6.1 Atmospheric and Seawater Weathering

6.1.1 Introduction

Weathering is defined here as all the interactions occurring between fluids and rocks at low temperature. It takes place at the interfaces between continents and atmosphere \((0 < T < 25 \, ^\circ C)\) and between oceanic basalts and seawater \((-5 < T < 4 \, ^\circ C)\). The penetration of meteoric or sea fluids into rocks causes destabilisation of their initial mineral components and favours the formation of new hydrated species. The chemical balance of these reactions is expressed as the loss of some elements that pass into solution whereas the most insoluble ones concentrate in solids.

Complex mineral or organo-mineral reactions take place at the interface between rock substrate and atmosphere: the meteoric alteration of rocks (weathering) and the formation of soils (pedogenesis). These are the two processes transforming the coherent rocks into a loose material partly composed of clay minerals. Like any interface, the weathered rock (alterite) and the soil form a polarised domain:

- polarisation from bottom upwards: the weathering patterns are rather governed by the progressive fading of the petrographic features of the parent rock,
- polarisation downwards: soils invade the underlying rock over increasing thicknesses as functions of time. They depend on climate (rain, heat) and biological activity.

The mechanical stability of these two types of loose rocks depends on topography. Significant mass movements take place in surface horizons, even on low slopes, whereas deep horizons mostly remain in structural continuity with their parent rock. Therefore, the weathering profiles are often separated from the soil by a discontinuity marked by pebble beds. Most of the time, soils do not form a geochemical continuum with the underlying alterations. For this reason, these two loose formations will be discussed separately here.

Clay minerals are formed in surface environments by weathering of pre-existing minerals that have crystallised under very different temperature-
pressure-fluid composition conditions either in magmatic and metamorphic environments such as feldspars, pyroxenes, amphiboles, micas, chlorites and so on . . . or in sedimentary environments such as glauconites, sepiolites, zeolites etc . . . Any weathering process comprises three stages:

1. dissolution of the primary minerals that are out of their stability field,
2. transfer of the chemical elements so released from the dissolution zones to the precipitation zones (fluid circulation or/and diffusion),
3. precipitation of secondary minerals: clays, Fe–Mn oxyhydroxides . . . (nucleation, crystal growth). Oxides, hydroxides and oxyhydroxides of iron and manganese form a complex mineral family hereafter referred to as oxyhydroxides (Bigham et al. 2002; Dixon and White 2002).

Each stage is controlled by local physicochemical conditions. The weathering rate is determined by the slowest of the three stages.

When clays replace a primary mineral whose crystal structure is not that of phyllosilicates, it is called neogenesis. When they replace a phyllosilicate (biotite, muscovite, chlorite, serpentine), the alteration process may be either a neogenesis or a layer-by-layer transformation. The replacement can take place without any change in the volume or form of the parent minerals (pseudomorphosis); in such a case, the original structure of the rock is conserved. If not, by contrast, the original structure of the rock can be totally erased. The purpose of this chapter is first to survey as simply as possible the fundamental processes governing the formation of clay minerals in weathering conditions. Then, the main natural environments in which these processes take place will be presented. Subsequently, the crystallization sequences of clay minerals will be connected to the major types of alterites. The solutions recovered from springs and rivers retain the geochemical signature of the alteration profiles they have crossed. Only those data that help to understand the mineral reactions will be used here. The bases of the analysis of natural waters can be found in Drever’s book (1982).

6.1.2
Mechanisms of Formation of Clay Minerals

6.1.2.1
Dissolution of Primary Phases

Definitions
The literature contains a number of ambiguities regarding the concepts of congruent and incongruent dissolution. Indeed, the incongruent dissolution is generally considered to be typical of primary minerals yielding secondary minerals through weathering: plagioclase + solution A → kaolinite + solution B. In fact, this reaction consists of the congruent dissolution of plagioclase followed by the crystallisation of kaolinite. These terms will be used here according to the definitions suited to the petrographical observations:
congruent dissolution  incongruent dissolution  dissolution + cristallisation

Fig. 6.1a–c. Definition of the terms used in the text. a) Congruent dissolution. b) Incongruent dissolution. c) Dissolution and precipitation

- **congruent dissolution**: the crystal is destroyed in such a way that all the elements enter the solution with the same stoichiometric coefficients as those of the solid. The dissolution first takes place at the most energetical sites (vertices, edges, crystal defects on faces), then spreads in the form of corrosion zones formed by coalescence of the dissolution sites (Fig. 6.1a);

- **incongruent dissolution**: the crystal is partially destroyed so that the elements entering the solution do not have the same stoichiometric coefficients as those of the solid. Generally an alkali depleted amorphous material (gel) remains in the dissolved sites. Besides, another mineral particularity may influence the composition of dissolving solutions on a larger scale. Indeed, minerals whose composition may vary in large solid solution domains exhibit frequently a heterogeneous crystal structure: preferred zones are affected by the dissolution while other ones are spared (Holdren and Spyers 1986). The dissolution then spreads through preferred corrosion of some sectors of the parent mineral such as parts of the twin or of the chemical zonation (Fig. 6.1b);

- **dissolution and precipitation**: the dissolution can be congruent or incongruent; in both cases, if the solutions reach the required oversaturation, the nucleation and growth of secondary minerals are triggered. The corrosion zones are rarely empty of solid matter (porosity); they incorporate most often a mixture of parent mineral debris and newly-formed clays (Fig. 6.1c). The nucleation of secondary phases in altered silicates is made easier by structural connections with the parent mineral crystal lattice (Eggleton 1986).

**Chemical Potential Gradients**
Meteoric fluids essentially contain H₂O+CO₂ and accordingly are acidic. After more or less long paths through soils and rocks, they reach the open air in springs, and are subsequently drained towards rivers and streams or stored in water tables. Waters from springs, from rivers or ground waters are generally
diluted solutions (> 10 mg l\(^{-1}\)) whose composition is the result of interactions with the minerals encountered in the rocks (see Drever 1982).

Meteoric fluids penetrate the fissures of rocks and microfissures of minerals. The narrower the openings, the more slowly they flow. Therefore, their interactions with minerals, hence their composition and concentration, can vary from one point of the country rock to the other. Chemical gradients appear between fluids and the minerals they soak. These gradients govern the dissolution and crystallisation processes of clay minerals.

At the contact of the basaltic deep-sea floor, the chemical properties of seawater are nearly constant. As the water mass can be considered as infinite, the chemical potential gradients related to the interactions with rocks are maintained over very long periods. This explains that alterations have macroscopic effects, despite the very low temperature.

**High gradients (diluted fluid):** they generally lead to a congruent dissolution of minerals. Edges and vertices of crystals become blunt. Dissolution pits appear at the emergence of the screw or edge dislocations on their faces. The minerals become porous; the intercrystalline joints open (weakening of bonds), bringing about the shedding of crystals. The rock becomes friable and loses its mechanical coherence. Dissolved chemical elements are leached out by waters flowing in the connected pores. At the end of the process, only the less soluble minerals remain: Fe- and Al-oxides and hydroxides. The parent rock structure is faded out. Such gradients occur in zones where fluids are constantly renewed by rapid flows (surface horizons of intertropical soils; network of highly permeable fractures).

**Moderate gradients:** they bring about the new formation of clays often associated with Fe-hydroxides in the dissolution zones of the minerals. A heterogeneous microcrystalline matrix (plasma) composed of newly-formed minerals and fine debris detached from the parent minerals is formed. These gradients occur in arena-rich domains where the rock or the soil retains its original structure but becomes more and more loose.

**Low gradients (concentrated fluids):** these gradients occur in narrow microfissures where the fluids flow so slowly that they approach equilibrium with the minerals they soak. The dissolution zones are totally sealed by growing secondary minerals. These zones appear as pseudomorphoses, with illite replacing K-feldspars and saponites replacing pyroxenes.

**The Mechanism of Dissolution**

The dissolution process comprises five stages, whatever the mineral involved (Fig. 6.2a):

1. migration of the solvent through the solution up to the mineral surface;
2. adsorption of the solvent on the surface;
3. migration of the solvent into the crystal lattice up to the bonds it will break;
4. break up of the bonds and release of the ions from the lattice;
5. migration of the ions from the lattice to the solution.
Fig. 6.2a,b. Dissolution. a) Schematic representation of the five stages of the dissolution process. b) Theoretical states of the chemical gradients and dissolution rates for a diffusion- or surface-controlled system. C: concentration of a chemical element; C_{surf}: concentration of the element at the mineral surface; C_{sol}: concentration of the solution at an infinite distance from the mineral surface.
The rate of the whole process is controlled by the rate of the slowest stage (Fig. 6.2b). When dissolution is controlled by the diffusion of the dissolved elements in the solution, the concentration of the latter ranges between a maximum value at the mineral surface and a minimum value (infinite concentration state). The dissolution rate decreases as a function of time whereas the concentration of the dissolved elements increases. When dissolution is controlled by mechanisms of detachment of elements at the mineral surface, no concentration gradient can occur; the solution composition is controlled by the dissolution rate of the elements in the solid. The rate remains constant during the whole dissolution process. Under weathering conditions, the bond breaking stage at the mineral surface is slower than the migration rate of ions in the solutions.

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 quartz in water is a step-by-step process and involves the adsorption of water molecules and the hydrolysis of Si–O bonds (Dove and Crerar 1990; Fig. 6.3a). The dissolution is controlled by the coordination states of the chemical components at the surface of solids. Berger et al. (1994) thus show that the alteration of the basaltic glass takes place following two processes with different rates:

1. an 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.

Berger (1995) further shows that the rates of these two processes are similar to the dissolution rates of glass in open state (diluted solutions) on the one hand and of crystallised silicates (quartz, albite, anorthite, K-feldspar) on the other hand (Fig. 6.3b). 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 kaolinite 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 \( (E_a = 0.51 \pm 8 \text{ kJ mol}^{-1}) \). The activation energy of the smectite dissolution is very close to that of the tetrahedral sheet of kaolinites \( (E_a = 0.52 \pm 4 \text{ kJ mol}^{-1}) \).

6.1.2.2

Neogenesis

Neogenesis (new formation) is considered here as the result of two processes:

1. direct precipitation within the pores or fractures from the solutions (replacement of voids). This is the case of kaolinite precipitating in the dissolution pits of feldspars in altered granites.
Fig. 6.3a,b. Mechanism of dissolution. 

a) Dissolution of quartz (after Dove and Crerar 1990, modified): 1) Adsorption of water molecules on the crystal surface; 2) Break up of a Si–O bond (hydrolysis) and adsorption of another water molecule; 3) Repetition of the adsorption – hydrolysis process; 4) Release of a Si$^{4+}$ ion from the crystal structure in the form of a H$_4$Si$_4$O$_{10}$ molecule into water.

b) Arrhenius diagram showing the dissolution rates of basaltic glasses and silicates (after Berger 1995)

2. crystallisation of clays by pseudomorphosis of primary minerals other than phyllosilicates. Neogenesis mostly results in the partial or complete replacement (pseudomorphosis) of these minerals. This is the case of saponite replacing olivines.

**Direct Precipitation (Weathering Of Feldspars)**

Alkaline feldspars (orthoclase, microcline, sanidine, albite, anorthoclase) alter under surface conditions thus becoming more and more porous. As pores grow bigger and more numerous, they cluster into genuine caries partially filled with neogenetic clay minerals mixed with fine debris of the parent mineral. Porous “plasma” is formed, which constitutes a favoured pathway for the penetration
Fig. 6.4. Schematic representation of a dissolution pit in an orthoclase. A phyllosilicate (illite) starts crystallising in an amorphous substance (gel), partially filling the pit (after Eggleton and Busek 1980).

of fluids. In the very first stages of this destruction, amorphous silicate material (gel) and/or fine particles of phyllosilicates such as illite (Fig. 6.4) can be observed in some of the pores (Eggleton and Busek 1980; Eggleton 1986). Smectite appears in stages in which weathering is the most intense (Banfield and Eggleton 1990). Plagioclases (albite-to-anorthite series), which are even more sensitive to weathering than K-feldspars, frequently show the precipitation of kaolinite or halloysite in the dissolution pores.

**Preservation of the Chains of Tetrahedra (Pyroxenes, Amphiboles)**

Studies of altered pyroxenes by high-resolution electron microscopy (Eggleton and Boland 1982) have revealed the relationships between the crystal lattices of the primary mineral and those of its secondary products (Fig. 6.5). The phyllosilicates produced by weathering (talc and trioctahedral smectite) appear as the result of a topotactic growth because their crystal lattice is strongly oriented by that of pyroxene. This type of growth is very common in the biopyriboles described by Veblen and Buseck (1980). Lattice coherence favours a more rapid growth than that of totally reconstructed secondary phases.

**6.1.2.3 Transformation of Pre-Existing Phyllosilicates**

**Transformation of Micas**

Experimental studies of mica weathering have been extensively devised in the 1960s to answer an essential question: how was potassium, a vital element for the growth of plants, released or fixed in soils? These studies focused on the two types of micas most commonly found in rocks: biotites (trioctahedral ferro-magnesian mica) and muscovites (aluminous, dioctahedral mica). These two minerals were subjected to chemical attacks by organic acidic solutions
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Fig. 6.5. Growth of talc or tetrahedral smectite in the altered zones of an enstatite (after Eggeleton and Boland 1982). This type of transformation is said to be topotactic because the crystal lattice of pyroxene is in structural continuity with those of its alteration products (Robert and Pédro 1972) or inorganic acidic solutions (Scott and Smith 1966). Potassium is much more readily extracted from trioctahedral minerals than from their dioctahedral homologues (Fig. 6.6a). Newman and Brown (1966) have shown that the destruction process of mica occurs in several stages:

- replacement of K$^+$ by Na$^+$
- loss of those (OH)$^-$ released after the loss of K$^+$ ions. The charge of the 2:1 layer decreases, which entails the loss of additional K$^+$ ions.
- oxidation of the ferrous iron: $4$Fe$^{2+}$ + 4 structural (OH)$^-$/O$_2$ → $4$Fe$^{3+}$ + 4 structural O$^{2-}$ + $2$H$_2$O.
- loss of bivalent cations in octahedral position such as Mg$^{2+}$.

Generally, the progressive extraction of K$^+$ ions from the interlayer sheet causes the mica to transform into vermiculite then into smectite. The charge density decreases, bringing about the aperture of the interlayer zones, which are then able to adsorb polar molecules (water or organic molecules). The charge decrease is due to a significant rearrangement of the tetrahedral and octahedral sheets of the 2:1 layers, although the general appearance of the original mica crystal seems unchanged. HERTM observations confirm that vermiculite layers are inserted inside the mica ones (Jeong and Kim 2003; Mukarami et al. 2003). The vermiculitisation progresses from the edges of the biotite crystals (Fig. 6b).

These experiments that simulate the destruction of micas in soils have an additional interest. Indeed, alteration is used as a selective probe of the crystal structure at the beginning of the destruction process of mica. The first stages of the reaction forming regularly ordered mixed-layer minerals show that every second layer in the original mica fixes less strongly the interlayer potassium than its neighbour (Boettcher 1966). These data known since the early sixties have not been fully exploited with this view. They deserve new consideration.
The transformation of biotites differ according to the composition of the waters percolating into granitic rocks (Meunier 1977). In highly diluted solutions, biotites are transformed into di- and trioctahedral vermiculites + kaolinite + Fe-hydroxides assemblage (Fig. 6.7). If the solutions become charged with Ca$^{2+}$ ions during their percolation in the sedimentary rocks above granite for instance, they are transformed into a mica-trioctahedral vermiculite regularly ordered mixed layer + kaolinite + Fe-hydroxides.
Transformation of Chlorites

Chlorite weathering leads to the formation of vermiculite through a series of mixed-layer minerals. The most noteworthy step of this alteration is the formation of a vermiculite – chlorite mixed layer with a corrensite-type structure. Many attempts at reproducing experimentally these sequences observed in nature have been carried out: deshydroxylation of chlorite at 600 °C then acidic dissolution of the brucite-like sheet (Ross and Kodama 1974) or solubilisation of Fe by dithionite (Makumbi and Herbillon 1972). The formation of corrensite shows that the original structure of chlorite (IIb polytype) is retained in a weathering process where every second layer is transformed. Like for micas, weathering could be used as a probe showing heterogeneities of the crystal structure of chlorites.

It is generally accepted that “vermiculitisation” of chlorites is the result of the oxidation of Fe\(^{2+}\) cations. The change of valency has two effects: (1) in the octahedral sheet of the 2:1 unit, \([Fe^{2+}OH]^+ \rightarrow [Fe^{3+}O]^++ H^++ e^-\), and (2) loss of Fe\(^{2+}\) and Mg in the brucite-like sheet. In nature, it seems that the “vermiculitisation” of chlorite rather starts with the loss of a part of the Fe\(^{2+}\) cations of the 2:1 unit because the Fe\(^{3+}\) content does not increase significantly from chlorite to the corrensite-type regularly ordered mixed-layer mineral (step 1) then to vermiculite (step 2). The Mg cations are widely leached out.
from the octahedral and brucite-like sheets, leading to a relative enrichment in Si and Al (Proust et al. 1986). If step 1 is a layer-to-layer transformation, step 2 is a dissolution – crystallisation process.

**Transformation of Kaolinite**

Halloysite and kaolinite have the same chemical composition: Si$_2$O$_5$(OH)$_4$ for the half unit cell (1:1 layer). Nevertheless, halloysite differs in that water molecules occupy the interlayer position. Most often, halloysite layers have the property to roll up into cylinders. These two minerals are generally described in soils developed on volcanic ashes or in tropical soils. Halloysite is formed in environments where fluids have a high ionic concentration, conditions that favour disorder and fast growth (Giese 1988). The numerous crystal defects favour the hydration of the 1:1 layers. Kaolinite is formed much more slowly in well-drained areas where fluids have a low ionic strength. These conditions favour a slow growth and a smaller degree of disorder. The layers remain plain and are not hydrated. Plane or cylinder structures depend on the way the difference between the $a$ and $b$ dimensions of the tetrahedral and octahedral sheets are compensated for (Singh 1996). In halloysite, compensation takes place by layer bending while in kaolinite it takes place by rotation of tetrahedra (Fig. 6.8a).

![layer bending](image1)

![rotation of tetrahedra](image2)

**Fig. 6.8a,b.** Halloysite and kaolinite crystal structure. a) Compensation of $a$ and $b$ dimension differences between the tetrahedral and octahedral sheets by layer bending (halloysite) or by rotation of tetrahedra (kaolinite). b) Kaolinite to halloysite conversion by the rolling up of 1:1 layers along $b$ or $a$ direction after hydration (after Singh and Mackinnon 1996)
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In nature, kaolinite is considered as the stable mineral phase. The passage from halloysite to kaolinite takes place progressively over time through a dissolution-recrystallisation process. The experimental works by Singh and Mackinnon (1996) show that the reverse path can be travelled when kaolinite undergoes hydration. The kaolinite booklets roll up, thus forming elongated tubes along the $b$ direction, more rarely along the $a$ direction (Fig. 6.8b).

6.1.2.4 Sequence of Transformations in Profiles

Concept of Microsystem

Soils and alterites are not homogeneous environments. Their physical properties (permeability, porosity) and their chemical and mineralogical composition vary over very short distances. Therefore, the mineral reactions producing the clay minerals take place within microenvironments (from a few square microns to a few square millimetres). Like the rocks from the contact metamorphism zones described by Korzhinskii (1959), soils or alterites consist of a mosaic of reaction microsites.

Fig. 6.9a–c. The various types of reaction microenvironments along the open grain joints between muscovite and orthoclase (a), biotite (b) and plagioclase (c)
The example of the incipient weathering of granite provides a better understanding of the diversity of these microsites. At this stage, the meteoric fluids enter the interconnected microfissures that are mainly located at the grain joints. The systematic observation of the contact zones between muscovite crystals on the one hand and their various neighbours (biotite, orthoclase, plagioclase ones) on the other hand shows a clear relationship between the contact type and the forming secondary minerals (Fig. 6.9).

Within each reaction microsite, the dissolution and precipitation reactions (nucleation, growth) are controlled by local chemical conditions established by the interactions between aqueous solutions and the primary minerals at their contact. Each microsite can then be viewed as a microsystem composed of three entities: primary minerals, newly-formed minerals and solutions (Korzhinskii 1959). Then, classical thermodynamics can be applied at this scale.

The microsystem concept is an efficient tool for integrating the mineralogical observations and chemical compositions measured with the electron probe and for interpreting them in terms of phase equilibrium. Indeed, although chemical equilibria between phases are rarely reached, the observed assemblages of secondary minerals comply with the phase rule. The concepts of stability or metastability are not really important at this stage of the analysis of the observed facts. This point will be discussed later.

The identification of microsystems exclusively rests on the analysis of solids (X-ray diffraction on microsamples, electron microprobe analyses). At the moment, the fluids that triggered the reaction processes cannot be collected nor analysed. Their properties can be qualitatively inferred from the phase diagrams built from observations.

**Phases, Equilibrium, Stability and Metastability**

Theoretically, a phase for a given substance corresponds to a state of the matter such that its chemical composition and physical state are homogeneous in the whole system. Consequently, all the kaolinite crystals occurring in a granite weathering profile form the kaolinite phase. Obviously, the definition cannot be strictly respected in clay rocks where the chemical and physical homogeneity of crystals is not perfect. Crystal defects and scattered compositions in more or less extended solid solutions bring about a great variability as a function of the physico-chemical properties of the microenvironment. Nevertheless, all the crystals from a given clay species will be considered as forming a phase. Thus the trioctahedral vermiculites are considered as a phase in the granitic arena, although their composition varies according to the type of microsystem in which they are formed.

At equilibrium, the phases involved do not show any gradient in the intensive variables (temperature, pressure, chemical potentials . . .). At constant temperature and pressure (classical weathering conditions), equilibrium is reached when the chemical potentials of some elements are identical in all the phases involved. For instance, at orthoclase – smectite – illite equilibrium, \( \mu_{Si} \) is equivalent in the three phases although the SiO\(_2\) concentration in each phase is different (see Sect. 3.1.5.2). A phase is stable in a domain defined by the
intensive variables. However a phase may exist outside this domain for reasons of reaction or crystallisation kinetics. Then it is called metastable. This does not influence the phase rule, which remains a universal mark in the analysis of weathering profiles. A detailed discussion of the concepts of stability and metastability applied to clay minerals has been proposed by Essene and Peacor (1995).

6.1.3 Weathered Rocks

6.1.3.1 Granitic Rocks

Weathering Profile

Arenas (regolith) form discontinuous mantles at the surface of the granitic or gneissic rock massifs. While, on a large scale, the general organisation presents a fresh rock polarity to the topsoil, in the detail of the outcrop, this vertical logic is rarely obvious. Indeed, this order is disrupted by the action of erosion or by the preferred weathering of the fractured zones, which leads frequently to the observation of little weathered rocks on top of pulverulent arena (Fig. 6.10).

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Fig. 6.10. Example of a weathering profile developed on a granite: La Rayrie, Deux Sèvres, France (Meunier 1980)
This heterogeneity can be found at the centimetre scale where small fragments of apparently fresh coherent rock lie within highly friable levels. Therefore, the use of rock facies is better suited for the description of weathering profiles than the use of horizons, which are only suited to soils. Thus, four great facies can be distinguished: (1) fresh rock, (2) coherent weathered rock, (3) saprock or structure-maintained friable arena and (4) saprolite or structure-modified friable arena (difference with the definition given by Taylor and Eggleton, 2001). The clay mineral content increases from 1 to 4.

**Fresh Rock**

All the granitic rocks outcropping at the surface of the continents incorporate weathering minerals, even the most apparently fresh ones. Indeed, the dissolution reactions of primary minerals are triggered by the meteoric water impregnating their microporosity (grain joints, cleavages, microfissures etc.). Plagioclase, biotite and amphibole are the most affected minerals by these early stages of weathering. Clay minerals (kaolinite, ferriferous smectites) precipitate in the voids created by dissolution. Clay crystals, in spite of their small size (> 1 µm), can be observed by transmission electron microscopy.

The connected porosity (permeability) of a granite is low: $10^{-18}$ to $10^{-20}$ m$^2$. The study of its distribution is very difficult, even in a two-dimensional space like a thin section, because of the very narrow openings of pores or microfractures. Only the autoradiography imaging technique applied to sections of rocks impregnated with a radioactive resin ($^{14}$C-polymethylmethacrylate) whose viscosity is lower than that of water (Hellmuth et al. 1993) proved efficient. The mineral map is obtained by processing the images acquired after the various species have been stained: quartz, K-feldspar, plagioclase, ferromagnesian minerals. It is subsequently superposed on the porosity images obtained by autoradiography (Fig. 6.11). This technique allows the porosity distribution to be analysed and the exchange surfaces between the fluids and the various mineral species to be measured (Sardini et al. 2001).

Considering the narrowness of the microfractures, the solid-fluid interfaces are very large, thus facilitating the chemical exchanges. The solutions retained by the significant capillary forces and the double layer at the surface of the minerals does not flow in a measurable manner. Since the solutions remain unchanged, their composition is controlled by the dissolution of primary minerals with which they are in contact. In this manner they reach the supersaturation state necessary for the precipitation of the hydrated phases: clays and Fe-hydroxides.

**Coherent Weathered Rock**

The original structure of the rock is perfectly maintained, although some primary minerals show “caries” in which their debris are mixed with newly-formed clays. Weathering occurs in microsites isolated from each other (Fig. 6.12a). It brings about an increase of both the porosity and the amount of alteroplasma (microcrystalline assemblage of clays, Fe-oxyhydroxides and fine debris of primary minerals). The mechanical strength of the rock is
Fig. 6.11. 2-D image of the connected porosity for each mineral species in a granite obtained by superimposition of the mineral map (staining method) on autoradiography (impregnation of a granite with a radioactive resin: $^{14}$C-polymethylmethacrylate), from Sardini et al. (2001)
Fig. 6.12a–c. Variation of physical properties of granitic arena with increasing alteration degree. a) Amounts of weathering plasma (clays + oxides + fine debris of primary minerals) and voids (measured using point counting on thin sections). b) Resistance to a uniaxial stress. c) Young’s modulus

weakened—decrease in the compressive strength, decrease in Young’s modulus (Fig. 6.12b,c)—but yet remains that of a coherent material (Baudracco et al. 1982). The density decreases from 2.6 to 2.1. It is inversely correlated with the increase of the porosity (Righi and Meunier 1995). The chemical composition of the fresh rock does not vary significantly; only the water content increases noticeably.

The new mineral phases, particularly clays, are then formed in a multitude of microsites a few tens of microns in size located in the grain joints, cleavages or microfissures. The weathering process operates like a mosaic of independent microsystems. Although numerous, these microsystems come in three categories only: the contact microsystems, the plasmic microsystems and the fissure microsystems (Meunier 1980). In the contact microsystems, considering the narrowness of the voids, the activity of water is greatly below 1 (see Sect. 5.1.2.2). Flows are slow and low; the chemical transfers are carried out over very short distances only. The system can be considered as closed when its size is that of the microsite. The plasmic microsystems progressively open as the secondary porosity created by the dissolution of primary minerals increases. The activity of some chemical elements is then controlled by the environment outside the system. Finally, developing in the connected lattice, the fissure microsystems are widely open. The activity of silica and alkaline elements in particular are controlled by the external environment.

Inside the coherent weathered rock, most mineral reactions occur in the contact microsystems. The assemblages of clay minerals depend on the facing primary minerals. The example of the intercrystalline joints between muscovite and other primary minerals provides a better understanding of how clay minerals are formed at this stage (Fig. 6.9):

- the neighbouring mineral is orthoclase: the K⁺ content of the fluids is high enough for illite to form locally in replacement of feldspar. Muscovite does not look weathered (solution undersaturated with respect to K-feldspar but close to equilibrium with respect to mica);
– *the neighbouring mineral is plagioclase*: the K⁺ concentration in solutions is too low, only kaolinite can form within the plagioclase. Muscovite transforms layer by layer along the joint by loss of the interlayer K into aluminous dioctahedral vermiculite;

– *the neighbouring mineral is biotite*: both micas lose K and their layers are transformed into vermiculite. Two types of polyphase assemblages appear: trioctahedral vermiculite + kaolinite + Fe-oxyhydroxides in biotite, dioctahedral vermiculite + kaolinite in muscovite;

The weathering processes taking place along the other joints (feldspar-quartz or feldspar-feldspar) operate like the internal weathering processes (plasmic microsystems) of feldspars along their internal microfractures:

– plagioclase → kaolinite
– K-feldspars → dioctahedral vermiculite + kaolinite.

The fissure microsystems, at this early stage of rock weathering, already display the mineral assemblage typical of the end of the evolution in temperate climate: kaolinite + Fe-oxyhydroxide.

**Saprock**

The structure of the rock is maintained although its mechanical strength is very reduced. Porosity ranges from 10 to 20%, resulting from the dissolution of primary minerals and the formation of new fractures generated by local variations in the stress state. The contact microsystems are no longer operative. They disappear in the weathering plasma that develops within each parent mineral (*alteroplasma*). Illite formed at the muscovite-orthoclase joints is no longer identifiable. The plasmic microsystems still retain the signature of the parent minerals (Fig. 6.13):

– K-feldspars: dioctahedral vermiculite+kaolinite (± beidellite)
– plagioclase: kaolinite
– biotite: trioctahedral vermiculite + kaolinite + Fe-oxyhydroxides
– muscovite: dioctahedral vermiculite+kaolinite

New fractures open up and are connected with the pre-existing network of fissures. The resulting network drains throughout the whole weathering profile. The solutions flow faster and are more diluted. They transport clay particles and Fe-oxyhydroxides that settle on the fissure walls in red concentric deposits (*cutans*). The only stable clay in these fissure microsystems is essentially kaolinite.

**Saprolite**

In temperate climate, saprolite forms more or less deep zones within the regolith. In tropical climate, it makes up most of the weathering mantle (Nahon
Fig. 6.13a–c. Mineral composition of plasmic microsystems (alteroplasma) in the saprock. (Laurens et al. 1991; Tardy 1993). The initial structure of the rock is no longer recognisable (difference with definition given by Taylor and Eggleton, 2001). The mechanical strength and Young’s modulus are very low and correspond to those of unconsolidated rocks. Porosity is high in places (about 40–50% in the remaining small pieces of saprock) and much more reduced in others, owing to the settlement of arena under its own load. The debris of the parent minerals mixed with their weathering products form a new environments (pedoplasma), imposing different chemical conditions that bring about a second generation of mineral reactions. Particularly, in the vicinity of dissolving K-feldspar debris, the illite+kaolinite assemblage replaces the aluminous dioctahedral vermiculites (Dudoignon 1983). Fe oxidation grows more intense and the trioctahedral vermiculites disappear to the benefit of ferriferous dioctahedral vermiculites.
Fissures
Fissures – whose opening ranges from the micrometre to the centimetre – form a connected network throughout the whole profile, including the fresh rock. They are coated with cutans composed of the kaolinite + Fe-oxyhydroxide assemblage, whatever their size. This network is used as a drain by the solutions percolating in the granitic massifs and reappearing in springs. The chemical analysis of these “granitic waters” show that they are in equilibrium with only one clay species: kaolinite (Feth et al. 1964). This indicates that the other possibly transported species (vermiculites, smectites, illites) are dissolved.

Geochemical Processes of Granite Weathering
The petrographic observations carried out in the weathering profiles developed in various climates show that particular mineral assemblages are formed in each type of microsystem (Harris and Adams 1966; Bisdom 1967; Wolff 1967; Sikora and Stoch 1972; Gilkes et al. 1973; Rice 1973; Eswaran and Bin 1978; Dudoignon 1983; Boulangé 1984):

Fresh rock: K-feldspars, plagioclase, biotite, muscovite, quartz.

Coherent weathered rock:

- mica-orthoclase contact microsystems: illite
- mica-mica, mica-plagioclases, quartz-feldspars, orthoclase-plagioclase contact microsystems: di- and trioctahedral vermiculites + kaolinite ± Fe-oxyhydroxide ± beidellite, each parent mineral giving its own secondary products as it does in alteroplasma microsystems (see below).

Saprock (alteroplasma):

- plasmic microsystems in micas: di- and trioctahedral vermiculites + kaolinite ± Fe-oxyhydroxide ± beidellite
- plasmic microsystems in K-feldspars: dioctahedral vermiculite (aluminous or ferriferous) or beidellite+kaolinite
- plasmic microsystems in plagioclases: kaolinite

Saprolite (pedoplasma):

- temperate climates: illite+kaolinite
- tropical climates: kaolinite + Fe-oxyhydroxide + gibbsite

Fissure microsystems:

- temperate climates: kaolinite + Fe-oxyhydroxides
- tropical climates: gibbsite + Fe-oxyhydroxides.

To simplify the chemical system representing the weathering processes of granitic rocks, the differences between biotites and muscovites may be ignored because the solubilized Fe is rapidly fixed in the form of minerals that remain inert: oxyhydroxides. Magnesium plays a part in the determination of
the secondary phases only in the very first stages of weathering, when trioctahedral vermiculites form. The latter subsequently transform into dioctahedral vermiculites by oxidation of the Fe$^{2+}$ ions. Let’s consider here that biotite and muscovite alter into a vermiculite + kaolinite assemblage. The secondary parageneses can then be represented in a phase diagram Na,K–Al–Si (Garrels and Christ 1965).

Plagioclases are always replaced by kaolinite (or halloysite). No other phase with a greater silica content (smectite, micas, zeolites, albite) crystallises. The absence of micas can be explained by the fact that only the potassic species (illite) can form under surface conditions, margarite and paragonite crystallising at higher temperatures. The K$^+$ contents are too low for micas to form. Likewise, zeolites and albites are forbidden because the activity of the silica in solution and the pH value are not high enough. The activity of the alkaline elements is too high for smectites to crystallise. The too low local pH value reduces the kaolinite + albite + zeolite stability field to the kaolinite – solution tie line (Fig. 6.14a). Quartz, although theoretically stable, cannot crystallise under surface conditions. Amorphous silica occurs for higher Si activities only. Therefore, in the absence of these minerals, the Si$^{4+}$ activity is buffered by the newly-formed phase having the greatest silica content: smectites.

In the weathering process, the mineral reactions take place in microsystems that are first closed then more and more open as porosity increases. Some of the most soluble chemical components, Na and K in particular, then behave like mobile elements (calcium being clearly less abundant; Garrels and Howard 1957). Their chemical potential ($\mu_{\text{Na,K}}$) is an intensive variable playing a strategic part in clay crystallisation. Moreover, since hydrolysis reactions can be considered as the introduction of H$^+$ protons into solid phases, the pH of the solutions too becomes one of the most important intensive variables in the weathering process. The system to be considered should then be Si–Al–$\mu_{\text{Na,K}}$, pH. However, another simplification can be brought: the pH being rapidly buffered by minerals, it varies by only two units between the microfractures of the fresh rock and rainwater. The variation of the potential $\mu_{\text{Na,K}}$ is greater because the alkaline element concentration becomes infinitely low in highly diluted solutions flowing in fractures. The really active chemical system can then be reduced to Si–Al–$\mu_{\text{Na,K}}$ and readily derived from the ternary system by the equipotential method (see Fig. 3.10).

The decrease in the potential $\mu_{\text{Na,K}}$ as the weathering intensity increases can be represented by a succession of equipotential lines in order of decreasing values, from the highest values (concentrated solutions, low permeability) to the lowest values (diluted solutions, high permeability). The number and rules of line plotting (see Sect. 3.1.5.2) are determined by the number of three-phase assemblages and their position in the ternary diagram (Korzhinskii 1959; Spear et al. 1982; Meunier and Velde 1986). The plotting of these lines ($7 + 2 = 9$) is determined by the sequence of secondary minerals observed in the various microsystems (Fig. 6.14b).

The Si–Al–$\mu_{\text{Na,K}}$ system (Fig. 6.15) shows how the composition and nature of solids (extensive variables Si, Al) vary as functions of those of solutions ($\mu_{\text{Na,K}}$).
Fig. 6.14a,b. Phase diagram in the system Na,K–Al–Si. a) Diagram representing the assemblages of clay minerals identified in the granitic arena, assuming that the three components (alkaline elements, Si and Al) are inert. b) The highly soluble alkaline elements are considered as mobile elements. Plotting of the equipotential lines $\mu_{\text{Na,K}}$ describing the assemblages identified represented by dotted paths. The $[\text{K}^+]/[\text{H}^+]$ ratio of solutions is buffered by the muscovite-K-feldspar contact microsystems at a value such that K-feldspars are no longer stable. Illite (low-temperature equivalent of muscovite) forms and grows within feldspars. No secondary mineral forms along the quartz-K-feldspars contacts because the solutions are not buffered by mica; they reach equilibrium with feldspar. Along the K-feldspar–plagioclase contacts and in plasmic microsystems (internal alteration of minerals in granite), the solutions are buffered for lower values of $\mu_{\text{Na,K}}$. The Si and Al contents in the solutions are controlled by illites, vermiculites, smectites and kaolinite. In temperate climates, these solutions flowing freely in fissures are much more diluted, and only kaolinite is stable. The main part of the saprolites developed in tropical climates is also composed of this monomineral assemblage. The latter
disappears in the most intensively drained zones to be replaced by gibbsite. The illite+kaolinite assemblage is typical of granitic saprolites developed in temperate climates. Indeed, the new friable rock formed by the collapse of the structure-maintained arena is a mixture of clays and debris of primary minerals. The new rock containing less soluble silica (quartz is abundant but little soluble), the alkaline element potential – and notably the K potential – is still high because of the abundance of K-feldspar debris.

