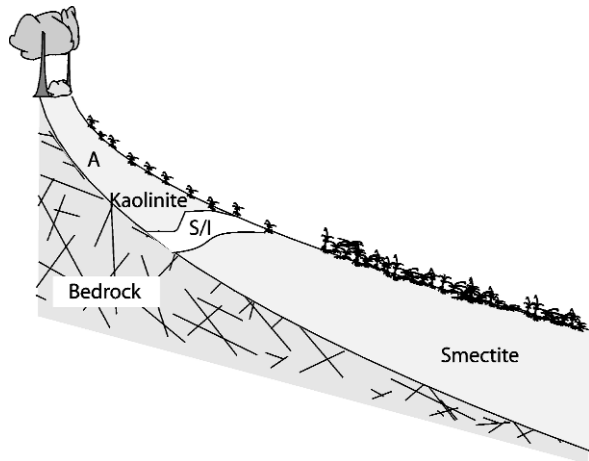
Bocquier (1973) reports on two toposequences from Tchad formed under tropical conditions. The overall dimensions, or relative dimensions, of the different soil profiles in the sequence are quite striking as outlined in Fig. 7.7. The granite source rock is biotite-rich, providing a clay mineralogy of kaolinite plus detrital biotite in the zones of high slope. Down slope movement of clays gives a strong concentration in the B horizon which rises almost to the surface on the toe slope region. A thin surface zone of transported clays is present there. However at shallow depth one finds some interstratified minerals and almost exclusively kaolinite and a large amount of smectite at some depth. The high slope part of the sequence is covered by a treed savannah with a decrease in trees in favor of grasses in moving down slope.

The smectite is considered by the author to be formed in the soil and subsoil. The soil sequence from high slope to toe slope is one of tropical drained red soils to black vertisols. The movement of material is accompanied by a change in mineralogy, where the silica-poor 1:1 mineral kaolinite is replaced by the more siliceous smectites.

Here it is clear that an increase in active silica (higher activity in soil solutions) is the cause of mineral change. One finds a notable thickening of the B clay-rich horizon at the expense of the more clay-poor A horizon. Since there is significant movement by erosion and some by transport of clays within the soil itself, one can pose the question of the circulation of materials with respect to the plant cover (savannah prairie type). Bocquier (1973) and other authors have argued for the accumulation of dissolved ions in solution which are concentrated upon evaporation. If the majority of the material displaced arrives from erosion deposit, then the soils are developed from the top downward, i.e. with successive deposits gradually incorporated into the



**Fig. 7.7.** Description of the clay facies in the catena described by Bocquier (1973) for a tropical drained soils on a slope with black soil, saturated (hydrologically) soils at the toe of the slope where smectite is found. The influence of slope on clay mineralogy under similar climatic conditions in more than evident



soil plant/silicate interaction zone from above. If this mechanism is dominant, the clays in the developed soil and alteration profile are largely of depositional origin and will have been affected by plant interaction before burial. This is a similar situation to that of loess deposition, except that the transport medium is water and not air.

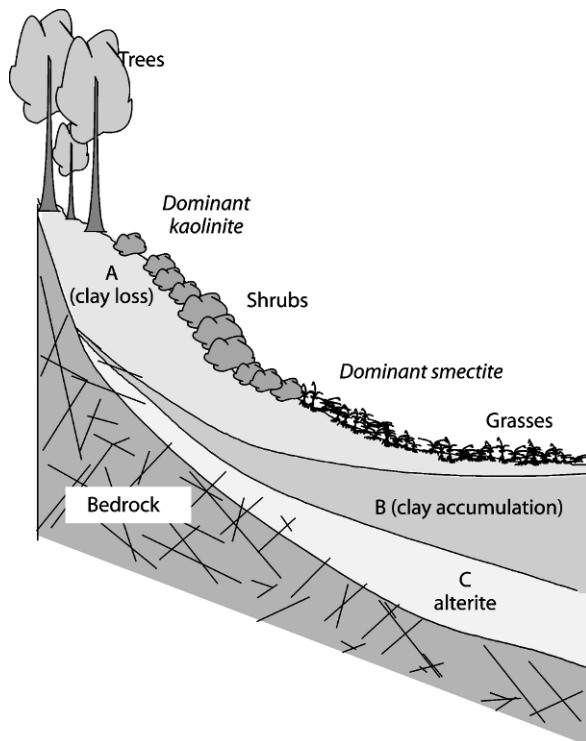
Paquet (1977) insists on the importance of montmorillonite (smectite) formation at the lower portions of slopes in arid to semi-arid climates due to the accumulation of dissolved ions through capillary action to the surface under strong evaporative conditions. Her extensive research and observations under these climates at sites in Lebanon, Morocco and Tchad indicate the prevalence of the 2:1 expanding mineral at the base of slopes and their presence on outwash plains or flat basins. She felt that the explanation for this mineral, and its "invasion" of the soils under these climates was due to a concentration of dissolved elements which concentrate under conditions of lower water flow. In fact she sees a relation between these smectites and the formation of sepiolite and palygorskite in truly arid soils. This is possible, but there is perhaps another, more simple explanation related to plant/silicate relations. In the situations of slopes in semi-arid climates, there seems to be a tendency to form sparse forests on the upper portion or the plateau part of the slope. On the slope itself one finds scrub growth. In the lower portion or on the outwash zone, one finds grasses, the savannah. In each portion of the catena, different plants dominate. At the bottom of the slope prairie forms and this is where one finds smectites.

We know that grasses are good sources of phytoliths (amorphous silica) and that the savannah plant occupation of the surface is more dense than the more sparse vegetation of the treed savannah regime. One can expect that the movement by chemical uplift of silica in grasslands in such a situation would be greater than that of the sparse shrub lands of the higher slopes. It will be longer lasting in that the slope is low and the effect of uplift will be longer lasting than on a slope where erosion occurs. Hence a chemical pressure (activity of silica) would be applied by the grasses to form a more silica-rich mineral than the 1:1 mineral kaolinite in the soil (plant/silicate interaction) zone. Thus we can imagine a sequence of kaolinite-rich sediments which react with silica brought to the surface through the action of grasses in the form of highly reac-

tive phytoliths. One should remember that, as Paquet suggests, the soil solutions flowing into the basin will concentrate silica also.

In such a situation, there is a continuous importation of soil clay minerals, dominated by 1:1 types and oxides. These will be brought into the upper, soil (plant/clay interaction) zone. Although the rain events are periodic, they are regular when considered on a year to year basis. Thus one finds a renewal of clays at the surface formed under different conditions from those of the prairie. It is highly possible that the plant/clay interaction, essentially one of the introduction of silica through phytoliths, can change the 1:1 clay mineral type into a more silica-rich 2:1 mineral type, smectite. Each yearly input will be fully or partially transformed into this new phase and subsequently buried by the continued input from upslope. Transfer of fine-grained material by gravity movement effects a change in mineralogy through the uplift of silica by plants to the surface where it is combined with a silica-poor clay mineralogy to produce smectite. In this way one can explain the high clay content profiles in the flat basins remarked by Paquet (1977) and demonstrated by Birkeland (1984, p. 238) where there is a concentration of fine material at the foot of slopes (Fig. 7.8). This fine material is sedimented, and the soil profiles formed are renewed from the top where plant/clay interaction is predominant. One can propose then that a least a part of the smectite forming vertisols under semi-arid climates is due to down slope transportation of clay material and interaction with plants.

**Fig. 7.8.** Illustration of the relations of clay minerals assemblages as a function of position on a slope in alteration under a contrasted climate regime. High slope and low plant cover produce kaolinite, scrub produces kaolinite and lower slope prairie type vegetation results in a smectitic mineralogy (data after Paquet 1977). The change in mineralogy is essentially due to two factors, one is better drainage and low transit times of water in the soils (low concentration of dissolved ions in solution) and low vegetal activity and low input of translocated elements. Toe slope environments show higher plant activity and an accumulation of transported clays with the result that water transits more slowly and is more saturated with the elements present in the clays. Plants translocate K and Si to the surface



### *Red and Black Soils*

A special case, at least from a soil color point of view, is found in the red-black soil sequences. These soil types, or the association of these soil types, are well known in savannah climates where soils are formed on basalts on slightly hilly terrain (Herbillon et al. 1981; Böhmann and Grubb 1991; Vingiani et al. 2004). Basically one finds kaolinite-iron oxide soil clay assemblages at the top of the plateau and slope alteration profiles developed from basalt. In the lower portions (alteration zones) smectite is common (nontronite) which is gradually replaced by kaolinite towards the surface. The plateau and slope soils tend to be sandy and red with a thin A horizon whereas the toe slope soils have a deeper brown to black color and a more strongly developed A and B horizon with more clays present. The clays in the lower toe slope zone contain smectite and kaolinite/smectite interlayered minerals. The soil color is deeper and one finds a change from hematite in the slope soils to goethite in the toe slope soils. Relative proportions of elements in the clay fraction do not seem to change much, however the oxidation state of iron does change following the color. The smectite in the lower, more reduced soil zones in the landscape is largely nontronitic, i.e. containing high amounts of Fe the majority of which is  $Fe^{3+}$ .

Undulating hills form local zones of clay accumulation and this is expressed as the black part of the red-black sequence. However the plant regime changes some, with more hydromorphic plants in these shallow basins. Hence one can suspect that the reduction in iron is to a large extent driven by increased plant activity and accumulation of organic matter. The impact of this reduction in oxidation state is to favor smectite, containing some ferrous iron. Thus one goes from a kaolinite-hematite oxidized assemblage on the slopes to one of a more reduced kaolinite/smectite plus or minus an independent smectite phase in the depressed zones. The clays at the very surface of the profiles, those of most recent migration, tend to be kaolinite and hematite rich. In the B horizon one finds the mixed layered and smectite mineral associations.

Basically, one finds that smectite (nontronite type) forms upon alteration of basalts and is gradually replaced by kaolinite and iron oxides in alteration and soil profiles on well drained sites. These are the red soils. However, in poorly drained sites the tendency is to find kaolinite/smectite minerals and even smectite (nontronite and iron beidellite, Vingiani et al. 2004) in the zones of clay accumulation. It appears that the reaction smectite to kaolinite + iron oxide is reversed in poorly drained areas. The transformation of kaolinite to smectite occurs through an interstratified mineral.

Here we can see the impact of topography on clay minerals at the surface. One can imagine, though most papers published on the red-black sequences do not mention the plant regime, that the lower, dark soil areas indicate an increase in prairie plant activity and development of a stable humic layer which favors the reduction of iron from hematite to ferric forms. Since ferrous iron is not stable in solution in the presence of silicate minerals, one finds that kaolinite is transformed to smectite in a mixed-layer phase. In better drained sectors, on slopes or plateau zones oxidation is stronger under the conditions of a savannah (contrasted season) climate. Again, in the more reduced soils, increased plant activity might bring an increase in phytoliths with a resulting increase in silica activity.

Red-black soils sequences demonstrate the importance of slope and most likely plant regime. The clay minerals change rather rapidly, since they follow the influx of

eroded material (either by surface action or within the profile itself) rather closely.

In these examples we have seen that lateral movement of soil clay material and eventual deposition in low lying areas often produces a smectite mineralogy. Smectites are the most silica-rich of the soil clays and hence need an abundant source of silica to maintain their presence. This source is most likely that of plant phytolith deposition at the surface. In clay-rich sediments, little clay movement can be expected by elutriation or vertical water movement within the soil and hence the clay assemblage will be stable as it is continually buried by further sedimentation due to down slope movement.

#### 7.4

### Summary

Movement of surface materials is very important in understanding soils and their clay mineralogies. Transport of fine grained material can change the surface layers, or in fact much of a soil sequence if the material is deeply buried. In such instances the clay mineralogy is relatively static having come to surface chemical equilibrium. Should the plant regime change, one would expect to see changes in clay mineralogy in the soil zone. Chemical loss by water-silicate dissolution is minimal, compared to that which occurs when water is in contact with highly unstable high temperature minerals which transform into clays. In such situations one could even propose that there is a high proportion of chemical transport that occurs through plant chemical uplift.

Much of human activity has been centered in the areas where clays have been transported and concentrated, in the presence of water or not. Initially, of course the necessity of transportation and water resources for a population invited grouping of people around rivers or delta areas. The population concentration occurred largely because early on men began to get along poorly with their neighbors and needed to build protective systems for their well being. This led to concentrations of population within the protective walls even though overall the population density of an area was small. In any event, water resource became important. Transportation by water rapidly became important also as trade in needed external resources became evident. With the advent of agriculture, given a concentration of habitation on local sites, one needed a close source of fertile soil. River and lake or sea side sites were extremely well adapted in that soils, frequently with humic material, were deposited in such sites, soils which were adapted to grain growing. Further, if a water source were sufficiently important one could correct for nature's forgetfulness in times of drought by irrigation. As a result of these causes, people used the renewable resources of river and peri-maritime transportation of fine grained alteration products to the benefit of developing mankind.

If one wishes to understand the reasons for the presence of vertisols at the base of long slopes in semi-arid climates, it is probably in the relations between clay mineral transport and the development of prairie ecosystems. Certain positions in the landscape are conducive to the formation of smectitic minerals. Observations of mineralogy and site in the landscape were often made without the insight concerning plant ecosystem relations. If one combines the physical transportation of a specific type of mineral with the impact of plant interaction one can easily conclude concerning the origin of the clay minerals observed. Reading the landscape involves both vegetal and mineral elements.

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## Suggested Reading

- Allen PA (1997) Earth surface processes. Blackwell Science, 404 pp
- Birkeland PW (1984) Soils and geomorphology. Oxford University Press, 372 pp
- Fitzpatrick E (1983) Soils. Longman, London, 353 pp
- Millot G (1964) Géologie des argiles. Masson and Cie, Paris, 499 pp (English translation 1970: Geology of clays. Springer-Verlag, New York, 429 pp)
- Smith K, Ward R (1998) Floods: physical processes and human impacts. John Wiley and Sons, New York, 382 pp

# The Place of Clay Mineral Species in Soils and Alterites

## Introduction

Throughout the book thus far one can find the crystallo-chemical descriptions of clay minerals, their specific chemical properties as well as the probable reasons for their formation and lack of crystal size development. The transformation of unstable high temperature minerals into clays by the interaction of meteoric water and rock silicate minerals producing fine-grained crystallites is given in detail. These are the classical accounts of clay mineral formation under the influence of surface water-rock interaction. They depend essentially on the ratio of water to rock or altering mineral during the reaction period. Clay minerals formed at the rock interface are present in the saprock and eventually saprolite zone, and they are eventually submitted to the direct interaction of meteoric water at the soil surface in the context of plant/silicate interaction chemistry. Attention has been drawn to the importance of plants on clay mineral stabilities and occurrences. Observing the literature one can see that different clay mineral assemblages are found in the soil zone, compared to the zone just below, C horizon and saprolite. The relations of the clays in the plant/silicate interaction zone do not always follow a sequence of alkali loss and silica loss which should be the case for continued water/silicate interaction under non-organic chemically controlled conditions. This observation leads us to a non-conventional and usual approach to understanding clay mineral origin and occurrence in soils and alteration profiles. Hence we will summarize and develop here the observations which have been made on the interactions which concern the major clay mineral forming factors: water/rock interaction compared to climate and vegetation.

First we must recall our nomenclature of the transition between rock and soil. We divide the profile that one might obtain by digging a hole into the ground into three major parts: (1) rock/water interaction zone, (2) alterite zone (saprolite) and C horizon where one finds altered rock and alteration products as dominant phases, mostly clay minerals and (3) the soil horizon where the effects of plant and silicate are predominant in forming the type of clay mineral present. This is the part of clay mineralogy which affects mankind the most today, that of agriculture and the biosphere.

### 8.1

## Where Clay Mineral Types Occur in Alterites and Soils

In the previous chapters we have indicated the ways in which clays form and how they form. The demonstrations have dealt with different chemical environments which produce clay mineral assemblages. The initial motor of formation is the inherent in-

stability of high temperature minerals, those forming rocks, which are not at equilibrium under surface conditions in the presence of meteoric water. This action forms clay minerals and a large portion of dissolved matter carried away in aqueous solution. It is very important to remember that clays, for the most part in situations of surface alteration, form groups of minerals occurring together. Most often the initial clay assemblages formed by water/rock interaction are multiphase when one considers a sample of several grams. One finds assemblages of clay minerals the composition of which depends upon the climate, position in the alteration profile (soil zone, alterite zone or interaction zone) length of time of alteration and interaction, as well as the composition of the materials which are being altered. It is very rare to find a mono-mineral clay deposit in surface reaction zones due to rock/water interaction. As one moves upward in an alteration profile, clay assemblages become less complex.

This being the case, it is evident that the interpretation of the importance of a given clay mineral will depend upon its neighbors, i.e. the clay assemblage. However, clay mineral types do occur under certain general conditions and their strong concentration is due to specific conditions of the chemical environment. In general, the forces of alteration (interaction of rainwater with silicates) tend to reduce the alkali and alkaline earth content of the assemblages with a loss of Na, Ca, K and Mg roughly in that order. Concomitantly, but to a lesser extent, there is a loss of silica in the early stages of alteration. Eventually the surface, clay material will be composed of aluminum hydroxy and iron oxyhydroxide minerals given enough time and interaction with meteoric water. Such material is of course infertile to plant life, i.e. organisms with roots.

However, often one finds 2:1 clay minerals at the surface, and often with kaolinite (1:1 mineral) in the B and C horizons. This would seem to be a contradiction to the normal trend of weathering via silica loss and alkali loss. It seems useful to summarize where one finds the different types of clay minerals under alteration conditions.

Below we give a general summary of the conditions under which one is likely to find different clay mineral types.

### 8.1.1

#### The 2:1 Minerals

The 2:1 minerals tend to dominate the clay mineral assemblages of the soil zone in latitudes other than those of tropical rain forests. As suggested in the introductory Chap. 1, it is possible to consider several of the 2:1 clay mineral types found in soils as variations on a theme. That theme is a charged 2:1 layer structure with various cations present in the interlayer space. These phases are called HI minerals with partially filled sites and dioctahedral chlorite when Al-OH polymeric complexes are found in the interlayer site. Expanding minerals (smectites) with exchangeable hydrated cations in the interlayer sites having a high charge are usually called vermiculite and those with a low charge are called smectites. Finally, illite is the 2:1 mineral with anhydrous potassium as the interlayer ion. This mineral sequence of different interlayer ion occupancy is determined by layer charge and the site of the charge. The mineral names traditionally given to the different clay types are based upon the interlayer cation occupancy: illite with potassium, HI with aluminum ion complexes and smectites with exchangeable hydrated cations. The different types of 2:1 minerals are:

**HI minerals.** Here the interlayer ion is based upon an  $\text{Al}(\text{OH})_2^+$  or  $\text{Al}(\text{OH})_3$  interlayer structure. In order for such a mineral to form, the activity of alumina must be relatively high. At pH values above 4 low amounts of free alumina (near 6 ppm) will precipitate to form gibbsite or the more hydrous form of alumina and silica, allophane. However at these conditions enough silica is present to form other minerals (silicates). In fact one often finds gibbsite occurring along with HI minerals (Harris et al. 1989; Burkins et al. 1999; Soller and Owens 1991 for example) in the soil zones or in the alterite portion of the profile at pH below 4, where alumina solubility increases dramatically. The availability of alumina depends upon two factors: low pH which puts alumina into solution without precipitating gibbsite and a lack of complexing organic matter which allows the movement of alumina into the clay structures. Thus acid soils are instrumental in forming HI minerals. Such acid soils are often associated, at least in the minds of pedologists, with organic matter. The HI and gibbsite can be found together in different parts of the horizon. Gibbsite indicates a maximum of alumina activity in solution. However, pH is not the only factor in that many acid soils do not form HI minerals. This is undoubtedly due to the complexation of Al by organic acids and other organic molecules which fix alumina and restrict the formation of HI minerals at low pH.

HI minerals also seem to be a product of the initial stages of alteration of high temperature phyllosilicates, either trioctahedral or dioctahedral. The trioctahedral forms are less resistant to the chemistry of soil weathering and they generally are transformed into other minerals (see the demonstration by Righi et al. 1999). HI minerals are frequently considered to be a transient stage of transformation of phyllosilicates (biotite, chlorite and muscovite) towards a final smectite mineral. However, HI minerals have been observed to form in the soil zone (plant/silicate interaction) from other phyllosilicates (Sect. 3.4.1).