6.1.3.2

**Ultrabasic Rocks**

**Grained Rocks (Lherzolite)**

The case of lherzolite, whose weathering profile has been described by Fontanaud and Meunier (1983), shall be taken here as an example to facilitate the understanding of the petrographic analysis of the ultrabasic rock weathering. The
Fig. 6.16a,b. Weathering of a lherzolite (after Fontanaud and Meunier 1983). a) Weathering profile. b) Schematic representation of the weathering sequence. The fresh lherzolite (stage 1), essentially composed of olivine and pyroxenes (clino- and orthopyroxenes), has been serpentinised (metamorphism): formation of calcite and chrysotile veins; local crystallisations of amphiboles and magnetite (stage 2). In levels where the rock microstructure is maintained (saprock), weathering causes the early crystallisation of talc in pyroxenes (stage 3) then of saponite and Fe-hydroxides (stage 4). Finally, the rock loses its structure (saprolite) in which nontronite and an amorphous substance (gel) precipitate (stage 5).
lherzolite weathered over a thickness of 50 to 60 cm is covered by a thin soil 20–25 cm thick (Fig. 6.16a). A five-stage petrographical sequence has been defined from the freshest rock to saprolite (Fig. 6.16b). Initially formed of olivine, clino- and orthopyroxenes (stage 1), the lherzolite has widely been serpentinitised during a hydrothermal alteration or metamorphic episode, which caused the formation of calcite and chrysotile veins (stage 2). Amphibole and magnetite crystals appear locally. The serpentinitised rock is in turn subjected to weathering, the early stages of which leave the rock microstructure unchanged (saprock). Clay minerals and Fe-hydroxides are formed in microsites along the cleavages or microfissures of pyroxenes. Talc and Fe-oxides appear in pyroxenes whereas chrysotile and calcite are not weathered (stage 3). Fissures open up and increasing oxidising conditions cause Fe-oxides and hydroxides to settle on the microfissure walls. Saponite crystallises under various habits; the serpentinitised rock microstructure is still maintained although pyroxenes, talc and chrysotile are weathered. Calcite is dissolved and magnetite is oxidised (stage 4). The final stage of weathering leads to the drastic change in the microstructure: the crystal frame inherited from the parent rock disappears to the benefit of a mainly microcrystalline and highly fissured new material: saprolite. New minerals are formed: large plates of nontronite and an amorphous substance along fissures (gel). Nontronite concentrates into deposits (cutans) sealing the fissures (stage 5). From stage 4 to stage 5, the saponite composition changes. It’s Al and Fe content becomes increasingly higher. Chrysotile, talc, saponite and nontronite do not form a paragenesis, although X-ray diffraction and chemical microanalyses show their coexistence in the < 2 µm fractions in most of the samples collected.

Five different clay phases (including gel) as well as oxides and Fe-hydroxides have been formed by weathering of lherzolite. The compositions of the phyllosilicates are given in Table 6.1. Three groups of chemical components seem to be essential in these compositions: Si, the trivalent elements $R^{3+}$ ($Al^{3+}, Fe^{3+}$) and the divalent elements $R^{2+}$ ($Fe^{2+}, Mg^{2+}$). The cations able to integrate the interlayer sheet of some phyllosilicates are for the most part $Mg^{2+}$ and $Ca^{2+}$, and for a minor part $Na^+$ and $K^+$. Weakly bonded to the 2:1 structure (exchangeable cations), their concentrations vary according to the fluid composition. These variations do not alter the crystal species. These elements globally represented by an equivalent $M^+$ such that $M^+ = 2Mg^{2+} + 2Ca^{2+} + K^+ + Na^+$ can be ignored in a first step because they do not control the mineral phase formation. The active chemical system is then reduced to three groups of components $Si^{4+}$, $R^{2+}$ and $R^{3+}$.

Figure 6.17a shows a phase diagram in the system $R^{2+}–R^{3+}–Si$ summarising the observations. The tie lines are consistent with petrographical observations and delineate 6 three-phase assemblages if one considers that quartz or amorphous silica can precipitate. Talc does not co-exist with nontronite. The magnesian gel is a metastable substance appearing when saponites transform into nontronites (stage 5). The saponite-quartz line forbids the talc + Fe-oxides assemblage. These two species can be observed at stage 3 but oxides are not hematite (maghemite?) and are inherited from the serpentinitisation.
episode; thus talc + Fe-oxides are not a paragenesis. The chemical parameters controlling all the observed mineral reactions are the Mg$^{2+}$ leaching and the Fe$^{2+}$ oxidisation. They operate simultaneously and reduce the concentration of the bivalent elements (R$^{2+}$), which are consumed in the formation of trioctahedral clays (Fe$^{2+}$ and Mg$^{2+}$ are assumed to substitute for each other in all proportions). Therefore, the driving force during the weathering process of ultrabasic rocks appears to be the chemical potential of these elements: $\mu_{R^{2+}}$. The sequence of observed mineral reactions can then be represented by a series of equipotential lines plotted in order of decreasing chemical potential values $\mu_{R^{2+}}$ from $a$ to $h$ (Fig. 6.17b).

The $\mu_{R^{2+}}$–R$^{3+}$–Si diagram shows that the rock composition changes as the chemical potential of the bivalent elements decreases (dotted paths, Fig. 6.17c). Notably, silica losses lead to the accumulation of Fe-oxyhydroxides, which form compact and thick horizons in tropical climate. Saponite takes part in two different two-phase assemblages, with talc on the one hand and nontronite on the other. The petrographic observations show a change in its habit, meaning that saponite recrystallises and experiences also chemical modifications: Mg-rich when stable with talc, it becomes richer in Al and Fe$^{3+}$ when stable with nontronite. Saponite is unstable for low values of $\mu_{R^{2+}}$, yielding nontronite and a metastable magnesian phase: gel. The latter disappears in highly permeable zones.

Knowing the compositions of the minerals formed by weathering of the serpentinised lherzolite (Table 6.1), it is possible to calculate their dissolution equation so as to determine the equilibrium conditions with the solutions in the system SiO$_2$–MgO–H$_2$O at 25 °C, 1 atmosphere.

**Saponite**

\[
\text{Si}_{3.44}\text{Al}_{0.56}\text{O}_{10}\text{Al}_{0.09}\text{Fe}_{0.03}\text{O}_{0.53}\text{Mg}_{0.20}\text{(OH)}_2\text{Fe}^{2+}_{0.53}\text{Mg}_{2.80}\text{(OH)}_2\text{M}^+_\text{al}_{0.56} + 4.52\text{H}_2\text{O} + 5.70\text{H}^+ \\
\rightarrow 3.44\text{H}_4\text{SiO}_4 + 0.65\text{Al(OH)}_3 + 0.27\text{Fe}_2\text{O}_3 + 2.35\text{Mg}^{2+}
\] (6.1)
Fig. 6.17a–c. Phase diagram in the system $R^{2+} - R^{3+} - Si$. a) The soluble bivalent elements do not form a mineral phase: $Fe^{2+}$ is oxidised into $Fe^{3+}$ (oxyhydroxide), $Mg^{2+}$ remains in solution and is subjected to leaching. b) The assemblages observed from the fresh rock to saprolite are described by the eight equipotential lines (see Figure 6.16). c) Phase diagram in the system $\mu_{R^{112+}} - R^{3+} - Si$
Atmospheric and Seawater Weathering

\[ K_{\text{sap}} = \frac{a^{3.44}_{\text{H}_4\text{SiO}_4} \cdot a^{2.35}_{\text{Mg}^{2+}}}{a^{4.70}_{\text{H}^+}} \]  

(6.2)

\[ \log K_{\text{sap}} = 3.44 \log a_{\text{H}_4\text{SiO}_4} + 2.35 \log \left[ \frac{(a_{\text{Mg}^{2+}})}{(a_{\text{H}^+})^2} \right] \]  

(6.3)

\[ \Delta G_r^\circ = \left[ 3.44 \Delta G_{f,\text{H}_4\text{SiO}_4}^\circ + 0.65 \Delta G_{f,\text{Al(OH)}_3}^\circ + 0.27 \Delta G_{f,\text{Fe}_2\text{O}_3}^\circ + 2.35 \Delta G_{f,\text{Mg}^{2+}}^\circ \right] \] 

\[ - \left[ \Delta G_{f,\text{sap}}^\circ + 4.52 \Delta G_{f,\text{H}_2\text{O}}^\circ \right] = 24.03 \text{ kcal mol}^{-1} \]  

(6.4)

\[ 3.44 \log a_{\text{H}_4\text{SiO}_4} + 2.35 \log \left[ \frac{(a_{\text{Mg}^{2+}})}{(a_{\text{H}^+})^2} \right] = +17.62 \]  

(6.5)

**Talc**

\[ \text{Si}_4\text{O}_{10}\text{Mg}_{2.80}\text{Fe}_{0.20}(\text{OH})_2 + 4.20 \text{ H}_2\text{O} + 5.6 \text{ H}^+ \] 

\[ \rightarrow 4\text{H}_4\text{SiO}_4 + 0.20 \text{ FeO} + 2.8 \text{ Mg}^{2+} \]  

(6.6)

\[ K_{\text{talc}} = \frac{a^{44}_{\text{H}_4\text{SiO}_4} \cdot a^{2.8}_{\text{Mg}^{2+}}}{a^{5.6}_{\text{H}^+}} \]  

(6.7)

\[ \log K_{\text{talc}} = 4 \log a_{\text{H}_4\text{SiO}_4} + 2.8 \log \left[ \frac{(a_{\text{Mg}^{2+}})}{(a_{\text{H}^+})^2} \right] = +20.66 \]  

(6.8)

**Gel**

\[ \text{Si}_2\text{O}_5\text{Al}_{0.09}\text{Mg}_{2.47}\text{Fe}_{0.40}(\text{OH})_4 + 4.94 \text{ H}^+ \] 

\[ \rightarrow 2\text{H}_4\text{SiO}_4 + 0.09 \text{ Al(OH)}_3 + 0.40 \text{ FeO} + 2.47 \text{ Mg}^{2+} + 0.33 \text{ H}_2\text{O} \]  

(6.9)

\[ \log K_{\text{gel}} = 2 \log a_{\text{H}_4\text{SiO}_4} + 2.47 \log \left[ \frac{(a_{\text{Mg}^{2+}})}{(a_{\text{H}^+})^2} \right] = +19.31 \]  

(6.10)

**Nontronite**

\[ (\text{Si}_{3.66}\text{Al}_{0.16}\text{Fe}^{3+}_{0.16})\text{O}_{10}\text{Fe}^{3+}_{1.82}\text{Mg}_{0.18}(\text{OH})_2\text{Mg}_{0.26} + 6.15 \text{ H}_2\text{O} + 0.88 \text{ H}^+ \] 

\[ \rightarrow 3.66 \text{H}_4\text{SiO}_4 + 0.18 \text{ Al(OH)}_3 + 0.99 \text{ Fe}_2\text{O}_3 + 0.44 \text{ Mg}^{2+} \]  

(6.11)

\[ \log K_{\text{nont}} = 3.66 \log a_{\text{H}_4\text{SiO}_4} + 0.44 \log \left[ \frac{(a_{\text{Mg}^{2+}})}{(a_{\text{H}^+})^2} \right] = -11.03 \]  

(6.12)

These equations enable the plotting of the different mineral phase solubility curves in the system \( \log[(a_{\text{Mg}^{2+}})/(a_{\text{H}^+})^2] \) as a function of \( \log a_{\text{H}_4\text{SiO}_4} \) (Fig. 6.18). The fluids are enriched in dissolved silica through both the serpentinisation and the weathering processes. The “microsystem” effect expresses itself
Fig. 6.18. Solubility diagram of weathering phases of a serpentinised lherzolite (Fontanaud and Meunier 1983). The variation in the composition of fluids is represented by dotted lines through differing paths according to whether solutions acquire their composition by weathering of serpentinised olivines or of pyroxenes. Serpentine and talc co-exist in the very first stages of weathering. As porosity increases with weathering, new conditions are imposed and erase the microsystem effects: saponite is the most abundant species in the rock. It becomes unstable in turn along the fissures where more diluted and more oxidising solutions flow, causing gel and nontronite (+ Fe-oxyhydroxide) to precipitate.

**Serpentinites**

The weathering of serpentinite can be compared to that of the studied lherzolite described above because both rocks are chemically very close (Al$_2$O$_3\%$< 2%). By contrast, the mineralogical composition and the microstructure are totally different (Ducloux et al. 1976). Serpentinite is mainly composed of phyllosilicates (antigorite, chrysotile, talc and Mg-chlorite) whose mean size is greatly below 0.1 mm. Contrary to lherzolite, serpentinite is a homogeneous rock of the mm$^3$ scale. Owing to the very high reactivity of the constituent mag-
nesian phyllosilicates under weathering conditions, the rock is extensively altered and shows a sudden transition between the alterite-soil system and the unweathered substrate. The thickness of the weathering profiles depends on topography: thin on the summit rock parts, they grow thicker on the slopes and reach their maximum in the depressions that generally correspond to fractures (Fig. 6.19a). The initial structure suddenly disappears: the saprock is very thin (a few cm). Clay-rich horizons (more than 50% clay) form with thicknesses differing according to the topographical situation of saprolite and exhibit a prismatic structure. They are topped by a thin soil composed of a horizon rich in organic matter (A horizon) and of a clay accumulation horizon (B horizon).

Fig. 6.19a,b. Weathering of serpentinites. a) The thickness of the weathering profiles varies with the slope (1: rock summit; 2: slope middle; 3: slope bottom, fractured zone). b) Representation of the composition of rock and unweathered minerals (black squares) and secondary minerals (grey squares and ovals) in the system Si–R²⁺–R³⁺ for profile 3.
The saprock becomes porous, thus testifying to the intense dissolution undergone by the serpentinite minerals. A secondary assemblage composed of a Si-rich chlorite and a Mg-saponite appears. This assemblage is destroyed in saprolite (prismatic horizon): saponite disappears whereas nontronite is formed. The composition of the Si-rich secondary chlorite changes with smectites until it has disappeared in saprolite to the benefit of a chlorite-vermiculite regularly ordered mixed layer (Fig. 6.19b). This sequence of mineral transformations is due to the progressive loss of bivalent elements through leaching ($Mg^{2+}$) or oxidation ($Fe^{3+}$ escaping from silicates to form oxides). The secondary silicates get progressively richer in $Al^{3+}$, which concentrates in the newly-formed minerals owing to its low solubility. These newly-formed minerals are richer in $Si^{4+}$ than the parent minerals because of the high level of the silica activity in solution (Barnes et al. 1978). The formation of kaolinite – and hence of gibbsite – is impeded by the activity of dissolved silica. These two phases can form only in a tropical climate where abundant rainfalls cause an intense leaching of the weathering profiles (Trescases 1997).

6.1.3.3
Basic Rocks

Grained Rocks (Gabbros, Amphibolites)
Like in all grained rocks (granite, lherzolite), the microstructure imposes the juxtaposition of very different microsystems in the first stages of weathering (Fig. 6.20). Four types of microsystems can be distinguished according to their petrographical position (Proust and Velde 1978; Ildefonse 1980):

- **contact microsystems** (amphibole – plagioclase) in the coherent weathered rock: formation of ferriferous beidellite,

- **internal microsystems of primary minerals (alteroplasma):**
  a) Amphiboles: they are replaced by the talc – nontronite – Fe-oxyhydroxides assemblage in the saprock and the trioctahedral vermiculite – Fe-oxyhydroxides assemblage in the saprolite,
  b) Plagioclases: they are transformed into dioctahedral aluminous vermiculite in the saprock and saprolite.

- **Secondary microsystems in the saprolite (pedoplasma):** both types of vermiculite recrystallise into ferriferous beidellite. The latter forms the clay matrix in which new trioctahedral vermiculites grow, with a composition differing from that of the previous ones,

- **Fissure microsystems:** cutans coating the fissure walls whatever their position in the profile are formed by the Fe-bearing beidellite+Fe-oxyhydroxides assemblage.

Like for ultrabasic rocks, the mineral reactions are governed by magnesium leaching and Fe oxidisation. The greater amount of aluminium within the rock should favour the formation of Al-bearing secondary minerals such as
Fig. 6.20. Weathering profile developed on the gabbro from Pallet, Atlantic Loire, France (after Ildefonse 1980). Insets represent the microstructure of the saprock (1), the saprock-saprolite transition (2), saprolite (3). plag: plagioclase; am: amphibole; ta: talc; Fe-be: ferriferous beidellite; no: nontronite; ve II: dioctahedral vermiculite; ve III: trioctahedral vermiculite; sm: mixture of smectites; Fe-ox: Fe-oxyhydroxides

chlorites, but this is impeded by the greater activity of dissolved Na\(^+\), K\(^+\) and Ca\(^{2+}\). Vermiculites then ferriferous beidellites are formed. The occurrence of nontronite is only transient in the very first stages of the internal weathering of amphiboles.

**Basalts**
Basalts form vast surfaces on the continents (trapps from Deccan, Parana, Karoo, Siberia, Columbia River . . . ). Generally, they are highly weathered and correspond to intensively cultivated areas in tropical climates owing to their fertility. Soils and alterites form a red mantle on the black rocks. Between the fresh rock and the organic soil, the material structure, porosity and chemical composition change according to four facies, which are in increasing order
of weathering: (1) the coherent weathered rock, (2) the saprock (boulder),
(3) the clay-rich saprock and (4) the saprolite (Fig. 6.21). The whole structure
is crossed by wide vertical fissures inherited from the prismation of the volcanic
flows.

Composed of phenocrysts (clino- and ortho-pyroxene, plagioclase and
sometimes olivine) and a microcrystalline or vitreous matrix, basalts contain
also clay minerals before being subjected to weathering. Indeed, vesicles and
diktytaxitic voids are often sealed by zoned crystallisations from diagenetic or
metamorphic mineral reactions (see Sect. 8.2.2.1) or even from direct crystalli-
sation from magma residual fluids (see Sect. 10.2.1). These high-temperature
phyllosilicates (saponite, chlorite, chlorite/saponite mixed layers, nontronite)
are in disequilibrium under surface conditions.

Fig. 6.21. Typical weathering profile on basaltic rocks. The thicknesses of the
various horizons vary according to climates.
Atmospheric and Seawater Weathering

Table 6.2. Mineralogical composition of the different parts of weathering profiles on basalts

<table>
<thead>
<tr>
<th>Altered level</th>
<th>Olivine</th>
<th>Glass or argillaceous mesostasis</th>
<th>Plagioclase</th>
<th>Pyroxenes</th>
<th>Fractures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh rock</td>
<td>Iddingsite</td>
<td>Cealadonite + saponite</td>
<td>–</td>
<td>–</td>
<td>Cealadonite + zeolites</td>
</tr>
<tr>
<td>Altered coherent rock</td>
<td>Fe-saponite + nontronite</td>
<td>Halloysite + Fe-beidellite</td>
<td>–</td>
<td>–</td>
<td>Cealadonite + calcite</td>
</tr>
<tr>
<td>Saprock (boulders)</td>
<td>Fe-beidellite + halloysite</td>
<td>Halloysite + Fe-beidellite</td>
<td>Halloysite + Fe-beidellite + goethite</td>
<td>Fe-beidellite + halloysite + goethite</td>
<td></td>
</tr>
<tr>
<td>Argillaceous saprock</td>
<td>Goethite + halloysite</td>
<td>Secondary porosity (dissolution)</td>
<td>Halloysite + Fe-beidellite + goethite</td>
<td>halloysite + goethite</td>
<td></td>
</tr>
<tr>
<td>Saprolite</td>
<td></td>
<td>Halloysite + gibbsite + Fe–Mn oxyhydroxides</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the early stages of weathering, the basaltic rocks form a mosaic of microsystems which are more or less independent. Thus, the forming secondary minerals are strongly influenced by the local chemical conditions (Table 6.2). Nevertheless, short-distance transfers of elements probably occur under the effect of local chemical potential gradients. This is particularly well observable in altered olivines: in spite of the fact that they do not contain aluminium, they are replaced by aluminium-bearing clay minerals (saponite, nontronite). Several sequences of mineral transformations can be followed as long as the rock initial structure persists (clay-rich saprock). The tendency to homogenisation of the secondary products whatever their origin (olivine, pyroxene, plagioclase) is related to long-distance transfers of the chemical elements which are evacuated by the fluid flow within an increasingly porous rock. The minerals making up the most weathered horizons (clay-rich saprock, saprolite) are composed of the less soluble elements: Al and Fe\(^{3+}\) (Table 6.2).

Glass is rare in basaltic rocks except in their chilled margins that have undergone a sudden quenching. The vitreous matrix is particularly unstable under weathering conditions. It rapidly dissolves (pore) or transforms first into hydrated glass then into very small-sized clay minerals (cryptocrystalline) to finally yield halloysite (Ildefonse 1987). However, massive basaltic rocks do not contain glass. The mesostasis more or less opaque under the polarising microscope generally accepted as being glass is in fact composed of a multiphase assemblage of clay minerals + K-feldspar ± quartz, which was formed early in the last stages of flow cooling (see Sect. 10.2.1). Zeolites formed during diagenetic transformations (see Sect. 8.2.2.1) or hydrothermal alteration stages (see Sect. 9.1.4.2). The meteoric fluids bring about the dissolution and recrystallisation of these early clays.

Weathering causes the Si and Mg depletion and the Al and Fe\(^{3+}\) enrichment of basaltic rocks. Saponite and nontronite formed in the very first stages are replaced by a ferriferous beidellite + Fe-oxyhydroxides assemblage. The collapse of the rock structure makes the weathered material homogeneous by mixing the various clay products and the debris of parent minerals. This
new environment imposes chemical conditions that bring about the disappearance of some species (feldspars) and the change in beidellite composition. These conditions favour the formation of the ferriferous beidellite + halloysite + Fe–Mn-oxyhydroxide assemblage.

The common point in the weathering of basic and ultrabasic rocks is the Al and Fe$^{3+}$ progressive enrichment of alterites whereas Si and Mg are evacuated by fluids, as indicated by the composition of spring or river waters (Drever 1982). Thus, the chemical potentials of Si and Mg (mobile components) will be the driving forces for the crystallization of secondary phases while the amounts of Al and Fe$^{3+}$ will control their respective quantities. Therefore, the phase diagrams $\mu_{\text{Si,Mg}} - \text{Al} - \text{Fe}^{3+}$ enable the major mineral reactions of the weathering process to be represented (Fig. 6.22). Ultrabasic rocks differ essentially from basic ones by their low aluminium, alkaline and alkaline-earth elements contents. Nevertheless, these elements do not influence identically the formation of secondary phases. Indeed, the low aluminium contents of ultrabasic rocks are not an obstacle for the precipitation of Al-bearing phases since chlorite and chlorite/smectite or chlorite/vermiculite regularly ordered mixed layers (structure similar to that of corrensites) are formed. It only controls their relative quantities. On the contrary, these phyllosilicates do not appear in weathering profiles of basic rocks because the chemical potentials of Na and Ca are too high and favour the crystallisation of trioctahedral vermiculites.

Fig. 6.22. Tentative phase diagram in three-dimensional space: $\mu_{\text{Na,Ca}} - \mu_{\text{Si,Mg}} - \text{Al} - \text{Fe}^{3+}$ corresponding to the weathering of basic and ultrabasic rocks. \textit{ch}: chlorite; \textit{co}: corrensite; \textit{no}: nontronite, \textit{Fe-ox}: Fe-oxyhydroxides; \textit{sa}: saponite; \textit{ve III} and \textit{ve II}: tri- and dioctahedral vermiculites; \textit{Fe-be}: ferriferous beidellite; \textit{ka}: kaolinite; \textit{ha}: halloysite
or high-charge saponites. This difference is increased in microsystems where weathering is more intense. The trioctahedral vermiculites disappear while the ferriferous beidellite – dioctahedral vermiculites – Fe-oxyhydroxides assemblage forms in saprolite. Saprolites in ultrabasic rocks are characterised by the nontronite+Fe-oxyhydroxides assemblage because aluminium is too scarce to produce ferriferous beidellites or dioctahedral vermiculites.

6.1.3.4 Sedimentary and Metamorphic Rocks with Phyllosilicates

Glauconite (Limestones and Sandstones)
The glauconitic rocks are mainly limestones or sandstones. Weathering produces the same effects in both cases; only the thickness of the profile varies (Courbe et al. 1981; Lovel 1981). The greater the drainage of the environment (high porosity, slopes or hill tops), the deeper the profiles. Glauconites are potassium dioctahedral phyllosilicates that generally come in the form of very well-calibrated rounded grains, 75% of which have a diameter contained between 100 and 200 µm (see Sect. 7.2.3). In the first stages of weathering, the external boundaries of these grains become fuzzy and a greenish alteroplasma forms. The latter becomes increasingly red as weathering gets more intense. Electron microprobe analyses show that Fe and K contents gradually decrease in clay minerals (white arrow, Fig. 6.23). Potassium is leached out from the rock by percolating waters (long distance transfer) while the Fe goes out of phyllosilicates (short distance transfer) to precipitate as an independent phase (oxyhydroxides).

Glauconite progressively transforms into iron-rich illite/smectite mixed layers then into smectites. Smectites close to montmorillonites seem to co-exist with nontronites. In upper horizons, cutans bordering fissures are made up by a kaolinite + Fe-oxyhydroxides assemblage. All mineral reactions can be represented in the system $\mu_{K-Al-Fe}$. The more intense the weathering, the lower the $\mu_K$ and the less available Fe for phyllosilicates. The final stage in temperate climates is then the kaolinite + Fe-oxyhydroxides assemblage. The comparison of the phase diagram inferred from weathering observations with the one representing glauconitisation (Fig. 7.15) is interesting. The weathering sequence is opposite to that of the sediment glauconitisation (Hower 1961; Velde 1976) indicating that the formation of glauconite is a reversible process at Earth surface conditions.

Illite (Marl)
The weathering of a low-permeability Toarcian marl has made possible the observation of the early stages of the diagenetic illite transformation under surface conditions (Lafon and Meunier 1982). The fresh rock mainly composed of the illite + chlorite + pyrite + dolomite assemblage is black. Small amounts of large-sized quartz and detrital micas are observed. The rock becomes ochreous (pyrite oxidation) without disturbance of the sedimentary structures. Carbonates are dissolved and porosity increases. Chlorite and il-
Fig. 6.23. Weathering of glauconites in the system $\mu_K$–Al–Fe$^{3+}$. The arrow is plotted on the electron microprobe point compositions of the grains, the green and red weathering plasmas and the cutans coating fissures. *gla*: glauconite; *il*: illite; *I/S$_{Al}$, I/S$_{Fe}$*: aluminous and ferriferous illite/smectite mixed layers, respectively; *sm* and *no*: smectites close to montmorillonite and nontronite respectively; *ka*: kaolinite; *Fe-ox*: Fe-oxyhydroxides

...lite disappear while a new assemblage is formed: illite/smectite mixed layers + kaolinite + Fe-oxides. Owing to the very low permeability of the fresh rock, the weathered zones are thin.

The invasion of the rock by weathering fluids brings about pyrite oxidisation and pH depression in microsystems. Carbonates and chlorites are dissolved under the imposed acidic conditions. Since illites show a greater specific surface than detrital micas, they react more rapidly by losing potassium. The K- and Al-depleted layers become expandable. Illite transforms into illite/smectite mixed layers and the released aluminium is consumed in the kaolinite crystallisation. Fe-oxidisation is accordingly the driving force of these chain reactions in acidic environments (Fig. 6.24).

**Chlorite and Micas in Gossan (Micaschists)**

The particular interest of the gossan system lies in the fact that it imposes chemical conditions that are totally different from those of common alterites or soils. The selected example is the Rouez gossan (Sarthe, France) that has developed on a huge lens of sulphides (mainly pyrite) and has been exploited for its precious metal concentrations of high economic value (Bouchet 1987). The sulphides are embanked in a quartz-rich brecciated gangue intersecting...
pelitic rocks (or schists) at the anchizone-epizone boundary. They are composed of chlorites and micas intermediate between illite and phengite. The chemical compositions of these phases change within a metasomatic aureole developed about the sulphide body. Notably, the Fe content of chlorites increases significantly (Fig. 6.25).

The gossan structure comprises from top to bottom:

- an oxidised zone: kaolinite + Fe-rich chlorite/saponite mixed layers;
- an intermediate zone: several types of talc/smectite mixed layers are formed according to the composition of smectite: ferrous smectite, stevensite, saponite.
- a cemented zone: sepiolite + talc/smectite + chlorite/saponite + kaolinite.
- a cemented pelitic zone: kaolinite + sudoite/smectite mixed layers.

The fissure walls in the whole weathering profile are coated with Fe-rich amorphous silicates.

The weathering of sulphides is controlled by oxidation-reduction cells (Thornber 1975, 1983). Electron exchanges take place between a conductor (sulphides) and an electrolyte (weathering solutions). Cathodes are located in zones where
Fig. 6.25. Gossan developed on the Rouez sulphide body, Sarthe, France (after Bouchet 1987). Oxidation causes the formation of electric cells through the exchange of electrons: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ and produces local pH gradients (Thornber et al. 1981)
the oxygen dissolved in water is reduced (generally above the hydrostatic level) according to the following reaction:

\[
O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^- 
\]  

This reaction is the starting point of oxidation. It shows the relationships between (OH)\(^{-}\) concentration and electron exchanges. These relationships are readily calculated and classically presented in the form of \(Eh\)-pH diagrams (Fig. 6.26). Anodes are located under the water table. Sulphides are transformed into sulphates and locally change the pH value:

- metal/sulphur ratio < 1: pH becomes acidic

\[
FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ 
\]  

Fig. 6.26. \(Eh\)-pH diagram (after Sato 1960) showing the natural condition domain (shaded area). The main clay species making up the Rouez gossan are indicated in the zones corresponding to their formation conditions
metal/sulphur ratio > 1: pH becomes basic

\[
\text{Cu}_2\text{S} + 2.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Cu}^{2+} + \text{SO}_4^{2-} + 2(\text{OH})^-
\]

(6.15)

Hydroxides are formed: \( \text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+ + e^- \). The effects on pH stop when oxidation is complete.

Several cell systems are observed in the Rouez gossan. Some of them are now fossil systems (oxidised zone) while others are active in the zone of water table fluctuation or even in the cemented zone at the contact between diabase and ore. Local variations in pH explain the juxtaposition of clay minerals of differing compositions such as kaolinite and sudoite on the one hand and talc, stevensite, sepiolite on the other hand.

6.1.3.5

Seawater Weathering of Basalts

Seawater weathering mostly refers to interactions between totally cooled basalts and seawater (−5 to 4 °C). This process is difficult to identify because it is usually superposed on previous alteration stages related to the sudden cooling of lava or to hydrothermal circulations. Seawater weathering forms a black halo on the rock surfaces in contact with seawater, either on those surfaces not coated with sediments or on the walls of open fractures in the ocean floor (Andrews 1977; Alt and Honnorez 1984). The most relevant criterion which differentiate seawater weathering from the other types of alteration (postmagmatic or hydrothermal) is that the development of black halos is a function of the basalt age. Suboceanic research programs (DSDP then ODP) have permitted the study of series of samples ranging from 0 to 23 My in age. The thickness of halos ranges from a few millimetres to 1 or 2 centimetres. Since basalt vesicles remain empty, they are generally composed of an external amorphous zone (no clay crystals determinable by X-ray diffraction) and an internal dark zone in which are formed the potassium and ferriferous clays, which sometimes yield a diffraction peak at 14–15 Å that moves towards 17 Å after ethylene glycol saturation. Most of the time, the small size of the coherent scattering domains does not allow us to go deeper into the mineralogical identification. The chemical composition of these clays is scattered in a domain contained between that of nontronite and celadonite.

The process governing seawater weathering is the chemical diffusion between seawater and the rock vitreous parts. The chemical balance of exchanges is K and H\(_2\)O enrichment and a Si, Mg, and Ca depletion of the rock (Thompson 1973). Whether Fe\(^{2+}\) migrates to the water is difficult to know because its decrease in the halo may be due to oxidation (the Fe\(^{3+}\) content increases). Diffusion rates are slow owing to the very low temperatures (< 4 °C). Nevertheless, considering the immensity of the ocean reservoir, the potential gradients are maintained for very long times and the effects become perceptible after 3 to 6 million years (Hart 1970; Staudigel et al. 1981). The formation of these K-nontronites buffers the \( K^+ \) content of seawater (Bloch and Bischoff 1979) by consuming the inputs of those streams draining the continents.
6.2
Soils

Introduction

Soils are loose rocks in which biological (plants, animals) and microbiological activities trigger two types of reactions altering the organic as well as the mineral matter. The dissolution of the minerals of the constituent rocks of the substratum is influenced by the conditions imposed by the wetting processes ($Eh$-$pH$-$P_{CO_2}$). Each one of the dissolved minerals forms a microsystem in which clays occur either through genuine neogenesis or through the transformation of pre-existing phyllosilicates (micas, chlorites). An overall presentation of the relationships between the microstructure, clay minerals and the geochemical behaviour of soils can be found in some general papers (Pédro 1989–1993; Lynn et al. 2002) or books (Brady and Weil 1999 among others). The purpose of this section is first to present the major mechanisms involved, then to give the mineralogical characteristics of the main types of soils. The soil nomenclature used here is that recommended by the Soil Survey Staff (1998–1999).

6.2.1
Clays in Soils

6.2.1.1
Soil Forming Processes

Biological Factors

In a soil, vegetation adds organic matter to the mineral components thus forming a litter whose mass varies with latitude (Fig. 6.27a). The amounts of organic matter in the soil then depends in the first place on the abundance of litters but

![Fig. 6.27a,b. Organic matter in soils. a) Variation in the amount of litter produced by vegetation as a function of latitude. b) Transformation process of organic matter in soils](image-url)
also on the resistance of plant debris to biodegradation. Indeed, microorganisms, through their own biological activity, transform the litters into CO$_2$, NH$_4^+$ and NO$_3^-$ (mineralisation). The organic residues become humic components (humification). Humification is a slow and complex process in which both soil microorganisms and non-biological physico-chemical reactions take part. The amount of organic matter in the soil is influenced by the difference in velocity between mineralisation and humification processes.

Humification is a complex process leading to the degradation of lignin and to the synthesis of aromatic compounds (Fig. 6.27b). The action of organic acids (humic and fulvic) is double: they provide protons and they are complexing agents of metals, Al and Fe notably. Both actions are very important in the weathering of primary minerals and in the transport of dissolved elements.

**Mineralogical Composition of the Parent Rock**

In temperate climates, the crystallochemical nature of rock has an obvious effect on the soil nature, as shown by the rather accurate superimposition of the large-scale soil distribution maps (1/100,000$^{th}$) upon geological maps. The soils developed over ancient massifs composed of magmatic and metamorphic rocks stand out against those formed over sedimentary rocks. The soil map of Fontenay-le-Comte for instance (Ducloux 1989) is framed by the metamorphic basement of the Armorican Massif to the North, the Quaternary sediments of the Marais Poitevin to the south and the Jurassic calcareous plain to the centre.

In tropical or equatorial climates, soils are very thick and mainly formed of kaolinite or halloysite in combination with Fe-oxides. The initial composition of the parent rock is not as determining as in temperate areas except for trace element distribution. The rock is of decisive importance in thin, relatively recent soils only; this influence decreases in thick and ancient soils, where weathering is intense.

The rock microstructure is a factor as significant as its chemical composition: the soils developed on lherzolites are different from those developed on serpentinites. Although chemically very close, these two types of rocks are composed of minerals of very different size and crystal lattice: pyroxenes+olivine on the one hand, antigorite-chrysotile (1:1 ferromagnesian phylllosilicates) on the other hand (see Sect. 6.1.3.2).

**Age and History of Soil**

The formation of soils, and hence of clay components, is a slow process on the human life time scale (several centuries to several million years). Changes in climatic characteristics take place over equally long periods. Consequently, a soil is hardly ever the result of a constant process, taking place in fixed conditions. Most of the time, the interpretation of soil characteristics using the influence of actual processes alone is erroneous. In most cases, such processes incorporate the superimposition of different pedogenetic processes that follow one another over time at the rate of climatic oscillations. Relicts of soil structures typical of hot climates are frequently found reworked by a pedogenetic process in cold climates.
The soil structure itself is not the result of a single process taking place at a constant rate. Accordingly, incorporation of organic residues into the surface horizon requires a few tens of years whereas the effects produced by the leaching of clays into deep horizons are visible only after several millennia. The formation of a kaolinitic horizon several meters thick, like in Brazil or Africa, requires at least one million years (Tardy and Roquin 1992). The most ancient geomorphological surfaces in West Africa date from the middle of the Tertiary Period. The soils developed on these surfaces are very ancient and are deeply eroded.

6.2.1.2 Kinetics of the Mineral Reactions in Soils

A few studies have attempted to measure durations for the transformation of clays in soils. Such durations not only depend on the kinetics of the mineral reactions involved but also on the rate at which the fluids come in contact with these minerals individually. This rate is controlled by climatic factors, seasonal variations and the microstructural characteristics of the materials determining the soil permeability. Measuring a duration is difficult, if not impossible, except in some favourable cases where temporal reference points permit measurement of time. These soils are then referred to as forming a chronosequence.