HI minerals are most often associated with acid soils, forest soils in temperate climates to tundra climates. This is especially true for coniferous forests. HI minerals are defined by the presence of hydroxyl alumina complexes. Such complexes are to be found in acid soil solutions. High alumina content of soil solutions is often a limitation of plant survival. Wolt (1994, p. 235) indicates the toxicity thresholds for some common plants, crops and trees. It is clear that agricultural field plants are highly susceptible to high alumina contents with thresholds 100 times or less than those for many species of trees, especially conifers. Thus the presence of HI minerals is a sign of potential crop plant toxicity. Common practice in converting forest soil to crop culture involved in the pioneering past of the United States "sweetening" the soil, either through the burning and distribution of tree alkali ashes or by liming which lowers the pH and thus diminishes the alumina content of the soil solutions. This action essentially destabilizes the HI minerals which become more common 2:1 forms, smectites or in the case of high charge HI minerals they can convert to illite.

In general one can expect to find HI minerals in young soils where they represent the initial stages of mineral transformation of high temperature phyllosilicates such as chlorite, muscovite or biotite formed under acidic conditions especially in conifer forest soils. The conditions of formation are a high activity of alumina in solution which is controlled by the pH due to the presence of organic material which does not complex the alumina.



**Illite.** This mineral is a high charge, potassic clay mineral which can be formed through the weathering of muscovite or formed through mineral reaction during mineral weathering. The occurrence of illite in the coarse clay fractions seems to indicate a detrital mineral origin, coming from muscovite or diagenetic-metamorphic illite material. However, it would seem that a significant part of illite in soils can be relatively easily transformed into smectite (or a mineral having a smectite behavior) and perhaps *vice versa* (see Sect. 3.4.1). Most likely then soil illite has different sources and probably different compositions. The amount of charge and charge site in soil illite are not known. Illite is commonly reported in almost all types of soils and alteration zones except those formed upon basic rocks (basalts, diabases, serpentines, etc.) and glassy eruptive rocks. Illite is rarely reported in tropical forest soil and alterite zones nor does it seem to be present in laterites. To a certain extent there is an antithesis between illite and kaolinite, at least when large amounts of kaolinite are present in soils.

Illite is commonly a component of smectite-illite mixed layer minerals in soils. This type of mineralogy is specifically common in prairie soils. It is also common in deciduous forest soils (see Sect. 3.4.1). Relations between illite-smectite proportions in agricultural soils can change dramatically (Sect. 5.2). Hence there is a strong inter-relation between illite and smectite in soils mineralogies. It is highly probable that illite can be "transformed" into smectite or a mineral with a smectite behavior quite easily under the action of plants.

Thus illite can have an origin in the weathering cycle (water/rock interaction) and be strongly affected by plant activity. It occurs in water/rock alteration and soil environments of temperate to cold climates on rocks containing abundant aluminum and potassium. The parent material such as granite, and acid intrusive rocks, metamorphosed pelites and most common sedimentary rocks are conducive to the formation of illite. These conditions are in fact those of most of the fertile agricultural zones today. Illite can be closely associated with agricultural fertility.

**Smectite.** This mineral is a variation of the theme of charge and charge site under conditions of low potassium or aluminum availability. Higher charge smectites (vermiculite) can form either illite or HI minerals when significant amounts of the requisite cations are present in solution, either K or Al. Smectite minerals are most frequent in temperate climate soils and in the rock/water interaction stages of alteration. Smectites can be either di- or trioctahedral and contain either Al or Fe ions. For the most part such minerals can form HI minerals but only aluminous dioctahedral smectite seem susceptible to form or be associated with illite.

In fact pure smectite behavior (expandability) is extremely rare in soil clay mineral assemblages. It is usually interstratified with another 2:1 mineral or, more rarely, with kaolinite. Smectites form the basis of soil clay mineralogy in vertisols, which are usually formed under dry prairie conditions. High altitude prairies form smectite-rich clay mineral assemblages also under humic, cool conditions which favor low pH soil solutions. However, smectites are found as precursor assemblages in high intensity alteration such as laterites and tropical forests. They are found in acid and basic soils and alterites. Most alteration assemblages of crystalline rocks contain smectite minerals. In general, smectites are found in most alteration zones.

The different types of 2:1 minerals in alteration products are responses to the constraints of chemical composition imposed by the environment (potassium for illite,

available aluminum in solution for HI minerals, more “neutral” pH conditions for smectite types). The mineralogical range is unstable, different plant regimes can change the clay mineral type, maintaining the 2:1 structure basically intact. Mixed layer minerals of the different interlayer types, illite/smectites, HI/illite, HI/smectites are responses to the cation activity in the solutions saturating the 2:1 clays.

### 8.1.2

#### **Kaolinite and Kaolinite/Smectite Mixed Layer Minerals**

The 1:1 almost exclusively aluminous mineral kaolinite is ubiquitous in soils. It is present in the early stages of most weathering in crystalline rocks, at least in minor amounts. Hence it is found in alterites and eventually in most soils. Under conditions of intense weathering, tropical contrasted season climates, kaolinite can be seen to become predominant in alterites. It is often dominant in portions of tropical forest soils also. Kaolinite is replaced by aluminum hydroxide (gibbsite) in laterite formation. Thus kaolinite is found to form and persist in most soil climates and under most conditions of alteration.

The overall tendency in alteration sequences is to lose silica compared to alumina in soil clay assemblages. Then alumina in its turn is lost (Pedro 1966). The loss of silica relative to alumina marks the difference between temperate climate soils and humid tropical alteration. This change in overall chemistry is applicable to the clay minerals, phyllosilicates and hydroxyl-oxides. It does not include quartz. In fact Lelong (1969) demonstrates that in tropical rain forest soils based upon granite, the quartz (and hence silica) content increases in many cases towards the surface while kaolinite content decreases. However on basalts, the clays show a decrease in aluminum hydroxides in favor of iron oxy-hydroxides. As a result humid tropical soils do not show much smectite content. Most commonly one finds kaolinite as the clay mineral present for several meters depth in such soils (Schultz and Ruhiyat 1998). In general, it is apparent that soils under high rainfall tend to contain kaolinite at the expense of 2:1 minerals. Kaolinite and muscovite have the same Si/Al ratios (near one) whereas smectite has a higher relative silica content than kaolinite. In fact if one considers the phyllosilicate transformations from micas and chlorite (high temperature minerals) to soil clays under temperate climate conditions, the initial equilibrium is towards more silica-rich phase, smectite in most cases. One can contrast then the clay assemblages in temperate climate to humic tropical soils as being more silica-rich than those formed under high rainfall.

### 8.1.3

#### **Gibbsite**

The hydroxyl aluminum mineral is restricted to two conditions of formation: one where highly acid conditions produce the precipitation of the mineral indicating the destruction of other alumino-silicate minerals, with loss of silica. It is the buffer to aluminum exportation. Gibbsite is also found in the early stages of granite alteration under temperate climates. Braga et al. (1989) have made some very interesting observations on the presence of gibbsite in the early stages of granite alteration, the arenite facies. They find a zonation from north to south in Europe, through temperature and climatic zones

essentially. In the non-glaciated regions (Norway, Sweden, Scotland to western France) the dominant alterite minerals are 2:1 types with kaolinite. Gibbsite becomes apparent in the more clement climatic areas which have not been glaciated and hence are older alteration profiles. One can equate the low mountain regions of France (Vosges) with the Scandinavian type of alteration in their analysis. In the older alteration zones of Spain and Portugal (equally at higher temperatures) gibbsite is more apparent and can become dominant. Gibbsite is however rare in soil clay assemblages based on these altered rocks. As one moves upward in the alteration profiles more 1:1 and then 2:1 minerals are present.

One reason that gibbsite is rare in the plant/silicate interaction zone is that the amount of soluble alumina necessary to produce this phase is sufficiently high that it will poison many plant species (Wolt 1994). High concentrations of alumina cannot be tolerated by plants. However, if the plants send roots to sufficient depths, they can probably extract silica that is the product of mineral dissolution and bring it into their biotic sphere as phytoliths. This silica, in the form of phytoliths, will be recombined with gibbsite to form kaolinite and probably smectites (becoming HI mineral in most cases) in the soil zone.

One must remember that the water which reaches the water/rock alteration zone at the base of alteration profiles is probably often present because of rapid drainage along major fracture or pore systems. It is not charged with ions from dissolution or equilibration of clays with the aqueous solution. Thus the presence of gibbsite in the early stages of weathering is due to a structural cause in the geometry of weathering. However, in the cases of tropical weathering, the great influx of unsaturated aqueous solution induces the dissolution of most minerals and only the most insoluble ionic species, Al and Fe, remain, forming gibbsite and hydrated iron oxides. Of course this analysis is valid for aluminous rock types, shales, gneiss and granite. More basic or calcareous types will not lead to the formation of gibbsite.

#### 8.1.4

##### Iron Oxyhydroxides

Iron oxides are ubiquitous in soils. They are present in most types, showing a color in the reds under low pH and high weathering intensity, yellow under higher pH and lower water flux and brown to black under conditions of interaction with organic matter. However, iron oxide and hydroxide is present everywhere. Under conditions of high weathering intensity, laterite formation occurs with a strong concentrations of iron forming a semi-impermeable crust near the surface of an alteration profile.

#### 8.1.5

##### Imogolite and Allophane

These minerals are often precursor phases to others. They are formed through the rapid precipitation of Si-Al allophane of various Si/Al ratios and Si-Al imogolite with Al = Si during the alteration of vitreous rocks or under conditions of alteration under high pH control (Farmer and Lumsdon 2001; Farmer 1999). Imogolite can also be strongly fixed to organic material in acid soils, especially the E horizon of podzols. In such situations the soil chemistry is of low pH and silica is exported. Since imogolite has a high alumina to silica ratio, it is the result of low silica activity in solution under these con-

ditions. The key to the presence of both imogolite and allophane is a continuous humid condition. Under conditions of contrasted climate they are no longer present and are probably transformed into smectite for allophane and kaolinite for imogolite. They represent humid alteration conditions, and the presence of highly reactive substances, for the most part. The allophane and especially imogolite minerals are most likely very important in processes of chemical transfer from surface to lower horizons in acid soils under temperate climate conditions.

For the most part one thinks of imogolite and allophane as alteration products of glassy volcanic rocks. These rocks and their alterite and soils need to be kept humid in order to maintain the hydrous, amorphous or nearly amorphous materials.

### 8.1.6

#### Chlorites

Soil chlorites are found in two different types of situations, one dependent on source rock and the other on plant activity. To a large extent they indicate special chemical conditions of the source rock, either a strong iron content in the absence of alumina or a situation of low alumina activity with minimal alkali activities. Basalts and especially ultrabasic rocks are found to form trioctahedral iron chlorite in the weathering process (Velde et al. 1976). Magnesian trioctahedral soil chlorites are probably rarer, due probably to the same conditions but in the absence of iron activity. These chlorites are unstable at low pH values, but since magnesian and iron-rich rocks are “basic”, i.e. weathering to form high pH soils, these minerals are the result of high Mg and Fe activity in solution. The trioctahedral chlorites are dependent on the presence of a basic (Fe- and Mg-rich) source rock.

A second situation for the formation of soil chlorite is that of a soil (zone of plant/silicate interaction) where the activity of alumina in solution is very high and this situation has pertained sufficiently for the formation of a completely hydroxyl aluminous interlayer in 2:1 mineral structures. These minerals are di-octahedral in composition, and hence largely aluminous. Dioctahedral, aluminous chlorites are a type of end member of the 2:1 minerals where no alkali ions are present. They are of low silica content. This represents situations in soils where silica is lost with the resultant formation of an aluminous 2:1 mineral. Usually such soils are found to have a very low pH and are formed under coniferous tree cover.

### 8.1.7

#### Palygorskite, Sepiolite

These magnesian minerals formed in deserts where capillary action precipitates saturated solution material to form magnesian silicates. They are not stable at the surface, in the soil zone (Paquet 1977). Hence they are most likely to disappear in many soil formation processes. They are relegated to areas of very low water activity at the surface where rainwater is not likely to be saturated with Mg, Al and other ions which form these minerals. In fact much of their presence is due to highly concentrated solutions, desert lake and other closed basin sedimentation in the presence of carbonates or sulfates (see Velde 1985, ch. 7). Hence these minerals are in fact present in the C horizon, usually in sediments where soil is little developed at the surface.

## Summary

In this section we have attempted to outline the conditions under which the various components of clay assemblages formed in the alterite and soil zone will occur as a function of climate and hence plant regime. The predominance of 2:1 clay minerals (HI, vermiculite, smectites and illite with their cortege of interlayered minerals) is typical of temperate climate situations. They occur in young soils and mature ones in regions of reasonable rainfall and temperature variations from alpine to Atlantic or mid-Continent ranges. In areas of high rainfall and high temperatures, those climates where it never freezes in the winter, there is an increase in the presence of kaolinite at the expense of the 2:1 minerals. Eventually gibbsite and iron oxide minerals dominate under conditions of high and constant rainfall. These minerals lead eventually to a very low fertility of the soil zone for plant growth. As long as plants can maintain a biotope, especially the forest system, a fertile surface can be artificially maintained. If this system is destroyed, plants have difficulty in maintaining the artificial balance of silica and alkalis in the soil zone. Cutting a rain forest will lead rapidly to a loss of Si, K and other nutrients in the surface layer which cannot be maintained by crops which tend to exhaust these nutrients instead of re-enforcing their presence.

When gibbsite [ $\text{Al}(\text{OH})_3$ ] and iron oxides are present it is difficult to maintain a reasonable plant biotope. Plants cannot grow well on such impoverished soils (tropical and laterite), needing essential alkali and alkaline earth cation nutrients. The smectite-illite clay minerals are potassium and cation-rich, chemical attributes which contribute to plant growth and fertility (Black 1968 for example, pp. 238–272).

## 8.2

### Clay Minerals Present in Soils as a Response to Climate

#### 8.2.1

##### Physical Factors and Their Effect on Alteration and Soil Clay Mineral Facies

Dry climates (arctic or desert), either by lack of water or lack of liquid water produce fine grained material which is most often little reacted chemically. Soil forming processes are largely mechanical due to differential thermal expansion properties of materials, either individual grains in a rock or the difference between rock and water. This material becomes fine grained but often is composed of the unstable high temperature minerals of which it is made. If the source rock is composed of sedimentary rock minerals, as is often the case on continents, the clay sized fraction will be one of diagenetic or low grade metamorphic phyllosilicates such as aluminous mica (illite) and chlorite with varying amounts of diagenetic mixed layer smectite/illite minerals. Other rocks, such as granites or higher grade metamorphic rocks will produce micaeous materials in the fine fraction and the sand fraction will be composed to a large extent of tectosilicates and other minerals in more minor quantities. These are the surface materials of arctic climates or dry deserts. This material cannot rightfully be considered to contain clay minerals in that the phyllosilicates have not come into chemical equilibrium with atmospheric aqueous solutions at low temperatures. However one of the early mineral transformations in desert zones is one of oxidation and

the production of a red coloring due to the formation of hematite. Usually this iron oxide is not abundant.

Temperate climates have contrasted seasons (wet and dry) and contrasted temperature regimes. Under such conditions forests can prosper and when rainfall is not sufficient, prairies prosper. One can see such situations in going from north to south on the Eurasian continent or east to west in North America. The same changes can be observed on many oceanic islands of modest dimension (Hawaii, Azores, Galapagos, etc). Much work has been done to characterize the soils in regions of contrasting climate as summarized in Jenny (1994) and Birkeland (1984).

Rainfall is very important, of course, in that it controls the saturation of dissolved elements in soil solutions and hence the tendency for silicates to dissolve in order to come into equilibrium with the aqueous solution. For example Jenny (1994, p. 132) indicates that the clay content of soils based upon loess is three times greater with three times the rainfall at roughly constant temperature. Hence dissolution and reaction to form clays is greater under conditions of abundant rainfall. Demonstrations concerning the effect of temperature are somewhat more scarce. Nevertheless Jenny (1994, p. 172) proposes convincingly a relation between rainfall and temperature which indicates the rate of rock weathering and soil formation from granites and gneiss (pelitic or aluminous rocks which contain micas as a major phase). The demonstration of muscovite-chlorite mineral conversion to illite-smectites mixed layer minerals in (see Sect. 3.4.1) indicates that a change in average temperature from mountain to temperate climate in grass-dominated soils can change the reaction time in soil clay mineral transformation by a factor of  $10^3$ . This suggests that a serious estimation of average temperature is necessary in assessing the rate of alteration and soil clay mineral formation. These comparisons of course involve both temperature and plant activity which may not follow the same reaction rates and hence the effect of plants can be greater than would be seen in the water/rock interaction zone as a result of temperature differences.

One factor which has not been taken into consideration sufficiently in many cases is that of the plant regime which pertains in the soil environment. Biological activity is strongly governed by rainfall and hence such values as nitrogen, organic carbon, pH and so forth are determined by this factor. The impact of biologic variables on clay mineralogy is less well documented (see Birkeland 1984, chapter 10 for example). In general, forests favor a lower soil pH, a stronger dissolution of silicate materials and the formation of a sandy horizon (E horizon) almost devoid of clay minerals which lies under the surface, humic layer. Clay accumulation occurs below the E horizon with the formation of a clay-organic horizon. By contrast prairies favor the accumulation of clay minerals in the humic horizon with some clay accumulation in the lower B horizon. One can imagine that the plants will have a greater effect than climate alone concerning the type of clays in the soil horizon.

One very important relation in temperate climates, at least in the northern hemisphere, is the non-correlation between change in temperature and rainfall. Much work has been done and reported by Jenny (1994) and Birkeland (1984) on the different effects of these two variables concerning the major characteristics of soils such as pH, carbon, nitrogen and clay content of the soil horizons. If we consider that the influence of temperature on clay reactions is an exponential function of temperature and

that of rainfall a linear function, it is clear that the relations of climate in such situations, as measured by temperature and rainfall will be complex. Further, as showed by Jenny (1994, chapter 6), the relations of rainfall and temperature are not necessarily correlated. For example in North America, temperature is essentially a north/south variable whereas rainfall varies from east to west yet most soil chemical trends are east to west. Overall, if one looks at plant biotopes they follow rainfall for the most part. The amount of reaction between clays and plants will depend upon the thermal input which drives the intensity of the chemistry imposed by plants (and other biological action by bacteria and other organisms in the soils). However, variations of rainfall within a yearly cycle can change the plant regime. For example, the north Moroccan plains have a similar annual rainfall to that of western France. The plant regime is very different in the two areas. If rainfall comes in concentrated periods followed by long dry spells (contrasted climate) the overall effect is to reduce plant growth. Hence plant growth regime is perhaps more important in many cases concerning the effect on clay mineralogy. This is a very important factor in the development of clays, especially in the soil (plant/silicate interaction) zone. Therefore we can consider that there are three factors which will affect the development of clay minerals in soils; temperature, rainfall and above all plant regime. Plant regime is an integrator of the temperature and distribution of rainfall over a yearly cycle.

Tropical climates, especially those of tropical rain forests are dominated by unsaturated aqueous solutions and luxuriant plant growth. Six to seven meters of rainfall is quite a lot. These aqueous solutions will attempt to come into equilibrium with silicates or, by default, aluminous minerals. In doing so the alkali and silica content of the solids is diminished. The 1:1 clays (kaolinite and its hydrous equivalent halloysite) are dominant and eventually in older alteration sequences, hydrous aluminum and iron oxides (allophane and goethite) are the only survivors of the initial silicate rocks which have been altered. However, if the rainfall is alternated with periods of low water influx, contrasted tropical climates, the effect is to dry out the clays and produce gibbsite and hematite. Here the clay mineral types follow the seasons as well as total water input.

The generally accepted ideas on clay formation in alteration are that rainfall and temperature are the major variables which continue to change clay minerals in soils as a function of reaction progress or time. These relations are indicated in Fig. 8.1.

Overall, we would suspect that climate and hence plant regime are very strongly inter-related in the formation of clays in the surface layers of the alteration zone. One should probably look first at the type of plants forming the soil first before considering the clay mineralogy of a soil profile. The alteration zone (water/rock interaction) is surely less dependent upon plants and should respond to temperature and water influx in a more regular and predictable manner.