Chronosequence of Clay-Rich Soils in the Marais Poitevin (Western France)

The study of a time sequence of clay soils (over 60% clay) developed in similar pedogenetic conditions has been made possible by the conquest of seven polders over the sea from 1665 to 1912 (Sodic Entisols – Aquic Entisols). The most ancient soil has been developing for 330 years, the most recent for 80 years. The $< 0.1 \, \mu m$ clay fraction extracted from soil samples collected at a depth of 36 cm is the most reactive. The potassium of the micaceous phases has been transferred to the expandable phases: smectite+mica $\rightarrow$ illite + mixed-layer minerals. The energy necessary for this reaction is provided by the wetting-drying cycles, the effects of which are assumed to remain the same at constant depth. The progress of the reaction is not a linear function of time (Fig. 6.28). At first rapid, it tends towards equilibrium after 200 years.

Chronosequence of Podzols (Spodosols) on Till Deposits

Two examples are selected in post-glacial environments. In Finland, soil age is easily given by the present day altitude above sea level because the isostatic upwelling rate of the Baltic Shield after the last glaciation is perfectly known. A chronosequence of podzols developed on highly homogeneous tills (ground moraines) has been studied for ages ranging from 6,600 and 10,000 years bp (Gillot et al. 1999). The clay reactions take place essentially in the E horizon (eluvial horizon) of those podzols over 6,600 years in age. The more ancient the soil, the more significant the Al, Fe$^{3+}$ and Mg depletion brought about by leaching (Fig. 6.29a). At the same time, the amount of mixed-layer minerals decreases with time until only smectite remains in the most ancient soil
Fig. 6.28a,b. Soil-geological formation dependence. a) Simplified pedological soil map from the 1/100,000th Fontenay-le-Comte map (Ducloux 1989). b) Sodic and aeric entisols from the Marais Poitevin (western France). Migration of the XRD peak position of the Ca-saturated and air-dried $< 2 \mu m$ fraction as a function of time: smectite (1), illite/smectite mixed layers (2)

(10,000 years). The smectites formed are dioctahedral with a variable tetrahedral charge (beidellites): high charge and low charge coexist in each sample. High-charge layers disappear as a function of time (Fig. 6.29b).

The age of the soils developed on the Mont-Blanc Massif moraines ranges from 80 to 6,600 years (Righi et al. 1999). The podzolic features have progressively developed over this period. While mineral transformations are very
discrete in accumulation horizons (B horizons), they are by contrast intense in eluvial horizons (E horizons). The trioctahedral primary phases (biotite + chlorite) have disappeared within 1,000 years, yielding mica/smectite dioctahedral mixed layers. The weathering of the dioctahedral primary phases has then taken over, yielding mica/smectite regularly ordered mixed layers. These mineral reactions have caused a logarithmic increase in the soil clay mass as a function of time (Fig. 6.30).

Fig. 6.29a,b. Mineralogical and chemical evolution of E horizons of podzols (spodosols) from a chronosequence in Finland as a function of the evolution duration ($10^3$ y). a) Chemical depletion. b) Progressive weathering of the trioctahedral then dioctahedral phases into high-charge smectites (h. c. smect) and low-charge smectites (l. c. smect)
Transfers and Accumulations

The soils developing in humid climate experience significant mass movements that take place at various rates (Fig. 6.31). The most immediate and rapid process is the leaching of cations (\(\text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}\)) that brings about the decrease in the soil solution concentration, which in turn causes the desaturation of clay minerals. Clays are dispersed through solutions then dragged down to the deep zones of the profile where they accumulate (B horizon). They may migrate laterally if topography shows slopes steep enough to cause lateral flow. These transfers of clay particles are described under the term illuviation.

The organic matter produced by humification is fixed on the surface of clays. Attached to its support, the organic matter moves only if clays move themselves. Nevertheless, in acid soils such as podzols for instance, some organic compounds may migrate as solutions or as colloids. Generally, these compounds are organic acids complexing metals, notably Al and Fe. They accumulate in depth forming a Bh horizon.

6.2.1.3 Example: Acid Soils in Temperate Climate (Inceptisols)

Mineralogical Evolution

Acid soils develop in temperate climate in areas composed of magmatic (granites) or metamorphic (gneiss) quartzo-feldspathic rocks. The example chosen here is a soil developed on weathered granitic rocks in the area of the Millevaches plateau in France (Righi and Meunier 1991). This soil (\(\text{pH} = 6\)) comprises four horizons from top to bottom: the A1 horizon rich in organic matter, the partially leached A2 horizon, the clay-rich Bw horizon and the C horizon forming a transition with the weathered granite. The C-horizon is in great part formed of the minerals inherited from the underlying granitic
Soils

Fig. 6.32. Schematic representation of the transformation of phyllosilicates inherited from the weathered granitic rock in the A1, Bw and C horizons of a brown acid soil (dystic inceptisols). Fragmentation takes place either by chemical weathering or by mechanical deformation. At the same time, the inherited phyllosilicates transform either into mica/smectite or mica/vermiculite mixed layers or into intergrade minerals in which the interlayer sheets are blocked by deposits of organic compounds or of Fe–Al-oxyhydroxides.

rock: feldspars, quartz and primary or secondary phyllosilicates (muscovite, chlorite and vermiculite). Feldspars are dissolved and are not found in upper horizons. Particle-size analyses show that the fraction of fine clays (< 0.2 μm) has increased by more than 60%. The amount of fine (1 to 0.2 μm) and very fine (< 0.2 μm) particles increase from the C-horizon to the A1 horizon. This attests to the formation of clay minerals in the soil. The inherited coarse-grained minerals are fragmented and can be found in the very fine grain size fractions. At the same time, they are transformed into a complex assemblage of mixed-layer and intergrade minerals. Organic compounds or deposits of Fe-Al-oxyhydroxides settle in the interlayer sheets (Fig. 6.32).

The phyllosilicates inherited from the weathered granite (muscovite, vermiculite and chlorite) are progressively transformed into minerals having increased expandability (smectite and vermiculite). The electron microscope observations show that the peripheral part of the partially chloritised biotite coarse-grained particles is widely transformed (Fig. 6.33a). One portion looks like an amorphous silicate and seems to be the cause of the increase in the intensity of the fluorescence domes observed in the X-ray diffraction patterns of these particles. The smaller these particles, the higher the transformation rate. Transformation occurs by elimination of the bivalent elements of the crystal lattice: oxidation of Fe$^{2+}$ into Fe$^{3+}$ and Mg solubilisation (Fig. 6.33b).
Fig. 6.33a–d. Transformation of the phyllosilicates inherited from granite and new formation of smectite. a) Photograph-derived representation of a chloritised biotite particle observed by transmission electron microscopy. b) Chemical analyses of the coarse soil fractions extracted from the C horizon (squares) and of the fine and ultra fine fractions extracted from the A horizons (arrows). c) Relationship between the exchange capacity (CEC) and the size of the clay fractions. d) Relationship between the fixed organic carbon content and the K$_2$O content.
The very fine grain size fractions (0.1–0.2 µm and < 0.1 µm) incorporate swelling minerals whose \( d \)-spacing reaches 16.6 Å after glycol saturation. These are smectite-rich mixed-layer minerals that crystallise in the environment of the dissolving large particles. Their crystal lattice cannot form directly from the inherited phyllosilicates by loss of bivalent cations. Their tetrahedral and octahedral sheets, interlayer charge and bulk chemical composition clearly differ from those of the vermiculites resulting from the transformation of the large particles. They are probably the result of a genuine new formation. Their partial expandability (16.6 instead of 17 Å) shall be explained later. Each dissolving large particle form a single microsystem that controls the chemical composition of the “montmorillonitic” clays.

**Evolution of the Chemical Properties of Clays**

The cation exchange capacity regularly increases from 8.6 to 34.4 cmol kg\(^{-1}\) as the size of the analysed clay fractions decreases (Fig. 6.33c). The CEC varies in inverse proportion to the K\(_2\)O content of these various fractions. This shows that the larger the fractions, the greater their unweathered mica content. These results are confirmed by X-ray diffraction when the intensity of the mica diffraction peaks is compared with that of weathered minerals (vermiculite and chlorite).

Smectite- and vermiculite-like minerals in this acid soil have a strong tendency to show total or partial expandability after ethylene glycol saturation or heating at 300 °C. This is classically interpreted as the characteristic of intergrade minerals, namely those having portions of brucite- or gibbsite-like sheets in their interlayer zone. These discontinuous sheets are dissolved by a sodium citrate treatment. When applied to the soil studied here, this treatment has revealed a noteworthy difference between the minerals with an intergrade tendency from the A horizon and those from the B-horizon. The first incorporate Fe-Al-oxyhydroxides in their interlayer sheet whereas the others contain brucite-like sheet residues from the chlorites they replace. Consequently, the first are the result of a precipitation process of these Fe-Al-oxyhydroxides in the interlayer zone of expandable minerals while the others bear witness to an unachieved weathering process of the structure inherited from the parent chlorite.

The 1–2, 0.2–1, 0.1–0.2 and < 0.1 µm soil clay fractions show noteworthy organic carbon contents after hydrogen peroxide treatment. Figure 6.33d shows that the organic carbon content is inversely proportional to the K\(_2\)O content, namely to the amount of mica present in the fraction being analysed. The organic carbon content is a direct function of the amount of expandable minerals. The organic carbon is strongly fixed in the interlayer zones of these minerals and hence escapes the classical chemical extractions.
6.2.2 Soils in Cold or Temperate Climates

6.2.2.1 Podzol – Cambisols (Spodosol – Inceptisol)

In temperate climate, podzolization never affects all surfaces exposed to pedogenesis. This process is only triggered in favourable sites in quartz-rich sandy rocks. Podzols are generally combined with acid cambisols, both being characterised by differing associations of clay minerals. These soils are organised in sequences in the landscape. All pedogenetic factors are identical with the exception of the organic matter behaviour. Indeed, podzols are characterised by high complexing organic acid contents.

A sequence has been thoroughly studied in the Medoc area (south-west France). Righi et al. (1988) have shown that for a same parent rock composed of quartz, mica, vermiculite and chlorite/vermiculite mixed layers, clay minerals in cambisols (acid brown soils) are clearly distinct from those in podzols (Fig. 6.34). In the first, micas are transformed into intergrade vermiculite. In the others, micas are transformed into smectite. This difference is due to the fact that Al and Fe are highly complexed with the organic matter in podzols and are not available to precipitate in the form of oxyhydroxides in the interlayer sheets of the expandable minerals.

![Fig. 6.34. Sequence from podzol (spodosol) to cambisol (acid brown soil; dystic inceptisol) observed in the Médoc area, south-west France (Righi et al. 1988). Smectite accumulates in the podzol E horizon whereas intergrade minerals are formed in cambisols.](image-url)
6.2.2.2
Leached Loess-Soils (Ultisols)

The loess is an accumulation of wind-laid particles predominantly of silt size (2–60 µm). Distributed essentially in the Northern hemisphere, they cover about 10% of the continental surfaces. They were formed during the Quaternary Period in periglacial areas. This explains the weak weathered state of their constituent minerals. Micas and chlorites are often intact. They are combined with kaolinite and smectites arising from ancient soils disintegrated by erosion. Most of the time, loess contains a lot of calcite.

The first stage of pedogenesis is marked by the dissolution of calcium carbonates. The dissolved elements are leached out of the soils. The loess becomes darker and divides into polyhedra. Mica and chlorite crystals experience a beginning of mechanical fragmentation attested by their occurrence in fine grain size fractions. Decarbonatation brings about the suspension of clays by lowering the Ca\(^{2+}\) concentration of soil solutions. Suspended clays are moved and redeposited lower, forming typical zoned deposits: cutans (Fig. 6.35a). This process (illuviation) modifies the distribution of clay fractions in the soil by depletion of upper horizons and enrichment of deep horizons (Fig. 6.35b).

The later stages of pedogenesis bring about very significant changes in the soil structure. Thick clay accumulation horizons are formed in depth by the intense illuviation. These horizons form impervious layers retaining a temporary perched water table in the wet season, the level variations of which control the oxidation-reduction conditions. Iron reduced to Fe\(^{2+}\) is solubilized and moves with solutions. It precipitates in the form of nodules fixing Fe\(^{3+}\) ions when oxidation conditions make it possible in the dry season. Subsequently, those accumulation horizons that have reached a threshold thickness begin to divide into columns or prisms. The outlining fractures make up preferred drains for the solutions. Desaturation causes dispersion of accumulated clays. The eluvial

![Fig. 6.35a–c. Characteristics of leached loess-soils. a) Cutan: zoned deposit of clay particles suspended in soil solutions and redeposited at the bottom of fractures. b) Distribution curves of the clay fraction (< 2 µm) in leached soils. c) Variations in the CEC as a function of depth](image-url)
horizon is disintegrating. Spectacular profiles show leaching “tongues” separating clay blocks (glossic structure). The suspended clays accumulate in turn at the bottom of these “tongues”.

Clay minerals are slightly transformed during their migration in the soil. The only noteworthy change is the progressive desaturation of swelling species that lose their interlayer adsorbed cations (Ca$^{2+}$, Mg$^{2+}$). The latter are replaced by aluminous polycations that polymerise in the form of hydroxides in the interlayer zones. The expandable phyllosilicates are then partially transformed into intergrade minerals. An accurate study of the mineralogy of those smectites contained in the leached soils developed on moraines has shown that beidellite concentrates to the expense of montmorillonite in E eluviation horizons (Spiers et al. 1986). The exchange capacity decreases near the surface (Fig. 6.35c). Using the chemistry of oxygen isotopes, these authors have shown that the observed enrichment was not resulting from the new formation of beidellite but rather from the preferred leaching of montmorillonite.

6.2.2.3
Clay-Rich Soils (Entisols)

Soils developing on clay-rich sedimentary rocks are themselves clay-rich soils and exhibit a particular structure. During the dry season, their upper part is heavily crackled. Gaping shrinkage cracks due to desiccation form a connected network, isolating prisms that are themselves crackled by smaller aperture fissures (Fig. 5.7a). This structure controls water pathways and soil macroporosity. Very fine clay particles (< 0.1 µm) are leached out from the soil. Losses of the order of 400 kg ha$^{-1}$ have been measured (Nguyen Kha et al. 1976). Owing to these selective transfers, the structure changes with seasons. During winter and early spring, rainwaters cannot penetrate in the soil and run off at the surface. By contrast, during the dry season (summer and fall), the wide fractures opening from the surface make up a connected network thanks to which rainwaters penetrate in the upper part of the soil. Fine clays are then dispersed, forming stable suspensions that are themselves leached out towards brooks and rivers. The consequence of this process is the relative enrichment of the upper soil horizons with those mineral species that are dispersed with difficulty. Smectite and vermiculite are progressively leached out whereas kaolinite, mica and fine quartz are concentrated.

6.2.3
Soils in Tropical Climate

6.2.3.1
Worldwide Distribution of Soils

Soils in tropical climates are generally very thick. The mineral reactions (weathering of primary minerals, formation of secondary minerals) are pushed to a more intense degree than in temperate areas, owing to the joint action of two factors:
1. high mean temperatures;

2. very long evolution durations; some surfaces date from the Tertiary. Indeed, these regions have not been planed by glaciers that, after melting, have uncovered surfaces freed from their weathering products in the cold temperate zones (Europe, North America and Northern Asia).

The crystallisation of weathering minerals (clays and Fe–Al-oxyhydroxides) is controlled by climatic parameters, and notably by rainfall distribution and intensity during the year. Abundant and steady rainfall all year round imposes diluted soil solutions and favours the formation of kaolinite (oxisols). Light rainfall followed by periods of intense evaporation lead to soil solutions with a high Si, Ca and Mg content that favour the crystallisation of smectites (vertisols, xeric soils). These different soil types mark the pluvial and arid regions in the intertropical space (Fig. 6.36).

### 6.2.3.2 Oxisols (Laterites) in Wet Equatorial Zones

The lateritic soil profiles (oxisols) not affected by erosional truncation are organised classically into three zones from the weathered rock at the bottom up to the surface organic horizon, as shown in Fig. 6.37. (Bocquier et al. 1984; Muller and Bocquier 1986; Tardy 1993).

1. **Lower zone (A).** The weathered rock at the bottom of the profile retains the initial structure of the parent rock. The primary minerals are weathered to a greater or lesser extent and replaced by highly crystallised kaolinite, hematite and goethite. This horizon is friable and porous. In its upper part, it gradually passes to a material composed of debris of the weathered rock
Fig. 6.37. Schematic representation of a lateritic soil profile (oxisol), after Muller and Bocquier (1986). A, B and C indicate the major pedological horizons. 1: saprolite; 2: compact red matrix; 3: friable yellow matrix; 4: ferruginous lithorelict; 5: clay-rich ferruginous nodules; 6: compact yellow matrix; 7: accumulation zone of organic matter
embedded in a red matrix, a mixture of poorly-crystallised kaolinite and Fe-oxyhydroxides. This intensively red zone (prevailing hematite) gradually passes to the yellow intermediate zone (prevailing goethite).

2. **Intermediate zone (B).** This zone is formed by a nodular horizon. The large-sized nodules (20–80 mm) are ferruginous relics in which the parent rock structure is retained. They are composed of large-sized kaolinite and hematite. These nodules are numerous in the central part of the intermediate zone. Their border is not well defined and forms a gradual transition with the enclosing hematite matrix. The small-sized nodules (< 20 mm) are round-shaped and are composed of microcrystalline kaolinite combined with hematite. The initial structure of the parent rock has totally disappeared. These nodules are the most abundant and are often concentrated in the upper part of the intermediate zone. They are dispersed in a hematite matrix similar to that of the large-sized nodules. Nevertheless, this matrix becomes abundant and highly compact.

3. **Upper zone (C).** Nodules are scarce and the red hematite matrix is gradually replaced by a goethite yellow one. The replacement is complete 1 m from the surface. The upper part of this zone is porous and impregnated with organic matter.

The major mineral phases forming in oxisols are kaolinite, hematite and goethite, as well as gibbsite in the nodular level of the intermediate zone. This can be explained by the intense leaching of Si\(^{4+}\), Mg\(^{2+}\), Ca\(^{2+}\) and Na\(^{+}\) ions, which reduces the soil-solution interactions to the chemical system Fe\(_2\)O\(_3\)–Al\(_2\)O\(_3\)–SiO\(_2\)–H\(_2\)O (Trolard and Tardy 1989). The range of the Fe–Al solid solutions of hematite and goethite depends on water activity (Fig. 3.8). A part of these oxyhydroxides is fixed on the surface of kaolinite crystals. The aggregates so formed behave practically as a silt. Surface properties are annihilated and the CEC is reduced. Kaolinite properties are partially restored by Fe depletion treatments. In nature, the destruction of oxyhydroxides is triggered either by Fe-complexing organic compounds or by water logging due to the perched water tables that impose reducing conditions.

### 6.2.3.3 Vertisols

These soils develop in tropical climates with contrasted seasons that are characterised by a dry period lasting 4 to 8 months. The small amount of rainfall imposes a very limited soil drainage, and hence a moderate leaching of the soluble Ca\(^{2+}\) and Mg\(^{2+}\) ions. The latter concentrate in the pore solutions by evaporation of water (solvent elimination; see Fig. 1.19). High concentrations and pH values close to neutrality are conditions favourable to the crystallisation of smectites. Topographically, vertisols cover the surfaces of Ca\(^{2+}\)- and Mg\(^{2+}\)-rich rocks (basalts, shales, limestones or volcanic ashes) or develop in the lower portions of slopes where ions accumulate by height leaching. They are particularly observed in India, Australia or Sudan (Fig. 6.36).
The chemical composition of smectites in vertisols is variable and is influenced by that of the parent rock, notably as regards Fe contents. Generally, while the compositions of smectitic minerals are scattered between the end members montmorillonite – beidellite – nontronite, the great majority belongs to the domain of ferriferous beidellites (Wilson 1987; Bradaoui and Bloom 1990). The Fe content of clays is proportional to that of the parent rocks.

Smectites in vertisols are poorly ordered. The X-ray diffraction patterns reveal the heterogeneity of their structure. Some of these smectites show an expansion up to 18 to 20 Å after ethylene glycol saturation. These unusually high d-spacings are classically attributed to the presence of organic matter between layers. They could be due also to an interstratification of smectite layers with two glycol sheets (17–17.2 Å) and kaolinite layers (7.15 Å) combined with the effects of low coherent domain size. The latter is perceptible in the diffraction patterns of air-dried samples showing unusual basal spacings for minerals that are not interstratified.

In most cases, clays in vertisols result from the mixture of phyllosilicates inherited from the parent rock (micas, illite/smectite mixed layers) and clays newly formed by direct precipitation or by transformation (beidellites ± rich in Fe). The latter process is a weathering of micas or I/S mixed layers by Fe$^{2+}$ oxidation and K$^+$ loss. The growth of smectite has been shown by Kounestron et al. (1977). The formation of montmorillonite – rather than beidellite – is made possible by the presence of chlorite releasing much more Mg$^{2+}$ in solutions. When the parent rock itself contains smectites, the latter are subjected to significant compositional changes by the vertisol development. Their global charge increases essentially by the growth of the substitution rate of Al for Si in tetrahedra. High-charge beidellites are then formed (Righi et al. 1998).

The smectites in vertisols undergoing the wetting-drying cycles imposed by the season alternation have their crystalline nature modified. They irreversibly fix the potassium available in soil solutions. Some layers remain collapsed at 10 Å whereas others retain their expandability. The stacking sequences become more ordered. Smectites progressively transform into illite/smectite mixed layers whose chemical composition differs from that of the minerals inherited from the diagenetic parent rock.

The wetting-drying cycles cause significant volume variations in the soil. These variations produce stresses (shear stresses) that result in the clay matter re-organisation (Fig. 5.26b). Cracks appear at the surface and propagate down to 160 cm. The fine granules in the surface horizon disintegrated by drought fall into these cracks that seal in the dry season. The clay and organic matter of the soil is then stirred and homogenised naturally.
6.2.4 Soils in Arid or Semi-Arid Climates

6.2.4.1 Xeric Soils (Aridisols) with Sparse Vegetation

In regions where most rainfall is concentrated during the hottest periods of the year, the water escaping runoff percolates into soils. A significant part is subsequently evaporated during the long dry periods that follow rainfall. The remaining part is stored perpendicular to the sparse clumps of vegetation. In Mexico's arid areas, Delhoume (1996) has shown that a sequence of soils of varying thickness marks the transition between the bare zones (regosols) and the clumps of vegetation, although the parent rock is strictly homogeneous (Fig. 6.38a). The formation of a thicker clay horizon under the clumps of plants is due to mineral reactions and not to a clay enrichment by lixiviation of upper horizons as attested by the absence of cutans (Fig. 6.38b). The parent rock is a lutite composed of beidellite + illite/smectite mixed layers. Clay-rich horizons (B horizons) are mainly composed of montmorillonite. Fibrous clays (palygorskite) occur in thicker soils. Both minerals often co-exist because they develop in similar chemical conditions (Elprince et al. 1979). The solutions extracted from these soils are rich in Mg and Si and happen to be very close to the stability domain of montmorillonite and palygorskite (Fig. 6.38c).

6.2.4.2 Saline Soils Without Vegetation (Aridisols)

In arid or semi-arid climate, intense evaporation causes an alkaline-element overconcentration in soil solutions. Salts precipitate forming more or less temporary crusts at a precise soil level controlled by capillary forces (Fig. 6.39). Evaporation increases the concentration of elements in solution. The precipitated salts are of various natures. Usually, calcium carbonate makes up the main part of the crust, but sulphates and other salts have been observed too. The pH reaches 7.8 (precipitation pH of calcite), sepiolite can form (Van den Heuvel 1966). Palygorskite is not systematically related to the precipitation of calcite. Soils with crusts of salt or gypsum occur in plains or depressions (schot, sebkha). The pH conditions are even higher (pH = 9). The Si and Mg high concentrations reached in solutions are favourable to the precipitation of palygorskite- or sepiolite-like magnesian clay minerals (Paquet 1983). In these soils, the inherited clay minerals are the Al-bearing species. They become unstable in those horizons where evaporation concentrates Si and Mg. If the reaction takes place in a closed system, Al being the inert element, an aluminous phase is necessarily associated to the magnesian fibrous clays (sepiolite and palygorskite):

\[
\text{Al-clay minerals (smectite, illite) + Si}^{(aq)} + \text{Mg}^{(aq)} \rightarrow \text{palygorskite-sepiolite + kaolinite}
\]

In this case, the Al contents of magnesian clays must be in equilibrium with this phase. This is the case of the soils described by Van den Heuvel (1966), in
Fig. 6.38a–c. Xeric soils (Aridisols) with sparse vegetation. a) Sequence of regosol towards the most differentiated soil under vegetation (after Delhoume 1996); A: surface horizon; AB: subangular polyhedral structure; B: polyhedral-to-prismatic structure; C: weathered lutite; lutite: fresh parent rock. b) Variation in clay content in the most differentiated soil. The B-horizon is enriched by neogenesis and not by lixiviation of upper horizons. c) Phase diagram calculated at 25 °C, 1 atmosphere in the system Si–Mg–Al–H₂O (after Leprince et al. 1979)

Fig. 6.39. Schematic representation of the mineralogical zonation and water movements in a xeric soil (Aridisol). The dark area corresponds to the calcareous crust
which the Al$_2$O$_3$ content of palygorskite is 10.7% and that of sepiolite is 5.4%. In a closed system, the composition of the present phases is controlled by the tie line between sepiolite-palygorskite and kaolinite.

Nevertheless, it is probable that these precipitation horizons by evaporation do not completely constitute a closed system. Transfers by chemical diffusion or by slow flows of solutions are inescapable. Under these conditions, equilibria are modified and differentiated horizons are formed, concentrating the magnesian and aluminous species separately. Under these particular chemical conditions, palygorskite and sepiolite contain less and less aluminium.

6.2.5
Soils on Volcanoclastic Rocks

6.2.5.1
Imogolite and Allophane (Andisols)

Soils developed on volcanoclastic deposits (andisols) cover significant surfaces in highly cultivated areas (and intensively inhabited) owing to their fertility. These deposits are very reactive to the pedogenesis conditions because they are essentially formed of vitreous debris of dacitic-to-rhyolitic composition, typical of explosive volcanoes. Andisols can be found in the Pacific volcanic belt, in the Caribbean, Mediterranean and Canary Islands, in Italy etc. They are characterised by the presence of particular substances that used to be said to be poorly crystallised: imogolite and allophane. In fact, these are minerals whose crystal structure is ordered over short distances (small size of X-ray diffraction coherent domains). Their characteristics have been defined by Cradwick et al. (1972) and Wada (1989):

- imogolite: (OH)SiO$_3$Al$_2$(OH)$_2$; it is related to nesosilicates and comes in the form of tubes 20 Å in diameter (Fig. 6.40a);

- allophane: (SiO$_2$)$_{1-2}$Al$_2$O$_3$(H$_2$O)$_{2.5-3.0}$; amorphous in X-ray diffraction, it comes in the form of hollow spheres 35 to 50 Å in diameter.

Imogolite and allophane are formed in various types of climates (humid, temperate, or tropical). In fact, the presence of glass in the rock is the decisive factor for their occurrence because of its high reactivity under surface conditions. Their stability is maintained in those soils that retain nearly constant moisture content. By contrast, they are unstable under extensive drying conditions and rapidly transform into halloysite. The activity of silica in solution is increased by the drying process and cristobalite can precipitate (Lowe 1986). The greater the SiO$_2$ content of the glass in the parent rock, the greater the increase in the activity of silica in solution: the Si/Al ratio is higher for rhyolitic glasses than for andesitic glasses. Humus-bearing horizons of andisols are thick. The accumulation of organic substances is facilitated by the formation of allophane-humus complexes. Once in abundance, the organic matter directly forms complexes with the aluminium released by the dissolution of vitreous debris, which inhibits the formation of allophane.
Fig. 6.40a,b. Imogolite and allophane. a) Crystal structure of imogolite (after Cradwick et al. 1972).

b) Variation in the cation exchange capacity (CEC) and anion exchange capacity (AEC) of allophane as a function of pH (Wada 1989).

The cation 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 (Fig. 6.40b):

- pH = 4: the CEC is almost zero, the AEC is close to 20 cmol kg\(^{-1}\);
  \[ \text{Al}^{VI}(\text{OH})(\text{H}_2\text{O}) + \text{H}^+ \rightarrow [\text{Al}^{VI}(\text{H}_2\text{O})_2]; \]

- pH = 8: the CEC is close to 30 cmol kg\(^{-1}\), the AEC tends towards zero;
  \[ \text{Si(OH)} + (\text{OH})^- \rightarrow \text{SiO}^- + \text{H}_2\text{O} \] (Wada 1989).

6.2.5.2

Kinetics of the Glass-Clay Reactions

The influence of time on the weathering of volcanic glass and on the formation of imogolite, allophane and halloysite in natural environments has been
approached thanks to a sequence of palaeosols developed on recent rhyolitic tephras in New Zealand (Hodder et al. 1990). The age ranges between 14,700 and 770 years and the weathering periods (duration separating two successive deposits) vary from 670 to 3,320 years. The authors show that the weathering process comprises two stages with differing kinetics:

1. hydration of glass following a parabolic kinetic law of type $C = k_P t^{1/2}$ where $C$ is the concentration of one element in solution, and $k_P$ is the dissolution rate constant.

2. formation of clay minerals following first-order kinetics $\frac{dC}{dt} = -k_a C$ where $C = C_0 \exp(-k_a t)$, $k_a$ is the reaction rate constant, and $C$ and $C_0$ are the concentration of one element at times $t$ and $t_0$ (starting point), respectively.

The activation energies of the various stages have been calculated taking into account the Si/Al ratio of volcanic glasses. The first precipitates are rich in Al (imogolite). The activation energy is close to that required for a diffusion process. Subsequently, the solids become increasingly richer in Si (allophane, halloysite). The activation energies correspond to the dissolution processes of a gel.

**Suggested Reading**


White AF, Brantley SL (1995) Chemical weathering rates of silicate minerals. Reviews in Mineralogy 31, 583 pp


7.1
Mineral Inheritance

Introduction

Clay rocks make up nearly 70% of the sedimentary rocks (Blatt et al. 1980) and about a third of the rocks outcropping at the surface of continents (Meybeck 1987). Clays in sediments are derived from different sources: (1) erosion of soils and weathered rocks (more than 60% of the Earth’s surface), and (2) crystallisation by reaction between saline solutions and silicates. The first form rocks whose granulometric and mineralogical characteristics depend on transport and deposit processes. The second replace minerals or seal pores in rocks that are already formed. The first are inherited from disintegrated rocks; the second are totally neoformed. Between these two end members, intermediate types are possible. Accordingly, clays formed in a continental environment by dissolution of silicates under the influence of diluted solutions undergo chemical modifications – and even recrystallisations – when settled in a saline environment (early diagenesis or eodiagenesis). Several books give a thorough description of the interest of clays as indicators of palaeoclimates, sediment sources and geotectonics (Chamley 1989; Weaver 1989). Only the physico-chemical interactions between sedimentation environments and clays will be presented here, with the exclusion of those controlling weathering (Chap. 6) or diagenesis (Chap. 8). This chapter comprises two separate parts presenting the mineral inheritance and its use as an indicator of sediment sources and climates on the one hand, and the early chemical transformations in the sedimentation environment and the neogenesis of clay minerals on the other hand.

7.1.1
Transport and Deposit

7.1.1.1
Transport Energy and Particle Size

Sediments, and more particularly clays, are transported in the form of suspensions (internal moraines, solid load of streams, aerosols) or fluid beds (flows
of mud or pyroclastic debris, turbidites etc). The transporting agents, be it ice, water or wind, are fluids with differing intrinsic characteristics (viscosity, dynamic viscosity, temperature, density). Flows (relative velocities) depend upon both these properties and the forces involved (gravity, frictions and impacts). The mass or size of the transported objects as well as the transport distance are complex functions of these parameters (Fig. 7.1). Allen’s book (1997) presents the principles of fluid mechanics whose knowledge is indispensable for understanding how fine sediments – and particularly clays – are put into motion. The question raised for clay mineralogy is whether mineral reactions occur at the time of contact with the transporting agent (fresh water, seawater, air) or at the time of changes in the state of clay particles (division, crystal defects, etc). This point will be addressed for each process.

**Entrainment**

Basically, clays are transported in two forms: isolated minerals and aggregates. Therefore, clay particles range in size between 0.01 and over 20 µm. Fluid (river) or gas (wind) flows can displace the particles within this size range by exerting frictional forces. These forces are proportional to the relative velocity of the particle with respect to that of the flowing fluid. The hydrodynamic force vector is written as follows:

$$\vec{F}_d = \xi (\vec{U} - \vec{V}_p)$$

(7.1)

- $\vec{F}_d$ hydrodynamic force vector (N)
- $\xi$ friction coefficient kg s$^{-2}$ ($\xi = 6\pi\mu(T)a_p$)
- $U$ fluid velocity vector (m s$^{-1}$)
- $V_p$ particle velocity vector (m s$^{-1}$)
- $\mu(T)$ dynamic viscosity (kg m$^{-1}$ K$^{-1}$)
- $a_p$ particle radius (m)
The relationship between dynamic viscosity and temperature is given by the Bingham formula: $\mu(T) = 0.6612 (T-229)^{-1.562}$. The size of transported particles is controlled by the fluid density and viscosity. Accordingly, a glacier can move both finely divided mineral debris – or rock flour – and boulders weighing several tons whereas wind only transports small-sized particles.

Two types of process are involved in the entrainment of clay particles: the suspension process (low clay concentration) and the fluidised beds (high clay concentration). Suspensions can travel great distances. At the mouth of rivers, they form plumes of material that are distributed in the surface water height of the ocean owing to the difference in density between fresh water and seawater. Fluidised beds are moved on continental or marine slopes. They are described under the terms mud flows and turbidites. They behave like Bingham fluids (see 5.2.3.2).

**Brownian Motion**

The Brownian diffusion coefficient $D_{BM}$ for spherical colloidal particles is given by the Stockes-Einstein equation:

$$D_{BM} = \frac{kT}{6\pi \mu(T)a_p}$$

(7.2)

- $k$ Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$)
- $T$ absolute temperature (K)
- $\mu(T)$ dynamic viscosity of the fluid (kg m$^{-1}$ K$^{-1}$)
- $a_p$ particle radius (m)

**Deposition**

The velocity of a solid particle falling into water first accelerates (prevailing gravity effect) then decreases under the effect of resistant forces and buoyancy forces. The bigger the particle, the greater this velocity. The balance of the forces present permits calculation of the falling velocity of particles (Stockes’ law). If particles are assumed spherical, calculation yields:

$$V = \frac{2gr^2(\varphi - \varphi_0)}{\mu}$$

(7.3)

- $V$ falling velocity of particles (m s$^{-1}$)
- $g$ 9.81 (m s$^{-2}$)
- $\varphi$ density of particles (kg m$^{-3}$)
- $\varphi_0$ density of liquid (kg m$^{-3}$)
- $\mu$ viscosity of liquid (kg m$^{-1}$ s$^{-1}$)
- $r$ particle radius (m)
Since clay minerals are not spherical but plate-shaped, \( r \) is referred to as “equivalent” radius and \( 2r \) is referred to as equivalent diameter (or Stockes’ diameter). In reality, suspensions become unstable because the particle size increases by aggregation. Accordingly, in oceanic environment, wind-borne clay particles are aggregated by the organic matter and rapidly fall to the bottom (marine snow). In the same manner, the mineral particles of aerosols aggregate under the effect of impacts in the presence of droplets and fall with the rain.

### 7.1.1.2 Deposition of River-Borne Sediments

A colloid is a particle whose size is contained between 1 nm and 1 \( \mu \text{m} \). Over 1 \( \mu \text{m} \), it is referred to as a suspended particle. The settling velocity of colloids is greatly slowed down by the Brownian motion (see Chap. 5). Colloids always have a large specific surface. This definition is well suited to smectites whose particle size is most of the time below one micron.

In rivers, sediments are mostly transported through the suspension of detrital particles. This is possible only if the vertical component of the resultant of the forces applied to each particle is not high enough to cause its fall. In fact, gravity is opposed by flow turbulence as regards coarse particles and by the Brownian motion as regards colloidal particles. The transfer towards the mouth of the river takes place through a sequence of falls and resuspension according to the local conditions of flows. The other displacement process (minor) is the flow of fluid beds on bottoms as regards the heaviest particles.

The analysis of the sediments transported by the Amazon River (Gibbs 1967) shows that the great majority of the colloidal particles are smectites whereas the coarsest particles (> 4 \( \mu \text{m} \)) are debris of quartz, feldspars, micas and chlorites. Kaolinite forms a clay load intermediate in size (Fig. 7.2). The total sedimentary load is supplied both by the physical disintegration of the rocks outcropping in the watershed and by neoformations of clays in soils and alterites. Thus, Gibbs (1967) has shown that the mineralogical composition and the grain size distribution of the various solid components of the sedimentary load of the Amazon River are identical to those of its tributaries from the Andes high reliefs. This is also the case for the dissolved components. The affluents of the tropical basin carry much smaller amounts of suspended solids (the major contribution is kaolinite) and dissolved elements (the total salinity is 5 to 6 times lower). The persistence of the suspended minerals from the Andes down to the mouth of the river over thousands of kilometres shows that chemical alterations in the river waters are too slow to be measurable. For this reason, the smectite making up the colloidal particles is supplied by the Andean affluents and does not result from the degradation of detrital phyllosilicates during the fluvial journey.
7.1.1.3 Deposition of Wind-Borne Sediments

Since air density and viscosity are very low as compared to those of water or ice, wind-borne particles are very well screened and belong to the granulometric domains of silts and clays (Fig. 7.3). The suspension of these particles depends on the wind strength (Tsoar and Pye 1987). Silts mostly form temporary suspensions that limit their transit distances. By contrast, clays form stable suspensions that can travel long distances, especially if they reach the altitude of jet streams. Their small size does not permit a direct entrainment by the wind; the exposed clay rock surfaces are subjected to a polishing process and take an aerodynamic shape. The suspension of clays is due to impacts with bigger grains (Nickling 1994). Dust clouds can be several kilometres high and may transport clays over thousands of kilometres. Air suspensions become unstable when clay particles start forming aggregates. This change of state is not controlled by the Brownian motion but rather by impacts with droplets. The fall of these aggregates far from the coastal zones is the main sediment source in oceans.

Aeolian sediments are derived from bare areas (arid and semi-arid deserts whatever the climate) and from intensively cultivated surfaces. Significant masses are so displaced: soil erosion alone is considered to produce $500 \times 10^6$ tons of dust per year in the atmosphere. Dust concentration decreases with distance. No mineral alteration seems to take place during these transits in atmosphere where even the physical fracturation of aggregates is reduced.

On continents, loess are the typical wind deposits. They cover vast regions in the northern hemisphere (Fig. 7.3b). Loess are composite sediments in which
7.1.1.4 Deposition of Glacier-Borne Sediments

The action of glaciers is noticeable only in high-altitude or high-latitude areas, namely 10\% of the Earth's surface today. During glaciations, more than 30\% of the Earth's surface was covered with ice, which explains the abundance of tillites (Edwards 1986). The viscosity of ice depends both on temperature and on the state of stress. Therefore, ice behaves like a non-Newtonian fluid (see Sect. 5.2.3.2). Flow rates can reach several tens of meters a year. The motion and pressure of ice exerted on rocks cause their abrasion and yield a rock flour composed of fine debris or disintegrated parent minerals. Since its viscosity is
much higher than that of water and air, ice transports debris of any size without screening. This is the main feature of moraine deposits. The finest grains are often composed of isolated primary minerals and show no weathering trace. They are subsequently put back in motion either by subglacial torrents that carry them to great rivers, as is the case with the Amazon River and its Andean tributaries (Fig. 7.2), or by drift ice in the ocean. Glacial clays are then essentially detrital and are formed of minerals occurring in fresh or altered and eroded rocks: illites, chlorites and vermiculites make up most of these tillites or the varved deposits that mark the seasonal cycles.

Wind-borne silts and clay particles can form suspensions congealed in ice when over-freezing conditions are imposed by sudden temperature drops. These “frozen suspensions” form along shallow coasts. Significant amounts of matter subsequently drift with the pack ice (Ehrmann et al. 1992; Kuhlemann et al. 1993). In icebergs, sediments are aggregated in the form of grains up to one centimetre in size (sea-ice pellets). They make up a significant part of the sedimentary load in the Arctic Sea (Goldschmidt et al. 1992).

7.1.1.5
Fluidised Beds

The motion of turbidites is triggered by sliding on slopes. The driving force depends on the difference in density between the sediment and the ambient fluid (see the profile of the sedimentary particle concentration Fig. 7.4a), on the thickness of the fluidised bed and on the slope angle. When this force becomes higher than resistance (frictional forces), the motion is triggered and velocities are distributed according to a vertical gradient (Fig. 7.4a). The feeding of the head, which is lighter, goes more slowly than the rest of the bed. Its volume is increased and flow becomes turbulent (Fig. 7.4b). The ambient fluid flows in the opposite direction at the contact with the fluidised bed. When velocity slows down, the suspension becomes unstable and the deposition process is triggered. The feeding becomes thinner, loses its force and finally stops. The chemical interactions with the ambient fluid are poorly known. They are probably insignificant.

Other phenomena such as subsurface currents and storms cause more or less remote transfers of fine sediments and notably clays. Subsurface currents bring about the suspension and the entrainment of fine particles (12 µm on an average). When the current velocity decreases, these particles (nepheloid layer) re-settle. Storms modify the distribution of coastal sediments. Through the agitation of waves, surface layers of soft sediments are remobilised and transferred from high sea to the coast.

7.1.1.6
Physico-Chemical Transformations of Clays

No clay mineral reaction during suspension, transport and sedimentation could be clearly identified. The interactions with the transporting agent seem
Clays in Sedimentary Environments

Fig. 7.4a,b. The motion of fluidised beds or turbidites (after Allen 1997). a) Schematic representation of the sediment velocity and concentration profiles between the immobile bottom and the ambient fluid. The inset shows a three-dimensional view of a moving fluidised bed with the ambient fluid counter-current. b) The three stages of the motion: first, the head gets bigger because it goes more slowly than the rest of the bed; the flow becomes turbulent; when velocity decreases, particles settle

to be insignificant and reduced to ion exchanges. The exchange capacity of clays (notably smectites and vermiculites) formed in soils and alterites is saturated by several cations – Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\) principally. In rivers, saturation is dominated by Ca\(^{2+}\) ions. In oceans, saturation is dominated by Na\(^+\) (50%), the remaining part being shared between Mg\(^{2+}\) (30–40%), Ca\(^{2+}\) (10–20%) and K\(^+\) (5%) (Sayles and Manngelsdorf 1977). These mean data do not take into account...
the selectivity of the fixation of ions available in waters. Accordingly, potassium is fixed preferentially in the high-charge sites of vermiculites, thus reducing their exchange capacity. Weaver (1989) shows that vermiculites are relatively abundant in rivers of the United States (East Coast and Gulf of Mexico) whereas they are absent from estuarine and marine muds. The preferential fixation of K+ ions caused the expandable layers to collapse at 10 Å, thus reducing apparently the proportions of vermiculite and increasing accordingly the proportions of illite. This phenomenon explains the inversion in the proportions of smectite (or vermiculite) and illite observed in the estuary of the Guadalquivir River (Melières 1973) or of the James River (Feuillet and Fleischer 1980).

The stability of the suspensions depends on the nature of clay minerals. Smectites form much more durable suspensions whereas kaolinite, illite and chlorite settle more rapidly. This difference is due to the small size (< 1 µm) of smectite crystallites and to their ability to agglomerate into low-density aggregates. Therefore, a kind of selective screening is performed, smectites being carried off shore and the other species settling on coasts.

7.1.2 Detrital Signature in Marine Sediments

7.1.2.1 Interpretation of the Sedimentary Signal

Sediments are rocks in which detrital elements and neoformed minerals are mixed. These complex assemblages do not constitute parageneses for which formation conditions can be simply defined. The origin of the minerals varies both over space and time. Indeed, at a given instant, rivers and winds carry minerals that are derived from vast surfaces covered by mountains, hills or plains (Fig. 7.5a). Total inputs are received by the final repository. The sedimentary load of the Amazon River (Fig. 7.2) is a good example of the mixture of clays derived both from the Andes disintegration upstream and from the erosion of tropical soils downstream.

There are roughly four great groups of soils whose mineralogical composition exhibits enough contrasts (the most abundant or typical minerals) to be identifiable sources of sediments: glacial soils (illite, chlorite), temperate soils (vermiculites), tropical soils (kaolinite, Fe-oxihydroxides), and arid and semi-arid soils (Al- and Fe-smectites, sepiolite, palygorskite). Variation over time is essentially related to the migration of boundaries between the different types of soils. These boundaries change with climatic evolutions or with tectonics (orogenesis, movement of continents). Any increase in altitude amounts to a displacement towards higher latitudes. Therefore, at a given place on Earth, weathering and pedogenesis conditions change over time owing to the combined effects of tectonics and climatic changes. These changes can be symbolised by a latitude–altitude–time path (Fig. 7.5b). The nature of the dominant clays in sediments change when going back in time in the stratigraphic column.
Fig. 7.5a,b. Schematic representation of the diversity of clay minerals making up the marine sediment. a) At a given epoch, the genesis conditions vary over space as functions of local climates determined by altitude variations. These variations themselves depend on the latitude of the geological site. b) At a given spot on the Earth, the genesis conditions vary over time as functions of the effects of tectonics and global climatic changes. The path represents the modifications of these conditions over time detectable in sediments.
7.1.2.2 Sediment Sources

In some favourable cases, the inherited clay fraction in recent or little transformed sediments (shallow burial) can lead to the identification of those continental zones which are input sources. The recent sediments in the Arabian Sea (Kolla et al. 1981) offer an example of the contribution of various sources (Fig. 7.6a):

- smectites are derived from the Deccan basaltic plateaus drained by coastal rivers and by the Tapali River. These smectites are transported by surface currents. At the far south of India, they mix with the smectites carried by surface currents of the Gulf of Bengal;
- illite and chlorite are mainly carried by the Indus River that drains the Himalayan Mountains. They are dispersed by turbidity currents that remobilise the delta sediments. These two minerals are also carried to the ocean by Northerly winds that sweep across the desert areas of Iran and Makran;
- illite and palygorskite are carried by westerly winds over the deserts of the Arabian peninsula and of Somalia;
- kaolinite is concentrated mostly in the equatorial current belt. It is derived from soil erosion in southern India, Madagascar and Africa.

The search for sediment sources can have a much finer spatial resolution. Indeed, when different rivers have their mouth on the same coast (Loire and Garonne in France for example), the sedimentary inputs of the various watersheds can sometimes be identified. Accordingly, Karlin (1980) has shown the respective contributions of the Californian rivers and the Columbia River (Oregon) to the sedimentation along the Pacific coast. The Californian rivers bring 90% of their sedimentary load – in which chlorite is greatly abundant – in winter. By contrast, the Columbia River discharges most of its mineral load – in which smectite is greatly abundant (weathering of basaltic plateaus) – in summertime. These sediments, although entrained by the littoral currents along the submarine canyons, clearly mark both types of input (Fig. 7.6b).

7.1.2.3 Palaeoclimatic Signatures

The purely palaeoclimatic interpretation of clay assemblages in sediments is erroneous if the global history of the genesis conditions is not taken into account. Error sources are numerous and have been analysed by Hillier (1995) and Thiry (1999, 2000). In addition to the variability effects over space and time, several other phenomena equally make the palaeoclimatic interpretation of sediments complicated:

- the formation of soils and the processes of their erosion are too slow for rapid climatic oscillations to be recorded;
Fig. 7.6a,b. Sediment sources. a) Supply zones of the Arabian Sea recent sediments (after Hillier 1995). I: illite; C: chlorite; P: palygorskite; Sm: smectites; K: kaolinite. b) Distribution of chlorite and smectite in the Oregon coast recent sediments, USA (after Karlin 1980)

- a mineralogical screening is performed during transport because clay species come in the form of particles of different sizes (Fig. 7.2);
- mineral reactions occur at the time of deposition (neogeneses at the sediment–seawater interface) or after deposition (transformations during diagenesis).

The sedimentary inheritance progressively fades as the burial depth increases. Some minerals are very reactive and rapidly disappear, such as Al–Fe-smectites and vermiculites. Others recrystallise, like supergene kaolinites made unstable by the presence of Fe$^{3+}$ ions substituted for Al$^{3+}$ and by their numerous crystal defects.

In reality, clay assemblages of sediments record the changes in the conditions of supply, among which climate only accounts for one factor among others (e.g. tectonics, hydrological process of rivers and marine currents and so on). Modifications of ocean currents have at least as much effect on the sediment composition as have climatic changes, but orogenesis remains the dominant factor (Chamley 1989). Only those sites tectonically stable over long periods record climatic changes. In the Mediterranean Sea, Chamley (1971) has shown that the cold and dry periods of the Quaternary glaciations are marked by totally unweathered illites and chlorites while the hotter and rainy interglacial periods are marked by kaolinite- and smectite-rich deposits. Similarly, studying the variations in the proportions of illite and palygorskite in the Arabian Sea sediments, Fagel et al. (1992) have established a correlation between the periodicity of these variations and the Earth's orbital cycles.
7.2
Neogenesis

Introduction

Sedimentary rocks are soft materials comprising mixtures of solid debris (minerals and rocks) with more or less diluted solutions. Typical of atmosphere or seawater interfaces, these rocks are characterised by a high porosity favouring the chemical exchanges between poral solutions and fresh or oceanic water. The presence of organic debris transformed by the microbial activity imposes \( \text{E}_h - \text{pH} - \text{P}_{\text{CO}_2} \) conditions that trigger dissolution and precipitation reactions of solid phases. Mostly carbonates, hydroxides, chlorides, sulphates and sulphides are formed, but neogenetic clays are formed too. They differ from detrital clays by their chemical composition and sometimes by their morphology. Some of them form species that are typical of sedimentary environments (glauconites). This section is aimed at giving a general presentation of the main neogenesis processes at water-sediment interfaces.

7.2.1
Magnesian Clays: Sepiolite, Palygorskite, Stevensite, Saponite

7.2.1.1
Salt Lakes and Sabkhas

The magnesian clays belong to two families: the 2:1 minerals (stevensite and saponite) and the fibrous minerals (sepiolite and palygorskite). The latter have a higher Si content owing to their structure (see Sect. 1.1.1.2). Since palygorskite and saponite contain more aluminium than sepiolite and stevensite, they are generally considered as resulting from the reaction between detrital minerals and Si- and Mg-rich solutions (Jones and Galan 1988). Sepiolite and stevensite are formed by direct precipitation from solutions.

Salt lakes in desert areas are closed sedimentary basins in which detrital inputs are essentially composed of kaolinite, and to a lesser extent of illite, chlorite and Al-rich smectite. These minerals are derived from the erosion of tropical soils. Their Fe, Ca and Na content is relatively low. The waters supplying these lakes are rich in Mg, Ca, Si and alkaline elements (Millot 1964). A zonation appears in lacustrine sediments between the banks rich in detrital elements (illite, chlorite, kaolinite, dioctahedral smectite) and the centre of the lake where the fibrous clays sepiolite and palygorskite precipitate (Fig. 7.7a). The passage from aluminous clays to magnesian clays has been observed in the Tertiary formations of the Paris Basin (Fontes et al. 1967) or of the south–east part of France at Mormoiron in Provence and at Sommières in the Languedoc region (Trauth 1977). The progressive evaporation of lakes leading to the precipitation of gypsum is accompanied by the formation of saponite, stevensite and sepiolite (Fig. 7.7b). The progressive Mg and Si enrichment of the neoformed phases yields the following compositional sequence (Trauth 1977):
Fig. 7.7a,b. Sedimentation in salt lakes. a) Present-day salt lakes in which the detrital inheritance is progressively transformed into a neoformed assemblage (after Millot 1964). b) pH Stratigraphic sequence formed by evaporation of the Tertiary lakes in the south-east part of France (after Trauth 1977)

1. detrital smectite: \([\text{Si}_{3.92}\text{Al}_{0.08}]\text{O}_{10}(\text{Al}_{1.21}\text{Fe}_{0.40}\text{Ti}_{0.03}\text{Mg}_{0.30})(\text{OH})_2\text{Ca}_{0.16}\text{K}_{0.21}\);

2. transformed smectite: \([\text{Si}_4]\text{O}_{10}(\text{Al}_{1.16}\text{Fe}_{0.24}\text{Ti}_{0.02}\text{Mg}_{0.60})(\text{OH})_2\text{Ca}_{0.12}\text{K}_{0.16}\);

3. neoformed saponite: \([\text{Si}_{3.79}\text{Al}_{0.21}]\text{O}_{10}(\text{Al}_{0.78}\text{Fe}_{0.24}\text{Ti}_{0.02}\text{Mg}_{0.135})(\text{OH})_2\text{Ca}_{0.16}\text{K}_{0.21}\);
4. neoformed stevensite: \([\text{Si}_{3.97}\text{Al}_{0.03}]\text{O}_{10} (\text{Al}_{0.25}\text{Fe}_{0.07}\text{Li}_{0.29}\text{Mg}_{2.29})(\text{OH})_2\text{Ca}_{0.08}\text{Na}_{0.08}\text{K}_{0.06}\);

Velde (1985) has proposed an explanation based upon the analysis of the mineral assemblages in a system with three inert components: Si–R\(^2\)(Fe\(^{2+}\), Mg\(^{2+}\))–R\(^3\)(Al\(^{3+}\), Fe\(^{3+}\)). The sequence observed in present-day salt lakes is described by assemblages 1 to 4 (Fig. 7.8a):

1. kaolinite–smectite–amorphous silica: detrital-dominated mineral assemblage. The amorphous silica can yield a flint-like phase (chert);

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**Fig. 7.8a–d.** Relationships between detrital aluminous clays and neoformed magnesian clays.  
*Fig. 7.8a.* Interpretation of the assemblages observed (Fig. 7.7a) in a closed system (after Velde 1985).  
*Fig. 7.8b.* Plotting of the equipotential lines \(\mu_{\text{SiO}_2}\) respecting the sequences observed in salt lakes and French Tertiary basins (Fig. 7.7b).  
*Fig. 7.8c.* \(\mu_{\text{SiO}_2}\)–R\(^2\)–R\(^3\) diagram inferred from Si–R\(^2\)–R\(^3\) diagram. Paths 1 and 2 correspond to present-day sebkas and Tertiary basins sequences respectively (see text for details).  
*Fig. 7.8d.* Calculation of equilibrium lines between solution, stevensite and sepiolite (after Gueddari 1984).
2. smectite–chert: the most aluminous detrital minerals (kaolinite, sometimes chlorite) disappear whereas dioctahedral smectites become more magnesian as shown by Trauth (1977);

3. smectite–palygorskite–chert: fibrous clays are formed owing to the high Si and Mg activity;

4. palygorskite or sepiolite–chert: only the fibrous clays are stable and nearly reach equilibrium with solutions.

The mineral sequence of the French Tertiary basins is represented by assemblages a, b, c, and d. Silica contents are lower than those observed in present-day salt lakes, which explains the presence of phases with a lower Si content than sepiolite and palygorskite: saponite and stevensite. In both geological situations, kaolinite and chlorite do not co-exist with fibrous clays. These minerals are dissolved as well as the detrital dioctahedral smectites in all likelihood. Velde’s point (1985) to justify a closed system lies in the frequent observation of three-phase assemblages: smectite–palygorskite–chert, palygorskite–sepiolite–chert, and palygorskite–saponite–sepiolite. Nevertheless, although most of the observed mineral reactions are accounted for by this method, two essential phenomena are ignored:

1. effect of chemical potential control by silica on the stability of the neoformed phases;

2. direct precipitation from salt solutions.

The first point can be easily addressed by deriving the phase diagram in the \( \mu_{\text{SiO}_2} - R^{2+} - R^{3+} \) system. The plotting of equipotential lines \( \mu_{\text{SiO}_2} \) respects the sequence observed in the lakes and Tertiary basins (Fig. 7.8b). The \( \mu_{\text{SiO}_2} - R^{2+} - R^{3+} \) diagram allows paths 1 and 2 corresponding to present-day and Mormoiron sequences respectively to be plotted qualitatively (Fig. 7.8c). The presence of amorphous silica in salt lakes buffers \( \mu_{\text{SiO}_2} \) at high values that favour the formation of fibrous clays to the detriment of magnesian trioctahedral smectites. In Tertiary basins, \( \mu_{\text{SiO}_2} \) is lower and permits formation of two- or three-phase assemblages involving trioctahedral smectites, sepiolite and/or palygorskite.

The second point is clarified by the chemical compositions of salt solutions that allow us to calculate the stability fields of sepiolite and stevensite. Stability was shown to depend on three parameters: the activities of Mg and Si in solution and the pH value (Gueddari 1984). Solutions from Chott El Jerid are undersaturated with respect to amorphous silica and the pH value varies between 7.5 and 8.3, which allows the formation of stevensite. However, the path determined by the increasing salinity (evaporation) gets close to the stability field of sepiolite. The activity of dissolved silica and pH are much higher in the Natron lake waters (pH = 9–10); these waters are oversaturated with respect to the two phases stevensite and sepiolite.

Sepiolite cannot form below pH 8 (Siffert 1962) and is destroyed at higher pH values. Its stability field corresponds to the one in which carbonates and
Neogenesis

salts precipitate together (Hardie and Eugster 1970; Gueddari 1984). Indeed, during evaporation, carbonates and gypsum are formed with sepiolite.

7.2.1.2
Ocean Floors

Palygorskite has been frequently observed in deep marine sediments far from any direct continental influence, as is the case for the Arabian Sea (Fig. 7.6). Sepiolite is much rarer. The origin of fibrous clays in this type of environment is still being questioned. Some facts argue for a precipitation at the interface between deep sediments and seawater (Couture 1977; Velde 1985), others for a detrital origin and an aeolian transport (Weaver 1989; Chamley 1989). However, the relative amounts of palygorskite and sepiolite seem to differ according to the type of environment under consideration. Sepiolite prevails in continental environments, palygorskite in deep marine environments. The assumption of a selective screening during transport is difficult to admit knowing that these minerals have very close shape and density. Consequently, the neogenesis assumption shall be seriously considered.

The sediments covering basalts in deep-sea zones form thin, poorly consolidated and very porous layers. Consequently, the mineral reactions taking place there are not due to burial diagenesis. They produce a typical palygorskite–dioctahedral smectite–clinoptilolite phase association (Couture 1997). The formation of these minerals necessitates Si, Mg and Al inputs. Silica is derived from diatom shells and volcanic ashes that have not been dissolved when falling into the ocean (Fig. 7.9). Ashes also provide aluminium, which can be found in interstitial waters despite its low solubility. The aluminium content increases near the interface with seawater (Caschetto and Wollast 1979). Magnesium is derived from seawater weathering of the basaltic surfaces in contact with seawater through sedimentary fluids (Lawrence et al. 1979). This type of alteration, although very slow, releases magnesium in solutions (see Sect. 6.1.3.1). The conditions of formation of palygorskite and of a zeolite (high activities of Si, Mg and alkaline elements, pH above neutrality) are then satisfied at the interface between sediments and seawater. According to Velde

Fig. 7.9. Neogenesis of palygorskite at the interface between deep sediments and seawater (after Velde 1985)
(1985), this paragenesis is practically a by-product of the sea weathering of basalts. High-temperature alterations actually yield other types of zeolites as well as saponite, and even talc (see Sect. 9.1.4.2).

7.2.2
Dioctahedral Smectites

7.2.2.1
Bentonites and Tonsteins

Sedimentary Origin
The formation of bentonites and tonsteins is related to the sedimentation of volcanic ashes in lakes, swamps, lagoons or shallow sea areas (Fig. 7.10a). Bentonites and tonsteins form even beds ranging in thickness from one centimetre to one metre (rarely more), the geographical range of which depends on the energy of the eruption and the power of air currents. These beds can cover huge surfaces and are commonly used as stratigraphic markers (Huff et al. 1991). The volcanic origin of these deposits is attested by two types of petrographical features:

1. presence of minerals inherited from the crystallisation of dacitic or rhyolitic (more rarely basaltic) magmas: β-quartz, biotite, sanidine, plagioclase, apatite, ilmenite, magnetite, zircon, rutile, sphene;

2. vitreous debris or their phantoms (glass shards with bubbles).

Ashes deposited on the surface of continents are subjected to weathering and to andosol-type pedogenesis (see Sect. 6.2.5.1), the eruptive cycles forming a series of buried palaeosols.

Bentonites and tonsteins are monomineral rocks composed of smectite (montmorillonite) and kaolinite, respectively. Their formation process is not fully understood yet. Most specialists think that ash alteration is very rapid and is not due to weathering (Grim 1968). Their chemical composition is not the decisive factor that determines the type of clay mineral formed: whether rhyolitic, dacitic or even basaltic, ashes are transformed into smectite in the presence of water or into kaolinite in the presence of organic acids. According to their thickness, tonsteins are formed in swamps where abundant vegetation produces thick organic deposits that are transformed into coal during diagenesis. Tonsteins may exhibit or not a mineral zonation: the thinnest ones are exclusively composed of kaolinite, the thickest ones contain smectite at the centre and kaolinite on the edges. It looks as if the initial matter (fresh or already altered ash?) was transformed from the interfaces between the volcanoclastic deposit and the organic sediments (Fig. 7.10b). On the basis of experimental studies by Eberl and Hower (1975), Bohor and Triplehorn (1993) propose a two-stage mechanism:

1. hydrolysis: rhyolitic glass + H₂O → hydrated aluminosilicated gel + cations in solution,
Fig. 7.10a,b. Formation of bentonites and tonsteins. a) Schematic representation of the alteration environment of ashes: andosols (continental surfaces), tonsteins (swamps), bentonite (lakes, lagoons, shallow sea areas). b) Influence of the thickness of ash deposits on the mineral zonation of tonsteins (after Bohor and Triplehorn 1993)
2. dissolution-precipitation activated by organic acids: hydrated aluminosilicate gel → kaolinite + hydrated silica + H₂O + cations in solution

The proposed reactions do not totally explain the alteration mechanism of ashes. Indeed, volcanic glass does not immediately alter into smectite in the presence of fresh or seawater. Vitreous debris has been observed in sediments several hundreds of thousands to several million years old (Hein and Scholl 1978; Keller et al. 1978; Imbert and Desprairies 1987; Weaver 1989). Their rate of transformation into smectite decreases with depth and remains constant at about 50% at 250 cm from the interface with seawater (Chamley 1971). Besides, the glass to smectite reaction is not stoichiometric. This reaction notably releases silica in amounts that should yield quartz or secondary opal. This is the case of the glass shards of the Otay bentonite from California (Berry 1999). Nevertheless, bentonites are practically monomineral in their body and contain no or very little opal. Their very rapid formation (a few hours to a few days; Berry 1999) is not consistent with an intensive leaching of dissolved elements. Chemical diffusion at the temperature of lake or seawaters is a process much too slow.

There are several alternative solutions which should be taken into consideration: ash alteration may take place either at the time of deposition in waters that are more saline or alkaline than seawater, or before deposition inside the volcano hydrothermal system itself, or after deposition during burial by diagenetic reaction. In the first case, ashes are transformed in lagoons where solutions are concentrated by evaporation. This is probably the case of Uruguay bentonites, which are calcic montmorillonites (Calarge et al. 2001). In the second case, glass is altered very early in its volcanic context and sedimentation involves already transformed ashes. Grim (1968) has suggested that alteration may take place during ash fall, which is improbable. The process proposed by Bohor and Triplehorn (1993) for the formation of tonsteins remains valid if smectite and not glass is assumed to be the starting point of alteration by organic acids. Nevertheless, how the complete transformation of glass into smectite may take place in the volcanic context must be explained. Great amounts of water and very large contact surfaces with magma are necessary. These conditions can be met only in phreato-magmatic systems where highly powerful eruptions produce great amounts of ashes mixed with high-temperature water vapour. Alteration might take place between the emulsion stage where glass is saturated with water and the eruption stage where suspended ashes develop huge surfaces with fluids. High temperatures and huge surfaces may explain a sudden alteration. Eventually, whatever mechanism may be involved partakes of a purely speculative approach to date.

**Diagenetic Origin**

The second alternative origin of bentonites is a diagenetic-like reaction. The vitreous pyroclastic deposits (not transformed into clay during volcanic processes) undergo mineral transformations during their burial process (Compton et al. 1999). The rhyolitic glass gets hydrated, and then yields smectite by a dissolution-recrystallisation process. The highly porous pyroclastic deposits
are gradually compacted; the dissolved elements are leached out along with poral fluids. Several facts support a diagenetic origin:

1. transformation progressivity measurable by the variation in the ratio of glass and clay amounts (mass ratio);

2. isotopic equilibration of hydrated glass and clays with resident waters (sea-water for the Monterey sequence, California for instance);

3. presence of CT opal in the adjacent sedimentary formations that could be related to the migration of silica by chemical diffusion from the volcanic glass dissolution zones.

Some problems have yet to be resolved. Indeed, the isotopic equilibrium with seawater \((^{18}O/^{16}O)\) is reached at temperatures higher than those found in the sedimentary environment \((40 ^\circ C)\). The \(\delta D\) values are not consistent with pure seawater and imply mixtures with fresh water. Despite these uncertainties, the diagenetic process – much longer than the sudden alteration of ashes at the contact with water – seems to be a better explanation of the nearly monomineral character of bentonites.

The diagenetic origin of some tonsteins is confirmed by the formation of pyrophyllite and sudoite along with kaolinite from bentonite beds in the Ardennes coal mine series (Anceau 1992, 1993). These minerals occurred owing to sufficiently acidic and reducing local conditions, as attested by the presence of pyrite. These local conditions have probably been imposed by the presence of cracking organic matter.

7.2.2.2

Sea-Water Hydrothermal Environments

Nontronites of Black Smokers

Seawater hydrothermal activity areas lined by the chimneys of black or white smokers form particular geochemical and biochemical environments characterised by sudden contrasts in physicochemical conditions (Hannington et al. 1995). Indeed, black smokers eject sulfurred acidic solutions at 300 celsius in an oxidising icy seawater \((2–4 ^\circ C)\): the mean oxygen content is \(4 \text{ml}l^{-1}\) (Fig. 7.11a). These contrasts explain the sulphide-sulphate mixture within the chimney walls (Fig. 7.11b). First sulphides then, farther, oxidised metals (mainly Fe and Mn) and nontronites are dispersed by the smoker plume. Purely ferriferous clays are formed by mixture of hydrothermal fluids with ambient seawater under low temperature conditions, namely below 70 celsius (Singer et al. 1984):

\[
\left[ \text{Si}_{3.67}\text{Fe}_{0.33}^{3+}\right]_0 \text{O}_{10} \left(\text{Fe}_{1.56}^{3+}\text{Mg}_{0.40}\right) (\text{OH})_2\text{K}_{0.15} (\text{NH}_4^+)_{0.34}
\] (7.4)

Crystallisation of these minerals can take place according to two different geochemical paths:
1. nucleation and growth under oxidising conditions. This process is slow (Decarreau et al. 1987). The conditions of formation of these nontronites have been calculated by Zierenberg and Shanks (1983) as functions of the sulphur and oxygen fugacities of solutions. Under oxidising conditions, nontronite and anhydrite precipitate (Fig. 7.11c);

2. initial formation of a polymerised ferrous or ferromagnesian precursor having a brucite-like structure (Harder 1978). This precursor serves as embryo on which siliceous trioctahedral layers polymerise in turn. The Fe valency changes, and the trioctahedral lattice subsequently becomes dioctahedral under oxidising conditions. A Fe\(^{3+}\) cation is released from the silicate and forms an independent oxihydroxide phase (hematite, goethite). This path is faster and is consistent with the working process of black smokers. The passage from reducing to oxidising conditions takes place by mixture with seawater as temperature decreases (Fig. 7.11b).

The role of the ferrous precursor has been specified by experimental studies by Decarreau and Bonnin (1986). The ferric smectite is formed according to the following reaction:

\[
\text{Si}_4\text{O}_{10}\text{Fe}^{2+}_2(\text{OH})_2 + 2\text{H}_2\text{O} \rightarrow \text{Si}_4\text{O}_{10}\text{Fe}^{3+}_2(\text{OH})_2 + \text{FeOOH} + 3\text{H}^+ + 3e^- .
\] (7.5)

The di-to-trioctahedral transition imposes that 2 out of 6 Fe\(^{2+}\) ions in the unit cell be released from the silicated lattice and form a Fe-hydroxide. The charge modifications imposed by the substitutions of Fe\(^{3+}\) for Si in tetrahedral sites are not accounted for by the reaction above. The nontronites formed in the ocean bed are exclusively K-nontronites. Their selectivity is noteworthy despite the presence of other cations in solution (notably Mg\(^{2+}\) and Na\(^{+}\)). This selectivity is probably related to steric conditions: the presence of Fe\(^{3+}\) ions in the octahedral or tetrahedral sheet increases the b cell dimension, hence its capacity to accept interlayer cations with a large ionic diameter (Eggleton 1977; Russell and Clark 1978).

**Ferrous Stevensite and Ferripyrophyllite of the Red Sea**

The structure of the Red Sea rift is characterised by the presence of basins full of hot brines at about–2,000 m in depth (Fig. 7.12a), of which three have been explored (Fig. 7.12b). These brines are derived from mixtures of hydrothermal fluids crossing the basaltic basement with solutions flowing in the evaporitic deposits that form the graben flanks. They are stratified, the lower brine having a density of 1.2 g cm\(^{-3}\) a chlorinity of 156%\(_0\) and a present-day temperature of 61 °C and the upper brine having a density of 1.10 g cm\(^{-3}\), a chlorinity of 82%\(_0\) and a temperature of 49–50 °C (Hartmann 1980). The bottom of these basins is covered with metallic ore deposits that have been studied owing to their potential economical value (Bäcker and Richter 1973; Zierenberg and Shanks 1983), and with clay sediments whose descriptions have been re-worked by Badaut (1988).
Fig. 7.11a–c. Nontronites in sea-water hydrothermal zones. a) Structure of black smokers and mineral deposits. b) Variation in the temperature and oxygen fugacity of hydrothermal fluids when mixing with ambient seawater (modified from Hannington et al. 1995). c) Phase diagram in the Fe–Al–Na–Si–O–S system at 200 bars, 60 °C showing the stability fields of nontronite and anhydrite (after Zierenberg and Shanks 1983)
Clays identified in the bore holes from the Ocean Drilling Programmes (ODP) are organised into three main groups:

1. detrital clays (illite, chlorite, kaolinite) commonly occurring in the Red Sea during the Pliocene epoch;

2. magnesian clays (talc, stevensite) derived from the alteration of basaltic rocks more or less rich in glass and sometimes associated with chrysotile;

3. Fe-rich neogenetic clays forming at the contact between sediments and brines and growing mostly in the form of regular laths on detrital clays.

Ferric clays are associated with silicates (hisingerite) and with more or less amorphous Fe-bearing oxyhydroxides (ferrihydrite, ferroxyhite, hematite). Ferrous clays (ferrous stevensite) are associated with sulphides.

The presence of a trioctahedral ferrous clay (\(b = 9.32 \, \text{Å}\)) has been revealed in sediments protected from the atmospheric oxidation at the time of sampling. They have a low Al content, they may contain a small amount of Zn, and the substitution rate in tetrahedral sites is low. These clays correspond to ferrous
Neogenesis

stevensites: \((\text{Si}_{4-\varepsilon} \text{Al}_\varepsilon) \text{O}_{10} \text{Fe}^{2+}_3 \text{(OH)}_2 \text{M}^+_\varepsilon\). They are very unstable under oxidising conditions and are transformed into nontronite according to the reaction described by Badaut et al. (1985):

\[
\text{Si}_4\text{O}_{10}\text{Fe}^{2+}_3\text{(OH)}_2 + 3/2 \text{H}_2\text{O} \rightarrow \text{Si}_4\text{O}_{10}\text{Fe}^{3+}_2\text{(OH)}_2 + 1/2 \text{Fe}_2\text{O}_3 \cdot n \text{H}_2\text{O} + 3 \text{H}^+ + 3 \text{e}^-
\]

(7.6)

These ferrous trioctahedral clays are close to the precursor devised by Harder (1978). Their isotopic composition \((^{18}\text{O}/^{16}\text{O})\) shows that they have been formed under temperature conditions that are high for the Red Sea site \((100–130 \degree \text{C})\).

Nontronites crystallise at the interface between the upper brine and met- alliferous sediments, probably by oxidation of ferrous stevensite and partial dissolution of detrital clays under relatively low-temperature conditions \((70–80 \degree \text{C})\). An example of typical unit formula is given by Bischoff (1972):

\[
[\text{Si}_{3.15}\text{Al}_{0.26}\text{Fe}^{3+}_{0.59}]\text{O}_{10}(\text{Fe}^{3+}_{1.60}\text{Fe}^{2+}_{0.24}\text{Mn}_{0.02}\text{Zn}_{0.15}\text{Cu}_{0.07}\text{Mg}_{0.19})(\text{OH})_2 1/2 \text{Ca}_{0.10}\text{Na}_{0.55}\text{K}_{0.09}
\]

(7.7)

The substitutions of \(\text{Fe}^{3+}\) for \(\text{Si}^{4+}\) in tetrahedral sites and of \(\text{Cu}^{2+}\) and \(\text{Zn}^{2+}\) for \(\text{Fe}^{2+}\) in octahedral sites are related to the chemical composition of those brines in contact with metallic ore deposits. Note that iron is not completely oxidised in these nontronites.

Ferripyrophyllite forms practically monomineral green clay deposits. De- spite the presence of a few expandable layers (charge compensated for by potassium), its chemical composition gets very close to the theoretical end member \(\text{Si}_4\text{O}_{10}\text{Fe}^{3+}_2\text{(OH)}_2\) (Badaut et al. 1992). It seems to have been formed by early diagenesis in very recent formations \((\text{less than } 25,000 \text{ years})\) under temperature conditions of about \(55–65 \degree \text{C}\) (Badaut et al. 1990).

7.2.2.3

Al-Fe Dioctahedral Smectites (Early Diagenesis)

Diagenesis begins right after the sediment-seawater interface; it is referred to as “early” when this burial does not lead to a noteworthy temperature rise (Chamley 1989). This mostly involves thicknesses of several hundreds of metres. In the present case, the term “early diagenesis” refers to the first tens of centimetres from the surface of the soft sediments. Their very high porosity (over 50%) allows for easy exchanges with seawater by chemical diffusion from the interface. This phenomenon has also been referred to as “reverse weathering” (Sillén 1961).