### 8.2.2

#### **Weathering Trend (Water/Silicate Chemical Trends)**

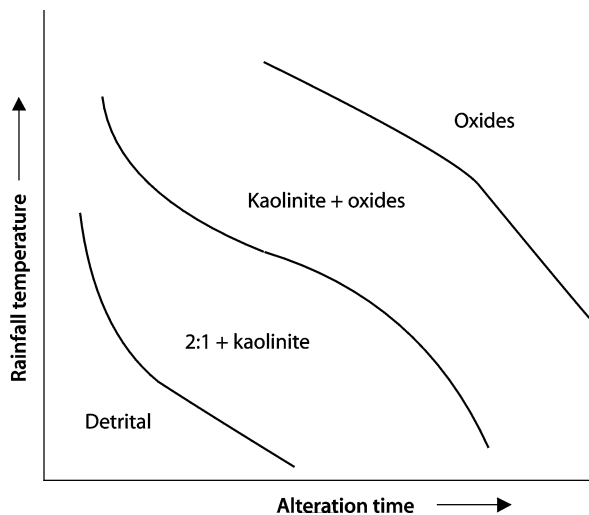
What happens when rainwater enters a soil? If rainfall is moderate, the capillary water composition would be more dominated by solids than under high rain input. White et al. (2005) indicate that potassium is more abundant in macro pore water at the surface of a soil profile. Ranger (2002) gives data for coniferous forest soils under moderate climatic conditions in France where capillary and macro-pore water has been

analyzed (Fig. 8.2). When comparing Si and Al concentrations in these solutions it is clear that the capillary solutions contain more silica compared to the macro-pore water and that the Al concentrations are nearly the same, i.e. in equilibrium. Under such conditions, the soil clays reflect stability of a silica-rich mineral, smectite (Si/Al 3 to 5.5), whereas the macro-pore water would tend to be in equilibrium with kaolinite (Si/Al 1.2–3.5). In this example of a temperate climate soil, there seems to be a stability of the more silica rich minerals determined by the solids in the capillary water which is in close contact with the clay minerals. However, the larger, macropores contain water which contains less dissolved silica. This material would be more likely to form a silica-poor mineral such as kaolinite. The macropore water undersaturated with silica is that which finds its way downward in the alteration profile and which eventually interacts with the unstable minerals in the alteration profile and in the altering rock.

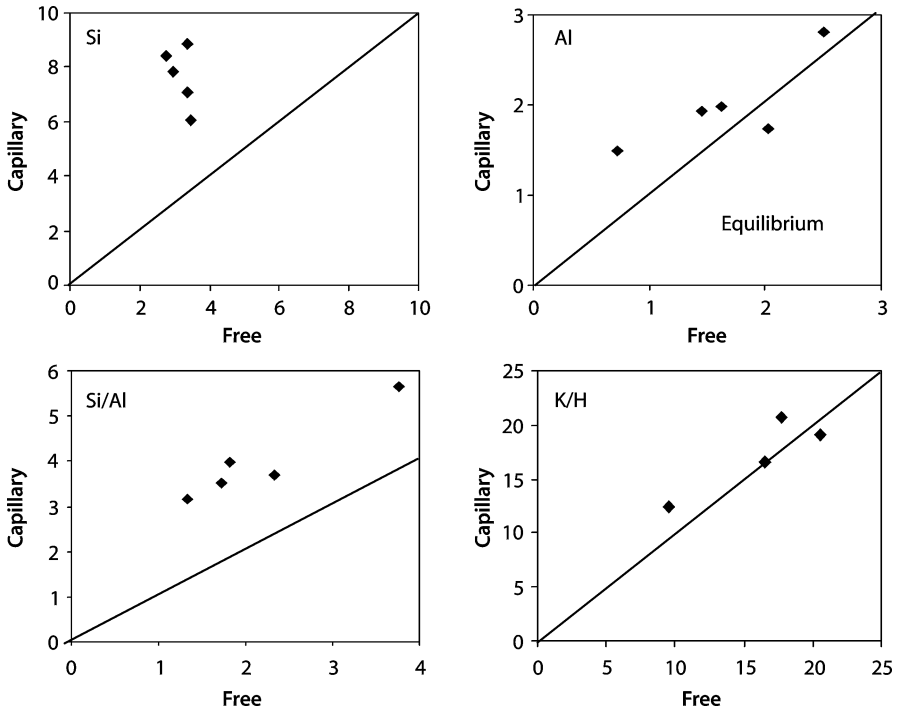
As we know (see Chap. 4) not only silica and alumina are involved in the formation of new clay minerals in alteration systems. The activity of alkalis, Ca, Na and especially K are fundamental parameters in mineral stability. Also one must consider hydrogen ions, which can temporarily replace K and Na ions in silicate structures causing de-stabilization and re-crystallization. The major motor for mineral change from high temperature, anhydrous minerals to hydrous clays is alkali/H exchange. The lower the activity of potassium for example, the lower the K/H ratio and hence one sees the transformation of potassium feldspar, into mica, and then mica into smectite, and so forth. In our case of macro-pore water and capillary water, one can compare the K/H ratios of the two fluids. In Fig. 8.2 it is apparent that the two values are similar for each of the samples, and hence one can assume equilibrium for these elements in both waters. The chemical pressure for change into clay minerals is the same.

Hence, using the major parameters of clay stability with respect to alkali-bearing minerals, the water analyses show that most elements are in equilibrium between capillary and macropore water in this example of a temperate climate soil with the exception of silica.

**Fig. 8.1.** Schematic representation of the clay mineral types as a function of climate considered as rainfall and temperature and alteration time.  
2:1 = three structural layer clay minerals





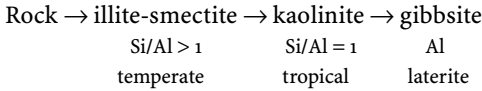


**Fig. 8.2.** Abundance of dissolved elements in free (macro pore = free) and capillary water in a forest soil (Ranger 2002); *points above the diagonal line* show enrichment in the capillary water, and those *below* enrichment of the element in the macro pore water; *points near the line* represent a near equilibration between the two types of soil water

This has potential importance for differences between tropical humid and temperate alteration mineralogies. If we can assume that macropore water is similar to that found in humid tropical profiles, the lower silica content would favor the formation of kaolinite compared to the more equilibrated water in temperate climate alterations which is more silica-rich and will favor the formation of 2:1 minerals such as smectites, illites and mixed layer minerals.

### ***Bulk Chemical Effect of Unsaturated Aqueous Solutions***

The chemistry of weathering (interaction of rainwater with continental rocks which are essentially silicate mineral assemblages) is an age old process which has been investigated for quite some time (Ebelmen 1847). The overall trends have been noted to be an initial loss of alkali and alkaline-earth cations and then silica, with a resultant concentration of hydrated alumina and iron oxides. More intense weathering shows loss of both alkalis and silica with a clear change in clay mineralogy from temperate to tropical to laterite soil types (Pedro 1966). The sequence can be indicated by the clay mineral relations:



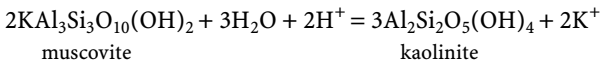
As discussed in Chap. 4, weathering is the result of two reactions engendered by the interaction of rocks and aqueous solution (1) the initial integral dissolution of minerals and (2) the hydration of others (i.e. exchange of hydrogen for cations) which leaves a clay mineral residue. These reactions are activated by slightly acid rainwater and in the surface soil zone one assumes acid products of plant growth (root exudates) as well as decomposition of plant material (Jenny 1980 for example) which in principle impoverish soils and eventually leads to their inevitable infertility (Mohr and Van Baren 1959).

### *Chemographic Analysis*

In order to understand the reaction sequence in soils it is important to understand the chemical relations of atmospheric alteration processes and the chemical relations between the basic forms of clay mineral.

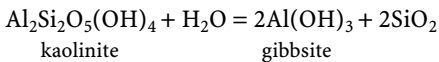
**Weathering (water/rock) reactions.** One demonstrative initial weathering reaction involves the high temperature 2:1 silicate mineral muscovite, used here as an example. It represents what should be a very common mineral reaction in the initial stages of weathering in the lower portions of alteration profiles (water/rock interaction) or in the upper portions of young soils.

*Hydrolysis (cation exchange) of muscovite to kaolinite (loss of K)*

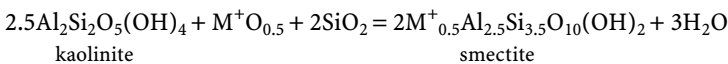


A second reaction step, that of intense weathering, would be the loss of the alkali-free kaolinite to the ultimate stages of weathering, the formation of bauxite.

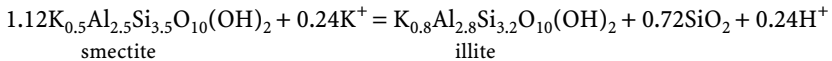
*Transformation of kaolinite to gibbsite (loss of Si)*



**Soil (plant/silicate) reactions.** Despite these weathering reactions, which are essentially rock/water interactions with their loss of alkalis and silica, we know that many soils tend to form smectite in the plant/silicate interaction zone (Righi et al. 1999) and probably illite (Reichenbach and Rich 1975). This process is can be envisioned in simple expressions such as:

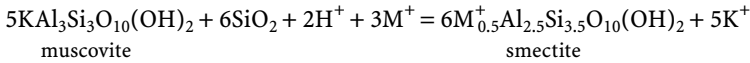


*Transformation of smectite to illite (gain of K, loss of Si)*

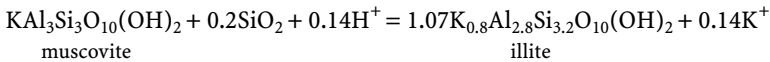


To complete the soil clay mineral transformations it is possible to directly form smectites or illite from high temperature muscovite:

*Hydrolysis of muscovite to smectite, via vermiculite (gain of Si, loss of K)*



*Hydrolysis of muscovite to illite (gain of Si, loss of K)*



We can represent these relations in a simplified version of chemical activity of Si and K with alumina considered as constant in its chemical activity in the system shown in Fig. 8.3 which involves the major clay minerals concerned. Here we can see that the loss of alkali will form kaolinite from muscovite or illite (arrow 1) and that the desilicification of kaolinite (arrow 2) will form gibbsite (aluminum hydroxide).

### 8.3

#### The Impact of Plant Regime on Clay Minerals in Soils

(This section is largely inspired from the PhD thesis of Pierre Barré, Ecole Normale Supérieure)

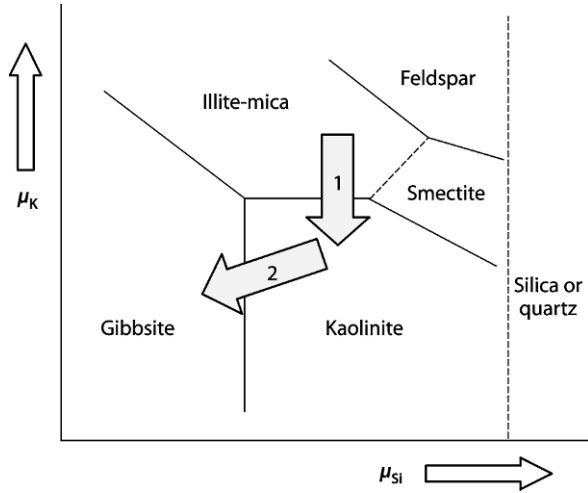
Normal weathering should give rise to a sequence of silica and alkali impoverishment as one moves from source rock at the bottom of an alteration profile upward to the surface. Older alteration profiles should show this tendency more than younger alteration sequences. This is the general idea given in most introductory texts which describe soil formation. This would mean that 2:1 minerals would be found at the rock/water interface and the base of the alterite portion of profiles and kaolinite or eventually gibbsite in the upper portions of soil profiles. Our observations in Chaps. 3 and 5 based upon published studies seem to invalidate this concept to a large extent, especially under conditions of temperate climate alteration where plants are abundant in the upper, soil portion of an alteration profile. Basically, one finds the 1:1 mineral kaolinite dominant only in regimes of high and continuous rainfall. What is the problem?

#### 8.3.1

##### Reactivity of Clay Minerals in Ecosystems

It has been noted in several places in the text that mixed layer minerals are almost exclusively found in the soil horizon and that these minerals are dominantly of the

**Fig. 8.3.** Effect of water–rock type interaction of mineral dissolution and loss of silica and alkali (potassium);  $\mu$  = chemical potential of the elements concerned



2:1 type, either illites or smectite/illite MLM typical of prairies or HI minerals typical of forests. How can one explain the strong presence of 2:1 minerals, which are the highest in silica content of the clays, in the soil horizons where the impact of unsaturated rainwater is the greatest? In order to do this one must compare the relations of normal water/rock interaction and the presence of clay types in the soil horizons.

It is known that plant ecosystems appear to affect the chemistry and clay mineralogy at or near the soil surface. Lucas (2001) has argued in favor of a stabilization of kaolinite in the place of aluminum hydroxide (gibbsite) at the soil surface under tropical forest cover due to siliceous plant phytoliths. Berner et al. (2005) have summarized this and other data which indicate the same influences. Hajek and Zelazny, (1985) summarize published data indicating that in old, strongly weathered largely forest soils in the Southeastern United States, the silica-rich minerals HI vermiculite and illite typically occur in the soil zone (plant/silicate interaction horizon) while kaolinite and gibbsite are found below this zone indicating that severe weathering occurs at depth. A sort of “chemical uplift” (Jobaggy and Jackson 2004; Reichenbach and Rich 1975, p. 81) or chemical translocation has also been invoked to explain that essential cations (K, Mg, Ca) are enriched as exchangeable elements in soil surfaces due to plant action in temperate climate soils. Birkeland et al. (2003), Velde (2001) and Reichenbach and Rich (1975, p. 81) have argued in favor of a stabilization and growth of the silica-rich clay minerals smectite and illite in prairie soils as a general feature. Thus various plant regimes appear to enrich the surface zone in silica-rich clays containing vital cations, especially potassium. Such effects are pointed out by White et al. (2005).

The clay minerals forming in the soil zone where plants determine the chemistry to a large extent must be a function of the type of plants present. This is due to the fact that plants are chemical agents in that they grow and decay in the soil, they exude various organic substances into the soil and their dead matter falls onto the soil and is incorporated in it through the action of bacteria and other living agents. Each plant regime has different types of organic material in it and thus influences the soils in different ways through the chemical controls engendered by its evolution.

In a very general way, prairies, deciduous or conifer forests can be considered to be the major ecosystem types, at least in temperate climate regimes. This has been discussed in Chap. 5 and it has been understood, intuitively and from experience by farmers for the last 2 500 years or so. It is still useful to return to these ideas and ancestral uses in that they are probably the key to an understanding of the effects of human intervention on soils clay mineralogy. The age old methods of keeping soils fertile involved rotations of crop plants (de Serres 1600) designed to favor the retention and renewal of mineral nutrients, potassium and phosphorous as well as supplying nitrogen. Nitrogen comes from the air, through plant and other biological activity while potassium and phosphorous are derived from the destabilization of high temperature minerals in the alterite (saproliite) and soil environment. In Sect. 5.4 concerning the plant chemical translocation effect, it seems that plants have a general tendency to preserve certain characteristics of soil chemistry which favor the presence of 2:1 clay minerals and especially smectites and illite. This involves the potassium cycle in soils and alteration zones. The preservation of potassium depends upon the presence of 2:1 minerals which is dependent upon silica activity that stabilizes these minerals. One of the major characteristics of plants is the presence of silica in their tissue, which when decomposed releases this element to soil solutions. The installation of plants on altering materials tends to slow down the process of alkali and silica loss.

Prairies are of particular interest in the plant/soil relations in that prairie type soils were those used by agricultural man to develop his favorite foods, grains, which can be stored and transported with greater ease than other food stuffs. The maintenance of soil fertility for agricultural purposes is in most cases related to the chemical conditions favored by grasses. It seems that these plants tend to form potassium-rich clays; smectites interlayered smectite/illite and illite. Intensive cropping tends to exhaust these clays, releasing potassium and favoring smectites. These smectites can be regenerated into illites given enough potassium in their chemical environment. Plant uplift of potassium from deeper parts of an alteration profile where high temperature minerals are continually altering to clays releases potassium which is incorporated into plant tissue by roots and re-deposited on the surface of the profile. In the soil zone, one finds the greatest root activity (root mass) where the re-utilization of the uplifted potassium can occur. Since potassium is not highly favored by cation absorbers (usually the potassium content of exchangeable ions in soils is 10 to 15% of the ions available), the incorporation of potassium into high charge smectites to form soil illite is a critical source of potassium for plants. Prairie soils seem to be particularly rich in potassic clays and hence lead to a source of potassium for crops.

By contrast, it appears that conifers tend to form soil HI minerals which will not capture nor retain potassium. They are antithetic to crops. It is possible to modify some of the HI minerals into other forms such as illite using different plant regimes such as oak trees (Tice et al. 1996) or of course prairie growth. Thus it is likely that one can manipulate soil clays to form a fertile assemblage using proper crop or plant sequences. This is of course nothing but classic, pre-1950 agricultural "wisdom" dating in fact from ancient greek times, practices recorded by classical writers (Toutain 1927, part 1). Crop rotations are just that, manipulation of soil chemistry to favor potassium-bearing minerals. However, once the 2:1 clays are degraded into kaolinite by intense weathering conditions, the problem is much greater and probably some time will be neces-

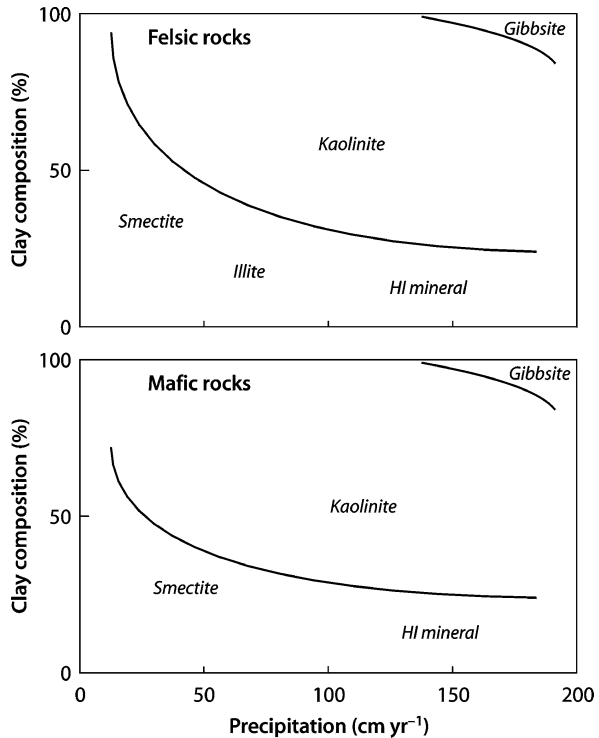
sary to convert kaolinite to a 2:1 mineral by the addition of silica through phytolith incorporation into the soil zone. We have no specific data on this problem.

### 8.3.2

#### Convergence of Soil Clay Mineralogies

There is some indication (Birkeland 1984, p. 287 reporting data of Barshad 1966) that plants can even overcome to a large extent the imprint of initial rock composition in the formation and transformation of clay material into soil clay mineral assemblages. Figure 8.4 indicates the soil clay minerals in the 0–15 centimeter depth zones of soils formed in the California Coast Range. The plot is one of relative clay mineral species content of the clay fraction versus rainfall and hence plant regime. The low rainfall samples form under prairie-scrub vegetation while those above 100 cm precipitation are formed under forest (mostly conifer) cover. Either felsic or basic eruptive or intrusive rocks give a very similar clay mineral family grouping if one considers the 2:1 versus 1:1 clay types or kaolinite versus illite, smectite and HI minerals. Smectite is more abundant under the prairie regime and becomes a minor phase compared to kaolinite in these soils formed on slopes. In fact one sees the formation of 2:1 minerals, aluminous for the most part, from alterite products and altered micas in felsic rocks. Certainly the presence of 2:1 minerals formed from basic rocks passed through a ferriic smectite (nontronite) to a more aluminous phase before becoming an HI mineral.

**Fig. 8.4.** Clay minerals formed in soils on different substrates (Birkeland 1984). Precipitation in cm per year. Substrate rock composition does not influence the clay assemblage to a great extent except for the absence of illite on basic rocks



The alteration of prairies favors smectites in the surface zone while forests (conifer) favor the presence of HI minerals. This top soil mineralogy appears to be largely independent of the rock material which the alteration profile is based upon. This indicates that the plant regimes tend to efface the chemical differences of inherited clays to form a series which is beneficial to their survival. The fact is that one rarely finds trioctahedral minerals in the soil zone, they seem to converge on different types of aluminous 2:1 minerals, smectites, illite or HI minerals depending upon the plant regime concerned. The imprint of rock chemistry is left behind in the alterite (saprock) zone of alteration. It should be noted that in the zones of lower rainfall, one finds more 2:1 mineral content in the clay assemblage.