Continental clay minerals remain seemingly inert when settled in oceans. Nevertheless, their exchange capacity is no longer saturated by the same ions, namely \(\text{Ca}^{2+}\) in rivers, \(\text{Na}^+\), \(\text{K}^+\) and \(\text{Mg}^{2+}\) in seawater (Sayles and Mangelsdorf 1977). Waters impregnating the first metre of sediment are systematically depleted in \(\text{K}^+\) and \(\text{Mg}^{2+}\). These seawater-derived elements being “consumed”
Figs. 7.13. Representation of overgrowths oriented by rotations at 60° on detrital clays and lath-shaped smectites

in solids, they diffuse in the solutions trapped in sediments (Sayles 1979). However, diffusion is unlikely to be maintained only by cation exchange reactions between fluids and clays. Although no unquestionable proof of the neogenesis of magnesian and potassium-bearing clays in the first metre of sediments has been provided to date, it seems that this process cannot be ruled out.

The neogenesis of phyllosilicates is a proved phenomenon in marine sediments. It is expressed by overgrowths on detrital clays (illite, smectite, kaolinite) or by the formation of lath-shaped smectites (Fig. 7.13). Studying black shales from the Albian stage, Steinberg et al. (1987) have shown that overgrowths on illite have an Al–Fe beidellite composition whereas those on smectites have a montmorillonite composition. Typical lath-shaped habits are found in sediments of different ages: Miocene red clays (Kharpoff et al. 1981), Atlantic sediments (Holtzapffel and Chamley 1986). The main factor in the formation of these minerals does not seem to be the burial depth but rather the duration of the exchanges with seawater by diffusion.

7.2.3 Ferric Illite and Glauconite

7.2.3.1 Ferric Illites

Ferric illites (or Fe-bearing illites or glauconite mica) are characterised by aluminium contents that are much higher than those of glauconies (Kossovskaya and Drits 1970; Berg-Madsen 1983). As shown by Velde and Odin (1975), there is no continuous solid solution between these two species (see Fig. 2.17). The crystal structure of these illites is still poorly known. They form in non-marine environments, such as lagoons (Porrennga 1968; Kossovskaya and Drits 1970), xeric soils (Norris and Pikering 1983), and fluviatile environments (Dasgupta et al. 1990; Backer 1997). They come in the form of green crystals sometimes included in cementing carbonates, thus showing that they crystallise during
sedimentation in the vicinity of the water-sediment interface. In xeric soils, they sometimes accompany sepiolite and palygorskite in horizons where salt solutions have been concentrated by evaporation.

7.2.3.2
Glauconies and Glauconite

Formation Environments
According to the Odin and Matter terminology (1981), the green sedimentary grains (glauconies) are mixed-layer minerals whose components are smectite and glauconite mica. The greatest part of the glauconies described in the literature is of marine origin. Nevertheless, some occurrences are reported in lacustrine sediments (see Sect. 7.2.3.1). Glauconies mostly come in the form of rounded grains. Some of them retain the morphology of the detrital elements they have pseudomorphically replaced: sponge spicules, foraminifer shells, volcanoclastic debris, faecal pellets and so on. Under present-day conditions, they form in all oceans except in icy parts. However, they are more abundant in the intertropical domain between −125 and −250 m (Fig. 7.14a). An open marine environment with a low terrigenous sedimentation rate is necessary (Porrenga 1967). The planktonic and benthic marine organisms provide the organic matters whose presence seems to be a decisive element in determining the chemical properties at the microenvironment scale (< 1 mm). Glaucony is formed by chemical exchanges between solid debris and seawater at the microsystem scale (Fig. 7.14b).

The glauconitisation process takes place at shallow depth (a few decimetres) in the vicinity of the sediment-seawater interface. The greater the size of the pores formed by the grain stacks in the sediment, the more efficient the process. Indeed, this condition facilitates exchanges between poral water and seawater (Odin and Fullagar 1988). The first glauconite glaebules grow in the mineral or in the plankton shell used as substrate, whatever its initial composition: siliceous (sponge spicules, diatoms), silico-aluminous (detrital clays, volcanic glass), or calcareous (bioclasts, oolites). These glaebules give way to flakes or rosettes that finally invade the entire solid substrate. The strontium isotopic ratios \( \text{Sr}^{87}/\text{Sr}^{86} \) show that dissolution of detrital phases and crystallisation of glauconite take place in a closed microenvironment that progressively opens up (Clauer et al. 1992). In the same time, the potassium content increases progressively. A time scale of these transformations (Fig. 7.14c) is given by Odin and Fullagar (1988).

Glauconitisation Process
The glauconitisation process is related to the chemical diffusion of those elements naturally in solution in water to which are added those directly solubilised in the poral waters of the microenvironment. The presence of organic matter imposes reducing conditions that permit local-scale solubilisation of the terrigenous Fe-oxyhydroxides. This presence causes the diffusion of these elements in the direction poral water to solid substrate by retaining a redox
Fig. 7.14a–c. Conditions of glaucony formation. a) Coastal marine origin (after Porrenna 1967). b) Glauconitisation takes place within microsystems that are close to the sediment-seawater interface and in which redox potential gradients ($\Delta E_h$) are established. c) The fixation of potassium increases with time and causes changes in the morphology of glauconitic corpuscles (after Odin and Fullagar 1988)

potential gradient ($\Delta E_h$), the excess ions in the solid entering the solution. This process leads to the epigenesis of clasts that retain their outward form: calcareous shells, siliceous sponge spicules and so on.

Although containing Fe$^{3+}$ ions principally, glauconite is sometimes associated with pyrite owing to the reducing properties of organic matter. The process is favoured but not controlled by the temperature conditions of tropical waters
since glauconies are formed under high latitudes. This has been confirmed by experimental syntheses from co-precipitates by Harder (1980). The significant parameter is the activity of silica in solution: when low, berthierines are formed, when high, glauconitisation is triggered. Using the phase rule, Velde (1985) shows that only aluminium remains inert in the microsystem. Indeed, the fact that glauconite is the only formed phase imposes that all the other variables be intensive ones (controlled by the environment out of the microsystem), the role of which depends on their chemical potential. In fact, even the inert element is likely to migrate, as shown by the epigenesis of the siliceous spicules or the calcareous bioclasts.

The proportion of interstratified smectite varies with the age of sediments (Fig. 7.14c): the more recent the sediments, the greater the smectite content. This variation is controlled by the amounts of potassium fixed in glauconies. Note that the same tendency is observed both for recent sediments (Odin and Fullagar 1988) and for diagenetic series (Thompson and Hower 1975; Velde and Odin 1975). The composition of the smectite component has long been considered to be of nontronite type. A reaction of glaucony formation from a precursor nontronite has been proposed by Giresse and Odin (1973):

\[
\text{nontronite} \left( 16\text{–}21\% \text{Fe}_2\text{O}_3 \right) + \text{K}^+ \rightarrow \text{glauconite}
\]

Nevertheless, this reaction is not consistent with the real chemical composition domain of glauconies, which is situated between celadonite-glauconite micas and beidellites (see Sect. 2.1.4.2). By contrast, the phase diagram proposed by Velde (1985) takes into account the real chemical composition domain and imposes a reaction between an aluminous phase (kaolinite) and a ferric phase (nontronite or Fe-oxyhydroxides):

\[
\text{kaolinite} + \text{nontronite or Fe-oxyhydroxide} + \text{K}^+ \rightarrow \text{aluminous mixed-layer mineral} + \text{ferric mixed-layer mineral} \rightarrow \text{glauconite}
\]

The presence of two types of mixed-layer minerals imposes a simultaneous increase in their mica content as the fixed potassium content increases. This is purely speculative and has not been shown by X-ray diffraction.

While the formation of a ferric smectite in the first stages of glauconitisation seems to be proved now, (a ferric montmorillonite in fact, Wiewiora, personal communication), nothing indicates that this precursor has the same composition as that of the smectite interstratified in the mixed-layer structure. This precursor is unstable and reacts with its environment to yield the two constitutive types of layers of glauconies: Fe-rich beidellite and glauconite mica. The reaction then becomes:

\[
\text{ferric montmorillonite} + \text{kaolinite} + \text{K}^+ \rightarrow \text{Fe-beidellite–glauconite mica mixed layer.}
\]

As emphasised by Velde (1985), the formation then the destabilisation of the precursor ferric smectite follows the inverse path of weathering (see
Sect. 6.1.3.4). This shows that glauconitisation is a reaction process of the Earth's surface involving true equilibria given its reversibility under the same conditions. Glauconitisation and weathering of glauconitic rocks should then be described using a single-phase diagram in the $\mu_{K^+} – Al – Fe^{3+}$ system (Fig. 7.15). Indeed, the glauconitisation diagram is very close to the weathering diagram (Fig. 6.22, Sect. 6.1.3.4); the slight differences are in fact due to the resolution of the petrographical analysis. This diagram shows that the precursor ferric montmorillonite is stable with kaolinite for very low values of $\mu_{K^+}$. As soon as these values increase, this assemblage is no longer stable and a Fe-rich beidellite-like dioctahedral smectite is formed. This is the “smectite” component of the interstratification. For higher values of $\mu_{K^+}$, the precursor disappears while glauconite mica is formed in the interstratification, as well as Fe-oxihydroxides if allowed by the chemical composition. Glaucositisation is not about solid-state transformations (SST) but a dissolution-recrystallisation process.

Fig. 7.15. Phase diagram in the $\mu_{K^+} – Al – Fe^{3+}$ system showing the relationships between the chemical composition of sediments and the formation of a precursor phase (ferric montmorillonite) before glauconitisation. Al–Fe–Sm: aluminous dioctahedral smectites. The composition of the mixed-layer smectite (Fe-beidellite) is stressed by the darker area; ka: kaolinite; glau mica: glauconite mica; Fe-sm: ferric smectites whose domain goes from nontronites to ferric montmorillonites; his: hisingerite or hydrated ferric silicates; Fe-ox: Fe-oxihydroxides
The “verdine” facies occurs in tropical environments where water temperature exceeds 20 °C (Porrentra 1967). This facies has not been observed in the intertropical space along the coasts bathed in cold oceanic currents (Odin and Matter 1981). Green grains are formed at shallow depth along the shores in the vicinity of the mouths of rivers carrying Fe-rich colloids (Fig. 7.16a). Coastal swamps and mangrove areas seem to play a major part as organic matter suppliers. The “greening” of sediments takes place between 10 and 60 m in depth, in the area where organic matter imposes reducing conditions that solubilise the iron of sedimentary oxides and hydroxides.

In ancient sedimentary formations, another facies is observed: oolitic ironstones. Formed of concentric deposits of iron oxides and clays, their origin is still questioned (Chamley 1989). A reliable reconstruction of the chemical processes taking place at the time of deposition is very difficult when the observed sediments have been subjected to diagenesis. The verdine and oolitic ironstone facies have in common the formation of Fe-rich phyllosilicates, which are neither glauconites nor nontronites. These are chlorites, the half-cell unit formulae of which are as follows:

1. berthierine (7 Å): \[ \text{[Si Al]}_5 (\text{Al Fe}^{2+}) (\text{OH})_4 \] for the Fe-rich end member,
2. chamosite (14 Å): \[ \text{[Si}_3 \text{ Al]}_10 (\text{Al Fe}_2^{2+}) (\text{OH})_8 \] for the Fe-rich end member,
3. odinite: \[ [\text{Si}_{4-x} \text{ Al}_x]_1 \text{O}_{10} (\text{R}_{2,2-2,8}^{3+} \text{ R}_{1,7-2,9}^{2+})(\text{OH})_8 \] (after Odin et al. 1988).

**Fig. 7.16a,b.** Odinite – berthierine. a) The verdine facies is formed at the mouth of rivers of tropical areas flowing into a hot ocean. b) The transformation of odinite into berthierine and into chamosite takes place by dissolution-precipitation reactions, and not only by reduction of the ferric iron.
Berthierine and chamosite have a triocahedral structure. Berthierine is characterised by high aluminium content. Odinite has a 7 Å-chlorite-like crystal structure intermediate between di- and triocahedral structures (Bailey 1988). The typical assemblages of the verdine and ironstone facies are odinite + Fe-rich smectite and berthierine + chamosite+swelling chlorite, respectively. It looks as if the crystal structures intermediate between di- and triocahedral are not stable under low diagenetic conditions.

Odinite can progressively transform into ferrous berthierine by reduction of iron, first yielding intermediate berthierines that retain the di-trioctahedral character: \([\text{Si}_{1.74} \text{Al}_{0.26}] \text{O}_5 (\text{Al}_{0.82} \text{Fe}_{0.28}^{3+} \text{Fe}_{1.01}^{2+} \text{Mg}_{0.46} \text{Mn}_{<0.01} \Box_{0.43}) \text{(OH)}_4\) (Hornibrook and Longstaffe 1996). Nevertheless, a moderate transformation does not mean that the reaction is limited to the change in iron valency. Indeed, odinite crystallises by filling bioclasts or porous detrital grains whereas berthierine forms coatings on the surfaces of the detrital elements outlining the rock pores (Fig. 7.16b). Therefore, the reaction implies both the dissolution of odinite (and of the accompanying detrital clay mineral assemblage) and the crystallisation of berthierine. The more reducing the environment, the closer to the ferrous triocahedral end member the composition of berthierine. Subsequently, the burial of sediments triggers diagenetic reactions that transform berthierine into chamosite. The mean conversion temperature is estimated at about 60 °C (Hornibrook and Longstaffe 1996).

The mineral sequence odinite – intermediate berthierine – trioctahedral berthierine results from the destabilisation of the detrital sediments carried by rivers of tropical areas. As regards fine particles, these sediments are mainly Fe-oxyhydroxides and kaolinite associated with organic matter. The reaction conditions have been very clearly analysed in an exceptional environment: weathering of a laterite submerged by swamps (Fritz and Toth 1997). They are as follows:

- low concentration of dissolved silica,
- low \(\text{Mg}^{2+}/\text{Fe}^{2+}\) ratio,
- high \(\text{CO}_2\) partial pressure,
- very low sulphate content, because during reduction, iron is trapped preferentially in sulphides (pyrite) to the detriment of phyllosilicates,
- moderate reducing conditions: \(Eh \approx -0.05\ \text{V}\).

These conditions correspond to those imposed by the discharge of fresh waters laden with oxihydroxides, kaolinite and organic matter into a hot ocean. The microbial activity is certainly one of the main factors taking part in the regulation of the \(\text{CO}_2\) and sulphur partial pressure.

**Suggested Readings**

CHAPTER 8

Diagenesis and Very Low-Grade Metamorphism

8.1 Sedimentary Series

Introduction

The physical properties and the mineralogical composition of sediments are transformed by diagenesis during burial in sedimentary basins. These physical and chemical transformations take place in the presence of complex fluids in which salt solutions, hydrocarbon compounds and gases are mixed. Burial at several kilometres in depth is possible only if the basin floor (basement) sinks gradually. This process, known as subsidence, is caused by sediment weight. The more abundant the sediment sources, the more active the subsidence.

During diagenesis, highly porous soft sediments (muds, sands) are transformed into less porous coherent rocks (shales, sandstones ...). This transformation is due to compaction (pressure effect) and cementation (mineral precipitations from over-saturated solutions). The resulting reduction in the pore volume causes the release of a great part of the water contained in the sediment. Mud and sand contain up to 80% and 30% water, respectively, whereas shales and sandstones contain a few percent only. The water released from rocks flows in high-permeability zones, notably in faults. The latter serve as drains, the activity of which being discontinuous over time (alternance of sealing and seism-induced reopening periods).

Diagenesis does not transform only the mineral matter. The organic components of sediments (river-borne soil organic matters, continental or oceanic living organisms) form hydrocarbon compounds and gases. These substances play a major part in the chemical environment, notably as regards redox conditions and solution pH. This chapter is aimed at showing the significant parameters of diagenesis, particularly those with an action on the mineral transformations of clays. The reactions will be detailed for two mineral sequences: the illite/smectite mixed layers (I/S) and the kaolin-group minerals.

Among the numerous books dealing with diagenesis, the general survey published by Larsen and Chilingar (1983), the subsidence process (Force et al. 1991), the review of organic matter evolution (Gautier et al. 1985; Gautier 1986), the methods for analysing the composition of fluids (Hanor 1988) and clay minerals (Eslinger and Pevear 1988) should be known. The reading of a few synthetic articles is strongly advised (Kübler 1984; Velde 1995).
8.1.1 Parameters of Diagenesis

8.1.1.1 Variation in Pressure and Temperature

Subsidence
The progressive sinking of the basement of sedimentary basins is due to the combined effect of slides along faults (tectonic subsidence) and volume reduction related to the cooling of this basement (thermal subsidence). The tectonic subsidence starts at the basin opening under an extension regime that induces the thinning and fracturation of the continental crust, thus forming a depression. The oldest sediments accumulate and their weight increases the downward movements (Fig. 8.1) until isostatic equilibrium has been reached. Thermal subsidence subsequently takes place (reduction in the basement volume by cooling process). The depression is sealed by increasingly recent sediments whose deposition is not disturbed by faults. Modelisation of these effects is now possible (Klein 1991). Nevertheless, the older the basins, the more complicated may be their tectonic history. Tectonic subsidence is sometimes interrupted by compression periods causing the reverse faulting of gravity faults. Finally, the basin structure itself is often greatly modified by the re-activation of gravity faults after the sedimentary filling period. Many basins are cut in “panels” in horst or graben position.

The various sinking, uplift and stability episodes experienced by the “panels” bring about variations in the pressure, temperature and permeability conditions of rock bodies. Therefore, successive processes of dissolution or precipitation of mineral phases take place in a same rock volume, yielding additional organic or inorganic chemical elements or, conversely, bringing about depletions by evacuation of some of these elements. These events are recorded in the petrographical structure of rocks, in the composition and shape of minerals, in fluid inclusions, and in the chemical and isotopic compositions of solutions collected in their environment. Accordingly, the history of diagenesis can be reconstructed gradually as shown by the North Sea example (Lacharpagne, personal communication), for which the sinking curve has been

![Fig. 8.1. Schematic representation of the subsidence of a sedimentary basin (Klein 1991)]
Fig. 8.2. Reconstruction of the diagenetic history of a sedimentary basin, North Sea (Lacharpagne, personal communication) plotted as a function of time and has been marked with mineral or organic reactions (Fig. 8.2).

**Lithostatic and Hydrostatic Pressures**
The pressure exerted at one point of the sedimentary pile essentially depends on the weight of the rock column above that point. The higher this column (depth
Diagenesis and Very Low-Grade Metamorphism

Fig. 8.3a,b. Pressure in diagenetic environments. a) The lithostatic pressure is exerted vertically (direction of gravity) on the framework of the rock-forming solids. b) The hydrostatic pressure is exerted isotropically on the pore walls. It tends to approach the lithostatic pressure when fluids are isolated from the surface by impermeable layers.

of the point involved), the greater the density and the higher the pressure. Since sediment porosity is never zero in the rock column, it can be connected up to the surface. In this case, pressure can be subdivided in lithostatic pressure (which is controlled by the mass of the solids) and hydrostatic pressure (which is controlled by the mass of the pore-filling fluids), both increasing with depth (Fig. 8.3a). However, considering the density difference in between solids and solutions, the lithostatic pressure increases at least twice as fast as the hydrostatic pressure (Fig. 8.3b).

Since permeability is reduced by compaction, fluids do not form a continuous column up to the surface. The hydrostatic pressure increases with the decreasing porosity and tends to approach the lithostatic pressure (Fig. 8.3b).
The relatively frequent occurrence of totally impermeable layers may induce a fluid overpressure, thus reducing the rock compaction rate, even at great depth. If overpressure exceeds the rock mechanical strength in its environment, the excess energy is released by hydraulic fracturation.

Compaction increases the density of sedimentary rocks by reducing their poral volume (Fig. 8.4a). Therefore, a great part of the ambient fluids is expelled, which results in the decrease of the solution/rock mass ratio. The higher the clay content in the sediment, the greater the decrease of this mass ratio. Accordingly, a mud containing 80% water yields a shale containing less than 20% water, whereas a sand containing a little more than 40% water is transformed into a sandstone containing only 30% water (Fig. 8.4b). From a geochemical standpoint, this means that during compaction, a sedimentary rock passes from an open system where fluid composition is controlled by the ambient environment to an increasingly closed system where this composition is controlled by equilibria with its mineral constituents and organic substances.

**Geothermal Gradient**

One of the effects of burial of a given sediment is the temperature changes it experiences with increasing depth. The average geothermal gradient for the continental crust is about $30 \degree{C} \text{km}^{-1}$. Nevertheless, the temperature increase is not a linear function of depth. Indeed, temperature rises fast in the first
100 km due to the production of heat related to the disintegration of radioactive elements (Vasseur 1988). A permissible approximation is that, in the crust, the temperature rises as a function of depth according to a law of the second degree:

\[
T = T_s - \frac{A_0 z^2}{2K} + \frac{q_0 z}{K}
\]

(8.1)

- \(A_0\) heat production (standard value: 2.4 \(\mu\) W m\(^{-3}\))
- \(K\) thermal conductivity (standard value: 3 W m\(^{-1}\) C\(^{-1}\))
- \(q_0\) heat flow (standard value: 60 mW m\(^{-2}\))

Nevertheless, for depths below 10 km, the geothermal gradient can be considered quite linear. In sedimentary basins, the gradient ranges between 15 and 35 \(^{\circ}\)C km\(^{-1}\) with a greater frequency for 25 \(^{\circ}\)C km\(^{-1}\) (Wood and Hewitt 1984).

### 8.1.1.2 Composition and Physical Properties of Rocks

The main types of rocks making up the sedimentary series observed in basins are sandstones, shales and carbonated rocks (limestones and dolomites). Rarer and much smaller are the salty rocks and the volcanoclastic rocks. Among the latter, bentonites are of great interest because they constitute stratigraphic markers (see Sect. 7.2.2.1) and particularly bear witness to diagenetic conditions (Sucha et al. 1993). From the standpoint of clays, the most important rocks are shales, bentonites and sandstones.

Sedimentary clays in muds or in clayey sands are generally mixtures of several species occurring in varying proportions: smectites, vermiculites, mixed-layer minerals, micas and so on. Large- and small-sized clays settle in the form of isolated particles (micas, kaolinite) and flakes (smectites, vermiculites), respectively (Fig. 8.5). The structures of these deposits are generally determined by edge-edge contacts, more rarely by edge-face contacts and never by face-face contacts (Fig. 5.22). This is due to the fact that the chemical bonds of the crystal framework of phyllosilicates are interrupted at the edges of crystals. When the pH conditions of the ambient environment are neutral or alkaline, flocculation is favoured by the unbalanced electric charges. Flocculation takes place when suspension in fresh water is dispersed in the sea.
The compaction rate increases according to the clay content of the sediment, thus introducing porosity contrasts. Accordingly, at 2 km in depth for instance, the porosity of a shale is about 10% whereas that of a clay-free sandstone is 30%. These differences not only affect the local water/rock ratio but also the solution flow. Therefore, shales behave like closed systems whereas sandstones constitute open systems. Bentonites are nearly monomineral rocks consisting of pure smectite (montmorillonite). Their extremely high compaction rate reduces their porosity and permeability more than for any other rock. Consequently, they form impermeable layers whose diagenetic evolution is less advanced than that of other clay rocks (Sucha et al. 1993).

8.1.1.3
Diagenetic Fluids

Open System – Closed System
The composition of the solutions impregnating sediments during their deposition is very close to that of seawater. The latter is an infinite reservoir that buffers the chemical activities of alkaline ions notably. Since compaction reduces porosity and permeability, then sandstones and shales form two systems with differing chemical behaviours. Accordingly, as fluids flow in sandstones, changes in their chemical composition are inferred from the chemical composition of seawater under the influence of interactions with solids (precipitation, dissolution). The marine inheritance is recorded in the isotopic compositions, as discussed below. The driving force for the displacement of solutions is the hydraulic gradient. Conversely, clay beds quickly acquire very low permeability and porosity. They contain small amounts of fluids, which flow very slowly, or not at all. In this case, the chemical activities of the dissolved species are controlled by the bulk chemical composition of the rock. The system is closed, and each clay bed undergoes changes independently of the others. Exchanges at the interfaces of these beds occur by chemical diffusion, the driving force being then the chemical potential gradients. To summarise, diagenetic reactions take place in open (Fig. 8.6a), half-closed (Fig. 8.6b) and closed (Fig. 8.6c) systems.

Isotopic Geochemistry
The isotopic composition of authigenic clay minerals is controlled by exchanges with the fluids from which they have been formed. At equilibrium, for a fluid with a given composition, the isotopic exchange rate depends on temperature (see Sect. 4.1.4). This has been shown in the Gulf Coast area where the isotopic ratios $^{18}O/^{16}O$ and $D/H$ vary with depth for the fine fractions only ($< 0.1 \mu m$), which must be considered as representing the authigenic fraction of clays (Fig. 8.7a,b). Yeh and Savin (1977) have shown that the $\delta^{18}O$ of this fine fraction depends on the temperature measured in the drill hole (Fig. 8.7c). The sudden variation of the $D/H$ ratio at about 3 km in depth indicates that the system is closing (Yeh 1980). The fine clay fraction reaches isotopic equilibrium with residual fluids mixed with dehydration fluids of shales.
Fig. 8.6a–c. Behaviour in open a), half-closed b) and closed c) systems of the major clay rocks in diagenetic series. The appropriate phase diagrams are represented in front of the rocks. In an open system, the chemical potential of all elements in solution is controlled by the external environment (significant fluid flows). In a half-closed system, the chemical potential of only a few chemical elements is controlled by the external environment. In a closed system, the chemical potential of all elements in solution are controlled by the rock composition.

It must be remembered that the isotopic composition of clays depends on three parameters: temperature, fluid/rock ratio and fluid isotopic composition. While the latter is readily controlled in supergene environments where it is known to depend on latitude, its determination is made much more difficult in diagenetic series. Indeed, fluids cannot be analysed most of the time, and even when possible, the fluids sampled in drill holes are not necessarily those that existed at the time of mineral formation.
Fig. 8.7a–c. Isotopic composition of the various grain size fractions of clay minerals derived from the Gulf Coast diagenetic shales. a) Variation of δ¹⁸O with depth according to data by Yeh and Savin (1977). b) Variation of the D/H ratio with depth (Yeh 1980). c) Relationship between the temperature measured in drill holes and the variation of the δ¹⁸O ratio.

Fig. 8.8a,b. The organic matter in diagenesis. a) van Krevelen diagram showing the three types of OM. b) The reflectance of vitrinite varies according to a factor time × temperature (Kübler 1985).
Diagenesis and Very Low-Grade Metamorphism

Geochemistry of Organic Substances
In the living world, the organic matter (OM) is composed of very long molecules. After death, burial leads to the rupture of carbon chains. The resulting molecules are increasingly short as temperature rises. This reduction brings about the release of carbon atoms then forming graphite. The OM from plant species yields coal whereas that from animals, phytoplankton and bacteria yields petroleum. The OM transformation stages have been clearly summarised by Tissot and Welte (1978) who defined three types of kerogens according to their hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios (van Krevelen diagram). Types I and II are dominated by aliphatic compounds (chains), type III is dominated by aromatic compounds (carbon rings). During the burial process, these three types form separate mineral sequences of increasingly short products (reduction of the H/C and O/C ratios), thus retaining the signature of the initial OM (Fig. 8.8a). In the same time, the solid compounds (organoliths) and notably vitrinite are modified during maturation (Kübler 1984). Their reflectance increases steadily as a function of the factor time × temperature (Fig. 8.8b).

The presence of liquid or gaseous organic compounds influences the mineral reactions in four different ways: (1) control of CO₂ and H₂S partial pressures, (2) prevailing influence on redox conditions, (3) influence on pH conditions (OM provides protons) and (4) capacity to form organo-mineral complexes that substantially modify the solubility of elements and increases mass transfers.

8.1.2
Smectite → Illite Transformation in Clay Sediments

8.1.2.1
Series of Illite/Smectite Mixed Layers (I/S)

From the Heterogeneous Sediment to the Formation of Smectite
Sediments are composed of very different minerals that do not make up stable assemblages. Some are debris of crystals formed under magmatic or metamorphic conditions (quartz, feldspars, micas . . . ), others have crystallised under surface conditions in alterites and soils (smectites, intergrade or partially interstratified vermiculites, kaolinite, halloysite, Fe-Mn oxides and hydroxides . . . ). Finally, at certain times, volcanic ashes may also have mixed with terrigenous sediments. By accumulating in sedimentary basins, these minerals or rock debris form mineral assemblages that are out of equilibrium under new imposed conditions (temperature and fluid composition). Velde (1995) proposes a highly pedagogical distinction between the first and the second kilometre in sedimentary basins having a normal geothermal gradient (25–30 °C km⁻¹). Indeed, whatever the value of this gradient, the temperature increase caused by shallow burials is not sufficient to trigger mineral reactions whose effects can be measured by X-ray diffraction. This is clearly shown in the Pleistocene series of the Colorado Delta (Jennings and Thompson 1987) where the sedimentary influence continues as long as a temperature of 80 °C has not been reached. Once said temperature has been reached, some mineral species of the
sediments react, notably clay species except micas. The reaction homogenises the clay composition by yielding pure smectite (low-charge montmorillonite). The older the sedimentary basin, the lower the reaction temperature: 80 °C for a recent age (Pleistocene), 50 °C for Cretaceous sediments. This means that smectite formation during burial is controlled by the parameter time × temperature (t × T). This phenomenon differs from “early diagenesis” that leads to lath-shaped overgrowths of Al–Fe clays at the interface between sediments and seawater (see Sect. 7.2.2.3).

**Smectite → illite Reaction**

The smectite previously formed by the reaction of the clay fractions in sediments in turn transforms as burial progresses, yielding illite. In the first stages of transformation, illite forms randomly ordered mixed-layer minerals with smectite. As the reaction progresses, the stacking sequence becomes ordered and the illite content rises (Fig. 8.9a). Such sequences are known in most of the sedimentary basins that have been drilled for oil exploration (Fig. 8.9b). From a chemical balance standpoint, this reaction consumes potassium, which implies an outside source for this element insufficiently present in smectite.

![Fig. 8.9a,b. Series of illite/smectite mixed layers (I/S). a) Diffraction patterns (air-dried and ethylene glycol-saturated oriented samples) of two examples of I/S minerals derived from the Paris Basin (Lanson 1990). b) Variation in the smectite content of I/S series derived from several sedimentary basins (Srodon and Eberl 1987)](image-url)
The source is derived either from the dissolution of some detrital minerals that had remained inert during the previous stage (smectite formation): micas and K-feldspars or from external solutions brines). The smectite → illite reaction can then be written in two different ways according to whether aluminium is considered (1) a mobile element (Hower et al. 1976) or (2) an immobile element (Boles and Franks 1979):

1. \[ \text{1 smectite} + \text{K}^+ + \text{Al}^{3+} \rightarrow \text{1 illite} + \text{Na}^+ + \text{Ca}^{2+} + \text{Si}^{4+} + \text{Fe}^{2+} + \text{Mg}^{2+} + \text{H}_2\text{O} \]
2. \[ \text{1.6 smectite} + \text{K}^+ \rightarrow \text{1 illite} + \text{Na}^+ + \text{Ca}^{2+} + \text{Si}^{4+} + \text{Fe}^{2+} + \text{Mg}^{2+} + \text{O}^{2-} + \text{OH}^- + \text{H}_2\text{O} \]

The first reaction does not entail any loss of mass (hence of volume) whereas the second reaction entails the loss of more than 35% of mass.

Both reactions can take place in all types of clay sediments as long as compaction has not established any permeability contrast between sandstones and shales. The composition of the sedimentary solutions is altered by the release of water and dissolved ionic species. Dissolved silica causes the formation of the first overgrowths on quartz. According to the CO$_2$ partial pressure value, the Ca$^{2+}$, Mg$^{2+}$ and Fe$^{2+}$ cations form carbonates or Fe-rich chlorites. Once compaction has reduced the permeability of shales, exchanges with sandstones are increasingly reduced. Shales behave as closed systems whereas sandstones keep connected with the external environment through faulting (Lanson et al. 1996). In closed systems, reaction 1 is supplanted by reaction 2.

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**Fig. 8.10a–c.** Variation in the mineralogical composition of sediments as a function of depth from Hower (1981). a) Progressive increase in the illite content of I/S mixed layers. The transition zone between the randomly ordered mixed-layer minerals and the ordered mixed-layer minerals is indicated. b) Progressive decrease in the K-feldspar content and increase in the chlorite content. c) Progressive increase in the K$_2$O content of the clay fine fraction dominated by authigenic minerals (I/S minerals) as the amounts of the coarse fraction dominated by detrital minerals (K-feldspars, micas) decrease.
Under diagenetic conditions, the illite resulting from one or the other reaction has never been shown to exist in the first place as individual crystals or particles. It comes in the form of layers interstratified with smectite (montmorillonite) in randomly ordered stacking sequences (R0 I/S minerals). As reactions progress, the illite content of R0 I/S minerals progressively increases up to values exceeding 50% (Fig. 8.10a). They are then replaced by ordered mixed-layer minerals (R1 I/S minerals) and illite crystals (see Sect. 1.2.4.2). In the same time, the proportion of chlorite increases and that of K-feldspars decreases (Fig. 8.10b). The K\textsubscript{2}O content of authigenic fractions increases (Fig. 8.10c). The simultaneity of these variations has been shown by Hower (1981).

**Series of Mixed-Layer Minerals: 2 Components (I/S) or 3 Components (I/S/V)?**

A direct reading of the diffraction patterns reveals a seemingly sudden transition between randomly ordered mixed-layer minerals (R0 I/S minerals) and ordered mixed-layer minerals (R1 I/S minerals) (Fig. 8.11a). Indeed, this transition corresponds to two criteria: (1) disappearance of the 17 Å band whose background in small angles increases with the illite content (increasing saddle/peak ratio), and (2) occurrence of a band near 13.4 Å typical of R1 structures (Fig. 8.9b). This is in fact a slower change. Decomposition of XRD patterns (Fig. 8.11a) and mostly the fit by calculated curves (Fig. 8.11b) show that R0 and R1 I/S minerals co-exist over greater depth than what was first supposed.

**Comparative Reactivity of Sedimentary Components**

Mineral components of terrigenous sediments do not all react at the same rate when burial depth increases (Fig. 8.12). The most reactive mineral components (unstable under diagenetic conditions) are clays formed under surface conditions (soils and alterites). All species (smectites, di- and trioctahedral vermiculites, mixed-layer minerals, illite, halloysite, allophanes and imogolites) mostly react to the change in the chemical composition of fluids (Velde’s first kilometre). Kaolinite itself, which is known to occur down to significant depths (at least 5 km), recrystallises and loses its supergene characteristics such as the presence of Fe\textsuperscript{3+} ions and a high density of crystal defects.

Debris of magmatic or metamorphic minerals persist over longer periods of time. They take part in the mineral reactions as providers of some chemical elements. Their dissolution produces a secondary porosity that adds to or replaces the primary porosity of the sediment. Quartz only dissolves on microsites under compression whereas overgrowths are formed in pore free space. Abercrombie et al. (1994) have shown that the dissolved silica content is first controlled by low-temperature amorphous silica, then by the dissolution of feldspars and finally by high-temperature quartz (Fig. 8.13).

Some minerals remain totally inert under the physicochemical conditions imposed by diagenesis. They then form a detrital inheritance that survives up to the very low-grade metamorphic domain. This is the case of garnets, zircons and magnetite-like oxides. Glauconite remains stable in practically the whole diagenetic domain. The only change is the progressive decrease in the proportion of interstratified smectite they may contain since their formation
Fig. 8.11a,b. Methods for interpreting X-ray diffraction patterns of illite/smectite mixed layers. a) Example of decomposition applied to a diagenetic bentonite sample (Aquitaine Basin, France): smectite + R0 and R1 IS MLMs + mica (°2θ Cu Kα). b) Calculation of the closest fit between the theoretical and the experimental pattern (from Drits et al. 1999)
Fig. 8.12. Reactivity differences between the mineral components of the terrigenous sediments under diagenetic conditions.

Fig. 8.13. Variation in the silica activity of solutions derived from the reservoirs of two sedimentary basins: San Joaquin and Gulf Coast offshore, U.S.A. (Abercrombie et al. 1994)
(Thompson and Hower 1973). They retain their characteristic pellet morphology and finally recrystallise yielding Mg-rich phyllites and stilpnomelane in the diagenesis-to-very low-grade metamorphism transition (Goy-Eggenberger 1998).

8.1.2.2
The Concept of the Smectite to Illite Conversion

Thermodynamic Models
Considering that smectite and illite are independent mineral phases, their stability field can be calculated in the chemical potential-temperature space (pressure seemingly playing a minor role) using their thermodynamic parameters. The problem is then to determine if these two components are independent phases in the mixed-layer structures or if, by contrast, they represent two pure end members of a solid solution. This problem is not straightforward and has been debated, particularly by Garrels (1984) who, using the data interpreted by Aagaard and Helgeson (1983) in terms of solid solutions, showed that they are equally coherent with smectite and illite viewed as separate phases (Fig. 8.14). Despite these defects in the coherence of thermodynamic data, numerous attempts have been made to characterise the variation in the stability field of the I/S minerals considered as solid solution as a function of temperature (Ransom and Helgeson 1993; Blanc 1996). The mineral transformations observed in di-

Fig. 8.14a,b. Representations of the solution composition in the sedimentary basin reservoirs in diagram Log \( \left( \frac{a_{K^+}}{a_{H^+}} \right) \) as a function of Log \( a_{SiO_2} \) at 25 °C (grey zone). a) Assumption of a solid solution between smectite and illite (Aagaard and Helgeson 1983). b) Assumption of independent phases (Garrels 1984)
agensis are not properly described by these attempts because crystal growth along $a$ and $b$ directions (see Sect. 1.2.4.2) is ignored.