### 8.3.3

#### Effect of Chemical Translocation by Plants on Clay Mineral Stabilities

The observation by Meybeck (2005) that K and Si are of the lowest abundance in contemporaneous pristine river waters compared to Ca, Mg, Na, Cl, and S ions is of great importance. This suggests that K and Si are withheld during the processes of alteration since their elemental abundance in most rocks is closer to that of the other ions compared. This is especially the case for silica of course. If the sea is salty (with NaCl) one can explain the extraction of Ca by animal action to produce carbonate shells, and eventually Mg incorporation into these materials. However the low abundance of potassium, two orders of magnitude, below other common elements should provoke some thought.

If plants can be associated with fertile, silica and potassium-rich clay minerals such as smectite and illite, how can they stabilize these minerals in the face of the assumed normal trends of weathering (alkali and silica loss)? The question which can then be posed concerns in fact a mechanism whereby plants control or at least limit the effects of water/silicate interaction, K and Si loss, which destroys the fertile clay minerals.

Most plants contain silica in the form of phytoliths (Farmer et al. 2005; Derry et al. 2005) which, upon the decomposition of the plant material will enrich the soil in a very active form of silica. This material is highly reactive because it is in an essentially amorphous or possibly in a crystalline state of high reactivity such as cristobalite whereas the stable form of silica, quartz, is of low chemical reactivity. Thus the high activity phytolith silica is brought to the surface by plant transport.

Further, most plants contain significant amounts of potassium in their different parts (Gain 1895 for example). Plants then accumulate potassium at the surface in the same way that they enrich soils in silica. This overall chemical effect can be seen in the chemical profiles of certain rock types, especially those which are initially potassium-poor. Data presented by Dahlgren et al. (1991) for grass and oak forest soil solutions in Japan formed from volcanic rocks indicates that silica concentrations in the organic horizon are significantly higher than in the lower horizons, by a factor of five, and potassium content is ten times higher than in pore water below the surface zone. The clays at the surface are 2:1 hydroxy-vermiculites which disappear below the upper horizon. Bonifacio et al. (1997) and Pion (1979) give chemical data for soils formed on serpentines, and basic intrusive and metamorphic rocks which are potassium-poor where there is an increase in potassium in the uppermost levels of the alteration profile. The potassium translocation effect can also be seen for weathering profiles on basic

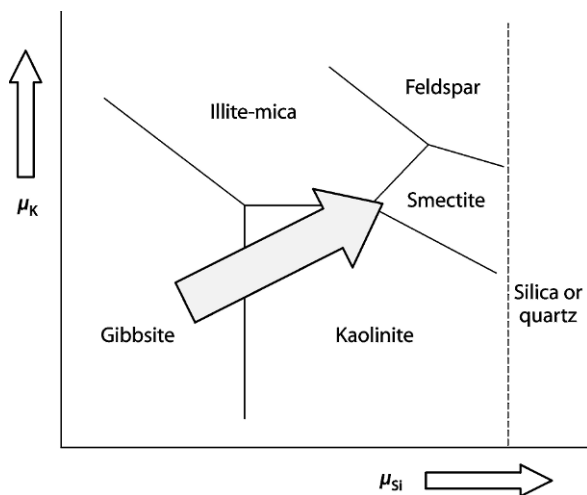
eruptive vitreous materials forming andosols and extrusive basic vitric materials (Meijer and Buurman 2003; Lorenzoni et al. 1995).

Plants then can move (translocate) material from the alterite (saprock) zone to the surface, plant/soil interface. This is indicated in Fig. 8.5 by an increase in silica and potassium activity in solutions. This action maintains and perhaps creates in some cases clay minerals of the 2:1 type which are the most silica-rich of the clay types found under weathering conditions. Silica is the key to their stability. Plants need the siliceous clay minerals smectite and illite to prosper. These are the clays that can furnish an abundance of potassium, calcium and magnesium to insure vigorous plant growth *via* cation exchange. Clays fix needed cations for use during the growing season of the plants. The normal trend of weathering (water/rock interaction) depletes the alteration zone of the elements essential for the stability of these clays (Si and K). Concentration of these elements in plant tissue by root action (chemical translocation) produces a surface layer in the soil horizons which favors the stability of these clays.

Of course each ecological system is more or less adapted to the soil type (substrate and alterite mineralogy) and the climate under which it prospers. These factors will influence the chemistry of the soil and the clay mineralogy independently of plant interaction. The evolution of each system depends upon the ability of soil minerals to conserve the specific ions extracting them from solution for their eventual incorporation either in plant tissue, to stock them in the clays or failing either, favorize their release to solutions and removal from the soil system.

Plants can only do so much against the forces of chemical dilution which engender the loss of silica and alkali ions. Although deeply weathered surfaces in the Eastern United States show high silica-rich clay content in the form of HI vermiculites (Hajek and Zelazny 1985; Norfleet and Smith 1989; Bryant and Dixon 1964) tropical rain forests appear to be devoid of fertile 2:1 clay minerals (Bravard and Righi 1988) and hence are significantly more fragile and less resilient to ecological changes such as de-forestation. This indicates that plants can arrange their surface soil chemical environment to a certain extent but eventually the dissolution of silicates, loss of silica and potas-

**Fig. 8.5.** Effect of chemical translocation by plants of Si and K which stabilizes the 2:1 minerals smectite and eventually illite.  $\mu$  = chemical potential of the element in solution



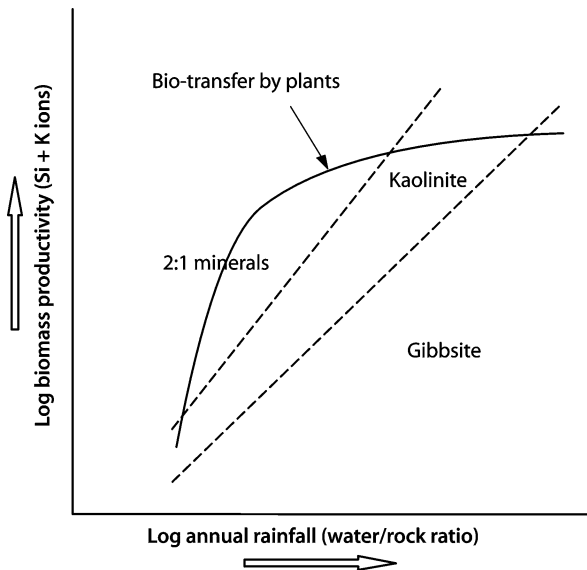


sium will impoverish the soil substrate. Just how much can plants do to counteract the normal trends of weathering by silicate/meteoric water interaction?

It is possible to consider such relations, rainfall, plant growth and elemental translocation as they could affect clay mineral species in the soil (plant/alterite reaction zone). It is known that there is a general, if not precise, relation between plant production (biomass) and rainfall (Lieth 1975). At low rainfall, biomass production is low and the translocation factor would be low. This should be reflected in loss of silica through the sparse but periodic rainfall in deserts. For instance, Manizhnan et al. (2006) indicate that kaolinite can in fact form in very deserts environments in western Australia. The interesting observation on the relations presented as a curve in Fig. 8.6 is that at high rainfall, the biomass does not increase greatly, certainly not as much as in changes under lower changes in rainfall regimes. This suggests that the production of biomass is not at all linear as a function of rainfall but attains as one would suspect a maximum. Biomass is also rather variable depending upon climate, i.e. the periods and intensities of rainfall throughout the year. For example the rainfall in western Europe is similar to that in North Africa, but the vegetation and bio-productivity is not at all the same. Biomass is in fact an integrator of the climate variables. Hence it cannot be directly compared to mean annual rainfall except in a very general way. Biomass production is an indicator of climate, seasonal effects of rainfall.

Now if we consider that biomass does not produce only carbon, nitrogen and oxygen-bearing material (atmospheric material), but also contains significant amounts of potassium and silica (mineral components) as indicated above, one can postulate the effect of biomass on the chemical composition of the soil. Increased productivity will increase the K-Si in the upper portions of the soil. This will favor 2:1 minerals compared to 1:1 minerals, the normal product of water/rock interaction, such as indi-

**Fig. 8.6.** Schematic diagram representing the effect of rainfall on plant activity (biomass) which indicates the amount of material translocated from depth to the surface soil mineral zone. The biomass curve shows that at high rainfall, the plant regime will not exceed a certain amount of translocation effect and hence dissolution of alkalis and silica proceeds producing the kaolinite and eventually gibbsite soil clay assemblages. Lower rainfall shows great changes in biomass, due essentially to the variations of rainfall throughout the year. Steady rainfall gives higher biomass production that does irregular, contrasted season rainfall where biomass production is lower

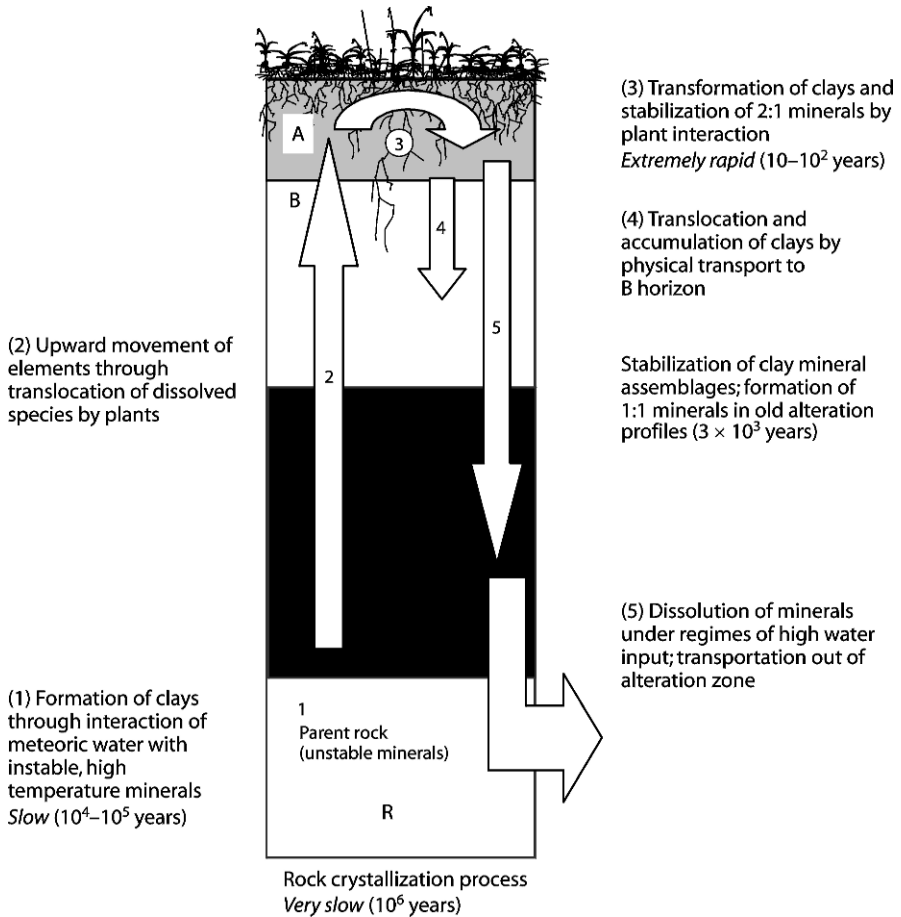


cated in Fig. 8.5 translocation by the arrows. Biomass increase shifts the equilibria to higher potassium activity and silica activity. However rainfall, the effect of diluting the solutions and hence transporting elements out of the system must be considered also. The important feature is that of the inevitable shift from 2:1 minerals towards kaolinite and gibbsite as a function of high rainfall even under high biomass production (tropical rain forest conditions). As rainfall increases, plants cannot keep up with the dissolution rate in soils due to rainfall. Here the influence of plants diminishes with rainfall. Moderate rainfall induces high plant input to the surface, favoring the stability of 2:1 minerals. As rainfall decreases, plant production decreases rapidly and the minimum stability of 2:1 minerals will be attained.

This schematic description of plant and clay mineral relations under different rainfall regimes is a potentially important tool which can be used to interpret different portions of soil sequences under different climate regimes. One very important point to consider is that such a diagram assumes maximum chemical equilibrium between water and clays. At each rainfall input, the silicates come to chemical equilibrium with the aqueous solution. One knows that in all soils there are macropore passages of high influx and capillary porosity which holds water for much longer periods of time. In the capillary situation one can expect chemical equilibrium whereas in the macropore situation this is less likely to obtain. The importance of macropores in a soil and alteration profile is a function, in general, of the clay mineral content. The more clay, the less macroporosity will occur during periods of humectation.

Another important point in considering rainfall averages is that they represent a yearly input. In climates of high seasonality, the rainfall can enter the system and leave without attaining chemical equilibrium with the clays. Such rainfall events will selectively affect the alteration profile in zones similar to those of the initial interaction of water and rock described in Sect. 6.3. Rainfall on a slope will move more rapidly leaving less time for chemical equilibration. These effects will exaggerate or magnify the effect of the amount of rain input into the system. Hence high rainfall, where biomass cannot over take the rainwater dilution factor will produce kaolinite and eventually gibbsite despite plant activity and translocation of Si and K. One should consider the case where plant activity and biomass input of Si and K are low due to low rainfall, and hence one could expect the presence of kaolinite and perhaps gibbsite in soil surfaces with low plant activity.

Overall one can propose a general schema for the change in clay mineralogy from top to bottom of an alteration profile. Alteration begins at the bottom, in the water/rock interaction zone. Here very local chemical forces come into play to form the individual clay minerals. In this process much matter is lost to solution, alkalies, alkaline earth elements and silica. The remnants of rock structure (saprock) keep the different new phases spatially separated which slows chemical interaction which would form new species. The loss of structure (saprolite) tends to form new clays which reflect the overall chemistry of the alterite. In these portions of the alteration profile, the minerals reflect local or more general chemical forces which are essentially determined by water/rock interaction (Fig. 8.7). The next zone of the profile (B) reflects the activity of the upper most part of the profile. This is the zone of physical displacement of clay particles associated with organic material fixed to these particles. Under conditions of high acidity (usually due to organic acids) the upper B is characterized by low clay content, and loss of these minerals. This is the E horizon of podzols.



**Fig. 8.7.** Overall movement of material in alteration profiles. *Arrow 2* shows plant translocation vector, *arrow 3* the deposition of elements by plant decay, *arrow 4* shows the movement of clays by movement in pore water to the B horizon, and *arrow 5* shows the movement of dissolved elements in solution which leave the system to be concentrated, eventually, in sea water

The A horizon is one of plant/silicate interaction. Here the chemistry is largely determined by biological processes, be it input from plant material by chemical translocation or the production of organic molecules which can interact with the silicate material. Many of the reactions are controlled by bacterial activity which controls the rate of the processes. Hence one can find a change of  $10^3$  in reaction rates of chlorite transformation to interlayered illite/smectites for example as demonstrated in Sect. 7.2.2. This change in reaction rate can be described as being one of temperature, which of course determines the bacterial action and growth. Minerals in the soil zone tend to be 2:1 types, which can retain cations useful to plants, such as potassium.

### 8.3.4

#### Equilibrium and Disequilibrium of Soil Clays

The initial stages of clay formation under atmospheric conditions are the water/rock interaction. This relationship is one of disequilibrium. Most rock materials are strongly out of equilibrium with surface conditions. They have formed under higher temperature conditions and for the most part in systems where the silicate solids are by far greater in mass than the liquids, mostly aqueous. These minerals are not in thermodynamic equilibrium with surface conditions where slightly acid water is abundant and the average temperature is nearer 10 °C than 50 °C where diagenesis begins or near 200 °C where metamorphism begins (see Velde 1985; Gharrabi et al. 1998). The hydration (hydroxylation) of silicate minerals occurs in the water/rock interaction. The disequilibrium between high temperature minerals and slightly acidic aqueous solutions is the motor of such reactions. The initial equilibrium attained during these reactions which form clay minerals is that determined largely by local (individual mineral grain) systems or grain contact regions. These minerals gradually come to a certain equilibrium as more and more of the high temperature material is altered. As alteration proceeds to the ultimate transformation of all of the rock into clay, the amount of altering fluids increases with time and the proportion of most soluble elements decreases. Alkali and alkaline earth elements are lost then silica. By the time the rock is totally altered, a large part of the soluble elements have been transported out of the system. The resulting clay assemblage at near total transformation is dominated by kaolinite, oxides and eventually gibbsite. Total transformation takes on the order of hundreds of thousands of years. This is the basic equilibrium towards which alteration is driven.

However, plants cannot thrive on kaolinite and gibbsite. They wish to have potassium available as well as minor quantities of calcium, magnesium and other elements. This can be effected by providing a chemical climate conducive to the stability of 2:1 minerals. Hence the equilibrium in the soil zone is controlled first by the activity of silica in solution, which favors the siliceous clays, the 2:1 minerals. This is the basic equilibrium maintained as much as possible by plants. The prairie regimes tend to favor smectites or illite minerals while the forest plants, especially conifers, favor HI minerals.

Now one must consider the effects of human activity. Changing the plant regime, mainly by exhausting the potassium supply, can create a new less potassic clay assemblage in periods of tens of years. We have no information indicating a change in clay mineral type, i.e. the loss of 2:1 minerals in favor of kaolinite for example. The changes in clay mineralogy appear to be reversible (when 2:1 minerals are still present). The traditional remedy was to change the plant regime, essentially by planting prairie in place of cash crops (see Washington 1801). Cycles of five and five years, prairie to cash or food crops were gradually reduced to one in three in the 18th–19th centuries (Patullo 1758; Seltzenberger 1912) by the use of the most efficient part of the prairie plant population, usually luzern or clover. These cycles were aided by the use of prairies as pasture where manuring was automatic. This type of land use can lead to disequilibrium or equilibrium depending upon the type and cycle of plants used. Of course one can

substitute chemicals to replace those taken out by plants. Thus in general one would expect that a 2:1 mineral would be favored by potassium fertilizer application, assuming that it replaces roughly what is taken out by crop plants.

Cutting trees and replacing them with cash crops will not help maintain the chemical equilibrium established by plants. This is especially true in tropical forest areas. Careful change to prairie type plants can bring deciduous forest soils rich in HI minerals to a mineral equilibrium compatible with cropping (smectite-illite). This has been done for about 6 000 years with success in Western Europe (Clark 1955).

The above analysis assumes that the transport of fine clays is not a dominant factor in the structure of the soils considered. If one produces new minerals of small grain size which are transported out of the alteration profile by water flow, not much can be done except to favor intense root growth at the surface to favorize physical stabilization of clays. Again plants come into play in such a situation.

## 8.4

### The Structure of Alteration and Clay Formation

The different chapters of this book have been devoted to a description of the different types of alteration mechanisms and the resulting products of chemical interaction at the Earth's surface. From this we can determine two major zones of interaction which pre-figure the chemistry and clay minerals produced. The first is the interaction of water and rock and the second is the interaction of plants and altered material, essentially clay minerals. The first interaction tends to produce multiphase clay assemblages while the second tends to produce more homogeneous clay assemblages. This effect is due to the nature of the chemical systems concerned.

#### 8.4.1

##### Water/Rock Interaction

Chapter 4 describes the interactions which are active in the early stages of water/rock interaction. The chemical constraints and interaction are determined on a very small scale, microns to millimeters. The context is one of unstable high temperature minerals which are put into contact with relatively dilute rainwater which first tends to dissolve the old, high temperature phases. The initial reactions are those of rapid dissolution, usually rapidly forming a new mineral when the immediate solution is saturated with low solubility elements. Thus high solubility elements such as alkalis and alkaline earths are put into solution leaving behind less soluble elements such as alumina, iron (ferric) and silica to form new phases. The role of magnesium is important in many alteration systems where ferro-magnesian rocks are altered. The higher temperature of formation of the source rocks, the faster they will react. Also, the higher the temperature of formation the greater difference between the old and new mineral phases. The clays formed in granite or gabbro rock alteration are greatly different from the clays formed from the alteration of sedimentary rocks. Low grade metamorphic rocks and sedimentary rocks contain to a large extent phyllosilicate material, excluding carbonate and quartz minerals, which is very close in mineral character to that of clay minerals. In any event, the systems of alteration are quite localized in space with single or two minerals reacting in the presence of unsaturated aqueous solutions. The

special distribution and segregation of the new clays is maintained until the old rock structure is destroyed forming the alterite zone. Here the inherited new minerals are brought into contact and they begin to react with one another. In this alterite zone, some parts of the initial rock, as mineral grains or rock fragments, still are present and they gradually react with unsaturated aqueous solutions.

The process of water/rock interaction is slow, taking up to a million years to be accomplished. The vector of alteration is downward into the substrate. Hence we have a lower interaction zone in an alteration profile that is slowly producing a multi-phase clay assemblage.

Due to the small size of the chemical systems forming clay minerals, one can find a large variety in different parts of the altered rock, saprock and lower saprolite zones. These multi-species assemblages are gradually effaced as the percentage of clays increases and the old rock structure is effaced, leading to a more general chemical system extending over larger and larger volumes.

### 8.4.2

#### Source Rock and Clays

Of course the basic importance of bulk rock composition cannot be ignored. One can distinguish basically three types of rock which contain large quantities of silicate minerals – acid eruptive, basic eruptive and their metamorphic equivalents, and pelitic metamorphic and sedimentary rocks. Carbonates and sandstones do not produce much clay material.

The acid crystalline and pelitic metamorphic and sedimentary rocks form aluminous silicates as clay minerals; kaolinite, 2:1 clays and oxy-hydroxides (Al and Fe) in the soil horizons. Basic rocks (those dominated by ferro-magnesian phases) tend to form ferric smectites and in some instances talc and chlorites. Oxidation and loss of silica tend to form, eventually, more aluminous smectite minerals. Most rocks under conditions of contrasted climates form dioctahedral 2:1 minerals in the soil horizon whereas the types of clay minerals formed in the rock/silicate interaction zone depends more strongly on the composition of the altering rocks. In these regions one will find trioctahedral minerals which become rare or non-existent in the superficial plant/silicate interaction zone.

When the eruptive rocks are glassy, containing much non-crystalline material, poorly structured minerals such as imogolite and allophane form under conditions of constant humidity. Here chemistry is less important than the high instability of the silicate material.

The imprint of rock type is seen in both the water-rock interaction zone as well as the soil/plant interaction zone, although the convergence of mineralogy towards the 2:1 minerals tends to efface the specificity of the initial rock composition to a large extent.

### 8.4.3

#### Plant/Soil Interaction

The upper, organic-rich portion of a profile, defined as the A horizon, is where most of the plant interaction occurs. Here the chemistry is determined by the action of plants,

their decay products and transformations by living organisms. For the most part, in soils developed by abundant plant regimes under conditions of moderate rainfall, the clay mineralogy tends to be similar, i.e. based upon 2:1 minerals with more or less minor amounts of kaolinite. These 2:1 minerals tend to form interstratified complexes probably with only two dominant types of inter layer ion present, potassium, exchangeable bases or hydroxyl alumina. This represents a strong homogenization of the clay suites found in the water/rock interaction zone where 1:1, 2:1 and hydroxy-oxides are found. If the clays are more homogeneous, in special terms, on a horizon scale, they must be responding to more general chemical constraints which affect the silicates over several tens of centimeters depth in the soil zone.

Different plant regimes (conifer, deciduous forests and prairie) tend to favor different types of clay minerals in the soil zone. This is the result of plant and bacterial actions as well as the effects of rainfall and temperature regime on these living organisms. Acid soils, those where pH is below 5, are normally the combined product of siliceous rock source matter and the presence of conifer or evergreen trees. Here one finds the aluminous interlayered 2:1 clays, HI and soil vermiculite. The high acid regime tends to dissolve the clays below the humic zone giving rise to an E horizon, dominated by quartz sand. Why the soil horizon contains 2:1 minerals and that just below shows their dissolution is a mystery at the moment.

Deciduous forest and especially prairie ecosystems promote the potassic 2:1 minerals illite and interlayered illite/smectites. These minerals stock potassium for use by the plants growing in the soil/plant interaction zone.

The clays dominant in the soil horizon are of the 2:1 type, either as pure or homogeneous phases or as interlayered minerals with components of two or perhaps more types of interlayer behavior.

#### 8.4.4

#### Clay Transport

Below the A horizon of plant/clay interaction one finds an accumulation of clay minerals coming from the humic, A horizon. This is the B horizon, developed by the physical transport of clay particles in percolating soil solutions. The vector of vertical displacement is not the only one possible. When the alteration profile is on a slope, some horizontal component of clay movement can be observed. In fact, even in areas of heavy vegetal cover, streams are known to be cloudy, and brown carrying fine clay particles after periods of heavy rain. This is not surface run off, but lateral transport of clays under percolation flow. The effect of mobilization of clay particles in suspension in moving fluids in the soil and alterite zones should not be underestimated. For example, clays are well known to carry absorbed charged molecules on their surfaces, such as exchangeable cations or more importantly charged organic molecules such as herbicide or insecticide metabolites. These vectors are not evident from surface observation, but it is well known that these potentially toxic organic molecules can be traced in ground water and especially in stream waters. For the most part they are not soluble but are attached to clay or other charged particles. This effect should be taken into account in studies of dispersion of industrial organic compounds.

### 8.4.5

#### Kinetics of Clay Change in the Soil Zone

In Chap. 6 one has seen the effect of agriculture on clay mineralogy of the soil zone. According to classical mineralogical definitions, new minerals such as illite can be formed or lost through agricultural processes. Transformation of chlorite to mixed layer minerals in illite-chlorite dominated source materials by plants can occur over periods of thousands or less than ten years. These reaction rates are very much greater than those for isolated silicate systems such as are found in diagenesis where temperature is the motor of mineral change. One can ascribe the differences in mineral reaction rate to the effect of biological action which will change the chemical intensity of the reactions by furnishing certain material at a great rate, which is in fact controlled by temperature also. However the impact of plants and bacteria seems to dominate in soil clay mineral stabilities.

One should take these observations as a function of their relative importance. If one considers most of the changes, they in fact occur between 2:1 minerals where the interlayer ion site changes occupancy giving a different X-ray diffraction characterization. In fact the difference between HI and illite is one of potassium availability in many instances as demonstrated by Tice et al. (1996) in field experiments and the observation on Arkansas agricultural soil clays (Chap. 5.5) with K-saturation in the laboratory. Shifts from smectites behavior to illite (closed layer, 10 Å spacings) can be effected by potassium saturation also. Reversal or this effect has been seen when corn is grown without fertilizer. Then one can form or lose HI, smectite and illite by manipulating the concentrations of ions in solution. This is not a true mineral change, in the sense that the different behaviors are due only to exchangeable ion site occupation. The interchangeable family of 2:1 mineral structures is in fact being manipulated by different plant regimes in the soil zone. This is a very important concept which should be kept in mind in studies of ecology and agricultural engineering. Rapid mineral change representing differences in the availability of potassium and other interlayer ions can be determinative concerning the productivity or in fact the presence of different plants in the soil zone.

### 8.4.6

#### Minerals Present and Their Change in the Soil/Plant Interaction Zone

If the rock/water interaction zone (saprock) is heterogeneous in its mineralogy from point to point, the mineralogy of the soil zone is mostly homogeneous as it is considered to be in a soil horizon by pedologists. This suggests that the plant regime tends to homogenize the chemistry of pore solutions in order to produce similar mineral phases from point to point in the horizon. The clay minerals present are dominated by 2:1 structural types of the aluminous, dioctahedral type such as the smectite/illite mixed layered minerals. Even HI minerals tend to become more aluminous with their evolution in the soil zone (Gillot et al. 2000). As far as we know the HI minerals in the evolved alteration sequences on various crystalline rocks in the south-eastern United States are also of an aluminous character (Rich 1960; Norfleet and Smith 1989; Bryant



and Dixon 1964; April et al. 2004). Hence it seems that there is a convergence of mineral type towards a dioctahedral 2:1 structure in the soil horizon. To a large extent, in reasonably mature soils one finds 2:1 minerals and kaolinite as the clay assemblage. Weathering intensity and time of interaction or low plant activity can favor the kaolinite over the 2:1 minerals. Thus one finds aluminous clays in the soil horizon in old soils of high rainfall.

The large portion of agricultural soils farmed today, for the most part in the northern hemisphere at least, is formed in reaction to rather recent climatic changes and effects, glaciation, loess deposits and river action. These soils are young, i.e. they have not reached an equilibrium with the plant regime and water influx that reigns. This is due to recent removal and transportation of surface materials and to the fact that the plant regime established today is rather recent. Here plants are the major actors in determining the chemistry of A horizon fluid compositions closely associated with the clays.

If plants control the local chemistry of soil solutions, this is the control of soil clay mineralogy. We have demonstrated that clay mineralogy can change (according to current mineral names) over periods of time that are much shorter than those necessary for mineral transformation and re-crystallization under conditions of diagenesis, those of higher average temperature than the surface. However, if one considers the changes observed, they concern mostly the 2:1 minerals. The changes involve soil vermiculite or HI minerals, smectite and illite. If one considers these minerals as a two layer TOT structure with different interlayer ions occupation, one can explain the “mineral” changes in a more simple manner. In fact, the “mineral” changes are due to changes in interlayer ion occupancy. The changes observed in the conversion of HI mineral to illite can be considered to be one of cation exchange of Al-OH material for potassium. Change of illite to HI mineral can be considered in the same light. Loss of illite to form smectites or interlayered minerals is simply one of loss of fixed potassium for a more easily exchangeable ion. These chemical changes can be effected by controls of the soil solution chemistry. Hence the apparent mineral conversions in the soil horizons are between members of a single 2:1 mineral family, for the most part dioctahedral and aluminous.

We propose the following schema then to account for the apparent rapid change (tens of years) in mineralogy:

- 2:1 mineral substrate – high charge
  - high alumina availability = HI mineral
  - high potassium availability = illite
  - low potassium availability = smectite
- 2:1 mineral substrate – low charge
  - smectites with exchangeable ions
  - high Al availability = Al exchanged smectites and HI minerals

At present we have little information on the possibility of change in the charge and ionic occupancy of the 2:1 mineral, but recent data (Bauer et al. 2006) indicates that internal ionic diffusion is possible at low temperatures (80 °C) which can modify the charge intensity in the interlayer site. It is quite possible that significant compositional change can be accounted for by internal diffusion as suggested by Gillot et al. (2000) for large crystals of phyllosilicates in soils.

Hence soil clays can be affected by changes in solution chemistry which changes the interlayer ion occupancy giving rise to differences in apparent mineralogy (tens of years), and on a longer time scale (perhaps hundreds of years) ionic diffusion can modify the charge intensity and charge site within the 2:1 structure. These time scales and reactivity contrast strongly with those found for the alteration of unstable rock minerals into clay minerals by water-rock interaction, occurring on the scale of thousands to hundreds of thousands of years.

#### 8.4.7

##### Conclusions

The exercise given above in these pages attempts to emphasize the relations between the major actors in the alteration of rocks to clays at the surface of the Earth. Much study has been done on different aspects of the panorama of change and chemical interaction. For the most part previous workers have concentrated upon the mineral chemistry aspect of the problem, the interaction of rainwater with inherently unstable high temperature minerals in rocks. However, the importance of plants and their chemical control of the chemistry of surface waters in the plant/silicate interaction zone (A soil horizon) has been underestimated in many cases. This last aspect is perhaps the most striking in that the interaction and control of major mineral properties (to the point of giving specific physical and chemical characteristics which have led to mineral names) is evidently a major influence of clay minerals in the soil horizon. Control and observation of these properties can lead to a better use of natural fertility as it is involved in the plant/clay interaction processes.

#### 8.5

##### Perspectives for Clay Mineral Science in Surface Environments: Challenges for the Future

#### 8.5.1

##### Soils and Crops

###### *The Cation Exchanger in Soils*

As with many resources, we find today that supply is not infinitely elastic concerning the soil. There are limits as to how much substitution one can do using factory or industrial products to replace natural soil fertility. Soil structure is controlled to a large extent by the organic matter present at the surface, its type and interaction with clays. One cannot continue to count the carbon atoms in the soil as an index to its fertility. Methods of sequestration do not consider the type nor the function of the carbon-bearing matter buried and held in the soil. Organic/clay interactions are the key to understanding soil structure.

Further, there is a general feeling that clays play a somewhat minor role in the capture and release of cations captured and fixed by plants. However, only some 10 to 15% of exchangeable base cations in common soils are potassium, one of the major fertilizing agents. The anhydrous potassic layers in 2:1 clays (illite) contain more than enough potassium to cover the needs of plants in most soils in temperate climates.

The destruction of these 2:1 minerals can seriously compromise the long term fertility of an agricultural soil. Following and predicting illite-potassium availability is the key to understanding long term fertility of agricultural soils.

### *Are Soil Quality Criteria Important?*

In the recent past the question was moot. It was, and still is in some circles, considered that modern chemical and mechanical manipulation of soils could be used to overcome weaknesses in soil characteristics. The development of crop plants dependent upon industrial nutrients was a strong goal for agro-industrialists. The cycle of higher productivity using more and more fertilizers, insecticides and phyto-sanitary products led us to the present state of affairs where much drinking water in many areas of the developed world are at the limits of normal sanitary consumption for well known chemicals or degradation products such as nitrates. We do not know about the many unknown products of biological degradation of the phyto-sanitary chemicals used in ever increasing amounts on the soils. Few controls are possible for molecules so powerful as to be effective at doses undetected by normal laboratory analysis of soils and water. Many people are beginning to think that more care should be taken in using modern chemical treatments of soils.

However, if one talks of reducing artificial treatments of soils, one must consider the alternatives. Can we go back to 30–40 bushel corn after the heady years of 80–100 bushels per acre? Can we reasonably reduce the productivity by 70% of the land in developed countries? It is hard to believe such a scenario. The challenge is then to understand the reactions and reversible processes inherent in crop rotation farming. We know that cycles of fertilizing and extracting crops maintained a balance in many agricultural lands. In France, much of the territory was first farmed 6 000 years ago and it did not lose its “natural” fertility until the post-War era. If one can make genetic strides in developing plants that need nitrogen and potassium to grow, cannot it be possible to develop ones that fix these elements in the soil? Such development must be accompanied by a careful study of the effects on clay mineralogy (illite-like behavior). In this way one can optimize the effects of plant selection.

Of course the corollary is to develop plants that can do with less nitrogen and can extract more potassium from the clay resource. In many cases one increases the illite (potassium) resource by the addition of potassium which, at least in part, is not plant extractable. Research must be done on the interaction of crop plants and different types of soil clay assemblages which form the basic soil clay types in agricultural areas. Each soil type will need a diagnosis as to what type of crop rotation is necessary with the varieties of crops planted. It is a multi variable problem, but one that can be solved with a little patience.

### *Soil/Plant Interactions: Soils and Ecology*

The interaction of plants and soils should be a fundamental (and will be in the future) of the study of land use. What are the limitations in converting a prairie into agricultural use? What can be done to convert forest soils into agricultural soil? What are the best methods of using agricultural lands in a forest-crop or prairie rotation plan? Very much has been abandoned to non-farming use (prairies and forest) for tech-

nical reasons; tractors with 12 row planters have a hard time on hills. However, less intensive farming can be accomplished for crops that need different soil types. The future of bio-carburants might just yield some new landuse schemes, with \$100 a barrel oil. Rotations of less profitable land abandoned under intensive farming techniques to different cropping methods can most likely free up some of the resources now neglected in many former farming areas.

Trees, grasses and agricultural plants are the basis of a new ecology of plant/soil interaction. Biotopes and their effects on the soil will need to be studied in order to develop the full potential of land use in the future. At present this is just a nascent field of endeavor. Ecological engineering must be studied from with a better knowledge of ecosystems as eco-engineers.

### 8.5.2

#### Soils as a Natural Safety Net for Modern Society

Contamination and accidental events are always going to occur, in one way or another. It is necessary now to study the natural capacity of soils to absorb and disperse high concentrations of anomalous chemical materials. Soils are in fact our natural barriers to disaster. Unfortunately little is known concerning the natural processes of fixing and dispersing elements which in high concentration are immediately harmful. Study should be done in understanding the natural processes of movement concerning for example Sr, Ni, U, As or other elements in a functioning soil system. When the basic systems are understood, one can commence working on methods to improve the capacity of fixation and dispersion over long periods of time for such elements. One can have an idea of the natural capacity of soils under stress and hence can estimate the limits and types of soils which will be most efficient to handle the problems that modern civilization will give them. Soils mean of course plant/silicate interactions, and hence ecosystem study is necessary to develop new soil types which can respond to the needs of society, another field of study to develop.

It is quite clear that many of the challenges of the future concerning clay science are those of developing a close relationship with biologists and ecologist in order to form a new science. One might call such an effort Geo-Ecology. Perhaps some young people with stars in their eyes will heed this call, and we can proceed into the 21st century on a better footing than when we left the 20th.

### Suggested Reading

- Birkeland P (1984) *Soils and geomorphology*. Oxford University Press, Oxford, 365 pp  
Black C (1968) *Soil-plant relationships*. John Wiley and Sons, New York, 789 pp  
Jenny H (1994) *Factors of soil formation*. Dover, New York, 281 pp  
Holland HD, Turekian KK (eds) (2005) *Treatise on geochemistry*, vol V. Elsevier, Amsterdam, 625 pp  
Wolt J (1994) *Soil solution chemistry*. John Wiley and Sons, New York, 345 pp

## Polytypes

### Definition

The way that layers are stacked in the clay crystallites determines the symmetry group and the dimensions of the unit cell (hexagonal (H), rhombohedral (R), orthorhombic (Or), ditrigonal (T), monoclinic (M) or triclinic (Tc); 1, 2, 3 layers or more). Therefore, several polytypes may exist for a given layer chemical composition. Two consecutive layers may be stacked with or without shift and rotation:

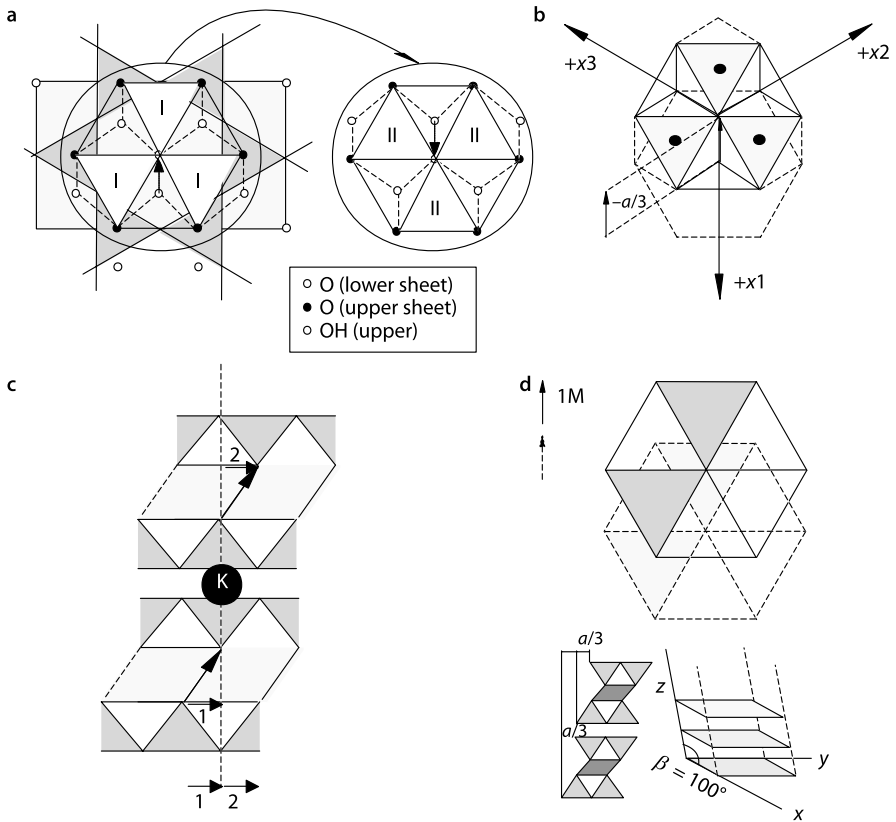
- *no shift*. The symmetry becomes orthorhombic, pseudo-hexagonal or hexagonal;
- *a:3 or b:3 shifts*. If no rotation occurs, the symmetry is monoclinic. If rotation occurs, angle  $\beta$  may be near  $90^\circ$  and the symmetry close to orthorhombic.

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. For instance, the structural formula of the 1M illite is based on a single unit cell ( $\text{Si}_8\text{O}_{20}$ ) while that of the 2M are based on a two-layer unit cell ( $\text{Si}_{16}\text{O}_{40}$ ).