**Kinetic Models**

Based upon kinetic laws (see Sect. 3.2.3), several models have been proposed either from observation of natural I/S sequences (Bethke and Altaner 1986; Pytte and Reynolds 1989; Velde and Vasseur 1992) or from experimentation (Eberl and Hower 1976; Huang et al. 1993). Values of reaction order, activation energy and pre-exponential factor vary according to whether illitisation is considered as a simple reaction (smectite $\rightarrow$ illite) or as a stage reaction (smectite $\rightarrow$ R0 I/S minerals $\rightarrow$ R1 I/S minerals . . . ).

In the smectite $\rightarrow$ illite simple reaction, the law of mass action is considered to affect the reaction rate. Huang et al. (1993) propose a rate formulation in which the relative K$^+$ content acts as a linear factor:

\[
\frac{-dS}{dt} = A \exp \left( \frac{-E_a}{RT} \right) \times [K^+] \times S^2
\]  

where

- $S$ % smectite in the I/S minerals
- $S^2$ indicates a second-order reaction
- $t$ time (s)
- $A$ frequency factor ($8.08 \times 10^{-4}$ s$^{-1}$)
- $E_a$ activation energy (28 kcal mol$^{-1}$)
- $R$ perfect gas constant (1.987 cal$^\circ$K$^{-1}$ mol$^{-1}$)
- $T$ absolute temperature ($^\circ$K)
- $K^+$ concentration (molarity) of K$^+$ in solution

By comparing the results of experiments carried out under the same temperature conditions (180 $^\circ$C) for different K$^+$ concentrations (Eberl and Hower 1976; Robertson and Lahann 1981; Howard and Roy 1985; Whitney and Northrop 1988; Meunier et al. 1998) have shown that a linear relationship appears between the potassium content and the reaction progress ($dS/dt$).

The major difficulty in this type of approach (simple reaction) is the selection of the reaction order, which is determined by its mechanism. What does a second-order (Huang et al. 1993) or a sixth-order reaction (Pytte and Reynolds 1989) mean? To avoid this problem, other kinetic approaches consider that illitisation is a stage reaction. Bethke and Altaner (1986) have tried to describe the I/S sequences observed in shales by successive reactions forming SSI then ISI structures from smectite S. Each of the forms S, SSI and ISI is characterised by a specific reactivity coefficient: 0.5, 1 and 1.1. The three
reaction constants $k_1$, $k_2$ and $k_3$ are calculated as follows:

$$k_1 = A \exp \left( \frac{-E_1}{RT} \right)$$

$$\frac{k_0}{k_1} = \exp \left( \frac{-[E_0 - E_1]}{RT} \right)$$

$$A = 10^{-3} \text{ s}^{-1}$$

$$E_0 - E_1 = 0.5 \text{ kcal mol}^{-1}$$

$$E_2 - E_1 = 1.7 \text{ kcal mol}^{-1}$$

This velocity rule has been successfully applied to shales which have undergone a deep burial but fails to describe properly the less advanced diagenetic transformations.

Velde and Vasseur (1992) have proposed an empirical kinetic model based on I/S sequences derived from seven basins of differing ages (1 to 200 Ma). This model rests upon the assumption of a two-stage smectite-to-illite transformation corresponding to the formation of two mineral structures with changing compositions (% illite). The first reaction describes the transformation of smectite into a randomly ordered I/S mineral (R0) whose percentage in smectite component ranges from 100% to 50%. The second reaction yields I/S minerals whose percentage in illite component ranges from 50% to 100%. The second reaction is dependent on the first one because, for each lost smectite layer in a R0 I/S mineral (relative increase in the illite content), a R1 50% illite crystal is formed. Subsequently, this crystal progresses towards the 100% illite composition, end of the reaction (Fig. 8.15). New R1 I/S crystals are produced as long as there are R0 I/S minerals with a composition tending towards the end of reaction 1 (50% illite). Therefore, the proportion of R0 crystals decreases as the reaction progresses.

The kinetic equations are as follows:

**Reaction 1 (randomly ordered I/S (R0) whose percentage in smectite component ranges from 100 to 50%)**:

$$\frac{dS}{dt} = -k_1 S \text{ with } \log (k_1) = \log (A_1) - \frac{E_1}{RT}$$

$$\log (A_1) = 24.4 \text{ Ma}^{-1} \text{ and } E_1 = 76.8 \text{ kJ mol}^{-1}$$

**Reaction 2 (regularly ordered I/S mineral (R1) with 50 to 0% smectite)**

$$\frac{dM}{dt} = k_1 S - k_2 M \text{ with } \log (k_2) = \log (A_2) - \frac{E_2}{RT}$$

$$\log (A_2) = 7.2 \text{ Ma}^{-1} \text{ and } E_2 = 37.4 \text{ kJ mol}^{-1}$$

This model gives a rather good description of the diagenetic transformations of the I/S minerals in shales, and even in bentonites. Its major drawback lies
Fig. 8.15. Empirical kinetic model of the smectite-to-illite transformation through two reactions (Velde and Vasseur 1992). Reaction 1: smectite → randomly ordered I/S mineral (R0) with 100 to 50% smectite (dotted curve); reaction 2: R0 → regularly ordered I/S mineral (R1) with 50 to 0% smectite (dashed curve); the sum of both reactions (full line) in a too early prediction (too shallow depth) of the end of the reaction end at 100% illite (Varajao and Meunier 1995).

The empirical model by Velde and Vasseur (1992) based on a mineral reaction between two phases is supported by recent works (Claret 2001). Indeed, the classical approach to the series of illite-smectite mixed layers in diagenesis has been modified by the fit of experimental XRD patterns by calculated ones using 3-component mixed layer minerals. The study of the diagenetic series in the eastern part of the Paris Basin and in the Gulf Coast area (USA) shows that the sample diffraction patterns result from the sum of the diffraction patterns of the discrete phases, of which the composition remains constant but the proportions vary with depth. This more rigorous but unfortunately very cumbersome new approach will undoubtedly become the most efficient procedure for interpreting diffraction patterns in the future, once the trial and error work performed by hand to date is somehow automated.

8.1.2.3
The Concept of Illite Growth on a Montmorillonite Nucleus

Basis of the Concept
The analytical data of a great number of series amount to three essential facts (Meunier et al. 2000):
1. smectite is a montmorillonite (no tetrahedral charge),

2. illite has a buffered chemical composition of type: $[\text{Si}_{3.30} \text{Al}_{0.70}]_0 \text{O}_{10}(\text{Al}_{1.80} \text{Fe}^{3+}_{0.05} \text{Mg}_{0.15})(\text{OH})_2 \text{K}_{0.90}$. The 2:1 layer then exhibits tetrahedral and octahedral charges. The interlayer charge clearly differs from that of micas,

3. the mathematical decomposition of samples composed of ordered mixed layers to illite reveals three populations of particles (Fig. 8.16a): WCI (well crystallised illite), PCI (poorly crystallised illite) and I/S minerals (illite-rich R1 I/S mixed layers). The size of particles increases with depth (Fig. 8.16b). Their shape changes gradually from laths (elongated rectangles) to more isotropic particles (hexagons).

Fig. 8.16a–c. The R1 I/S minerals in diagenesis (Lanson and Meunier 1995). a) Mathematical decomposition of the broad band near 10 Å. WCI: well crystallised illite; PCI: poorly crystallised illite; I/S: the two bands correspond to an illite-rich I/S mineral. b) Schematic representation of the relationships between morphology, size and composition of I/S particles under increasing diagenetic conditions. c) The different possibilities of illitisation for regularly ordered I/S minerals ($N$: number of layers in the coherent domain)
The illite content of I/S crystals progressively increases as they grow. This growth takes place simultaneously with the formation and growth of discrete illite particles. This means that the surrounding fluids are oversaturated with respect to illite (buffered composition) and not to mixed-layer minerals (illite+smectite). The montmorillonite component does not disappear from the growing I/S crystals, but is “fossilised” within the structure (see Sect. 1.2.5.1). Accordingly, the size and proportion of illite in regularly ordered I/S minerals can increase in four ways (Fig. 8.16c): (1) smectite to illite solid state transformation (N constant); (2) coalescence of I/S crystals of similar composition (limited increase in the illite content through interfaces); (3) nucleation and direct growth of illite crystals; (4) addition of illite layers on I/S crystals.

**Model of the I/S/V Crystal Structure**

At a first glance, the identification by X-ray diffraction of three types of layers in the I/S minerals (Drits et al. 1997) – montmorillonite (2 glycol layers), vermiculite (1 glycol layer) and illite (0 glycol layer) – does not seem consistent with the chemical compositions corresponding to a two component (montmorillonite + illite) mixture. This is only an outward discrepancy if these 3-component mixed-layer minerals are considered chemically identical to mixtures of illite and montmorillonite. In this case, layers with vermiculite behaviour are partly illites from the standpoint of tetrahedral and octahedral charges, but the interlayer zone is devoid of potassium (Meunier et al. 2000).

Indeed, a I/S/V mixed-layer mineral corresponds to a succession of interlayers bordered with tetrahedral sheets without substitution (Si$_4$O$_{10}$) compensating for octahedral charges (montmorillonite) and interlayers compensating for tetrahedral and octahedral charges (illite). If tetrahedral substitutions are added, the charge is increased and a 2:1 layer polarity is induced (Altaner and Ylagan 1997).

The growth of I/S/V minerals by addition of illite layers requires that the composition of the crystal outer surfaces be such that cumulative interlayer charges correspond to +0.90 per Si$_4$O$_{10}$. The outer interfaces of each I/S/V crystal have the chemical composition of a half illite layer (Fig. 8.17). When crystals are superposed in an oriented sample for instance, interfaces are saturated by the surrounding cations. If the latter are cations with a strong hydration power (Ca$^{2+}$, Mg$^{2+}$, Na$^+$), the joining interfaces form a pseudo interlayer sheet having a swelling power similar to that of vermiculite. Consequently, when examined by X-ray diffraction, mixed-layer minerals exhibit three types of layers: illite, montmorillonite and vermiculite. This model in which growth phenomena are accounted for is still hypothetical to date.

**Formation and Growth of I/S/V Minerals**

The addition of illite layers over a montmorillonite structure used as an embryo poses the problem of the nature of the solid-solution interfaces. To obtain an I/S mixed-layer structure similar to the one described in Fig. 8.17, it is necessary that low-charge montmorillonite interfaces be transformed into vermiculite interfaces whose charge is partly derived from tetrahedral substitutions.
Fig. 8.17. The symmetrical distribution of electric charges in the 2:1 layers about the interlayer zones corresponds to illite and montmorillonite in an I/S/V mixed-layer structure (Meunier et al. 2000)

(Fig. 8.18a). This type of transformation has been shown in experimental works (Howard 1981; Whitney et Northrop 1988). The reaction can be written as follows:

low-charge montmorillonite + Na–Ca solutions
→ vermiculite + Mg-smectite + quartz

The formation of quartz and magnesian smectite is due to the occurrence of substitutions of Al for Si in tetrahedral sheets and to the decrease in the sub-
**a Vermiculitization of the crystal outer interfaces**

![Diagram illustrating the transformation of specific interfaces of a low-charge montmorillonite into vermiculite by occurrence of charges in the tetrahedral sheet.](image)

**b the illite growth stage**

![Diagram showing the addition of illite layers and the growth process.](image)

**Fig. 8.18a,b. I/S/V mixed layers. a) Transformation of the specific interfaces of a low-charge montmorillonite into vermiculite by occurrence of charges in the tetrahedral sheet. b) Addition of illite layers. In the growth process considered here, the charge of the interface is equal to half the charge of an illite layer (0.45 per Si$_4$O$_{10}$)**

Substitution rate of Mg for R$^{3+}$ in octahedral sheets, which releases Si$^{4+}$ and Mg$^{2+}$ ions into solutions. Under higher temperature conditions, magnesian smectite is replaced by chlorite. In the case of high CO$_2$ pressure, magnesian phyllosilicates are replaced by dolomite. The increase in the size of I/S particles then takes place by addition of illite layers over vermiculite interfaces (Fig. 8.18b).

Illite layers grow over vermiculite interfaces such that the charge of the interlayer zone so created is equal to 0.9 per Si$_4$O$_{10}$ (Fig. 8.18b). The crystal then gains an additional layer (growth along the c direction) and the proportion of illite increases in the mixed-layer structure. In its new state, the crystal still exhibits vermiculite interfaces likely to fix a new layer. The process can take place continuously by spiral growth from a screw dislocation emerging on the (001) faces, as shown in Fig. 1.30. This type of growth, well known in micas, has been revealed in I/S crystals by Inoue and Kitagawa (1994). This process is much less energy consuming than direct nucleation of illite layers on the I/S (001) faces. This means that growth can be triggered for a much lower fluid oversaturation rate.
The growth of crystals or particles takes place in the three space directions, resulting in an increase in their thickness \((c)\) direction and lateral spread \((a\) and \(b)\) dimensions. The montmorillonite layers are then surrounded by illite layers (Fig. 8.19a,b). Illite growth in the \(a-b\) plane necessarily brings about the occurrence of crystal defects. Several types of growth are possible in this plane:

1. the initial montmorillonite layer changes laterally to an illite layer. A defect related to the change in thickness then appears;
2. two montmorillonite layers (15 Å) change laterally to three illite layers (10 Å). The boundary between the initial crystal of a mixed-layer mineral and the zone of lateral growth is marked by an intercalation defect of edge dislocation type (Fig. 8.19c).
3. the crystal morphology depends on the crystal growth directions (Güven 2001). Remember that the higher the growth rate along a given crystallographic direction, the more reduced is the corresponding face. Accordingly, the frequently occurring laths in I/S minerals and illites are due to a fast growth along \([100]\) and do not exhibit any \((100)\) face.

All I/S/V mixed-layer structures cannot be explained by the growth of illite over a montmorillonite nucleus, because the succession of several smectite layers is forbidden by the stacking sequence in ordered mixed-layer minerals (the probability of occurrence of S–S pairs is zero). Nuclei are not formed with a single montmorillonite layer. Consequently, the vermiculitisation process preceding illite formation is assumed to take place by solid state transformation of smectite layers within a stacking sequence, and not only at interfaces (Meunier et al. 2000).

**8.1.2.4 Direct Precipitation of Illite and I/S Minerals**

In sandstones, illite is not always formed by transformation of smectite. It may nucleate and grow directly on pre-existing solid supports, such as kaolinite or quartz notably. This has been shown by the study of the Rotliegende sandstone reservoir in the Broad Fourteens Basin, North Sea (Fig. 8.20). From the time of sedimentary deposition (275 Ma) to the Cimmerian orogeny (155 Ma), the burial diagenesis caused kaolinite to recrystallise into dickite. The faulting process during orogeny allowed hot and salted fluids derived from underlying formations (Zechstein) to flow. The sudden chemical disequilibrium imposed in the reservoir triggered the precipitation of illitic minerals (pure illite and I/S minerals), the morphology and crystallochemical characteristics of which did not depend on the stage of advancement of the classical reaction smectite → illite (Lanson et al. 1996). These characteristics (illite content of I/S minerals, illite / I/S minerals ratio, tridimensional crystal structure) reflect the temperature conditions established at the time of the crystallisation of these minerals. This is typically the result of a sudden hydrothermal phenomenon due to the invasion of the reservoir by K\(^+\)-rich brines.
Fig. 8.19a–d. Possible growth process of I/S crystals. a) Spiral growth from a screw dislocation emerging on the (001) face of a I/S crystal. The growth direction is given by the arrow. b) Growth along the three space directions. Iillite surrounds the montmorillonite layers that were used as a nucleus. c) Growth takes place from a crystal defect of edge dislocation type. Iillite; M: montmorillonite; V: vermiculite. d) Control of illite (or mica morphology by the crystal growth directions (Güven 2001)
The potassium source is derived from evaporitic deposits of the Zechstein Formation and not from the dissolution of K-feldspars. The solutions invading sandstones are oversaturated with respect to illite and K-feldspars. The higher oversaturation rate with respect to illite explains the precipitation of the latter whereas K-feldspars do not show any trace of dissolution. Since the input of K\(^+\) ions is not compensated for by the loss of H\(^+\) ions as is the rule for dissolution reactions, the \(a_{K^+}/a_{H^+}\) activity ratio decreases so that I/S minerals are more easily formed than illite.

8.1.3
Transformations of Other Clay Minerals

8.1.3.1
The Kaolinite-to-Dickite Transition

Kaolin-group minerals are Si\(_2\)O\(_5\)Al\(_2\)(OH)\(_4\) polymorphs. Kaolinite forms book-shaped triclinic flat crystals whereas dickite, although of monoclinic symmetry, exhibits rhomboidal prisms (Fig. 8.21a,b). Kaolinite (1-layer polymorph) comprises a layer stacking sequence whose vacancy is in the B position. Dickite (2-layer polymorph) is formed by the regular alternation of type B- and type C-layer stacking sequence (Fig. 8.21c). Nacrite is a monoclinic 2-layer poly-
Sedimentary Series

Fig. 8.21a–c. Crystallographic characteristics of kaolinite and dickite. a,b) Crystal shapes in diagenetic environments. c) The three types of vacancy position in the 1:1 layer (light grey: octahedral vacancy in A, B or C position; heavy lines: the three octahedra as seen through the hexagonal cavity of the tetrahedral sheet)

morph. Relatively rare in diagenesis, nacrite is known to be formed in rocks containing bitumen or coal.

The dimensions of the dickite unit cell are smaller than those of two kaolinite unit cells superposed along the $c^*$ direction. Therefore, its molar volume is smaller and dickite is viewed as the stable polymorph at high pressure. Ehrenberg et al. (1993) have proposed a kaolinite-dickite isograde in the pressure-temperature space, kaolinite transforming into dickite between 100 and 160 °C for pressures in the range 0.5–0.8 kbar (Fig. 8.22). Therefore, according to these authors, if pressure is known (calculated by the weight of the sedimentary column), the kaolinite-to-dickite transition can be used as a geothermometer.

In reality, isograde is a simplistic view of dickite crystallisation. Beaufort et al. (1998) have shown that dickite crystallisation takes place according to two simultaneous processes in the Rotliegende sandstone reservoir, Broad Four-
Fig. 8.22. Phase diagram proposed by Ehrenberg et al. (1993). Grey: occurrence fields of dickite

teens Basin, North Sea (Fig. 8.23). The first process is the accretion of matter derived from the dissolution of small kaolinite crystals or detrital minerals (K-feldspars then micas) on bigger kaolinite crystals. This process is similar to a ripening process although dickite and kaolinite do not crystallise in the same symmetry system. Randomly ordered dickite is formed first, and subsequently, while growing, it becomes ordered. The second process is a direct neoformation of ordered dickite from the solutions.

8.1.3.2 Corrensite and Magnesian Chlorite

Corrensite and minerals described as chlorite/smectite mixed layers are formed either in volcanic environments (volcanoclastic rocks, basalts) or in detrital or carbonated sedimentary series. Volcanic rocks will be discussed in a later paragraph. Since corrensite and magnesian chlorite are not directly formed by precipitation in present day evaporitic environments (Bodine and Madsen 1987), they were classically assumed to derive from the transformation of a magnesian smectite. The latter was believed to assume the role of precursor in the diagenetic crystallisation sequence: saponite → corrensite → chlorite (Fig. 8.24a). This sequence is not that commonly found because corrensite and magnesian chlorite occur in carbonated rocks (Hillier 1993) or in the fractures of the sedimentary basin basement. In fact, diagenesis of sedimentary series leads to the formation of these minerals only when brines impose very special local chemical conditions of pH and dissolved magnesium activity.
Fig. 8.23. Schematic representation of the two processes of dickite formation in the Rotliegende sandstone reservoir (Broad Fourteens Basin, North Sea): growth of dickite on kaolinite crystals, nucleation and growth of dickite crystals.

The source of chemical elements necessary for the crystallisation of corrensite or magnesian chlorites in carbonated rocks is double: dolomite for Fe and Mg; dioctahedral detrital clays and quartz for Si and Al. Two mineral reactions are considered:

\[ 5 \text{dolomite} + 1 \text{kaolinite} + 1 \text{quartz} + 1 \text{H}_2\text{O} \rightarrow 1 \text{chlorite} + 5 \text{calcite} + 5 \text{CO}_2 \]
Fig. 8.24a,b. Formation of corrensite and chlorites. a) Diagenesis of evaporitic series (Hillier 1993). b) Phase diagrams based on Hillier’s observations (1993) in the Mg–Fe$^{2+}$–(Fe$^{3+}$,Al) system showing the relationships between magnesian and ferrous mineral sequences (modified from Velde 1985). dol: dolomite, ank: ankerite, pyr: pyrite, mont: montmorillonite, I/S: illite-smectite mixed layers, bert: berthierine, corr: corrensite, Mg-chl and Fe-chl: magnesian and ferrous chlorites, respectively

(Zen 1959)

$$15 \text{dolomite} + 2 \text{illite} + 3 \text{quartz} + 11 \text{H}_2\text{O} \rightarrow 3 \text{chlorite} + 15 \text{calcite} + 2 \text{K}^+ + 2(\text{OH})^- + 15 \text{CO}_2$$

(8.10)

(Hutcheon et al. 1980)

In Devonian lacustrine clays of the Orcadian Basin (Scotland), Hillier (1993) has shown two essential diagenetic effects: (1) the amount of chloritic minerals increases as the amount of dolomite decreases, (2) a magnesian mineral sequence (corrensite, chlorite and corrensite-chlorite intergrowths) is formed
along with a chlorite having a higher iron content (Fig. 8.24b). This observation is important because crystallisation of chlorite is shown to take place according to two different processes depending on its iron content. The co-existence of two chemically different chlorite populations shows that equilibrium under the $P$, $T$, $\mu_X$ conditions is not reached. The predominating kinetic effects eliminate any possibility of searching for geothermometers based on the evolution of composition within the compositional range of a solid solution. The rock chemical composition is obviously of paramount importance for the formation of mineral assemblages in diagenesis.

Flows of hot brines at the interface between sediments and basement in sedimentary basins bring about mineral reactions in their flowing zones: porous sedimentary formations, fractures in basements. The example of the scientific drill hole at Sancerre-Couy (Géologie Profonde de la France programme) has shown that hot and highly salted fluids have infiltrated into the basement fractures and have reacted with the wall rock (gneiss and amphibolites). Their residence time has been long enough for them to reach the isotopic equilibrium with rocks, and for the formed secondary minerals to be exceptionally well crystallised (Beaufort and Meunier 1993). The formation of these minerals is controlled by the rock local chemical composition and not by temperature: saponite in pyroxene bearing rocks, corrensites in amphibolites, chlorites in gneiss.

The formation of corrensite, like the formation of magnesian chlorite, does not always take place at the same temperature. It depends on the local chemical composition, the geothermal gradient and the duration of diagenesis. Drill holes in which present-day temperature has been measured give a few indicators for the formation of corrensite (Table 8.1).

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Geological formation</th>
<th>Age</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>60–70</td>
<td>Detrital sandstones</td>
<td>Cretaceous</td>
<td>Chang et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>and shales</td>
<td>Tertiary–Upper Cretaceous</td>
<td>Pollastro and Barker (1986)</td>
</tr>
<tr>
<td>100</td>
<td>Carbonates</td>
<td>Jurassic</td>
<td>Kübler (1973)</td>
</tr>
<tr>
<td></td>
<td>Volcanoclastic rocks</td>
<td>Palaeocene–Oligocene</td>
<td>Chudaev (1978)</td>
</tr>
<tr>
<td></td>
<td>Volcanoclastic rocks</td>
<td>Miocene</td>
<td>Inoue and Utada (1991)</td>
</tr>
<tr>
<td>120–130</td>
<td>Volcanoclastic rocks</td>
<td>Upper Eocene–Lower Oligocene</td>
<td>Stalder (1979)</td>
</tr>
<tr>
<td></td>
<td>Volcanoclastic rocks</td>
<td>Tertiary</td>
<td>Kisch (1981)</td>
</tr>
<tr>
<td></td>
<td>Molasse</td>
<td>Tertiary</td>
<td>Monnier (1982)</td>
</tr>
<tr>
<td>160</td>
<td>Arkoses</td>
<td>Palaeocene</td>
<td>Helmold and van de Kamp (1984)</td>
</tr>
</tbody>
</table>
Corrensite and magnesian chlorite are often interlayered in composite crystals. The proportion of chlorite increases as a function of the time × temperature parameter. Pure magnesian chlorite does not exist below 100 °C; it is of polytype IIb ($\beta = 97^\circ$) and forms mostly platelets assuming a honeycomb pattern and covering the grain surface. It retains the porosity of sandstones by inhibiting the precipitation of quartz overgrowths on detrital grains (Hillier 1994). These coverings are frequently found in sandstones formed from Eolian sands (dunes, sebkas) reflecting desert climates and evaporitic conditions.

8.1.3.3 Berthierines, Glaucconites and Ferrous Chlorite

Berthierine-like iron-rich chlorites the half-cell formula of which is $\text{Si}_{2-x} \text{Al}_x \text{R}^2_+ \text{R}^3_+ \Box c \text{O}_5(\text{OH})_4$ are formed at the beginning of diagenesis (Walker and Thompson 1990; Hillier 1994; Ehrenberg 1993) or even under surface conditions in a reducing environment (laterite alteration under peat or lignite, shallow marine sedimentation). They can be found at varying depths (temperatures) according to the conditions imposed by the environment (presence of hydrocarbon compounds, carbonates, sulphides etc). They are subsequently transformed into a chamosite-like 7 Å chlorite. Temperature at the beginning of transformation is variable (Table 8.2).

The berthierine-to-chamosite transformation takes place through the interstratification of 7 Å layers with 14 Å layers. The number of serpentine-type layers decreases with temperature through a transformation process that is still poorly known (Ryan and Reynolds 1996). This transformation might take place by inversion of tetrahedra without variation in chemical composition (Brindley 1961; Jiang et al. 1994). The presence of 7 Å layers can be detected in ferrous chlorites up to 200 °C. These chlorites are of polytype Ib ($\beta = 90^\circ$) at first, subsequently transforming into polytype IIb ($\beta = 97^\circ$) above 200 °C. Ferrous chlorites are indicators of tropical sedimentary environments (great river deltas) in which ferric ooliths are formed (Hillier 1994).

Those glauconites scattered in sandstones or limestones were beidellite-glaucconite mica mixed layers at the time of their formation (see Sect. 2.1.4.2). The proportion of smectite depends on the local chemical conditions and particularly on the potassium concentration of the environment. Accordingly,
Fig. 8.25. Evolution of the chemical composition of glauconites as a function of their interstratified smectite content (data from Thompson and Hower 1975)

their heterogeneous composition derived from the sedimentary episode makes the diagenetic effects (time × temperature) difficult to grasp. Nevertheless, the series of samples studied by Thompson and Hower (1975) shows that the smectite content decreases with the increasing age of the formations: 5 to 10% for the Cambrian–Ordovician Period, 10 to 25% for the Jurassic–Cretaceous Period, 25 to 40% for the Eocene Period and 40–60% for the Eocene Period–present. Figure 8.25 shows that the K content is inversely correlated with the smectite content and with the Al/(Fe$^{3+}$ + Fe$^{2+}$) ratio. This confirms that, when interstratified with glauconite mica, smectite is an aluminous dioctahedral smectite and not a nontronite.

8.1.4
From Diagenesis to Very Low-Grade Metamorphism

8.1.4.1
Geology of the Diagenesis-to-Very Low-Grade Metamorphism Transition

The transition from diagenesis to the very low-grade metamorphism can be observed in four types of geological contexts: (1) extension tectonic basins (West of England), (2) subduction zones (California), (3) collision zones (The Alps), and (4) thermal metamorphism around magmatic bodies. The relationships between geodynamics and transformation facies of clays have been summarised by Merriman and Frey (1999). The very low-grade metamorphism
has long been a poorly known subject because isograde maps cannot be drawn by observing the occurrence or disappearance of some mineral or some mineral assemblage. Indeed, crystals in these rocks have a small size. Only X-ray diffraction analysis can detect differences in the crystal structure of several species – illites and chlorites principally.

**From Illite to Phengites**

Illites proved to be key minerals in the diagenesis-to-very low-grade metamorphism transition for two reasons: (1) they are very commonly occurring in sedimentary rocks, and (2) their crystallinity can be characterised using a very simple index: the 10 Å peak full width at half maximum (FWHM) or Scherrer’s width (Kübler 1964). When this method is applied to “true” illites (i.e. containing less than 5% smectite), the crystallinity index (or Kübler index) is shown to describe the variation in the coherent domain size of particles (Jaboyedoff et al. 1999). Diagenetic, anchizonal and epizonal conditions are defined by increasingly small crystallinity index values. This implies an increase in the coherent domain size of the I/S minerals and particularly in the number of consecutive illite layers in the stacking sequences (Fig. 8.26).

The illite-to-phengite transition seemingly takes place gradually in the epizone. Indeed, the potassium content passes from 0.9 to 1 per half cell (Si₄O₁₀) whereas aluminium and bivalent elements (R²⁺ = Fe²⁺ + Mg²⁺) contents do no longer vary independently but are controlled by the Tschermak substitution: (Mg, Fe²⁺) VI, Si IV ↔ Al VI, Al IV. However, electron microprobe analyses cannot be blindly relied upon because observations by transmission electron microscopy show that mica and chlorite often constitute intergrowths (Lee et al. 1984; Ahn et al. 1988), which alters the evaluation of the phengite substitution. The progressive transition from illite to phengites occurs through the increase in the coherent domain size, which passes from 15–25 layers to more than 60. Although the polytype change from 1M to 2M₁ is not as system-
atic as admitted for many years (Dong and Peacor 1996), 2M₁ still remain the prevailing polytype in the epizone.

**Chlorites and “Metamorphic Vermiculites”**

The chemical composition of chlorites changes during diagenesis. They become increasingly aluminous and the number of vacancies in the octahedral sheet decreases (Hillier and Velde 1991). Nevertheless, the variations are small and difficult to determine owing to contaminations. By compiling thousands of data, Zane et al. (1996) have shown that the chemical composition of chlorites and their host rocks are correlated. Therefore, any attempt to establish geothermometers from the composition of chlorites is fruitless. The only unquestionable fact is that the compositional range of solid solutions decreases with increasing temperature. “Metamorphic vermiculites” (Velde 1988) have optical properties and compositions intermediate between those of biotites and chlorites. Although low, their swelling property is unquestionable and makes them closer to randomly ordered chlorite/smectite mixed layers (Beaufort 1987).

A crystallinity index of chlorites has been modelled on that of illites, using the 14 and 7 Å diffraction peak full width at half maximum (Arkai 1991). The values of this index are rather well correlated with those of illite, which makes its use possible to establish a zoneography of the diagenesis-to-metamorphism transition. However, the coherent domain size of chlorites increases more slowly than that of illites. This is due to the greater deformability of chlorites when subjected to an increase in pressure. The coherent domain size is reduced by the resulting greater number of crystal defects.

### 8.1.4.2

**Mineral Zoneography of the Diagenesis-to-Metamorphism Transition**

The diagenesis-to-very low-grade metamorphism transition has been described in numerous geological sites (Merriman and Frey 1999). It has been thoroughly explored for many years in the Alps (Frey et al. 1980), and more particularly in the Morcles thrust sheet south-west of Switzerland (Kübler 1969; Goy-Eggenberger 1998). The intensity of the deformations in the structure of this thrust sheet regularly increases from the front zone (diagenesis) towards the root zone (epizone). The diagenesis–anchizone and anchizone–epizone boundaries are plotted from the crystallinity index of illite, 0.33 and 0.22 °2θ Cu Kα respectively (Fig. 8.27a). The mineralogical study of the various types of rocks (limestones, sandstones, shales) shows that the transition to metamorphism is emphasised by several reactions (Fig. 8.27b):

1. progressive transformation of glauconites into stilpnomelane in the anchizone;

2. disappearance of kaolinite (or dickite) in the epizone while pyrophyllite starts forming in the anchizone;
Fig. 8.27a,b. Diagenesis-to-metamorphism transition. a) Sketch profile of the Morcles thrust sheet with the diagenesis-anchizone and anchizone-epizone boundaries determined by the crystallinity index of illite (Goy-Eggenberger 1998). b) Mineral sequence observed in the thrust sheet. Pa-Ph: paragonite – phengite mixed layer

3. Crystallisation of rectorite, of a Na-mica – K-mica mixed layer and of chloritoid in the anchizone. These minerals subsequently disappear in the epizone, except chloritoid.

Rectorite, which has long been considered a regularly ordered smectite-paragonite mixed layer, is in reality a mineral phase sensu stricto like corrensite, its trioctahedral equivalent. Rectorite is definitely different from its potassic equivalent that should not bear the same name. In ancient literature, this mixed-layer mineral was referred to as allevardite. This mineral commonly occurs in I/S sequences typical of diagenesis. An improved knowledge of the
growth processes of these two minerals shall permit us to update terminology. The paragonite–phengite (Pa–Ph) mixed layer, contrary to rectorite, is a transient crystal structure that disappears by formation of separate phengite and paragonite crystals (Frey 1969).

The classical interpretations of the diagenesis-to-metamorphism boundary described above are substantially modified by the following observations:

1. chloritoid and pyrophyllite may occur in the anchizone in case of favourable chemical composition of rocks (aluminous shales);
2. kaolinite and pyrophyllite sometimes co-exist in the anchizone and epizone.

Sudoite is a relatively rare mineral whose occurrence is related to the reaction kaolinite + chlorite $\rightarrow$ sudoite + quartz + $\text{H}_2\text{O}$ (Fransolet and Schreyer 1984). This reaction is triggered at about 200°C. Nevertheless, sudoite may occur under diagenetic conditions of lesser intensity by transformation of smectites or I/S minerals in bentonite beds in the presence of organic matter (Anceau 1993).

8.2 Volcanic Rocks

Introduction

Volcanic rocks exhibit a significant distinguishing feature when compared to clastic sediments: they contain glass. Owing to the high reactivity of glass in the presence of fluids, the activities of the major chemical components of silicates, silica notably, are controlled by its dissolution. Rocks of volcanic origin are commonly found in series of detrital sediments in the form of relatively thin beds. Nevertheless, in the vicinity of island arcs, sedimentation is dominated by these glass-bearing rocks. They are transformed during the burial process; glass and some magmatic minerals disappear whereas zeolites and clays crystallise forming mineral sequences that vary with depth.

Such sequences can result from diagenesis (temperature rise due to burial by heat diffusion) or from hydrothermal alterations (temperature rise due to the flow of hot fluids: thermal convection). The respective roles assumed by diffusion and convection is not easy to define because volcanic areas are essentially regions with high geothermal gradient where hydrothermal flows are very active. In fact, their distinction cannot rest upon the local and instantaneous temperature because, in this case, the period of time during which this temperature has been stabilised is not known. Indeed, the reaction processes are controlled by kinetic laws. The significant parameter in diagenesis as well as in hydrothermal alterations is time $\times$ temperature. The difference between diagenesis and hydrothermal alterations is rather based on the importance of hot fluid flows, which can be measured by the water/rock ratio. Consequently, even when the thermal gradient is higher than the mean value of $30^\circ\text{C} \text{km}^{-1}$, the process will be referred to as diagenesis provided that the water/rock ratio remains low as compared to the values reached in geothermal fields.
8.2.1
Diagenesis of Ash and Vitreous Rock Deposits

8.2.1.1
Diagenesis of Bentonites

Bentonites are formed by alteration of volcanic ashes under conditions that are still poorly known (see Sect. 7.2.2.1). These are practically monomineral rocks composed nearly exclusively of montmorillonite-like smectite. They form reference stratigraphic layers and bear witness to the volcanic activity in the vicinity of the sedimentary basin. The thickness of beds ranges between a few millimetres to one metre (rarely more) owing to several factors, such as the distance to the ash-producing volcano or the flow turbulences in the atmosphere. The number of beds inserted in the sedimentary pile may be significant in some basins (e.g. the Slovak Basin described by Sucha et al. 1993).

Smectites persist in very old bentonites (Ordovician Period) even if the surrounding shales are composed of I/S minerals with a very high illite content.

**Fig. 8.28a,b.** Diagenesis of bentonites. a) Illitisation of the bed rims controlled by the diffusion of potassium (Altaner et al. 1984). b) Comparison of the advancement stage of the smectite → illite reaction as a function of depth between shales and bentonites in the eastern part of the Slovak Basin (Sucha et al. 1993). Bentonites react more slowly than shales.
Volcanic Rocks

(velde 1985). Nevertheless, mineralogical differences can be observed within bentonite beds according to their thickness and to the nature of the rocks with which they are in contact. When beds are 1 m thick or thicker, a zonation is clearly perceptible between the illitised rims and the centre that retains a high smectite content (huff and türkmenoglu 1981; altaner et al. 1984; brusewitz 1986). The potassium enrichment modifies the measured k/ar radiogenic ages (fig. 8.28a). This type of zonation takes place by chemical diffusion (pusch and madsen 1995).

When bentonite beds are thin (a few centimetres), their mineralogical composition is homogeneous and no zonation is perceptible. sucha et al. (1993) have compared the advancement stage of the illitisation reaction in a sequence of bentonites and shales in the eastern part of the slovak basin (fig. 8.28b). They have shown that the i/s series are seemingly identical in both types of rocks but that, for a given depth, the illite content is always higher in shales than in bentonites. The reaction is then slower in bentonites.