### An Example: The Mica or Illite Polytypes

For a given 2:1 mica layer, the octahedra may have two different positions referred to as *I* and *II* in Fig. A1.1a. Position *II* can be superposed on position *I* after a rotation of  $60^\circ$ . The tetrahedral sheets, represented by hexagons formed by apical oxygens, exhibit an *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  $60^\circ$ . The nomenclature of polytypes is standardized: the number on the left indicates the number of layers per over-unit cell in the stacking sequence, the letter indicates the symmetry system, the indexed number on the right gives the number of the stacking solutions for the same symmetry and the same number of layers contained in the over-unit cell.

Considering the hexagonal symmetry of octahedral sheets, configurations *I* and *II* both present three rotational possibilities (Fig. A1.1b). Therefore, two consecutive layers can be superposed after one or several  $60^\circ$  rotations, theoretically yielding six possibilities:  $0^\circ$ ,  $60^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$ ,  $300^\circ$ . Owing to the ditrigonal symmetry, rotations of



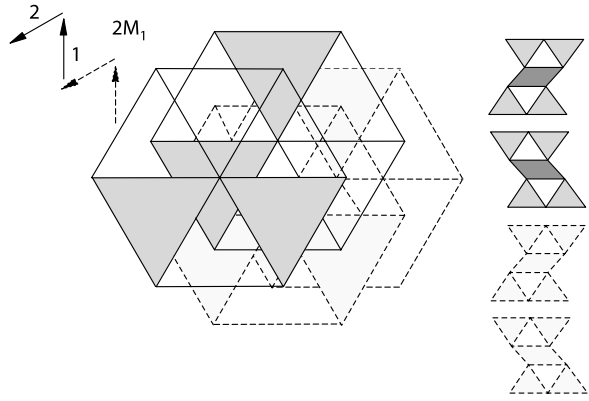
**Fig. A1.1.** 1M and 2M<sub>1</sub> mica polytypes; **a** the two groups of octahedral sites; **b** the three symmetry axes; **c** position of the translation vector in two adjacent layers; **d** section in the a-c plane (*o1o*) of a 1M polytype

60° and 300° on the one hand and of 120° and 240° on the other hand yield equivalent positions. Smith and Yoder (1956) have shown that there are theoretically six polytypes whose number of layers goes from 1 to 6. Of these, the most common are the 1M and 2M<sub>1</sub> polytypes:

- 1M polytype (Fig. A1.1c,d): layers stacked without rotation (0°); strongly monoclinic ( $\beta = 100^\circ$ ),
- 2M<sub>1</sub> polytype (Fig. A1.2): layers stacked with a rotation of  $\pm 120^\circ$ ; almost hexagonal ( $\beta = 95^\circ$ ).

Smectites and more particularly montmorillonites form crystallites characterized by the turbostratic stacking sequence of a small number of layers (non-rational rotation between layers within the stacking sequence).

Fig. A1.2. The  $2M_1$  polytype for illite or dioctahedral mica



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## Mixed Layer Minerals

### Conditions of Interstratification

A mixed-layer mineral may be randomly ordered (Reichweite = 0; R<sub>0</sub>) or ordered (Reichweite = 1;  $R \geq 1$ ), regularity being a particular R<sub>1</sub> case in which A = B = 50% (Fig. A2.1a). It is identified when its components, their proportions, and the degree of order of their stacking sequence have been determined. Let's consider a mixed-layer mineral composed of two components A-B occurring in varying relative proportions  $W_A$  and  $W_B$ . It will be fully described if the succession probabilities of A and B layers ("nearest-neighbor") are known:  $P_{AA}$ ,  $P_{AB}$ ,  $P_{BA}$  and  $P_{BB}$ . Generally, these six parameters are linked by four independent relationships:

$$W_A + W_B = 1$$

$$P_{AA} + P_{AB} = 1$$

$$P_{BA} + P_{BB} = 1$$

$$W_A P_{AB} = W_B P_{BA}$$

So there are six variables and four non-redundant equations which permit their calculation if two are fixed. Usually, the composition as well as one of the junction probabilities are fixed ( $W_A = 0.4$  and  $P_{BB} = 0.8$ , for instance). The development of probability calculations can be found in classical books (after Brindley and Brown 1980 for instance).

### Random Stacking Sequence (R<sub>0</sub>)

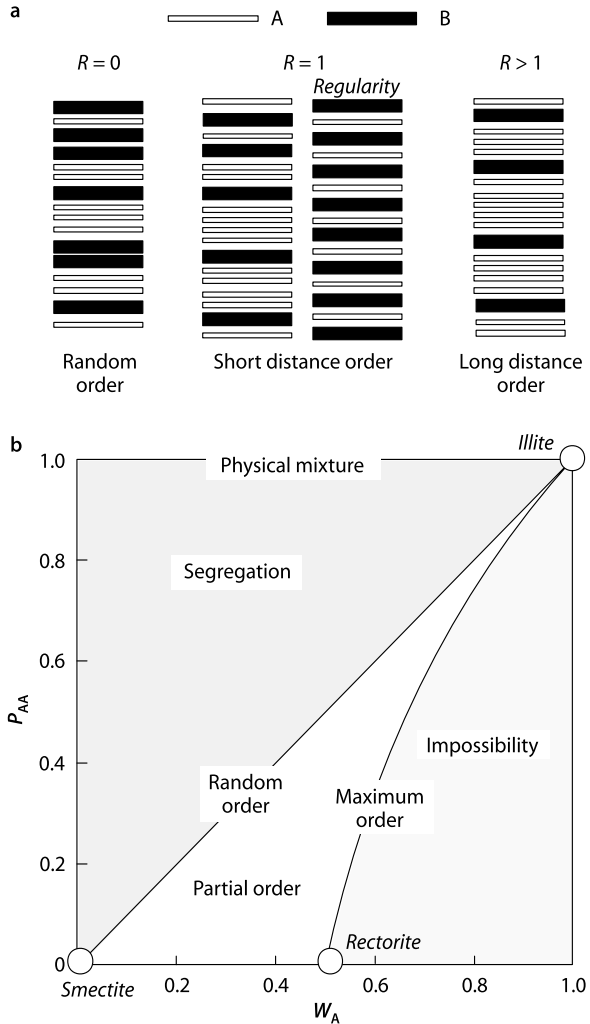
In a random stacking sequence, a A layer may be followed by a A or a B layer without any forbidden sequence. The succession probability of A and B layers depends only on the relative proportions  $W_A$  and  $W_B = 1 - W_A$ . Therefore, the probability for A to follow B is given by  $P_{AB} = W_B$ ; we know that  $P_{AB} + P_{AA} = 1$ , thus  $P_{AA} = W_A$ . The variation of  $P_{AA}$  as a function of  $W_A$  of the random stacking sequence is represented by a straight line whose slope is equal to 1 (Fig. A2.1b)

### Ordered Stacking Sequences (R<sub>1</sub>)

**Maximum degree of order.** If  $W_B \leq 0.5$ , the maximum degree of order is reached if the probability of finding a B-B pair is zero (Fig. A2.1b). Let's consider a 10-layer stacking



**Fig. A2.1.** Mixed layer minerals; **a** schematic diagram of randomly ordered, ordered and regularly ordered interstratifications of two types of A and B layers such as illite (10 Å) and smectite (17 Å); **b** relationship between succession probability of two illite layers ( $P_{AA}$ ) and illite content ( $W_A$ ) establishing mixing, segregation and interstratification domains (domain in white)



sequence containing 40% of B; a sequence such as B-A-B-A-A-B-A-B-A-A may exist, but a sequence such as B-A-A-A-B-B-A-B-A-A is forbidden. As  $W_B$  decreases, the probability of formation of B-A-B-type sequences becomes zero. Long-distance order may be established with at least two then three consecutive A after each B. Although the actual influence of the B layer on the subsequent layers is not established in terms of chemical or physical interactions, A-rich crystal structures can still be described using these long-distance ordering modes: order for a triplet  $R = 2$ ; order for a quadruplet  $R = 3$ ; etc.

In  $R_1$  stacking sequences, if A is the most abundant type of layer ( $W_A \geq 0.5$ ), the maximum order implies that no BB layer pair can exist ( $P_{BB} = 0$ ). Therefore, the following relations may be inferred:

$$P_{BB} = 0$$

$$P_{BA} = 1$$

$$P_{AB} = \frac{W_B}{W_A}$$

$$P_{AA} = 1 - P_{AB} = \frac{(W_A - W_B)}{W_A}$$

The variation of  $P_{AA}$  as a function of  $W_A$  for maximum order is given by the curve originating in the composition of rectorite in the case of illite/smectite mixed layers (Fig. A2.1b).

**Partial order (R1).** The partial order is an intermediate state between random order and maximum order: partial order =  $\alpha$  random stacking sequence +  $(1 - \alpha)$  maximum order stacking sequence. If A is the most abundant type of layer, then:

$$P_{AA} = \frac{\alpha W_A^2 + (1 - \alpha)(W_A - W_B)}{W_A}$$

$$P_{AB} = \frac{\alpha W_A + (1 - \alpha)W_B - \alpha W_A^2}{W_A}$$

$$P_{BA} = \frac{\alpha W_A + (1 - \alpha)W_B - \alpha W_A^2}{W_B}$$

$$P_{BB} = \frac{\alpha W_A^2 - \alpha W_A + \alpha W_B}{W_B}$$

The  $\alpha$  parameter varies between 0 and 1, which requires that  $P_{AA}$  vary between the values calculated for the random stacking sequence and the maximum order stacking sequence. The partial order domain is limited by the maximum order curve and the random order straight line (Fig. 1.10b).

**Segregation (R1).** This type of stacking sequence is intermediate between random state and physical mixing (Fig. 1.10b). Consequently  $P_{AA}$  must be fixed as a function of  $W_A$  in order to be located within the domain of segregation:

$$P_{AA} = \alpha + (1 - \alpha)W_A$$

$$P_{AB} = (1 - \alpha)W_B$$

$$P_{BA} = (1 - \alpha)W_A$$

$$P_{BB} = \alpha + (1 - \alpha)W_B$$

## References

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## Cation Exchange Capacity

The fundamentals for the study of the cation exchange capacity are detailed in McBride (1994).

### The Chemical Reaction of Cation Exchange

In a first step, one can consider the exchange equilibrium constant  $K_{\text{eq}}$  as the equilibrium constant of a classical reaction:

$$K_{\text{eq}} = \frac{(\text{MgCl}_2)(\text{CaX}_2)}{(\text{CaCl}_2)(\text{MgX}_2)}$$

The activity of solids is equal to 1 by convention,

$$K_{\text{eq}} = \frac{(\text{MgCl}_2)}{(\text{CaCl}_2)}$$

The constant  $K_{\text{eq}}$  imposes the following rule: as long as the solid can exchange  $\text{Mg}^{2+}$  ions, the activities of those ions in solution are constant. This is not the case in real exchanges because the  $\text{MgX}_2$  and  $\text{CaX}_2$  values vary with the number of exchangeable sites occupied by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . This means that the activity of solids is not equal to 1. The true variable is the ratio of the concentrations of adsorbed ions  $[\text{CaX}_2]$  and  $[\text{MgX}_2]$ :

$$M_{\text{Ca}} = \frac{[\text{CaX}_2]}{[\text{CaX}_2] + [\text{MgX}_2]}$$

$$M_{\text{Mg}} = \frac{[\text{MgX}_2]}{[\text{CaX}_2] + [\text{MgX}_2]}$$

Therefore, since the equilibrium constant  $K_{\text{eq}}$  does not describe the exchange phenomenon, it is replaced by a constant  $K_s$  – or selectivity coefficient – which is expressed as follows:

$$K_s = \frac{(\text{MgCl}_2)M_{\text{Ca}}}{(\text{CaCl}_2)M_{\text{Mg}}}$$

### Deviation from Ideality

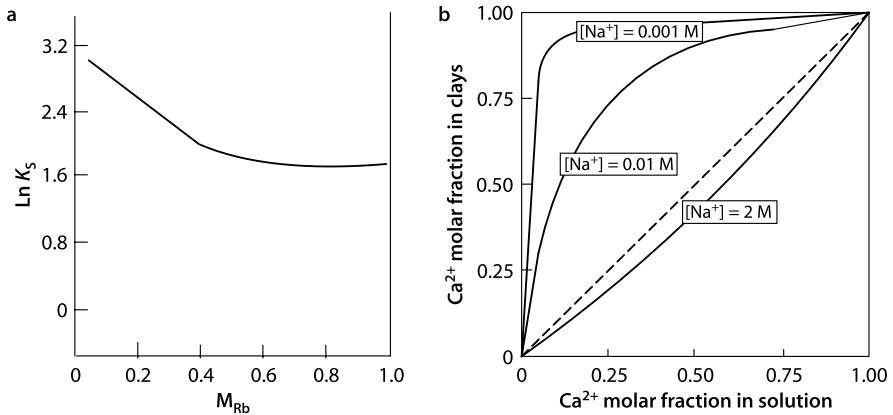
As the ion exchange modifies its composition, the clay may be considered similar to a solid solution. Thus, the selectivity coefficient is likely to deviate from ideality by the addition of an energy of mixing. The more similar the charges and diameters of ions, the lower this energy; the more different, the higher this energy. This means that the concentrations  $[\text{CaX}_2]$  and  $[\text{MgX}_2]$  needs to be “corrected” by selectivity factors:  $(\text{CaX}_2) = f_{\text{Ca}}M_{\text{Ca}}$  and  $(\text{MgX}_2) = f_{\text{Mg}}M_{\text{Mg}}$ . The exchange equilibrium constant then becomes:

$$K_E = \frac{(\text{MgCl}_2)f_{\text{Ca}}M_{\text{Ca}}}{(\text{CaCl}_2)f_{\text{Mg}}M_{\text{Mg}}} = K_s \frac{f_{\text{Ca}}}{f_{\text{Mg}}}$$

where  $K_s$  is the selectivity coefficient.

The example of the exchange of  $\text{Rb}^+$  cations in a Na-saturated montmorillonite shows that  $K_s$  is greater when fewer exchangeable sites have fixed this cation (Fig. A3.1a). For monovalent cations, the selectivity order is as follows:  $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ; for bivalent cations:  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ . This order is defined by the size (diameter) of the association cation/hydration sphere: the cation with the smaller diameter displaces the one with the greater diameter. Selectivity varies with electrolyte concentration: the more diluted the solution, the greater the selectivity (Fig. A3.1b). If the exchange is performed at constant temperature, the selectivity coefficient ( $K_s$ ) determines a cation exchange isotherm. Exchange isotherms are modified when pH conditions vary. Indeed, the behavior of the  $\text{H}^+$  ion is similar to that of the other cations with which it competes to bond to the variable or permanent charges. This imposes that the measurement of isotherms be performed under controlled pH conditions.

What does the selectivity coefficient mean at the crystallite level? Obviously, it corresponds to exchange energies that differ according to sites. If one considers smectites, for which variable charges are considered negligible, the exchange sites are located in the interlayer zone. Talibudeen and Goulding (1983) have shown through microcalorimetric analyses the occurrence of six groups of sites whose enthalpy of exchange (exothermal reaction) varies from 5.7 to 10.9 kJ eq<sup>-1</sup>. For low-charge smectites, the enthalpy of most of the exchange sites varies from 5.7 to 7.5 kJ eq<sup>-1</sup>. They have a few sites of higher enthalpy. These results have been confirmed by the study of Cs for Ca exchanges (Maes et al. 1985). Although not proved yet, it seems obvious that the variation in the exchange energy is related to the charge heterogeneities at the surface of 2:1 layers. These heterogeneities could result from the way in which ionic substitutions



**Fig. A3.1.** Variation of the selectivity coefficient  $K_s$ ; a  $Rb^+$ -Na-montmorillonite exchange.  $K_s$  varies as a function of the respective proportions of the exchangeable sites occupied by  $Rb^+$  and  $Na^+$  ions ( $M_{Rb}$ ); b relationship between  $Ca^{2+}$  contents in the exchanger (montmorillonite) and the solution. The more diluted the electrolyte, the greater the selectivity ( $K_s$ ) for  $Ca^{2+}$

are distributed between tetrahedral and octahedral sheets (Fig. A3.2). It should be noticed, first that two Si for Al substitutions in a group of four neighboring tetrahedra are very rare even if theoretically possible, second that  $Mg^{2+}$  cations are never segregated in a dioctahedral sheet (Vantelon et al. 2003). This excludes  $R^{2+}$ - $R^{2+}$  pairs, i.e. the -2 octahedral charge.

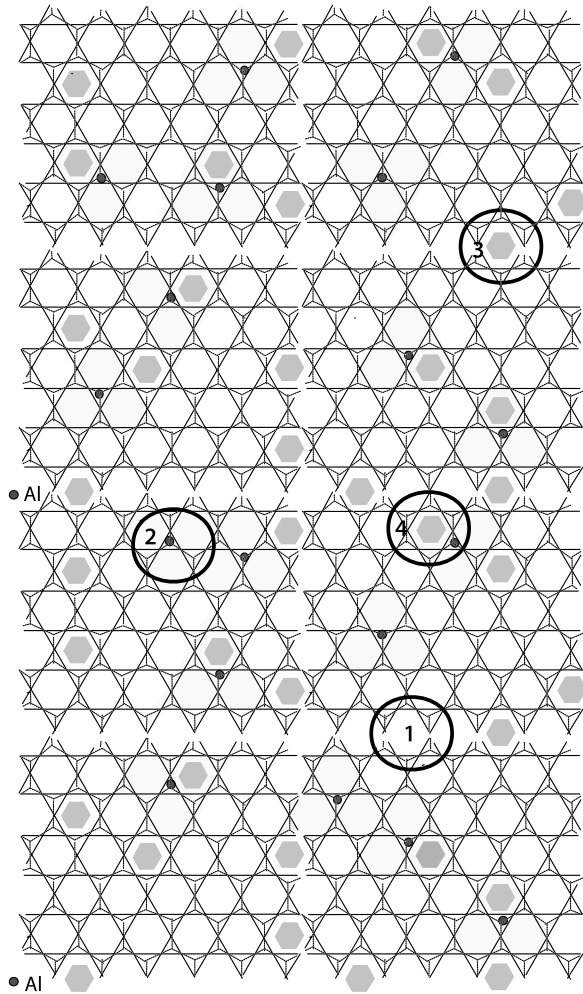
## The Variable Charges

The size of most clay mineral crystallites ranges between 10 nm and 10  $\mu m$ . 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  $R^{2+}$ -OH or  $R^{3+}$ -OH bonds interrupted by edges is very high. These interface sites are electrically charged. Neutrality is obtained only by adsorption of ions from surrounding solutions. Thus, in the case of kaolinite, two chemical functions appear: silanol (Si-OH) and aluminol (Al-OH) groups. The properties of these groups 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 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.

**Fig. A3.2.** The theoretical local charges of a dioctahedral 2:1 layer. *Insert* shows the origin of the octahedral charge (one  $R^{3+}$  cation is replaced by one  $R^{2+}$  cation in a three octahedron group). Four sites theoretically exist: 1: no charge; 2: tetrahedral charge; 3: octahedral charge; 4: tetrahedral + octahedral charges. *Gray triangles*: tetrahedral charge in the vicinity of a Si for Al substituted site; *gray hexagons*: octahedral charge located on a  $R^{3+}-R^{2+}$  site



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## Hydroxy-Interlayered Minerals (HIMs)

### The XRD Properties of Hydroxy-Interlayered Minerals

Hydroxy-interlayered minerals have similar basal “spacings” in their natural state. They all present a relatively narrow peak at 14.2 Å. The full width at half maximum intensity (*FWHM*) of that peak is less than  $0.9^\circ 2\theta$  CuK $\alpha$ . When saturated with bivalent cations, low charge smectites expand to 15 Å under ambient conditions. This spacing is dictated by the two water layer/cation complex in the interlayer sites. This is not the case for HIMs. Without chemical treatment, e.g. extraction of iron and/or aluminum hydroxides, hydroxy-interlayered minerals do not fully expand with glycol treatment. Additionally, the first order peak is intense while the other (*ool*) peaks are much less intense if not absent in the diffraction diagrams. This effect is due to less scattering intensity because of the incomplete structure of “gibbsite-like” layer in the mineral (Fig. A4.1).

Vermiculite minerals are high charge expandable clays, the  $d_{001}$  which changes shift from 14–15 Å in the air-dried state to about 16 Å after saturation with ethylene glycol (Douglas 1989). Soil vermiculite is a term used in the past to describe non- or poorly expanding soil clay minerals with a basal spacing between 14 and 15 Å (Wilson 1987). The poor expandability is due to the presence of polymerized Al ions in the interlayer zone. It is not uncommon to find normally expandable smectites and HIMs in the same soil sample (April et al. 2004). Hence the identification or determination of the behavior of the individual mineral species is difficult. In general, smectites have a larger peak centered near 15 Å while HIMs are centered at 14.2 Å.

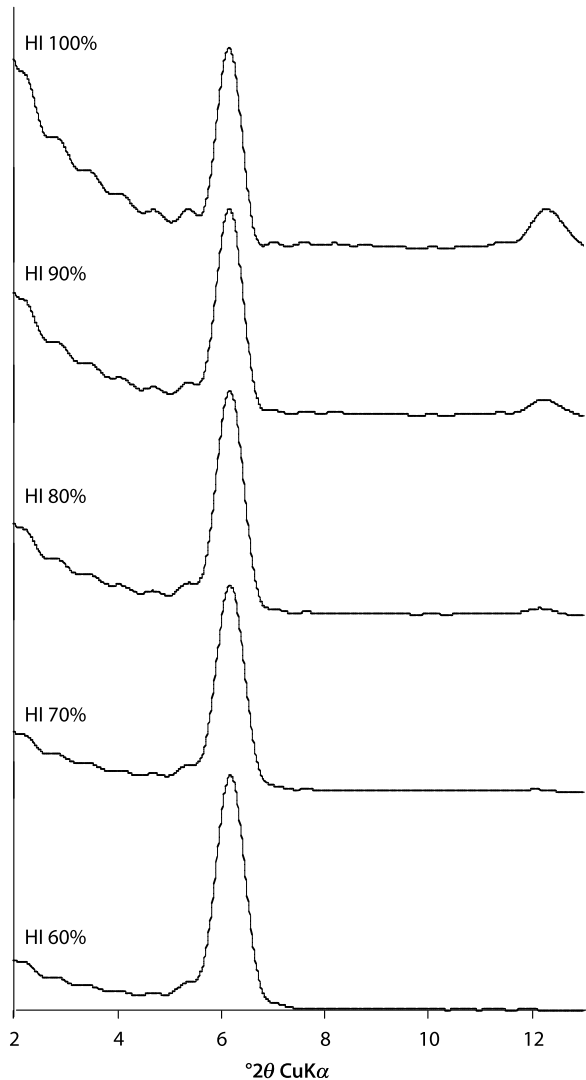
The specific position and intensity of the HIMs are quite well reproduced using NEWMOD calculations (Reynolds 1985) assuming that the “solid solution” assumption can be considered in a first step as an Al-chlorite and expandable layer interstratification. The first question is: how is a pedogenic or Al-chlorite different from a dondassite? Figure A4.1a shows the XRD pattern of an Al-chlorite with an incomplete “gibbsite-like” layer (60%). It is to be noticed that the (*oo2*) and (*oo3*) peak intensities are strongly reduced relative to that of the (*oo1*) peak. The interlayering of the Al<sub>60</sub>-chlorite with a dioctahedral smectite has been used to mimic a HIS mixed layered mineral series. The computed results show that the position and intensity of the (*oo2*) and the intensity of the (*oo3*) vary with the amount expandable layers (Fig. A4.2b,c).

### The Incorporation of Al Ions in the Interlayer Region of HIMs

The origin of the Al-polymers was debated in the eighties because of the evidence of the presence of the  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$  complex ion (or Al<sub>13</sub>) in the solutions as

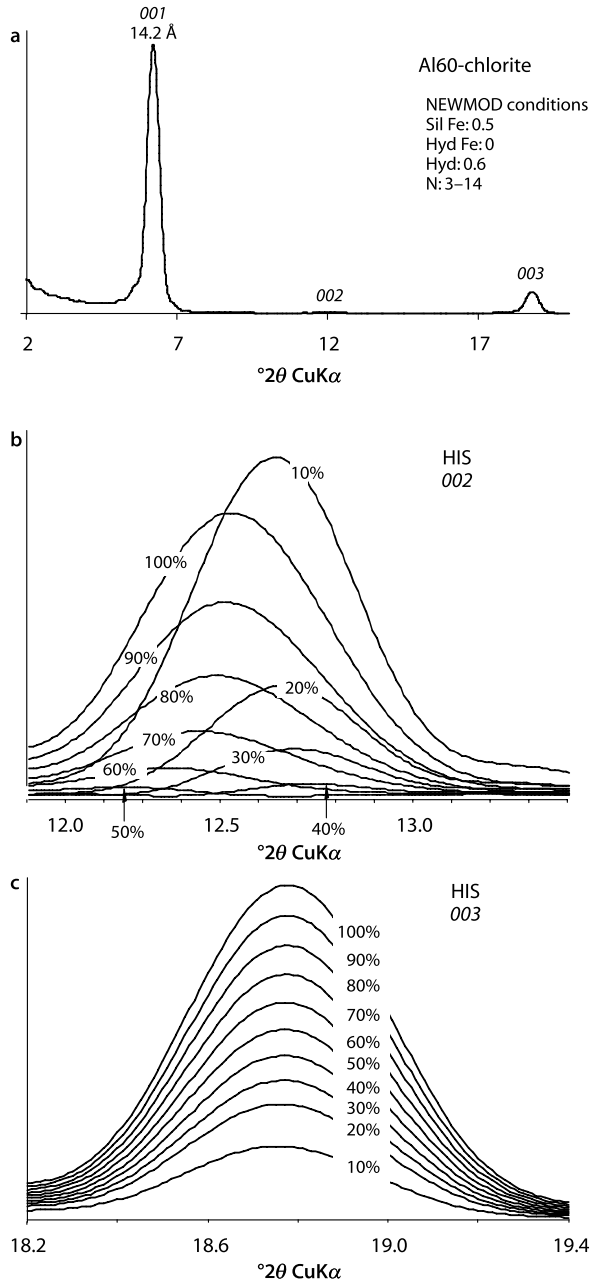


**Fig. A4.1.** Calculated XRD patterns using NEWMOD (Reynolds 1985), CuK $\alpha$ , di-dichlorite, Si/Fe: 0.5, N: 3–14 of HI-chlorites with 100, 90, 80, 70 and 60% of “gibbsite-like” layer



well as in the interlayer zone of experimentally prepared pillared clays (Plee et al. 1985; Schultz et al. 1987; Montargies et al. 1995). The  $\text{Al}_{13}$  complex ion is composed of two hexagonal rings of Al octahedra linked by an Al ion in tetrahedral coordination. However, Bertsch (1987) showed that this complex ion would not readily form in natural environments. He claimed that the HIV and HIS found in soils are not similar to pillared clays prepared artificially. Aluminum ions are not adsorbed as  $\text{Al}_{13}$  complex ion. If the case, the  $d_{001}$  values would vary between 17 and 19 Å (Montargies et al. 1995). This is incompatible with the measured 14.2 Å  $d_{001}$  value typical of HIMs. Besides, there is no evidence of the presence of tetrahedrally coordinated Al ions inside the interlayer

**Fig. A4.2.** Calculated XRD patterns using NEWMOD (Reynolds 1985), CuK $\alpha$ , di-dichlorite, SilFe: 0.5, N: 3–14; **a** di-dichlorite with 60% of the “gibbsite-like” layer (Al<sub>60</sub>-chlorite); **b** series of Al<sub>60</sub>-chlorite-dioctahedral smectite mixed layered minerals from 0 to 100% expandable layers: position and intensity variation of the (002) diffraction peak in the 11.9 to 13.4° 2 $\theta$  range; **c** intensity variation of the (003) peak in the 18.2 to 19.4° 2 $\theta$  range



zone. Consequently, when adsorbed, Al ions should be in the following 6-fold coordination state:  $[Al_n(OH)_x(H_2O)_y]^{x+}$  with  $x + y$  depending on  $n$  and on the type of polymer. Whatever the value taken by  $n$ , the thickness of the polymer formed from 6-fold

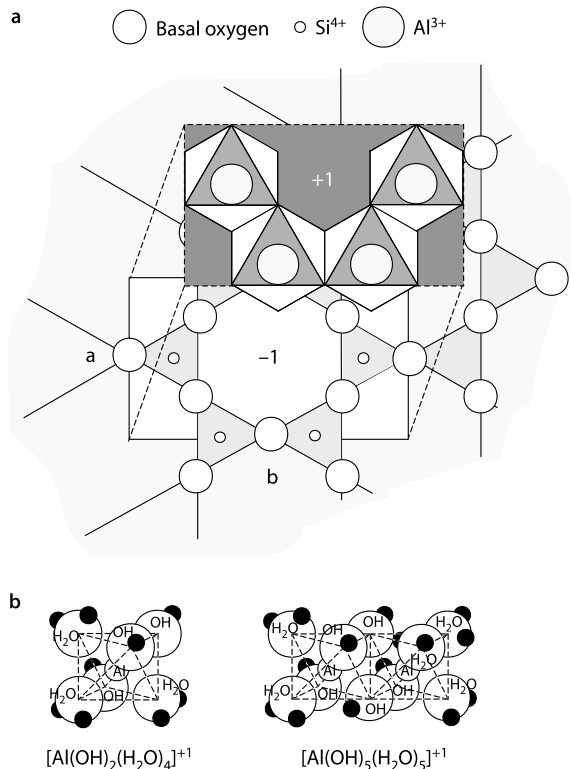
coordinated Al ions must not exceed that of a “gibbsite-like” layer in a chlorite-type structure.

The maximum number of 6-fold coordinated Al ions in the interlayer position which are housed in a unit cell is 4 (Fig. A4.3a). Of course, as they are fixed on isolated negatively charged sites of the 2:1 unit surface, their size is not limited to the unit cell, area. Al ions may form bigger polymers (more than 4 ions) if two conditions are respected:

1. the positive charge of the polymer must remain constant. Thus, the relative proportions of OH groups and water molecules are adjusted to compensate the local negative charge on the 2:1 layer surface (Fig. A4.3b);
2. the maximum number of Al cations in the polymer is ruled by the surroundings of the local negative charge, i.e. the relative location of the negative charges on the 2:1 layer surface (isolated, clustered).

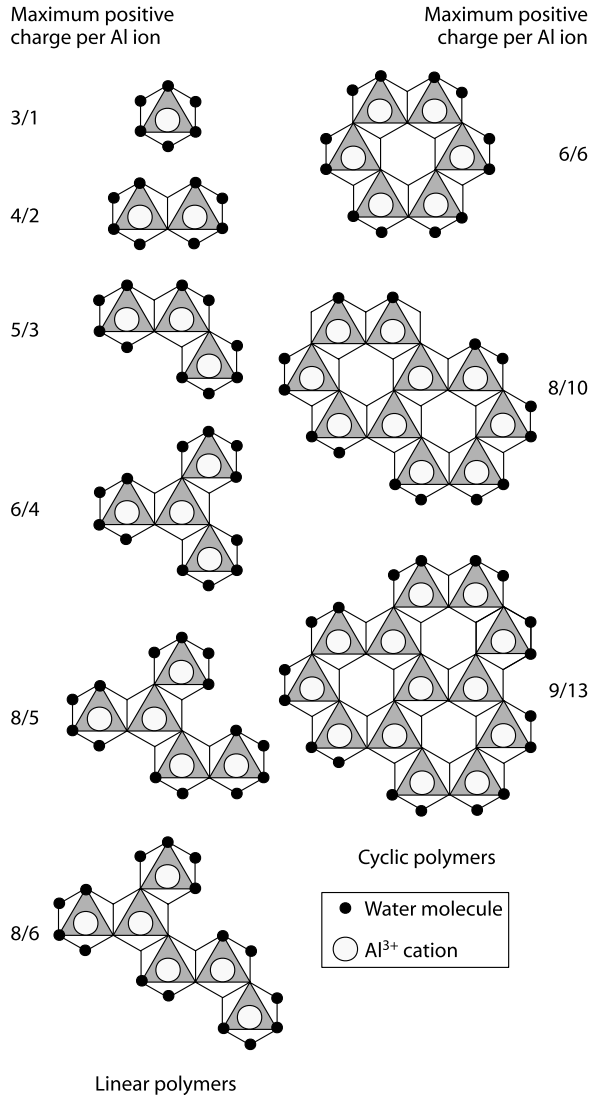
The maximum positive charge per Al ion decreases with the polymerization degree (Fig. A4.4) and is always higher for the linear polymers than for the cyclic ones. In both species, the positive charge is reduced through the replacement of water molecules by OH groups.

**Fig. A4.3.** Position of the Al-polymer in the HIV interlayer region; **a** maximum number of 6-fold coordinated Al ions per unit cell; **b** the 6-fold Al ion coordination may be adjusted by a variable number of OH groups and water molecules



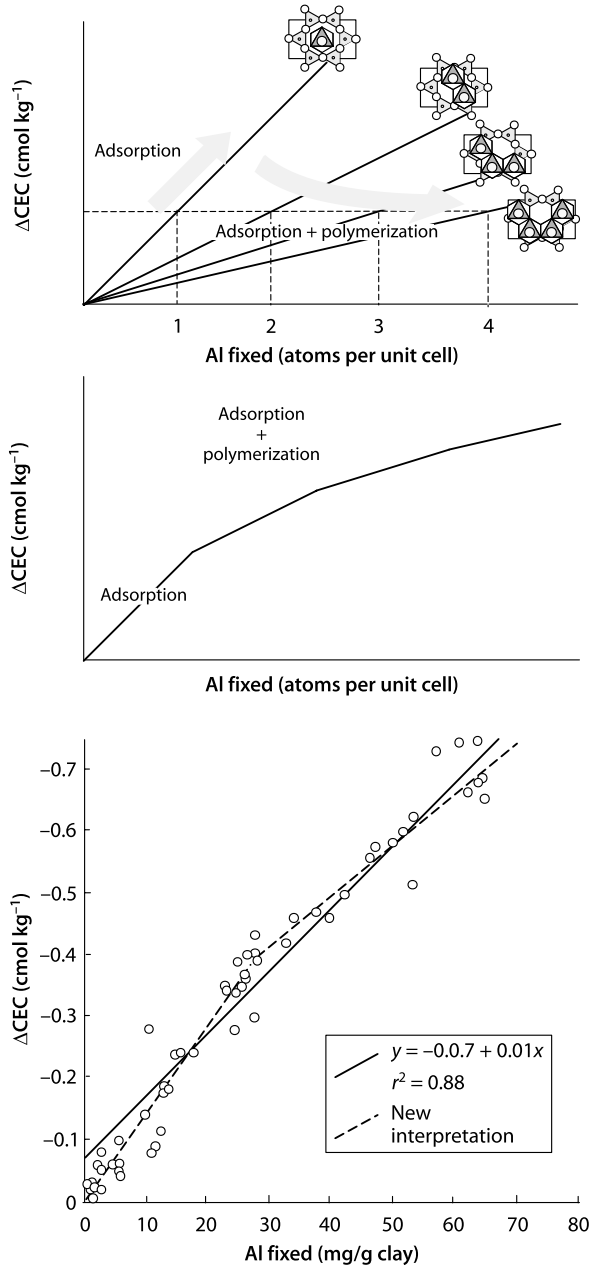
Because of steric constraints, the motion of Al-polymers inside the interlayer space of smectites or vermiculites in natural conditions (1 or 2 water layers) is made possible if their size is comparable to that of hydrated cations. Thus, only monomers or dimers are concerned by adsorption on the exchangeable sites of the 2:1 layer surface. Theoretically, the slope of the linear correlation between CEC and fixed Al would indicate what Al-polymer type is adsorbed at first on the exchangeable sites (Fig. A4.5a). The sharper the slope, the smaller the polymer. It is highly probable that only Al-monomers are concerned by the adsorption process. With increasing Al adsorption,

**Fig. A4.4.** Schematic representation of the relation between the positive charge and the polymerization degree when water molecules are present in the 6-fold coordination of Al ions (maximum positive charge)



the slope of the curve should decrease because some of the adsorbed Al are consumed by the polymerization process (Fig. A4.5b). The higher the charge of the 2:1 layer, the higher the polymerization degree. Thus, two steps should be considered during the

**Fig. A4.5.** Theoretical representation of the CEC decrease vs. fixed Al ion relationships; **a** the adsorption and adsorption-polymerization steps; **b** variation of the curve slope with progressing saturation of the exchangeable sites by fixed Al ions; **c** re-interpretation of the CEC vs. fixed Al relation (data from Barnishel and Bertsch 1989, p. 773)

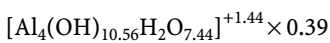


formation of HIMs: (1) Al-monomer adsorption; (2) Al-monomer adsorption and polymerization. This seems to be the case since the  $\Delta\text{CEC}$  versus Al fixed plot is more accurately fitted by two linear relationships than by one as did Barnishel and Bertsch (Fig. A4.5c).

## The Crystallochemical Composition of HIMs

In their review, Barnishel and Bertsch (1989) showed that the OH/Al ration varies between 2.5 and 2.9. They suggested that hydroxy-interlayered vermiculite (HIV) or smectite (HIS) could be considered to form a solid-solution series with the pure end-members consisting of dioctahedral vermiculite or smectite on one end of the series and aluminous pedogenic chlorite on the other end of the series. The negative 2:1 layer charges in HIV and HIS are considered to be partially compensated by a  $[\text{Al}_6(\text{OH})_{15}]^{3+}$  polymerized ring structure. Kirkland and Hajek (1972) presented an average HIV structural formula from the analysis of 12 Alabama soils:  $[\text{Si}_{3.24}\text{Al}_{0.76}]\text{O}_{10}(\text{Al}_{1.56}\text{Fe}^{3+}_{0.24}\text{Mg}_{0.20})(\text{OH})_2[\text{Al}_{1.56}(\text{OH})_{3.79}]\text{K}_{0.24}\text{Ca}_{0.08}$ . Other HIMs compositions have been proposed (see Barnishel and Bertsch 1989). However, all consider that the Al-polymer islands firmly bond the 2:1 layers and hold the interlayer region open in a sort of pseudo-zeolitic structure. Even if, as Barnishel and Bertsch wrote, the chemical composition of these minerals is highly variable, the structural formula above is indicative of the pedogenic chlorite trend: the charge of this 2:1 layer is  $-0.96$  per half unit cell that is near the theoretical value of  $-1$  for  $\text{Si}_4\text{O}_{10}$  encountered in chlorites. To be electrically neutral, the  $[\text{Al}_{1.56}(\text{OH})_{3.79}]$  member should have a positive charge equal to  $+0.56$ . The question is how these Al-polymers are integrated in the vermiculite interlayer region?

Because the  $[\text{Al}_{1.56}(\text{OH})_{3.79}]$  member must have a positive charge equal to  $+0.56$ , any of the polymers represented in Fig. A4.3 should incorporate hydroxyls to reduce their positive charges. Consider for instance that the positive charge is brought by a linear 4-polymer (18 octahedron apices) as shown in Fig. A4.4, then the formula of the  $[\text{Al}_{1.56}(\text{OH})_{3.79}]$  member must be re-written as follows:



What is the crystallographical meaning of the 0.39 (1.56/4) coefficient? If, for simplicity, one negative charge is considered to be located on a single hexagonal cavity, this coefficient is related to the degree of occupation of the cavities: 2.6 for 10 cavities. To be completely isolated each charged cavity must be surrounded by 6 neutral ones. In such a case, the coefficient is equal to 0.14. Consequently, for a 2.6 coefficient, several linear 4-polymers are necessarily in contact making higher polymers.

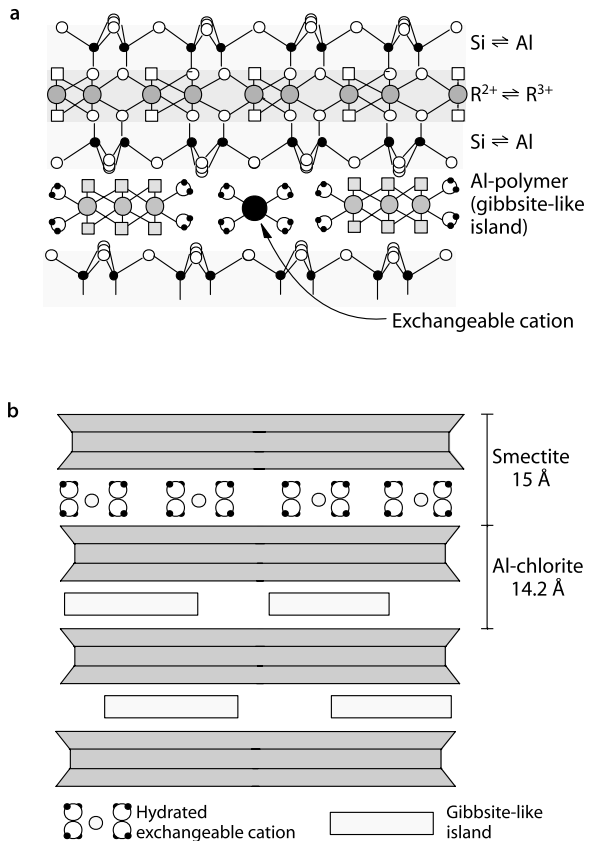
The number of the polymers fixed in the interlayer region of the expandable minerals depends on their size (number of Al) and shape (linear or cyclic) and the layer charge. However, even if the above calculation is only a theoretical exercise, it clearly indicates that a continuous gibbsite-like layer cannot be formed in HIMs because the positive charge becomes negligible when the polymer covers hundreds of unit cells. This confirms the presence of "Al islands" linked to water molecules in the interlayer zone of HIMs.