8.2.1.2 Diagenesis of Volcanoclastic Deposits

The abundance of zeolites is the signature of volcanoclastic deposits under diagenetic conditions (IIJIMA and utada 1966; coombs 1970 among others). Some basics of zeolite crystallochemistry may be recalled here. There are two main mineral sequences: Ca-zeolites (gismondine, laumontite, lawsonite, scolecite, chabazite, epistilbite) and Na-K zeolites (natrolite, analcite, clinoptilolite). Several species are common to both mineral sequences: phillipsite, stilbite, mordenite and erionite. These two mineral sequences differ by the value of their (Na + K + 2 Ca)/Al ratio (fig. 8.29a). The stability of zeolites in the pressure-temperature space has been studied by experimental synthesis of a few species. These works set the general lines of the diagenesis-to-metamorphism transition (Ghent et al. 1979), which spans the stability fields of analcite and laumontite (fig. 8.29b). For low pressures (shallow depths), the hydrothermal sequences (high geothermal gradient) result in wairakite, which can be viewed as the indicator of the boundary with thermal metamorphism.

The sequences observed in the deep drill holes of New Zealand volcanoclastic areas (fig. 8.29c) show that heulandite and analcite are the two main species characterising the upper part of the series where plagioclases are strongly albítised (low temperatures). Heulandite and analcite disappear to the benefit of laumontite and non-zeolitic minerals: prehnite and pumpellyite (Surdam and Boles 1979). Zeolites are commonly observed along with alkaline feldspars (albite, adularia) and illite/smectite mixed layers. Nevertheless, the complexity of zeolite solid solutions does not enable an accurate zoneography to be established, owing to the significant – if not dominating – effects of the local chemical composition.
Fig. 8.29a–c. Zeolites in the diagenesis of volcanic rocks a) The main zeolite species are represented in the $M^+–Al–Si$ chemical system ($M^+ = Na^+ + K^+ + 2 Ca^{2+}$). b) Analcite and laumontite stability fields in the pressure-temperature space (from Ghent 1979). c) Mineral sequence observed in volcanoclastic sediments in New Zealand (from Surdham and Boles 1979)
8.2.2
Diagenesis – Very Low-Grade Metamorphism of Basalts

8.2.2.1
Distinguishing Features of the Basaltic Series

Basaltic rocks are the most widely occurring rocks at the Earth’s surface. They make up the entire ocean floor and may form huge stackings on continents (trapps or flood basalts). Despite their relatively extended chemical compositional range (Juteau and Maury 2000), their differences are negligible from the standpoint of diagenetic alterations because their prevailing feature lies in high Mg and Fe\(^{2+}\) contents. Therefore, they differ from silicoclastic rocks, which exhibit higher Si, Al, Fe\(^{3+}\) and K contents. Diagenetic reactions are characterised by the prevalence of trioctahedral clay minerals and zeolites.

The observation of mineral transformations in continental basaltic series is for the most part made possible in natural outcrops and geothermal boreholes. Geothermal fields, apart from the intensely fractured zones where great amounts of hot fluids flow (heat transport by convection), exhibit sequences of zeolites and clay minerals that are close to those formed in zones with lower thermal gradients (heat diffusion by thermal conduction). These sequences are simply shortened. Accordingly, they will be described in chapter 9 along with the alterations of deep-sea floors (see Sect. 9.1.4.2). To avoid boring repetitions, only those aspects which are unquestionably related to burial under conditions of geothermal gradient and fluid flows typical of diagenesis will be considered here: 30–40 °C km\(^{-1}\), water of meteoric or marine origin.

Besides their chemical composition, basalts exhibit another characteristic that distinguishes them from sediments: the contrasted porosity within a single lava flow. The cooling magma flowing out to the open air degasses. Gas bubbles nucleate, go up in the lava flow and are vented to the atmosphere as long as permitted by magma viscosity (\(T > 1,150^\circ\text{C}\)). Below this threshold, they remain trapped and form vesicular levels at the top and bottom of the lava flow that surround a massive zone in between (Fig. 8.30). These massive zones are more or less roughly cut into prisms by fractures that spread once temperature has dropped below 700 °C. During burial, the vesicular or massive levels of basaltic flows form zones of contrasted permeability that behave like open or nearly closed systems, respectively (Levi et al. 1982).

8.2.2.2
Mineral Zonation at Various Scales

Regional Scale
The burial of basaltic series causes the crystallisation of zeolites and clay minerals whose assemblages form a large-scale mineral zonation. Whatever the age and the emplacement mode of basaltic series, the main facies are systematically observed: Achaean (Schmidt and Robinson 1997), late Precambrian (Bevins et al. 1991), Cretaceous (Lévi et al. 1982), and Tertiary (Neuhoff et al. 1999).
Four typical mineral assemblages can be distinguished in order of increasing intensity of metamorphism (Alt 1999):

1. smectite + alkaline zeolites and heulandite,
2. corrensite + laumontite,
3. chlorite + epidote ± prehnite,
4. chlorite + actinolite.

Local variations may appear according to $P_{CO_2}$ and $P_{S_2}$ whose values enable or impede the formation of carbonates and sulphides. The alteration of deep-sea floor basalts exhibits an additional phyllosilicate–celadonite, which persists in the corrensite facies.

Fig. 8.30. Structure of a basaltic flow and mineral and chemical zonation (from Schmidt and Robinson 1997)
Lava Flow Scale
Owing to the permeability contrast between the vesicular and massive levels, each lava flow exhibits an internal mineral zonation. In the basalts of the Chilean Andes cordillera (Jurassic, Cretaceous, Tertiary), Levi et al. (1982) have shown an increase in the albisation of plagioclases and in the ratio of the epidote amount to the prehnite + pumpellyite amounts from the massive levels to the vesicular and brecciated levels. Similar phenomena have been observed in other basaltic series, particularly in Iceland (13 Ma, Neuhoff et al. 1999) and in the metabasalts of the Keweenaw Peninsula, Minnesota, U.S.A. (Precambrian, Schmidt and Robinson 1997). Generally, smectitic minerals better withstand the condition changes imposed by burial in the massive parts of lava flows, which causes a shift of facies with the vesicular levels. Accordingly, for the same lava flow, saponite persists in the massive part whereas corrensite and chlorite are formed in vesicles. This shows that, within the greatest volume of basaltic series, thermodynamic equilibria are reached in microsystems only. The internal zonation subsists practically up to the actinolite zone.

Sample Scale
Clay minerals can be observed mainly in two types of sites: either they fill vesicles in which they form zoned deposits (Fig. 8.31a) or they replace a mesostasis classically considered to be formed of glass (Fig. 8.31b). Two essential pieces of information have been brought by the recent detailed petrographical studies (Mas 2000) on mesostasis: (1) glass is formed only on the lava flow margin, which is subjected to a sudden quenching, and (2) clay minerals are not always formed by alteration of phenocrystals along microfissures: they can precipitate directly on the unaltered crystal surfaces of these phenocrystals (Fig. 10.6). Their post-magmatic origin is now contemplated (see Sect. 10.2.1).

The physicochemical conditions imposed during diagenesis and very low-grade metamorphism differ from those imposed during the magmatic episode. Particularly, the circulation of fluids triggers interactions between solution and minerals, the products of which depend on the activity of ions in solution and on the water/rock ratio. Some of the initial mineral components become unstable under such conditions and react at different velocities. The nature of the secondary parageneses is controlled by the solid porosity: parageneses in the vesicular level differ from those in the massive level. Generally, whatever the reaction progress, the chemical compositions of altered and unaltered rocks are similar, except for water contents. Accordingly, cations are mobile over very short distances (a few millimetres), and only water is brought by the external environment. Neuhoff et al. (1999) have shown in Icelandic trapps that the filling rate of vesicles increases with the intensity of metamorphism (Fig. 8.31c). They distinguish two burial stages: replacement of 8% of the porosity by precipitations of celadonite and quartz (stage 1); hydrolysis of olivines, plagioclases and glass, feeding the crystallisation of chlorite/smectite mixed layers whose chlorite content increases with increasing depth, and of zeolites that seal 40% of the porosity (stage 2). Stage 3 is a hydrothermal alteration stage related to the emplacement of basaltic dykes. Zeolites precipitate and occupy 10% of the initial porosity.
Alteration patterns of primary components and conservation of rock composition are the petrographical and geochemical signatures of the metamorphic process. The mineralogical signature will be discussed later. The formation of clay minerals is fed by dissolution of primary components. However, since basaltic glass occurs only in lava flow chilled margins, its alteration remains problematical. The glass assumed to be present in the mesostasis is the final product of the fractional crystallisation and must be of rhyolitic composition, namely very different from the composition of its alteration products (saponite, nontronite and chlorite). There is no unquestionable petrographical evidence of the occurrence of this glass, except in the form of solid inclusions in plagioclase phenocrystals. Mas (2000) has shown that clays in the mesostasis are probably the result of a direct precipitation from residual fluids enriched with incompatible and volatile elements. Accordingly, these “initial clays” located in the porous zones of the rock—and not glass—would be transformed by metamorphism.

8.2.3
Di- and Trioctahedral Mixed-Layer Minerals

8.2.3.1
Celadonite – Glaucnite – Nontronite

Celadonite is systematically described in the vesicles of deep-sea floor basalts (Humphris et al. 1980; Laverne 1987; Kaleda and Cherkes 1991; Alt 1999) and more rarely in the vesicles of continental basalts (Neuhoff et al. 1999). This mineral always forms within the rock at the external interface of the vesicle (Fig. 8.31a). The first mineral sheet inside the vesicle comprises microcrystalline quartz. The following sheets show a zonation: they comprise trioctahedral minerals (saponite and C/S minerals) whose chlorite content is increasingly high inwards. The vesicle may be totally sealed by precipitation of zeolites.

The composition of celadonites is variable, ranging from the domain of sedimentary glauconites to the compositions of the theoretical end members of celadonite and glauconite micas (Fig. 8.32). This dispersion of values is due to three factors: (1) variation of the measured K\textsubscript{2}O contents in the range 6–9%, (2) presence of Al ions in tetrahedral position, and (3) presence of Fe\textsuperscript{2+} ions although the oxidation state of iron remains undetermined most of the time. Note that the compositional range of solid solutions rather extends towards the beidellite domain, and not towards that of nontronites. The latter have a limited chemical composition range close to the theoretical end member.

Celadonites and nontronites form in a wide range of temperatures. Indeed, low-pressure experimental syntheses have shown that the celadonite – biotite joint is reached at about 400 °C (Wise and Eugster 1964; Velde 1972; Klopproge et al. 1999). The higher the temperature, the closer the solid solution to the theoretical end member, and the lower the temperature, the greater the proportion of expandable layers. Stable isotopes show that celadonite can form at temperatures below 40 °C in marine environment (Stakes and O’Neil 1982...)
Fig. 8.31a–c. Clay minerals of basalts. a) Schematic representation of a vesicle totally sealed by deposits of clay minerals and zeolites. b) The three possible origins of mineral clays in the mesostasis: direct precipitation from post-magmatic fluids, glass ageing, alteration of glass and phenocrystals by external fluids. c) Temporal sequence of parageneses observed in Icelandic trapps (Neuhoff et al. 1999)
Fig. 8.32. Chemical composition of “celadonites” and nontronites formed by diagenetic alteration of basalts. The theoretical chemical composition domains of montmorillonites, beidellites and muscovites are indicated with shaded rectangles; the domain of glauconites and nontronites is determined by measured chemical compositions. Celadonites: rectangles (Humphris et al. 1980) and diamond shapes (Laverne 1987); nontronites: triangles (Koster et al. 1999)

among others). Celadonite persists all over the zeolite facies (Neuhoff 1999) and probably disappears when the prehnite-pumpellyite facies is reached. The metamorphism stage at which nontronite disappears is more difficult to determine because this mineral is not readily recognisable in the rock. Nontronite probably transforms very early once chlorite has crystallised. The reaction produces either a chlorite/smectite mixed layer or Fe-rich chlorite.

8.2.3.2 Chlorite – Corrensite – Chlorite/Smectite Mixed Layers

Chemical Composition Domains
Chlorite/smectite (C/S) mixed layers are described as typically derived from diagenesis of basalts. They form a complete series from 100 to 0% smectite (from saponite to chlorite). Their crystal structure has long been discussed and they are considered today to be saponite-corrensite and corrensite-chlorite (C/Co) mixtures rather than true smectite/chlorite mixed layers. However, the chemical compositions measured with the electron microprobe in basalt vesicles are not consistent with either model (Fig. 8.33). Indeed, a few compositions only are situated between the compositional ranges of saponites and those of chlorites, as should theoretically be the case. Many of them are situated in the saponite-nontronite-chlorite space. Unfortunately, in the absence of accurate
Fig. 8.33a–d. Representation of the chemical compositions of several series of smectite/chlorite mixed layers derived from the very low-grade metamorphism of basaltic rocks. a) Ophiolite from Point Sal, California (Bettison and Schiffman 1988; Bettison and Mackinnon 1997). b) Metabasalts from Keweenaw, USA (Schmidt and Robinson 1997). c) Basaltic trapps from Iceland (Neuhoff et al. 1999). d) Basalts from the Nesjavellir geothermal field, Iceland (Schiffman and Fridleifson 1991)

crystallographic data, the actual co-existence of nontronite with C/S or C/Co cannot be established.

Regardless of how the metamorphic sequence is described (saponite – corrensite – chlorite or a complete series of C/S minerals between end members saponite and chlorite), the chemical balance of the reaction is based on saponite disappearance and chlorite formation. Considering the theoretical compositions of these minerals (saponite: Si$_{3.7}$Al$_{3.3}$O$_{10}$R$_{2+}$$(OH)_2$M$^{+}.3$; chlorite: Si$_3$AlO$_{10}$R$_{2+}$$(OH)_2$–AlR$_{2+}$$(OH)_6$), and knowing that quartz and zeolites are to precipitate too, the global reaction can be written as follows:

$$1 \text{Saponite} + 1.7 \text{Al}^{3+} + 2 \text{R}^{2+} + 6(\text{OH})^- \rightarrow 1 \text{Chlorite} + 0.7 \text{Si}^{4+} + 0.3 \text{M}^+$$

The Si$^{4+}$ and M$^+$ ions released by the reaction are consumed by the precipitation of zeolites. This is consistent with the structure of the concentric deposits in vesicles.

Corrensite: a Mineral Indicator of Metamorphism

Corrensite has been identified in various natural environments spanning a large range of $P$, $T$, $t$ conditions: diagenetic evaporitic series (April 1981), geothermal fields (Inoue and Utada 1991), hydrothermal alteration of basaltic
rocks or ophiolites (Alt et al. 1985; Bettison and Schiffman 1988), and metamorphic formations (Shau et al. 1990; Goy-Eggenberger 1998; Alt 1999). By contrast, it has never been observed in rocks that have not experienced any diagenetic or hydrothermal alteration and whose chemical composition would yet be favourable to its formation (basalts, evaporites).

Corrensite has been synthesised from stoichiometric mixtures of oxides at 350 °C–2 kbar and 500 °C–2 kbar (Robertson et al. 1999). Authors have shown the importance of kinetics in its formation: 22 days at 350 °C and 6 h only at 500 °C. They have also shown that randomly ordered C/S mixed layers do not form and cannot be considered as precursors. Therefore, corrensite is truly a mineral phase like chlorites or micas. Its occurrence field is that of diagenesis or very low-grade metamorphism and that of long-time alterations like pervasive alterations or slow crystallisations in basement fractures visited by brines from sedimentary basin bottoms. Duration seems to have a very significant effect. Brief processes like alterations in active hydrothermal veins or cooling of lava streams in the presence of water (post-magmatic stage or sudden quenching in seawater) cause the formation of saponite or randomly ordered C/S mixed layers sometimes associated with chlorite (Fig. 8.34).

Fig. 8.34. Influence of the factor time × temperature (kinetics) on the stability fields of saponite (saponite-rich C/S minerals), corrensite and chlorite in the main geological processes.
Suggested Readings

CHAPTER 9

Hydrothermal Process – Thermal Metamorphism

9.1 Fossil and Present-Day Geothermal Fields

Introduction

Continental hydrothermal systems have been known since Antiquity for their potential ore deposits (copper, tin) and the “miraculous” properties of hot springs. However, their scientific exploration only began in the second half of the 20th century. Many works were undertaken in both fossil systems and active geothermal fields with the aim of searching for mineral zonations comprising sulphides, oxides and silicates. These zonations have been described in numerous books or reviews in which are explained the fundamental mechanisms of interactions between hot fluids and rocks: fossil systems (Lovering 1950; Bonorino 1959; Creasey 1959; Lowell and Guilbert 1970; Tittley 1982; Beane 1992; Pirajno 1992; Barnes 1997) and active geothermal fields (Steiner 1968; Ellis and Mahon 1977; Browne 1978; Elder 1981; Henley and Ellis 1983; Reyes 1990; Browne 1998).

The hydrothermal systems affecting the deep-sea floor basalts and ophiolites have been discovered recently even though the Cyprus copper was the primitive Greeks’ ore resource. Better known today thanks to oceanic research programs, these systems have been abundantly described. Their structure is rather well known from their roots in the dyke system to the floor surface from which they arise in the form of the famous “black smokers” (see Alt’s review 1999).

From the standpoint of clay minerals, fossil and active geothermal fields offer a great variability in their formation conditions: temperatures, composition and pH of solutions, fluid/rock ratio. Two processes operate simultaneously or successively depending on the location and activity period of the system: alteration of primary minerals and direct precipitation from oversaturated solutions. Considering the rapid changes in these conditions over time, several clay formation episodes may be recorded in the same rock. The result is then a complicated combination of different clay species that cannot be considered to form a single paragenesis, the analysis of which would permit the reconstruction of the accurate physicochemical conditions. Particularly, their use as geothermometers should be definitely avoided.
9.1.1 Geological and Dynamic Structure of Geothermal Fields

9.1.1.1 Conduction and Convection

Mineral Zonations in Hydrothermal Systems
The first classifications of alterations were based on the prevailing parageneses of secondary minerals. They have been used to define zones around the porphyry copper deposits: potassic, phyllicit, propylitic, and argillic zones (Creasey 1959). The classification proposed by Utada (1980) uses combinations of two variables: temperature and ratio of cation activities in hydrothermal solutions. This classification enables the major types of hydrothermal systems to be described (Table 9.1). Three groups are so distinguished according to the value of the cations/H$^+$ ratio: acid-type system (low ratio), intermediate-type system (medium ratio) and alkaline-type system (high ratio).

The deep roots of geothermal fields as they have been observed in the porphyry copper deposits are the seat of interactions of high-temperature (and mostly high-salinity) fluids and intrusive rocks with their immediate wall rocks. These interactions have been described as “phyllic alteration” and “potassic alteration” (Creasey 1959; Lowell and Guilbert 1970). The resulting secondary silicated minerals are not clays but white micas (muscovite and phengite) and K-feldspars. Nevertheless, it is important to know how to identify these early alterations, which can either be superimposed on an earlier propylitic alteration or be themselves followed by late low-temperature alterations. Since phyllic and potassic alterations do not produce clay minerals, they are not the subject of this book. On the other hand, the propylitic alteration will be described.

Table 9.1. Zonal arrangement of parageneses in the three types of hydrothermal systems defined by the value of the cations/H$^+$ ratio in solutions (Utada 1980)

<table>
<thead>
<tr>
<th>alteration type</th>
<th>cations</th>
<th>mineral zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>H$^+$</td>
<td>halloysite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>kaolinite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pyrophyllite</td>
</tr>
<tr>
<td>intermediary</td>
<td>K</td>
<td>smectite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I/S mixed layers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>illite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-feldspar</td>
</tr>
<tr>
<td>alkaline</td>
<td>Ca+Mg</td>
<td>smectite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I/S and C/S mixed layers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>chlorite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>epidote</td>
</tr>
<tr>
<td></td>
<td></td>
<td>actinolite</td>
</tr>
<tr>
<td>alkaline</td>
<td>Ca</td>
<td>stilbite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>heufandite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>laumontite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>welzite</td>
</tr>
<tr>
<td>alkaline</td>
<td>Na</td>
<td>mordenite-Na</td>
</tr>
<tr>
<td></td>
<td></td>
<td>analcite</td>
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<tr>
<td></td>
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<td>albite</td>
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Activityalkali + alkaline earth Activityhydrogen

<table>
<thead>
<tr>
<th>temperature</th>
</tr>
</thead>
</table>
Dynamics of Continental Systems

It is widely admitted now that active geothermal fields are the surface expression of a hydrothermal activity related to the emplacement of magmatic intrusions. These geothermal fields form the upper part of a greater system whose deep roots are the porphyry copper deposits (Henley and Ellis 1983) and whose intermediate parts are the epithermal ore deposits, as shown by Hedenquist et al. (1998) in the Far Southeast and Lepanto deposits in the Philippines. All these structures represent huge volumes of rocks submitted to interactions with hot fluids (Fig. 9.1).

Whether fossil or active, geothermal fields are geological structures that enable the heat stored in the Earth's crust to be dissipated. Two processes take place simultaneously or alternately: conduction and convection (Fig. 9.2). The emplacement of the magmatic intrusion is a slow process that enables the formation of thermal aureoles by conduction. The seismic activity opens faults, thus forming high-permeability networks that drain a major part of hot fluids. The most efficient process for dissipating the heat is then convection. The chemical and mineralogical interactions accompanying these circulations cause the sealing of the networks through deposits of secondary minerals (clays, carbonates, sulphates, sulphides, oxides). The permeability of the networks is reduced thus bringing about the predominance of conduction over convection. Such alternations may repeatedly take place during the activity period of the geothermal field, which itself depends on the amount of heat to

Fig. 9.1. Schematic representation of the organisation of a geothermal field around a strato-volcano. “Bubbles” represent the vapour-dominant levels. The fumarole symbolises the active geothermal field at the Earth's surface
Fig. 9.2. Displacement of the “thermal plume” in an active geothermal field according to whether the prevailing process is conduction or convection. The seismic activity opens faults that form permeable networks to be dissipated. Over time, the “thermal plume” is displaced according to the most efficient process for dissipating the heat. Consequently, a rock in a given location within the geothermal field may be altered first by fluids flowing in fractures (convection). After sealing, this rock undergoes transformations affecting the secondary products, notably clays, through a shift in the thermal system (conduction).

**Propylitic Alteration**

The greater the amount of heat (i.e. the size of the magmatic body), the greater the rock volumes in which temperature is increased by conduction. Thermal
models show that heat dissipation is a slow phenomenon owing to the very low thermal conductivity of rocks (Jaeger 1968; Cathles 1977; Norton and Knight 1977). The fluids entering these rocks through fractures and microfissures (intergranular joints, intramineral fissures) trigger mineral reactions: dissolution of primary minerals, precipitation of secondary ones. An aureole in which wall rocks are transformed forms around the heat source. These mineral transformations are described under the term *propylitic alteration*.

The mineral parageneses typical of the propylitic alteration have been abundantly described (Creasey 1959; Lowell and Guilbert 1970; Titley et al. 1986 etc). They are formed owing to local equilibria (microsystems) and they retain the rock initial microstructure (Meunier et al. 1984). Mass transfers take place over short distances of the order of magnitude of the size of primary minerals. The main mineral reactions are interdependent in that one reaction provides the elements in solution needed by another:

\[
\text{plagioclase} + K^+ \rightarrow \text{illite} + \text{Al}^{3+} \tag{9.1}
\]

\[
\text{biotite} + \text{amphibole} + \text{Al}^{3+} \rightarrow \text{chlorite} \pm \text{epidote} \pm \text{calcite} \pm \text{titanite} + K^+ \tag{9.2}
\]

Epidote or calcite is formed according to the value of the CO\(_2\) partial pressure. Quartz crystallises in microfractures by consuming excess silica. The amounts of fluids involved are so low that the composition of secondary phases is essentially controlled by that of primary phases (Berger and Velde 1992).

The study of the Saint-Martin fossil system, Lesser Antilles (Beaufort et al. 1992) has shown that the assemblages and chemical compositions of secondary minerals in the propylitic aureole vary with distance to magmatic body (Fig. 9.3a). The maximum temperature recorded by rocks (fluid inclusions in quartz + epidote veins) decreases as a complex function of distance. The ferro-magnesian minerals form an actinote – chlorite – chlorite-rich chlorite-smectite mixed layers series. Chlorites experience gradual changes in their chemical composition; their Fe content increases as the distance to the magmatic body increases. There is great temptation to consider that these compositions are controlled by temperature and that, as a consequence, they can be used as geothermometers. The reality is more complex because temperature is not the only parameter subjected to variation with the distance to the magmatic body. Particularly, the oxygen partial pressure (\(f_{O_2}\)) changes as attested by the presence of magnetite at short distance and of hematite farther. This parameter that modifies the oxidation state of iron is very important for determining the Fe\(^{2+}\) amounts taken up by the crystal lattice of chlorites. The chemical composition of the latter changes according to the minerals with which they are combined (Fig. 9.3b).

The temperature curve is not the best way for evaluating the amount of energy released by heat conduction. Indeed, not only is temperature higher near the magmatic body, but the duration of this “heating” before temperature has reached equilibrium with the wall rock temperature is longer. The \(\text{time} \times \text{temperature}\) parameter is the one that best accounts for transfers of energy. It
Fig. 9.3a,b. Alteration parageneses of the Saint Martin fossil geothermal field (Antilles). a) Variation as a function of the distance to the magmatic intrusion (hence of temperatures). b) Variation in the chemical composition of chlorites as a function of the minerals with which they are combined

is a determining parameter particularly for the crystallisation state: number of defects (order-disorder degree) and crystal size. Patrier et al. (1990, 1991) have shown that the order-disorder degree of epidotes increases with increasing distance to the magmatic body whereas their size decreases. Similar results have been obtained for chlorites from the width of their diffraction peaks on oriented samples (unpublished data).
9.1.1.2
Petrography: Example of the Chipilapa Field (El Salvador)

Geological Structure
The Chipilapa Field (El Salvador) belongs to the intermediate-type hydrothermal system as defined by Utada (1980). It developed in recent calcoalkaline volcanic formations (Pliocene to present day) where andesitic lava flows and dacitic pyroclastic deposits alternate. It seems that the hydrothermal activity has been established for about 16,000 years. It has experienced recent paroxysmal crises as attested by phreatic explosion craters. This field is fed by meteoric fluids that are heated up to 250 °C in reservoirs. The hot fluids are drained by faults that delineate a “thermal plume” (Fig. 9.4). Two reservoirs are exploited 600 to 800 m deep and 1,150 to 1,400 m deep. Drill hole CH 8 is far from the production area; it is used as a reference for the study of hydrothermal alterations in low-permeability areas where thermal conduction is the prevailing heat dissipation process. Drill hole CH 7bis is located at the centre of the “plume”. It

Fig. 9.4. Diagram of the geological structure of the Chipilapa geothermal field, El Salvador (Beaufort et al. 1995). The “thermal plume” is framed by three faults. Two reservoirs (A and B) are exploited by a series of drill holes
is used as a reference for hydrothermal alterations in high-permeability areas where convection is the prevailing heat dissipation process.

The surface geological formation (0–500 m) comprises rocks whose clay content increases with increasing depth. They form an impermeable layer (clay cap) that strongly slows down surface heat losses. Therefore, the thermal gradient is very high between 300 and 550 m: 60 to 80 °C over 250 m only. Surface reservoir A immediately beneath the clay cap contains high-temperature fluids (> 185 °C) with a significant vapour phase (steam cap). From 650 to 1,100 m, the permeability of rocks is low, as is the thermal gradient. The vapour amount of the deeper aquifer (reservoir B) between 1,100 and 1,400 m is small (prevailing liquid phase). Today, the boiling point of fluids ranges between 700 and 800 m in depth.

**Early Episode: Propylitic Alteration (16,000 to 4,000 Years)**

Referring to the distribution of calcium silicates, the vertical thermal gradient contemporaneous with the propylitic alteration episode in the Chipilapa Field must have been significant. Indeed, the clinoptilolite – stilbite – laumontite – wairakite sequence is established over 500 m in thickness. Epidote occurs at 750 m. Compared with other sequences in the world (Utada 1970; Cavaretta et al. 1982; Bird et al. 1984), the temperature must have exceeded 300 °C at 2,500 m and approached 100 °C at the surface. Anhydrite occurs from 1,000 m on, and prehnite and adularia from 2,400 m on. The mean temperatures estimated by the analysis of the fluid inclusions trapped in quartz and calcite (Bril et al. 1996) are much higher than those measured in present-day fluids at similar depth. The field is cooling down.

**Fig. 9.5.** Variation in the crystallinity measured by the full width at half maximum intensity (FWHM) of the (002) peak of the chloritic phases in the > 5 µm and < 0.2 µm fractions
The phyllosilicate phases of the propylitic alteration are mostly illite and chlorite. These minerals can be found all over the altered zone; only their crystallinity changes. Measured in the $>5 \mu m$ fraction by the full width at half maximum intensity (FWHM) of the (002) peak, the crystallinity of chlorite steadily increases with depth (Fig. 9.5). This means that the coherent scattering domain size (dimension along the c direction) increases whereas the number of crystal defects decreases; this is also so with the very fine fraction ($<0.2 \mu m$), except at about $-1,100$ m (reservoir B) where crystallinity clearly decreases. The mathematical decomposition of the (002) peak shows that the FWHM increases by addition of two effects: the presence of chlorite-rich chlorite/smectite mixed layers and the chlorite peak broadening. The minerals crystallising under conditions imposed by present-day hot fluid circulations are concentrated in the fine fraction whereas the coarse fraction corresponds to older crystallisations in the propylitic domain.

**Late Episode: “Clays – Carbonates” Alteration (4,000 Years – Present Day)**

Crystals from the illite – chlorite – epidote propylitic paragenesis show dissolution patterns when located in highly fractured rocks. Microfractures form very dense networks and are sealed by deposits of calcite, hematite and clay minerals (Fig. 9.6). Intense fracturation is due to the explosive expansion of fluids. The presence of hydrothermal breccia and the noteworthy compositional homogeneity of fluid inclusions in carbonates whatever the depth show that a sudden boiling phenomenon caused the hydraulic fracturation of the propylitised rocks. The new paragenesis sealing fractures is typical of the clays – carbonates alteration, as described by Steiner (1968), Browne and Ellis (1970), Lowell and Guilbert (1970), McDowell and Elders (1980), Beaufort and Meunier (1983), Beaufort et al. (1990).

![Fig. 9.6. Diagram (from photograph) of microfractures sealed by deposits of carbonates, hematite and clays](image-url)
Taking place at temperatures lower than those of the propylitic alteration (230–240 °C in the present case), the clay-carbonates alteration transforms pre-existing minerals (primary or propylitic) by modifying the physicochemical conditions. The system becomes open and oxidising, fluid/rock ratios are much higher. Consequently, the mineral reactions are no longer controlled by the rock, but by fluids (Berger and Velde 1992). Fluids have a low salinity and a meteoric origin, as shown by the biphased fluid inclusions in carbonates (salinity contained between 0.8 and 1.8 NaCl mass equivalent) and by the $^{18}O/^{16}O$ and D/H ratios of the neoformed minerals.

The clay minerals neoformed under these conditions are illite/smectite (I/S) and chlorite/smectite (C/S) mixed layers whose composition varies with depth. Their smectite content decreases with increasing depth (Fig. 9.7). In both cases, the variation is not progressive, but occurs in stages. For the I/S minerals, two different series appear depending on whether the drill holes go through the thermal anomaly (CH 7bis) or are far away from it (CH 8). Far away from the anomaly, the I/S minerals are randomly ordered (R0) and rich in smectite (> 90%) in the upper portion of the field. The major change occurs between 400 and 600 m, where temperature suddenly passes from 60 to 80 °C. The smectite-rich R0 I/S minerals transform into regularly ordered (R1) I/S minerals (50% smectite – 50% illite) then quickly into R1 I/S minerals with 60% illite. The illite content then increases steadily up to over 95% at −1,750 m. In the thermal anomaly (CH7 bis), transformations of the I/S minerals take place differently, with pure smectites and R1 IS minerals with 60 and 90% illite coexisting. There is no steady enrichment in illite.

Fig. 9.7. Variation in the smectite content of illite/smectite and chlorite/smectite mixed layers in drill holes CH 7bis and CH 8 of the Chipilapa geothermal field. Measurements were performed by mathematical decomposition of the diffraction patterns into Gaussian curves.
The smectite (saponite) – C/S series is similar in both situations: the upper portion of the field contains only saponite, then the gradient suddenly increases (400 to 600 m) and saponite is found to coexist with corrensite and C/S minerals with more than 95% chlorite. Saponite and corrensite disappear below 600 m. Corrensite reappears sporadically in low-permeability basaltic rocks between 1,000 and 1,100 m.

In the surface zone, down to −350 m, the clay cap of the field constitutes a low-permeability environment in which temperature is lower than 130 °C. Several smectite species co-exist: saponite, nontronite and a dioctahedral smectite whose composition is intermediate between beidellite and montmorillonite. R0 I/S minerals appear.

**Present-Day Episode: High-Temperature Smectites**

The alterations related to present-day fluid circulations can be observed in reservoir fractures only. They cause the formation of smectites, sometimes in combination with kaolinite and hematite, that are deposited as more or less continuous coatings on propylitic minerals or on minerals relating to the clays– carbonates episode (Fig. 9.8). Fluids locally impose physicochemical conditions that are similar to those of the clays– carbonates episode: temperature between 185 and 210 °C, low salinity, boiling state, oxidising environment.

The differences stem from permeability because fractures are not sealed by carbonated deposits. Ebullition brings about the oversaturation of the fluid phase, an increase in the oxygen fugacity and a decrease in pH.

![smectite + hematite](image)

**Fig. 9.8.** Schematic representation of the growth of smectites in combination with hematite over large crystal rosettes of chlorites of propylitic origin (from a micro-photograph, Beauvert et al. 1995)
Oversaturation is the driving force of the nucleation and growth of high-temperature smectites that are hallmark features of liquid-vapour reservoirs (Reyes and Cardile 1989; Reyes 1990; Zan et al. 1990; Inoue et al. 1992; Papanagiotou 1993). The forming clays have a tetrahedral charge: beidellite and saponite (Fig. 9.9). There is no montmorillonite component, like in the clay cap in the upper portion of the geothermal field. The assemblage of di- and trioctahedral phases is identical to what is produced by the experiments of high-temperature mineral syntheses by Iiyama and Roy (1963), Eberl (1978), Yamada et al. (1991), Yamada and Nakasawa (1993) (see Sect. 10.1.1.1).

9.1.2 Precipitation and Reaction of Clays in Geothermal Fields

9.1.2.1 From Field Dynamics to Mineral Reaction Kinetics

The Chipilapa geothermal field shows that the dioctahedral and trioctahedral phyllosilicates have syncrystallised under the same physicochemical conditions (identical chemical compositions of fluids and equivalent temperature) at two periods of the hydrothermal activity about 4,000 years apart. Despite these identical conditions, the two generations exhibit differing mineralogical and crystallochemical properties. Indeed, the minerals that are currently
crystallising \( (t_0) \) between 180 and 240 °C in the field’s active fractures are tetrahedrally charged smectites: beidellite and saponite. The clay minerals whose formation took place at about 240 °C about 4,000 years ago \( (t_{4,000}) \) are today’s saponite-chlorite and beidellite-illite mixed layer series. Their respective transformation rates towards the end members chlorite and illite increase with depth (Fig. 9.10). This shows that the crystallochemical properties of “ancient” clays do not reflect the temperature of their occurrence in rocks but rather the period of time during which the transformations of smectites (metastable)

![Diagram](image_url)

**Fig. 9.10.** Variation in the mineralogical composition of clays from the di- and trioctahedral series as a function of depth. Time \( t_0 \) corresponds to the precipitation of clays in fractures from boiling solutions. Time 4,000 years represents the duration of the local thermal anomaly (4,000 years at Chipilapa) that caused high-gradient diagenetic transformations in the rock
Hydrothermal Process – Thermal Metamorphism

into illite and chlorite have been thermally activated in various locations of the geothermal field over the last 4,000 years.

The progressive disappearance of the expandable components to the benefit of chlorite or illite at increasing depth indicates that during the considered time interval (4,000 years), the conductive thermal effect (mean geothermal gradient) prevailed over the convective effect (local thermal anomaly due to hydrothermal fluid circulation). Therefore, in active geothermal fields, clay minerals must be considered as indicators of the \( \text{time} \times \text{temperature} \) parameter rather than as geothermometers.

The first data on geothermal fields (Steiner 1968) showed that the illite content of I/S minerals progressively increased with depth. Therefore, hydrothermal series were considered equivalent to a high-gradient diagenesis. Based on this assumption, kinetic models were established on the smectite (montmorillonite) to illite conversion yielding a complete I/S sequence (Huang et al. 1993 for instance). These models, as sophisticated as they may be (see Sect. 8.1.2.2), do not fully succeed to represent the geological reality of geothermal fields for several reasons:

1. conduction alternates with convection according to the fractures opened by the seismic activity or phreatic eruptions. A plurality of rocks in a given location may be the seat of intense hydrothermal circulations, hence of formation of smectites at a given time. Once sealed, these smectites transform into illite or chlorite when the conductive regime is re-established.

2. clay minerals in reservoirs, notably dioctahedral smectites and I/S minerals, are not similar to those observed in diagenetic series. Indeed, beidellites predominate in geothermal fields and illites are much more aluminous (close to muscovite). Accordingly, the montmorillonite \( \rightarrow \) illite reaction is inappropriate.