## The Mixed Layer Model

During the adsorption process, the presence of mixed-site interlayers is unavoidable. Alkali cations and Al ones are surrounded by water molecules. However, it is not clear if the expandability of smectite or vermiculite is reduced at this early stage before Al ion polymerization. On the contrary, as soon as gibbsite-like chains or islands form, the smectite or vermiculite layer loses its expandability (chlorite-like  $d_{001}$  at 14.2 Å). Thus, HIMs can be considered as interlayered minerals as schematically represented in Fig. A4.6. Their expandability depends on the proportions of “chlorite-like” layers in the stacking. It is shown by the shift of the (001) peak in the ethylene glycol solvated state from 17 to 14.2 Å.

Expandable layers collapse to 10 Å after K-saturation heating to 300 °C while the  $d_{001}$  of the non-expandable layers (Al-chlorite) remain at 14.2 Å whatever the treatment. Consequently, after that treatment, the position of the (001) peak of HIMs is intermediate between 14.2 and 10 Å. With higher thermal treatment, the peak shifts toward 10 Å. Concomitantly, it widens and loses intensity. This indicates that the “chlorite-like” layers are deformed inducing defects in the stacking.

**Fig. A4.6.** The mixed-layered model for the interpretation of HIMs XRD patterns; **a** the “gibbsite” interlayer is discontinuous and hydrated exchangeable cations are still present; **b** schematic representation of the stacking of expanding and non-expanding layers in HIMs



We still ignore what is the proportion of fixed Al necessary for a given layer to lose its expandability and behave like a chlorite. Fortunately, this data is not absolutely necessary for a first approach of the interpretation of HIMs XRD patterns because the fixed Al proportions influence only the intensities of the (002) and (003) peaks and not their position. Thus, the variability of the HIS and HIV described in natural soils can be approximated by series of 17–14.2 Å and 16–14.2 Å randomly ordered mixed layers respectively.

## Conclusion

The mixed-layer model is the most appropriate one to explain how the “partial swelling” of HIMs leads to  $d_{001}$  values between 14.2 and 17 Å. Consequently, the difference between HIS and HIV is related to the number of 14.2 Å non-expanding layers (chlorite-like units) in the mixed layered minerals. In other words, HIS and HIV should not be considered as different mineral species but rather as mixed layered minerals of different Al polymerization degree.

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# Phase Diagrams Applied to Clay Mineral Assemblages

## Fundamentals

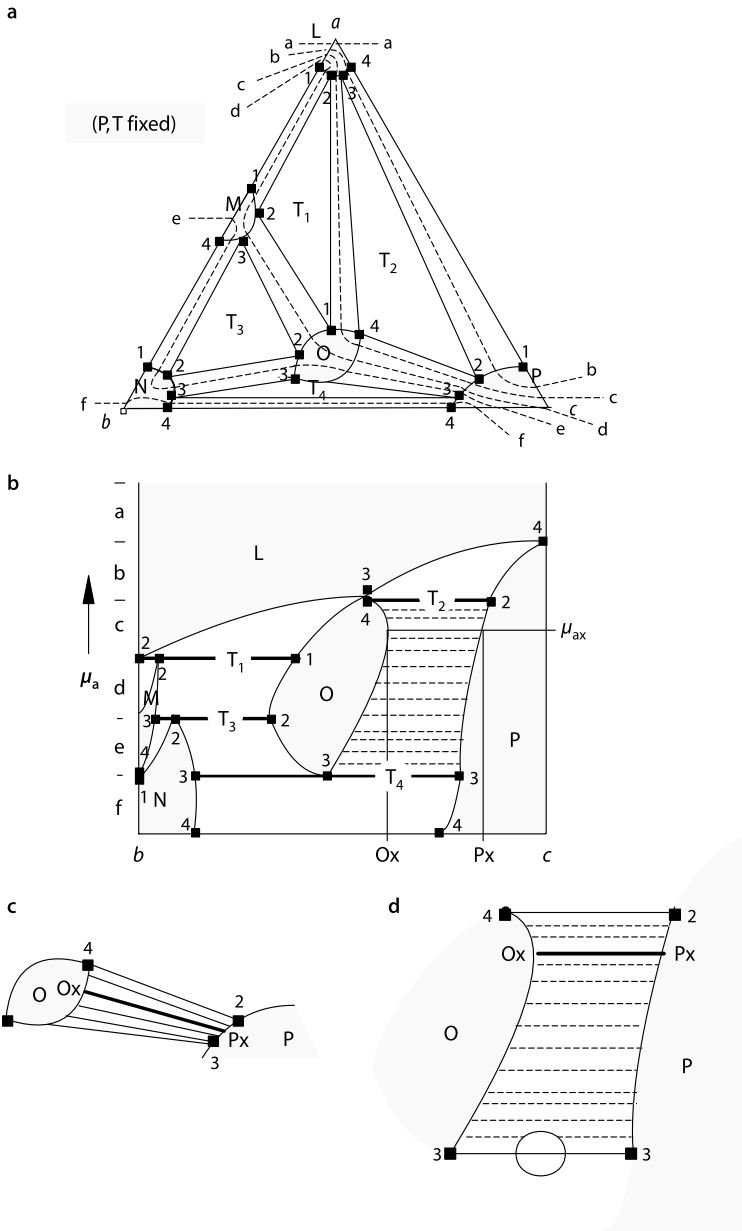
By definition, phases are said to be in equilibrium when the chemical potential(s) of the mobile element(s) is (are) the same in each of them. An equipotential line is then the geometrical location of a fixed value of the chemical potential of an element considered in the chemical projection used (Korzhinskii 1959). It may be visualized as paths leading from one phase to another with which it is in equilibrium. Each equipotential plotting must obey two strict rules:

1. to describe only once each three-phase assemblage;
2. never be crossed twice by any line passing through the vertex of the triangle representing the mobile elements.

A third rule requires that all two- and three-phase assemblages of the diagram be described without omission. A tie line between two phases of a triangular diagram is a portion of equipotential line. The number of equipotential lines necessary to describe any system is equal to the number of three-phase assemblages plus two. Details of the proof are given in Meunier and Velde (1986).

Several types of phase diagrams are commonly used for the study of assemblages of secondary mineral phases in weathering environments according to whether the physicochemical systems in which they are formed are more or less open. For instance, during weathering, a sequence of secondary minerals is formed in granites. This sequence is controlled by the increase of the porosity, i.e. the increasing quantity of fluids. Thus, mineral reactions are considered to occur in three different microsystems:

- *closed microsystems (dead ends)*: no mobile component. The mineral assemblages are determined by the rock composition ( $X$ ). If the simplified chemical system considered is reduced to three components or groups of components a-b-c, the phase diagram can be constructed in a triangular projection (Fig. A5.1a). The phases represented by points are interconnected by tie lines. Three-phase assemblages delimit sub-triangles;
- *partially open microsystems (>1  $\mu\text{m}$  wide microcracks)*: only one component out of three is mobile (a, for instance). The mineral assemblages depend on the chemical potential of this component in fluids and on the rock composition ( $\mu_a$ - $X_{b-c}$ ). An orthogonal potential-composition representation is used (Fig. A5.1b,c). Phases are represented by vertical line segments and three-phase assemblages by horizontal line segments;



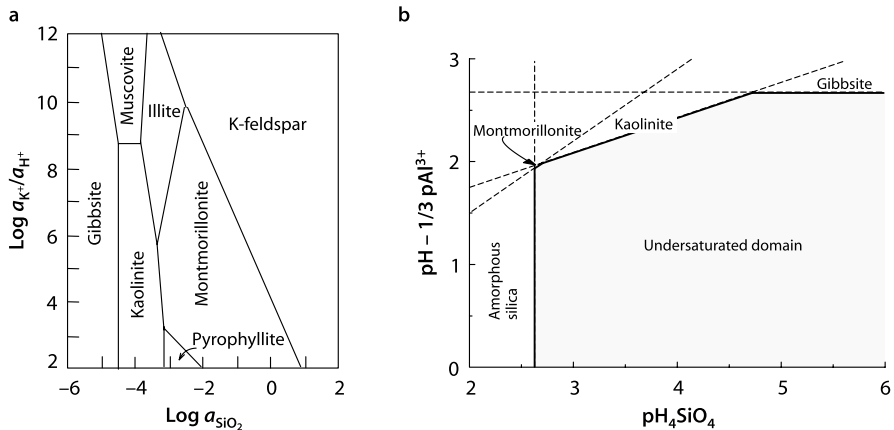
**Fig. A5.1.** Representation of equilibria between solid solutions in phase diagrams; **a** system without mobile component; the equilibria between solid solutions correspond to the two-phase fields covered by the various equipotential lines; **b** system with one mobile component; **a** the equilibria between solid solutions are defined by the chemical potential  $\mu_a$ ; **c** detail of *Part a* representing the equilibrium between solid phases for the phases *O* and *P* in the system without mobile component; **d** detail of the equilibrium between the same phases in the system with one mobile component

- *totally open microsystems (large fluid pathways)*: only one element remains inert, the two others are mobile (a and b, for instance). The mineral assemblages essentially depend on the chemical potential of the two mobile components ( $\mu_a - \mu_b - X_c$ ). This last type of diagram is readily calculated using thermodynamic parameters determined for each mineral phase (Fig. A5.2a). Phases are represented by surfaces, and three-phase assemblages by points intersecting these surfaces.

## Clay Minerals: The Stable Phases at Surface of the Earth

The very Earth's surface conditions may be summarized as follows: presence of water and low temperature. A great number of minerals form in these conditions: carbonates, phosphates, sulfides, sulfates, oxides, hydroxides, silicates. Among them, the clay minerals are the most widespread over the world because they form typically at the rock-water or rock-atmosphere interfaces. They are more or less consciously considered as representative of the very surface of the Earth because they have a determinant role in soils that is to say in our vital reserves. This leads to a fundamental question: why do clay minerals form instead of other silicates in the surface conditions? Thermodynamics may help us to find an answer to that question.

As soon as the difficulty to get a coherent thermodynamical parameters (mainly the standard free energy of formation) for clay minerals has been overcome, pioneer works showed that montmorillonite, kaolinite and gibbsite are stable phases at 25 °C and 1 atmosphere (Hess 1966 and references therein). A typical phase diagram is shown in Fig. A5.2a (from Garrels 1984). It gives a general picture of the stability domain of clay minerals compared to feldspar and mica: low  $a_{K^+}/a_{H^+}$  ratio, low  $a_{SiO_2}$ . Obviously, the low values of these parameters are related to the presence of water (dilution effect, increasing proton concentration). This fundamental aspect has been enhanced



**Fig. A5.2.** The thermodynamic stability of clay minerals at 25 °C, 1 atmosphere; **a** phase diagram in the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$  system (from Garrels 1984); **b** solubility diagram of some clay species (from Kittrick 1971)

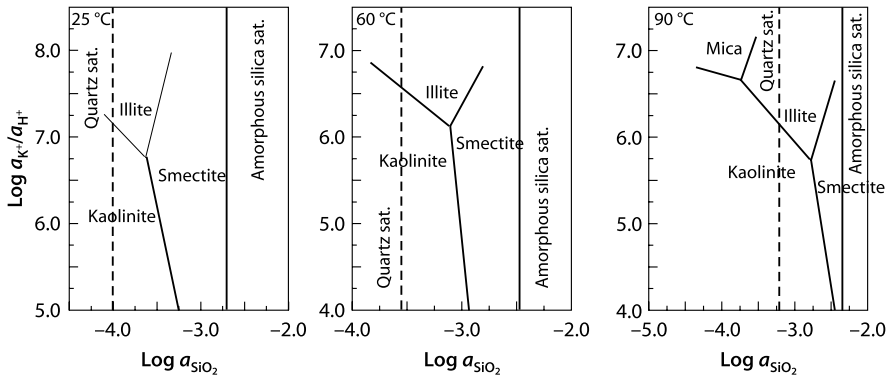


Fig. A5.3. Phase diagrams in the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$  system showing the presence of a mica-illite tie-line at elevated temperature (from Sass et al. 1987)

by Kittrick (1971) who conducted dissolution experiments in order to investigate the equilibria between clay minerals and the solution of the soils. He showed that, only one chemical activity of a component controls the equilibrium of a given soil mineral with the soil solution; the other components being controlled by associate minerals;  $\text{H}_4\text{SiO}_4$  activity being kinetically controlled (Fig. A5.2b).

Many natural solutions have been analyzed during the last four decades. Garrels and Mackenzie (1972), Drever (1982), Stumm (1992) among others, constantly showed that in many natural waters, the upper limits of dissolved silica on one hand and alkali on the other hand are far less than saturation with amorphous silica or mica respectively. Most of the water compositions in granitic areas are on the kaolinite/smectite tie-line (Garrels 1967; Drever 1982). In the same way, Karathanasis et al. (1983) showed that the solutions extracted from ultisols are over-saturated with respect to kaolinite and in equilibrium with intergrade vermiculite (HIV). In a summary, the Earth surface conditions favor the formation of clay minerals preferentially to other phyllosilicates.

The best example of the specificity of clays as mineral phases typical of Earth's surface conditions is the stability of illite rather than mica. Illite is a mineral phase which can be considered as a low-temperature equivalent of mica (see Meunier and Velde 2004 for a review). The dissolution experiments conducted by Sass et al. (1987) shows that a mica-illite tie line appears at 90 °C (Fig. A5.3). Below this temperature, no mica phase is stable.

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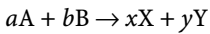
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# Kinetics

## Fundamentals

Mineral reactions are a response to changes in the system conditions. They make possible the change from a disequilibrium state to an equilibrium state with the required conditions. Kinetics deals with the reaction rate. Consider, in a closed system with constant volume, a reaction of type



$a, b, c, d$ : concentrations of minerals A, B, C, D respectively (simplification of normal symbols  $[a], [b], [c], [d]$ ).

The rate of the mineral reaction is measured by the negative variation in the concentration of the reactants A or B

$$-\frac{da}{dt} \quad \text{or} \quad -\frac{db}{dt}$$

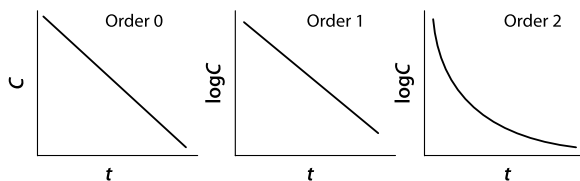
or the positive variation of the products X or Y as a function of time

$$+\frac{dx}{dt} \quad \text{or} \quad +\frac{dy}{dt}$$

Units are concentrations divided per time:  $\text{mol dm}^{-3} \text{s}^{-1}$  or  $\text{mol l}^{-1} \text{s}^{-1}$  or  $\text{M s}^{-1}$ .

The reaction rate has several mathematical expressions according to whether it is constant or varies with time. These expressions are graphically presented in Fig. A6.1.

**Fig. A6.1.** Variation in concentration as a function of time for order reactions  $n = 0, n = 1$  and  $n > 1$



**Zero-order reaction.** Concentration varies proportionally to the reaction time:

$$-\frac{da}{dt} = k \quad \text{or} \quad a = a_0 - kt$$

**First-order reaction.** The decrease in concentration becomes lower with time. Concentration tends asymptotically towards zero. The rate for any value of time is given by the negative slope of the curve concentration as a function of time:

$$-\frac{da}{dt} = ka$$

Rearranging and integrating the equation of time  $t = 0$ , for which the initial concentration is  $a_0$ , into the time  $t$ , for which the initial concentration is  $a$ , yields:

$$-\frac{da}{a} = kdt$$

$$-\int_{a_0}^a \frac{da}{a} = \int_0^t kdt$$

$$\ln a - \ln a_0 = -kt$$

$$\ln \frac{a_0}{a} = kt$$

$$a = a_0 e^{-kt}$$

A first-order reaction is recognizable from an exponential decrease in concentration as a function of time.

**Order reaction ( $n > 1$ ).** The order reactions ( $n > 1$ ) are expressed as follows:

$$\frac{da}{dt} = -ka^n$$

$$\frac{1}{a^{n-1}} - \frac{1}{a_0^{n-1}} = (n-1)kt$$

## The Fick's Laws

The diffusion process is triggered by the atom or molecule thermal agitation. When a difference of chemical potential is established across an interface between solids and/or

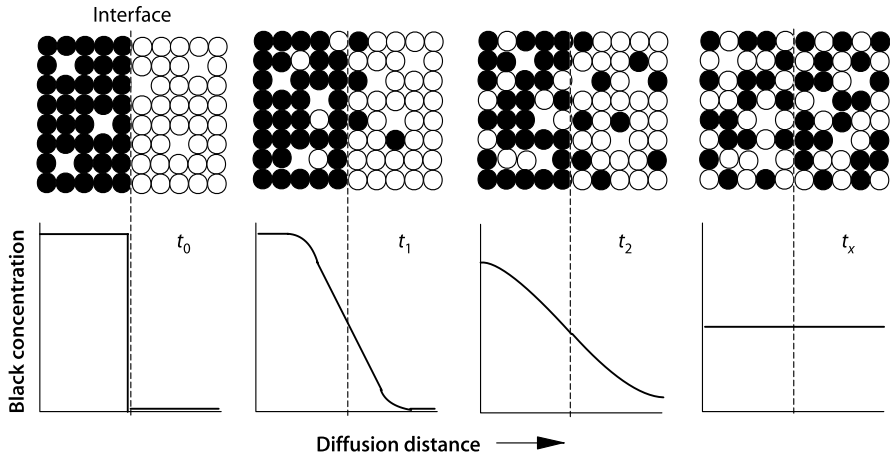


Fig. A6.2. Schematical representation of the diffusion process of black and white components through an interface between two solids

liquids, the probability of the atom or molecule movement is increased in the reverse direction of the potential gradient (high to low potential zones). The flux (balance of the migration through the interface) is entertained till the gradient exists (Fig. A6.2). In absence of a gradient, the thermal agitation persists but the flux is equal to zero. The number of atoms or molecules which migrate across the interface is similar in the two opposite directions.

The evolution of the potential (or concentration) with time is given by the first Fick's law which introduces two interdependent fundamental parameters: the flux and diffusion coefficient. Figure A6.2 shows the diffusion of black elements (A) into the white ones (B) and conversely. Considering the diffusion of A into a matrix of B, the 1st Fick's law gives the flux equation:

$$J_A = -D_A \frac{dC_A}{dx}$$

$J_A$ : flux of atoms through a unit area section perpendicular to the potential gradient (mol or at.  $m^{-2}s^{-1}$ )

$D_A$ : diffusion coefficient of component A in a matrix of component B ( $m^2s^{-1}$ )

$dC_A/dx$ : concentration gradient of component A at the interface ( $molm^{-3}$ )

The negative sign indicates that the flux is directed oppositely to the concentration gradient.

The 2nd Fick's law gives the diffusion rate equation:

$$\frac{dC_A}{dt} = D_A \frac{d^2C_A}{dx^2}$$



The diffusion coefficient ( $D_A$ ) depends on the temperature. The relation is an Arrhenius equation type:

$$D_A = D_0 \exp\left(-\frac{E_a}{RT}\right)$$

$D_0$ : matrix dependent constant ( $\text{m}^2\text{s}^{-1}$ )

$E_a$ : diffusion activation energy ( $\text{Jmol}^{-1}$ )

R: gas constant ( $8.31441 \text{ Jmol}^{-1}\text{K}^{-1}$ )

The deduction of the second from the first law imposes that mass is conserved. The distance of penetration of A into the B matrix or conversely is proportional to the square root of time:

$$L \equiv \sqrt{D_A t}$$

### Suggested Reading

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