\section*{9.1.2.2}
I/S and C/S Minerals: Discontinuous Series

\textbf{I/S Series in Geothermal Fields}

In geothermal fields, beidellite – and not montmorillonite – is the initial smectitic mineral whose transformation into illite as a function of the \( \text{time} \times \text{temperature} \) parameter yields a series of I/S mixed layers, contrary to what takes place in the diagenetic context. The total absence of the random interstratification (R0) stage in the series is noteworthy. Montmorillonite occurs in the clay cap of the geothermal field where R0 I/S minerals are equally observed. It seems that the random interstratification only occurs if smectite does not exhibit any tetrahedral charge. This fact raises questions that have not been satisfactorily answered yet.

Out of this surface portion, the I/S sequence begins with a potassic rectorite phase (regularly ordered mixed-layer mineral). A sudden transition makes them disappear to the benefit of R1 I/S minerals whose illite content and coherent domain size increase steadily with depth (Fig. 9.11). The crystal
morbidity passes from small-sized lath-shaped particles (60–80% illite) to more isomorphic and thicker large-sized particles (> 85% illite). In geothermal fields, the illitic component is close to muscovite. It greatly differs from that of diagenesis, which exhibits a high octahedral charge (see Sect. 8.1.2.3).

Unfortunately, the discrimination between coexisting beidellite particles and regular I/S minerals is difficult. There is seemingly no significant difference of size and morphology between them. Therefore, the standard reaction process is probably of STT type (solid state transformation). The adsorption of K⁺ ions brings about the irreversible collapse of high-charge layers. Subsequently, the increase in the illite content of I/S minerals with depth accompanied by size and morphology changes can only be due to a crystal growth phenomenon by addition of illite layers over I/S particles that is similar to the one described in diagenesis. Inoue and Kitagawa (1994) have shown that, in geothermal systems, the growth of I/S minerals and illites produces spiral steps originating from the emergence of a dislocation on the (001) faces (see Sect. 1.2.3.1).
**C/S Series in Geothermal Fields**

It was classically thought that the transformation of saponite into chlorite took place similarly to that of montmorillonite into illite through a continuous series of mixed-layer minerals (Chang et al. 1986; Bettison and Shiffman 1988; Bettison-Varga and Mackinnon 1997). However, some observations relating to active geothermal fields showed that the transformation rather took place discontinuously with randomly ordered C/S minerals (100 to 80% saponite) suddenly shifting to corrensite (50 to 40% saponite) then to “swelling chlorites”, which are in reality C/S minerals with 15 to 0% saponite (Inoue et al. 1984; Inoue and Utada 1991). As a general rule, saponite or R0 C/S minerals and corrensite on the one hand and corrensite and chlorite on the other hand co-exist in wide-ranging temperature domains. The successive disappearance of saponite (or R0 C/S minerals) and corrensite at certain depths enable the following reaction sequence to be written: saponite $\rightarrow$ corrensite $\rightarrow$ chlorite. Corrensite is in fact a true mineral phase (Beaufort et al. 1997). Reactions are probably of dissolution-crystallisation type.

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**9.1.3 Acid Hydrothermal Systems**

**9.1.3.1 Alunite – Kaolinite – Pyrophyllite Hydrothermal Systems**

These systems have been thoroughly described in Japan because they relate to recent volcanism and are sometimes exploited for kaolin. Figure 9.12a shows how the mineral zonation is established between deep propylitic zones and surface silica deposits. In the case of the Ugusu Mine, the post-Pliocene volcanic activity triggered circulations of acidic hydrothermal fluids (pH < 4 at 20°C) that deeply altered the volcanic formations over a few hundred meters. Under these pH conditions, aluminium becomes more soluble than silicon. Therefore, silica forms porous deposits in the centre of the altered zones where hydrothermal springs emerge. The first altered zone in the vicinity of these deposits is formed of kaolinite, dickite and nacrite. Pyrophyllite appears near alunite zones $(\text{KA}_3\text{Si}_3\text{O}_8 + 2\text{H}^+ + 9\text{H}_2\text{O} \rightarrow \text{Si}_2\text{Al}_2\text{O}_5\text{(OH)}_4 + 2\text{K}^+ + \text{H}_4\text{SiO}_4$ occurring during the decrease in the temperature of hydrothermal fluids. The total leaching of cations, including aluminium from rocks near the vents, is due to the pH stabilisation in the very acid domain by $\text{H}_2\text{S}$ oxidation. Therefore, the physico-chemical conditions (temperature – cation activity/proton activity log) probably change following the path indicated in Fig. 9.12b. The alunite precipitation is due to the $\text{H}_2\text{S}$ oxidation. Muscovite has not been observed. However, the presence of dioctahedral smectites near unaltered propylitic rocks shows that the cation concentration of solutions and pH values are higher away from the vents.
Fig. 9.12a,b. Acid hydrothermal alteration. a) Sketch profile of the acid hydrothermal system of the Ugusu Mine, Shizuoka Prefecture, Japan (Nagasawa 1978). b) Schematic representation of temperature and ion activity conditions (Montoya and Hemley 1985). The arrow symbolises the probable path of the temperature-composition conditions of fluids in the hydrothermal system.

9.1.3.2 Halloysite-Kaolinite Transition in Acid Lakes

Clay minerals react in acid and hot environments by dissolution of certain species and precipitation of others. The acid lake of the Ohyunuma crater (Japan) provides a unique opportunity to study these reactions because it is supplied by rivers that renew solutions (Inoue and Aoki 1999–2000). The mean residence time of water is 25.5 days. Two environments are superimposed (Fig. 9.13a):
Fig. 9.13a,b. The acid lake of the Ohyunuma crater (Japan) from Inove and Aoki (1999–2000). a) Variation in chemical parameters and temperature in the lake. b) The chemical composition of waters from the upper part (40 °C) and the lower part (80 °C) of the lake are represented by black dots. The slopes of solubility lines are determined from thermodynamic parameters calculated by Helgeson et al (1978)

1. a low-salinity, oxidising, well homogenised upper part, with a high sulphate content, a low chlorine content and with pH = 2.4, where temperature does not exceed 40 °C;

2. a high-salinity lower part, with high sulphide and chlorine contents, with pH = 2.7, where temperature increases from 40 to 121 °C at the bottom.
The distribution of the clay minerals composing the sediments at the bottom of the lake is controlled by several factors, such as the location of hydrothermal discharge zones, the composition of river-borne suspensions, the bottom topography, the flow direction. Nevertheless, these sediments are strictly composed of halloysite and kaolinite. Quartz and α-cristobalite are of allochthonous origin. Sulphur and pyrite precipitate in the entire water column; they are related to the very hot vents and are kept in suspension by turbulent flows. Alunite forms in the lower part.

The upper part is kept in an undersaturation state with respect to halloysite and kaolinite owing to the renewal of solutions by river inputs. Accordingly, the reactions relating to silicates amount to the dissolution of all suspended clays in rivers (smectite, halloysite and supergene kaolinite). The compositions of the solutions at various depths are represented in the diagram log $a_{\text{Al}^3+} + 3 \text{pH}$ vs. log $a_{\text{H}_4\text{SiO}_4}$ (Fig. 9.13b). The slopes of the solubility lines are determined from the thermodynamic parameters calculated by Helgeson et al. (1978). At 40 °C, they are greatly within the undersaturation domain.

In the lower part of the lake (mean temperature 80 °C), the compositions remain undersaturated with respect to halloysite but become oversaturated with respect to kaolinite. Accordingly, only the largest halloysite particles are not dissolved and settle at the bottom of the lake (Inoue et al. 2000). Kaolinite is formed first through a two-dimensional nucleation process due to the high oversaturation degree. The growth takes place by coalescence of small crystals agitated by lake currents. However, since the major part of the aluminium dissolved in solutions is consumed by sulphate precipitation (alunite), the growth of kaolinite is limited.

9.1.3.3 Donbassite and Tosudite in Granitic Cupola

The emplacement of granitic batholiths is a complex phenomenon that comprises different stages taking place over long periods. The physicochemical processes of the magmatic differentiation sometimes result in the formation of small granitic bodies having a high alkaline and volatile element content. The granitic cupola of Echassières (Massif Central, France), studied in the scope of the Programme Géologie Profonde de la France, is an example of this type of intrusion into a two-mica granite and micaschists. The presence of breccia adjacent to micaschists shows that the emplacement took place at very shallow depths (brittle domain). The magmatic body is divided into two entities: a phaneritic upper part and a lower part with a fluidal microstructure (Fig. 9.14a). Its mineralogical composition is dominated by albite (40–70%); other components are quartz (15–25%), K-feldspar (5–15%), lepidolite (10–25%) and topaz (1–5%). The rocks have been affected by two successive episodes of hydrothermal alteration:

- early alteration stages in veins, chronologically: quartz, muscovite, pyrophyllite, donbassite, tosudite, and kaolinite;
Fig. 9.14a,b. Hydrothermal alterations in the granitic cupola of Echassières, Massif Central, France (Merceron et al. 1992). a) Geological profile of the granitic cupola showing the intrusion of two magmatic bodies (phaneritic upper part, fluidal lower part) and the early alteration stages related to their cooling. The late alteration stages transform the fault wallrocks (post-magmatic tectonic event). b) Phase diagram in the Si–Al–Li–H\(_2\)O system, showing the extension of the stability field of donbassite as a function of its Li content (0 ≤ x ≤ 1)
late alteration stages in veins, chronologically: fluorite + quartz, illite + quartz, illite/smectite mixed layer + quartz.

Donbassite seals small-sized veins (0.2 to 0.7 mm) and replaces some pre-existing minerals: primary feldspars and lepidolites, secondary muscovites. It contains up to 1.6% Li$_2$O (in weight). Its mean unit formula is as follows:

$$[\text{Si}_{3.81}\text{Al}_{0.19}]\text{O}_{10}\left(\text{Al}_{3.81}\text{Li}_{0.52}\text{Fe}^{2+}_{0.01}\text{Mg}_{0.01}\text{Mn}_{0.01}\right)\text{(OH)}_{8}\text{Ca}_{0.02}\text{Na}_{0.07}\text{K}_{0.04}$$

(9.3)

The lithium content of tosudite (regularly ordered dioctahedral donbassite/smectite mixed layer) is a bit lower: 0.72%. Its unit formula is as follows:

$$[\text{Si}_{3.50}\text{Al}_{0.50}]\text{O}_{10}\left(\text{Al}_{2.95}\text{Li}_{0.22}\text{Fe}^{3+}_{0.01}\text{Ti}_{0.01}\right)\text{(OH)}_{5}\text{Ca}_{0.01}\text{Na}_{0.15}\text{K}_{0.18}$$

(9.4)

The salinity and temperature of solutions measured by fluid inclusions and by isotopic analyses of quartz and associated minerals are controlled by the cooling of the magmatic body after its emplacement. They range between 10 and 1% NaCl equivalent and between 400 and 150 °C, respectively. These fluids are acid and exhibit high chlorine and fluor contents. Upon reaction with alkaline granite, they yield a sequence of secondary minerals from 400 to 200 °C: muscovite – pyrophyllite – donbassite-Li$_{0.5}$ – tosudite – kaolinite. Donbassite and tosudite form at the end of this early episode between 300 and 200 °C preferentially to kaolinite owing to the presence of lithium in the system (Merceron et al. 1992). Indeed, the higher the Li content, the greater the temperature range of the stability field of donbassite (Fig. 9.14b). Late alteration stages relate to the opening of fractures and vertical faults that cut across the enclosing micaschists. Fluids are of meteoric origin. Their Fe and Mg contents are increased by their passage in the micaschist cover. The precipitated illite and I/S minerals have compositions that greatly differ from those of the minerals generated by early alterations.

9.1.4
Geothermal Systems with Seawater (Alkaline Type)

9.1.4.1
Active Geothermal Fields

The geothermal fields supplied with seawater are located in volcanic islands. The best known have developed in basaltic structures like Iceland, others are related to andesitic volcanic arcs (Bouillante, Guadeloupe), and still others form in fractured basements (Milos, Greece). Whatever their geological setting, they are characterised by the abundance of magnesium-rich trioctahedral phyllosilicates in zones of thermal diffusion (conduction) as well as in fractured systems where hot fluids flow (convection). Anhydrite is frequently observed (Tomasson and Christmannsdottir 1972).
Thermal diffusion in active geothermal fields establishes a zonation of zeolites and clay minerals similar to that developing in vast regions by diagenesis or metamorphism. The only singularity is the shortening of zones owing to the high geothermal gradient. The sequence as a function of depth (increasing temperature) summarised by Alt (1999) is based on the mineral transitions observed in Icelandic active fields. In this sequence the transitions in ferromagnesian silicates (phyllosilicates and amphiboles) and in Ca–Na silicates are paralleled (Kristmannsdottir 1975, 1977, 1978; Schiffman and Fridleifsson 1991): (1) smectite – chlorite-smectite mixed layers – corrensite – chlorite – actinote + epidote; (2) low-temperature zeolites (mordenite, stilbite, clinoptilolite, heulandite) – laumontite – wairakite – prehnite (Fig. 9.15a).

More or less similar parallel zonations are observed in active fields supplied with seawater. The example of the reservoir of the Milos geothermal field (Greece) enables this organisation to be verified in a non-basaltic context. The low-permeability upper portion of the field exhibits a mineral zonation related to heat diffusion by conduction. Low-temperature clays are montmorillonite, which disappears at 150 m in depth ($T < 150^\circ C$), and saponite, which persists beyond 250 m. Corrensite forms between 200 and 350 m in depth, from where it is replaced by chlorite. A non-expandable mixed-layer mineral of talc-chlorite type occurs in places. This regular zonation contrasts with clay minerals that are currently forming in permeable zones at temperatures over $300^\circ C$.

The reservoir is located in the basement composed of micaschists (blue schist and green schist metamorphic facies). The primary phyllosilicates of schist rocks are muscovite (phengite) and biotite. This dominating vapour reservoir is located in the seawater-boiling zone. All phyllosilicates forming at $300^\circ C$ are of trioctahedral type. Saponite reappears, combined with a talc/saponite mixed layer (T/S), talc and actinote (Fig. 9.15b). This combination is totally out of thermodynamic equilibrium. It results from the kinetics of the nucleation of these various phases and only depends on the composition of fluids. This effect of kinetics has been confirmed by experiments of basalt alteration between 375 and $425^\circ C$ that have shown the coexistence of smectite with chlorite-epidote or chlorite-actinolite-tremolite parageneses (Berndt et al. 1988).

9.1.4.2 Hydrothermal Alteration of Oceanic Basalts

Pillow Lavas (Seawater at 2–4°C)

The rims of pillow lavas are formed by very thin exfoliation structures produced by the thermal shock with seawater (Fig. 9.16a). These structures transform gradually into green breccia (Scott and Hajash 1976; Juteau et al. 1979). The interaction between seawater and glass yields an alteration micro-profile a few millimetres thick (Fig. 9.16b), which is not to be confused with the black halo caused by sea-water weathering (see Sect. 6.1.3.5). The external part is formed of green palagonite (altered glass) that gradually transforms (variolitic zone 2 to 3 mm thick) into an apparently unaltered brown basaltic glass. The green palagonite has a perlitic structure, each “pearl” being zoned concentrically. The breccia is formed of green palagonite pieces cemented together. Voids are sealed
Fig. 9.15a,b. Active geothermal fields supplied with seawater. a) Mineral zonation related to heat diffusion by conduction (Alt 1999). b) Contrast between the diffusion-related zonation in the upper portion of the Milos geothermal field (Greece) and the forming paragenesis in the reservoir (Beaufort et al. 1995)
Fig. 9.16a–c. Pillow lava. a) Schematic representation of an alteration profile at the surface of a pillow lava (Juteau et al. 1979). b) Diagrams of microstructures in palagonite fractures and massive basalt. c) Example of diffraction pattern of clays extracted from veins in palagonite by polyphased deposits: calcite, zeolites, and hematite. Several different species of zeolites co-exist in the fractured zones (analcite, chabasite, gismondine, faujasite).

Phyllosilicates in the glassy zones of pillow lavas are often difficult to identify because their diffraction patterns exhibit only broad and low-intensity bands (small size X-ray scattering coherent domains) while their chemical composition, even measured with the electron microprobe, always corresponds to phase mixtures (Fig. 9.16c). Most compositions so measured are located in the domains of celadonite, saponite and chlorite although only smectite can be identified by X-ray diffraction.
Alteration of the Deep-Sea Floor (Sea Water 10–50°C)

Hydrothermal alterations of the deep-sea floor have been extensively studied. Alt (1999) has published an excellent data synthesis. During the first two million years, the seawater-basalt interactions produce a black halo composed of a mixture of nontronite, celadonite and Fe- and Mn-oxihydroxides. Clay phases have very small-sized coherent scattering domains as is the case for the palagonitised zone of pillow lavas. This halo ranges between a few millimetres and 1 or 2 centimetres in thickness. The basalt vesicles remain empty. This is seawater weathering; see Sect. 6.1.3.5.

Older samples (2 to 10 My) show the presence of a saponite zone between the unaltered rock and the halo. The presence of this clay is interpreted as the superimposition of a hydrothermal alteration subsequent to the formation of the black halo by fluids derived from seawater and heated (< 50°C) in fractures. The hotter the fluids, the more intense the alteration. At this stage, olivines are totally altered. Saponite remains the dominant phyllosilicate but talc may occur in vesicles in combination with pyrite and calcite. The vesicles are then totally sealed.

The hydrothermal alteration under similar conditions (seawater, 50°C) of rocks that have been exposed for 10 to 23 Ma still exhibits the black halo. The zone intermediate with the fresh rock is characterised by an aluminous saponite + ferriferous beidellite + K-feldspar mineral assemblage. The sequence of occurrence of alteration minerals as a function of age (Fig. 9.17) shall not be interpreted as the replacement of the magnesian saponite by an aluminous equivalent. The change in composition is not a question of relative stability but of chemical composition of the altered environment. The presence of secondary minerals relates to the destabilisation of plagioclases.

Alteration of the Dyke Zone (Seawater, < 150°C)

Underneath basalts, the deep-sea floor structure comprises a layer formed by an agglomeration of dykes corresponding to the feeding conduits of submarine volcanoes. The intensely fractured rocks are crossed by heated fluids (> 50°C)
derived from seawater. Chlorite is the dominant phyllosilicate combined with epidote. In rifts, fracturation is sufficiently intense for basalts to be totally recrystallised. They are replaced by massive deposits of sulphides and by a rock composed of illite (or paragonite) and chlorite. The more abundant the fluids (whose temperature ranges between 250 and 360 °C), the more intense the alteration (Alt 1999).

The very hot sulphide fluids emerge at the deep-sea floor surface thanks to a network of interconnected faults. Chimneys several meters high are formed by complex pyrite, chalcopyrite, sphalerite and anhydrite deposits. Thermal shock and decompression of the hot fluids exiting into seawater at 2 °C bring about a tremendous oversaturation. Minute crystals suspended in these fluids emphasise the plume of the “black smokers”. Away from the vents, the hydrothermal fluids mix with seawater. Then a deposit of Fe- and Mn-oxihydroxides combined with nontronite is formed.

**Hydrothermal Alterations in Guyots (Sea Mounts)**

The general structure of guyots is typically organised as follows: a summit formed by air lava flows, a base formed by submarine lava flows and an inner framework of dykes. The Mururoa and Fangataufa atolls have been widely studied thanks to the numerous drill holes exploring their mechanical stability (Dudoignon et al. 1989; Dudoignon et al. 1997). The hydrothermal systems that have developed there have experienced several activity periods leading to successive mineral deposits. During the most intense activity at Fangataufa, the thermal gradient was 300 °C km⁻¹. Alterations have led to the formation of a sequence of clay minerals: from top to bottom, beidellite, saponite, saponite + randomly ordered C/S minerals, randomly ordered C/S minerals + corrensite, chlorite. The last activity period (150 °C km⁻¹) has caused the sealing of fractures by calcite deposits.

The sequence of trioctahedral minerals exhibits a general organisation that is similar to those described in the deep-sea floor or in Icelandic-like systems. However, their distinguishing feature is the formation of beidellite replacing plagioclases (Fig. 9.18). Beidellite co-exists with randomly ordered C/S minerals (190–240 °C) and corrensite (260–320 °C). The occurrence of illite/smectite mixed layers might be expected in these temperature ranges. Their absence is due to a chemical microsystem effect: plagioclase does not contain potassium.

9.2 Small-Sized Hydrothermal Systems

**Introduction**

Small-sized hydrothermal systems are often used as natural analogues in human works for the study of chemical component transfers or mineral reactions owing to similar size and duration scales. When the order of magnitude is a hundred years or more, any experimental reproduction of the phenomena is unthinkable. These systems are considered as natural laboratories and the
Fig. 9.18. Sequence of clay minerals in the hydrothermal system of the Fangataufa guyot (Sea Mounts), French Polynesia (Dudoignon et al. 1997). Palaeotemperatures have been determined by the stable isotope composition of phyllosilicates and carbonates.

Observations are treated like experimental data. Notably, the safety of the radioactive waste storages requires that the thermal and chemical behaviours of the various barriers be modelled over relatively long durations. Two points have been particularly developed:

1. The long-term stability of the bentonite engineered barrier has been modelled using natural situations in which this material underwent transformations triggered by the local temperature increase around volcanic rock intrusions;

2. The mechanisms involved in the transfers of chemical elements related to the circulations of hot fluids in fractures have been deciphered by the study of hydrothermal veins crosscutting different types of rocks.
9.2.1
Thermal Metamorphism of Clay Formations

9.2.1.1
Thermal Diffusion in Shales

The solution of complex equations of heat transfers is beyond the scope of this book. The principles are published in numerous books now. To simplify, the one-dimensional solution proposed by Carslaw and Jaeger (1959) and its application to magmatic intrusions (Jaeger 1964) will be used here:

\[
T = T_0 \sum_{n=0}^{\infty} \left[ \text{erf} \left( \frac{(2n + 1)L + x}{2\sqrt{\kappa t}} \right) - \text{erf} \left( \frac{(2n + 1)L - x}{2\sqrt{\kappa t}} \right) \right]
\]  

(9.5)

\text{erf}: \text{error function:}

\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-\xi^2} d\xi
\]

(9.6)

\(T\) temperature (°K)

\(T_0\) magma temperature (°K)

\(L\) thickness of the magmatic body (m)

\(x\) distance to the magmatic body (m)

\(\kappa\) thermal diffusivity of bentonite (mm² s⁻¹)

\(t\) time(s)

This type of modelling has been applied by Pytte (1982) to a contact metamorphic zone produced by basaltic intrusions in smectite-rich Cretaceous shales (Fig. 9.19a). The \(\kappa\) value for shales is 0.64 mm² s⁻¹. The result is expressed graphically in Fig. 9.19b, which shows that the thermal peak is reached faster when the considered point is closer to the magmatic body. The intensity of this peak decreases with distance. In other words, these graphs show that the amount of absorbed heat is proportional to the \(\text{time} \times \text{temperature}\) parameter: the closer the point to the heating body, the greater this parameter.

9.2.1.2
Kinetics of Mineral Reactions

\textit{Smectite} \rightarrow \textit{Illite Transition}

The progressive increase of the illite content and the decrease of the smectite content in illite – smectite mixed layers (I/S) in diagenetic or hydrothermal formations are classically thought to be due to a single mineral reaction of
smectite $\rightarrow$ illite type. Therefore, the reaction progress can be measured by the variation in the smectite ratio $S$. The kinetic expression is as follows: $-\frac{dS}{dt} = kS^a$ where $a$ is a constant determining the reaction order. The rate constant $k$ is given by the Arrhenius equation (see Sect. 3.2.2.1): $k = A \exp(-E_a/RT)$ where $A$ is the frequency factor, $E_a$ is the activation energy of the reaction and $T$ is the temperature expressed in K. The general kinetic equation is written as follows:

$$-\frac{dS}{dt} = S^a \left( \frac{a_K}{a_{Na}} \right)^b A \exp \left( \frac{-E_a}{RT} \right)$$

(9.7)

The transformation of smectite into illite brings about potassium consumption. As a consequence, the reaction does not only depend on temperature but also on the potassium activity $a_K$ in solution. In the case of the thermo-metamorphism of shales described by Pytte, an indirect measurement of $a_K$ was performed.
from the observation that the amount of K-feldspars increases with distance whereas that of albite decreases. Therefore, the K/Na activity ratio calculated by the orthose-albite equilibrium at all considered temperatures is a correct approach of the potassium role. The ratio $a_K/a_{Na}$ is given by the Van’t Hoff equation:

$$a_K/a_{Na} = 74.2 \exp\left(-\frac{2490}{T}\right)$$  \hspace{1cm} (9.8)

Integers $a$ and $b$ are added to determine the reaction order. Pytte and Reynolds (1989) give the following values: $a = 5$, $b = 1$. Using these values after integration of the differential equation yields:

$$S^4 = \frac{S_0^4}{1 + 4 \times 74.2 t S_0^4 A \exp \left( -\frac{2490}{T} - \frac{E_a}{R T} \right)}$$  \hspace{1cm} (9.9)

Parameters $A = 5.2 \times 10^7$ s$^{-1}$ and $E_a = 33$ kcal mol$^{-1}$ have been determined by fitting methods. The results have been compared to data relative to other environments where the smectite→illite reaction occurs (diagenesis, metasomatism). Pytte and Reynolds (1984) have calculated $A$ and $E_a$ using time and temperature values for which I/S minerals with 80% illite form more than 90% of the clay fraction under various geological conditions (Table 9.2). If $S_0 = 1$ (clay fraction with 100% smectite) and $S = 0.2$ (I/S mineral with 80% illite), the above equation becomes:

$$\ln \left( \frac{t}{T} \right) = \frac{1}{T} \left( \frac{2490 + E_a}{R} \right) - \ln(A) + 0.743$$  \hspace{1cm} (9.10)

The resulting numerical values are consistent with those extracted from the line presented in Fig. 9.20a. $A$ and $E_a$ values are $5.6 \times 10^7$ s$^{-1}$ (mineral reactions assumed to be first-order ones) and 33.2 kcal mol$^{-1}$, respectively. They

<table>
<thead>
<tr>
<th>Estimated time</th>
<th>Estimated maximum Temperature value (°C)</th>
<th>Geological conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 years</td>
<td>250</td>
<td>Contact metamorphism</td>
<td>Reynolds (1981)</td>
</tr>
<tr>
<td>10,000 years</td>
<td>150</td>
<td>Geothermal fields</td>
<td>Jennings and Thompson (1986)</td>
</tr>
<tr>
<td>1 My</td>
<td>127</td>
<td>Burial diagenesis</td>
<td>Perry and Hower (1972)</td>
</tr>
<tr>
<td>10 My</td>
<td>100</td>
<td>Burial diagenesis</td>
<td>Perry and Hower (1972)</td>
</tr>
<tr>
<td>300 My</td>
<td>70</td>
<td>Burial diagenesis</td>
<td>Srodon and Eberl (1984)</td>
</tr>
<tr>
<td>450 My</td>
<td>70</td>
<td>K-bentonite</td>
<td>Huff and Turkmenoglu (1984)</td>
</tr>
</tbody>
</table>
Fig. 9.20a,b. Thermometamorphism of shales (Pytte and Reynolds 1984). a) Time–temperature relationship of the formation of more than 90% of illite/smectite mixed layers with more than 80% illite in the clay fraction (values extracted from Table 2). b) Variation in the illite content in shales with distance to the basaltic vein (full dots). The solid line represents the curve calculated from the kinetic equation using the values indicated in the text.

are very close to those determined by means of the fitting method. The simulation (continuous curve) is relatively consistent with the measurements of the proportion of expandable layers in the I/S minerals (Fig. 9.20b).

**The Montmorillonite → Saponite + Illite Reaction**

The smectite → illite transformation such as classically admitted is based upon the assumption that a smectite layer yields an illite layer. Although the true transformation processes of one into the other are still poorly known (dissolution – crystallisation, solid state transformation, growth of illite over smectite), the chemical balance of the reaction cannot be drawn up. Assuming that smectite (montmorillonite) and illite have the following compositions:

\[
\begin{align*}
\text{Si}_4\text{O}_{10} & \left( \text{Al}_{1.65}\text{Fe}^{3+}_{0.05}\text{Mg}_{0.30} \right) \left( \text{OH} \right)_{2}\text{Na}_{0.30} \\
\left[ \text{Si}_{3.25}\text{Al}_{0.75} \right]\text{O}_{10} & \left( \text{Al}_{1.80}\text{Fe}^{3+}_{0.05}\text{Mg}_{0.15} \right) \left( \text{OH} \right)_{2}\text{K}_{0.90}
\end{align*}
\] (9.11)

the reaction is written:

\[
\begin{align*}
1 \text{ montmorillonite} + 0.90 \text{Al}^{3+} + 0.90 \text{K}^+ \\
\rightarrow 1 \text{ illite} + 0.75 \text{Si}^{4+} + 0.15 \text{Mg}^{2+} + 0.30 \text{Na}^+
\end{align*}
\] (9.12)

The source of K⁺ and Al³⁺ ions is generally related to the dissolution of K-feldspars or primary micas.
Since the mobility of aluminium is very low, the balance can be written otherwise. It is no longer 1 layer for 1 layer but 1.54 for 1:

\[
1.54 \text{montmorillonite} + 0.90 \text{Al}^{3+} + 0.90 \text{K}^+ \\
\rightarrow 1 \text{illite} + 2.91 \text{Si}^{4+} + 0.03 \text{Fe}^{3+} + 0.31 \text{Mg}^{2+} + 0.46 \text{Na}^+ 
\] (9.13)

The potassium source is always external (dissolution of K–feldspars–K or micas). This montmorillonite \(\rightarrow\) illite reaction significantly increases the \(\text{Si}^{4+}\) and \(\text{Mg}^{2+}\) contents in solutions. When the reaction is performed experimentally (closed system without \(\text{CO}_2\)), these elements are consumed in the precipitation of smectites of saponite-stevensite type (Beaufort et al. 2001). If \(\text{CO}_2\) is present, Fe–Mg carbonates are formed.

The formation of magnesian trioctahedral smectite has been observed in experiments simulating nuclear waste storages in the Stripa site (Sweden) where a clay barrier formed of a kaolinite/smectite mixed layer (K/S) has been heated for many years. Despite the low magnesium content of these K/S minerals, the chemical diffusion near the heating body has caused the precipitation of saponite (Bouchet et al. 1992). Without potassium, illite does not form. It is replaced by a dioctahedral smectite whose layer charge is mostly located in the tetrahedral sheet. The saponite + beidellite assemblage has been observed in alteration experiments (Yamada and Nakasawa 1993) and natural hydrothermal systems (Beaufort et al. 1995).

9.2.2 Hydrothermal Veins

9.2.2.1 Mineral Zonations

The circulation of hydrothermal fluids in fractures causes two types of mineral reactions:

- the precipitation of minerals that finally seal the fracture, referred to as a “vein”;
- the alteration of wall rocks whose colour changes over a variable distance to the fracture, referred to as an alteration “halo”.

Even reduced to a few microns in thickness, the halo is most often zoned. Mineral assemblages change with the distance to the vein. These zonations were described very early in mineralised systems (Lovering 1949; Bonorino 1959). Each zone is characterised by an assemblage or by a dominating mineral whose proportions vary with distance (Fig. 9.21). These two authors had already established that zonations resulted from a chemical diffusion process under isothermal conditions (the heat diffusion rate being higher by several orders of magnitude than the chemical diffusion rate). They considered that the width of the halo was dependent on the system temperature, among other factors.
The origin of zonation was subsequently reconsidered as resulting from crystallisation kinetics (Page and Wenk 1979). These authors based their conclusion on the observation of a sequence of phyllosilicates from the vein to the altered rock: 2M\textsubscript{1} phengite, 1M then 1Md illite, illite/smectite mixed layers (I/S). Assuming isothermal conditions, they considered that I/S minerals are metastable precursors of illite and phengite.

The generally admitted isothermal conditions have been questioned in recent studies. Indeed, thermal gradients at various scales have been shown using different techniques:

- 200 °C over 100 m in the Amethyst vein (Horton 1985),
- 60 °C over 6 m in uranium veins (Al Shaara 1986),
- 75 °C over 11 mm in a phengite vein (Turpault et al. 1992b).

The detailed study of the mechanisms of alteration propagation in the vicinity of the phengite veins crosscutting the La Peyratte granite (Deux Sèvres, France) has shown that the thermal gradient is stabilised by a pulsed flow of hot fluids in the fracture. The hydrodynamic regime was reconstructed from temperatures measured in secondary fluid inclusions in the wall rock quartz crystals. The residence time of fluids in the fracture and the expulsion frequency are of the same order of magnitude as those observed in surface geysers (Turpault et al. 1992a).

The statistical analysis of veins 20 to 300 µm in width in the La Peyratte granite shows that the wall rock alteration obeys the two following processes:

1. formation of mineral reaction “fronts” bounding chlorite, albite or plagioclase dissolution (oligoclase) zones;
2. propagation of fronts such that the various zones do not vary independently (Fig. 9.22). This means that the alteration propagation is controlled by
Fig. 9.22. Schematic representation of the propagation of alteration fronts in the wall rocks of fractures crosscutting the La Peyratte granite, Deux Sèvres, France (from Turpault et al. 1992a,b). t\textsubscript{1}: mechanical strains open a fracture that brings granite minerals and hydrothermal fluids into contact; t\textsubscript{2}: dissolution of the fracture wall rocks; t\textsubscript{3}: wall rock alteration maintained by the establishment of chemical potential gradients. The crystallisation of phengites in the fracture starts at this stage as the last link in the chain of mineral reactions; t\textsubscript{4}: alteration propagation by displacement of the mineral reaction fronts.
a single chemical mechanism maintained during the entire “life time” of the fracture.

This alteration propagation phenomenon in wall rocks cannot be explained by the dissolution of primary minerals at the contact of fluids alone. Once the chemical equilibrium between hydrothermal solutions and the mineral has been reached, the alteration rate becomes infinitely low. Therefore, in the absence of a thermal gradient maintaining a chemical potential difference for every element, mass transfers are believed to be reduced to values that cannot be measured in hydrothermal veins.

The chemical balance of alteration is achieved as follows: (1) transfer of H\textsubscript{2}O from the fracture to the wall rock, (2) transfer of Si\textsuperscript{4+}, Al\textsuperscript{3+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Na\textsuperscript{+} cations from the rock to the fracture and (3) total consumption of cations in the mineral reactions with the exception of Si\textsuperscript{4+} and Ca\textsuperscript{2+}. The mobility of low-solubility cations like Al\textsuperscript{3+} is maintained by the chemical potential difference of this element between the “source” site (dissolution front of plagioclases) and the “consumption” site (biotite → chlorite and oligoclase → albite reaction front). The variation in the size of the plagioclase dissolution holes accounts for the progression of alteration fronts (Meunier 1995).

Alteration involves several mineral reactions thus forming a “trophic chain” of which the ultimate consumer is the crystallisation of phengites in the open space of the fracture. This chain starts operating at the opening of the fracture and stops when one of the constituent reactions stops. In the present case, the crystallisation of phengites ceases when the whole open space is occupied (Berger et al. 1992). The vein is definitively sealed by the precipitation of fluorite ± pyrite. The bulk rock chemical balance (fracture + altered wall rocks) shows that only Si\textsuperscript{4+} and Ca\textsuperscript{2+} are exported outward. Oddly, the alteration process took place in a nearly closed system from the cation standpoint. Considering the quartz solubility at the alteration temperature (about 300 °C), one can calculate the number of litres of fluids that have flowed per volume unit of fracture to drain off the silica lost by the rock. The retrograde path (cooling of the system) is recorded in the rock by the precipitation of illite/smectite mixed layers that are increasingly rich in smectite near the vein in the plagioclase dissolution holes.

9.2.2.2

Hydrothermal Alteration of Clay Rocks

Clay rocks may be fractured and hydrothermalised under certain geological conditions. They form small-sized systems, which exhibit also a mineral zonation composed of mixed-layer mineral assemblages whose composition varies with distance to the vein. The recent argillised dacitic rocks from the Trois Ilets quarry, Martinique (Bouchet et al. 1988), are mainly composed of I/S minerals the smectitic component of which comprises more than 80% of high-charge layers (irreversibly fixing K\textsuperscript{+} ions). The fumarolic alteration (< 100 °C) causes the gradual decrease in the proportion of these layers down to zero in the vein.
(Fig. 9.23). The mineral reaction is of type:

$$\text{high-charge smectite} + \text{Si}^{4+} + \text{K}^+ \rightarrow \text{low-charge smectite} + \text{illite}$$  (9.14)

$\text{Si}^{4+}$ and $\text{K}^+$ cations are brought by hydrothermal fluids.

At the Pointe de la Caravelle site (Martinique), the rock is a dacitic conglomerate belonging to the ancient island arc (36–22 Ma). The clay fraction is dominated by randomly ordered I/S minerals with 55–60% smectite. A network of hydrothermal veins caused an intense alteration over about ten centimetres. The clay fraction of the wall rocks comprises kaolinite and two types of I/S minerals: randomly ordered with 80% smectite and ordered with 5% smectite. The proportion of ordered I/S minerals increases near the vein whereas that of high-charge smectite layers in the randomly ordered I/S minerals decreases.

Zonations in the vicinity of veins can be disturbed or erased during the hydrothermal activity period. Indeed, several successive reopenings of fractures initially sealed by mineral deposits are frequently observed. This is a commonly occurring phenomenon in seismically active geothermal fields, well known in metamorphism (“crack-seal”). Each episode imposes new interactions between fluids—whose chemical composition has most often changed, and the previously altered rock. The superimposition of alterations brings about the juxtaposition practically in the same sites of minerals that have formed under very different conditions. These assemblages do not constitute a paragenesis.
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