3 Origin of Clays by Rock Weathering and Soil Formation

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3.1 Introduction

It is a fact that mankind's domain of influence at the surface of the planet is roughly that of clay mineral formation: soils, weathered rocks, diagenetic series, continental and marine sediments, geothermal fields. These clay resources have been exploited since the discovery of fire. It is now important, for environmental studies, to know as well as possible, how and where these minerals form. Curiously, among the numerous works published until now, only a few are devoted to the mechanisms of clay formation at the scale of a soil profile, i.e. the metric scale in temperate zones. Indeed, more is known at the scale of a country (km) or the mineral–fluid interface (nm). For example, at the scale of a country, weathering can be considered as a homogeneous process. As a consequence, it is possible to model chemical transfers and clay-mineral stability fields using calculation codes. On the other extreme, the intimate dissolution–recrystallization mechanisms at the fluid–mineral interface scale are studied on isolated pure crystals in order to simplify the chemical system.

The major difficulty of studying clay formation at the scale of eye observation (m to µm) lies in the heterogeneity of natural materials which results in an enormous variability of chemical and mineralogical properties. Nevertheless, it is only at this scale of observation that important problems in environment conservation can be approached. The aim of this chapter is to show that the apparent variability is not an effect of chance, but that it is in fact governed by a few general laws. Consequently, a methodology will be proposed to researchers involved in clay formation problems.

Any student concerned with soils and weathered rocks must be aware of the difficulty of drawing a boundary between these two formations. Besides the intrinsic complexities of soils and weathered rocks, one reason for this difficulty is that they were most often studied by different categories of researcher; i.e. pedologists and geologists. As no definition is completely satisfying, a distinction will be proposed here in order to enhance what is important for us and to avoid unnecessary details. It is hoped that the reader will be informed of the current knowledge regarding the processes controlling the formation of clay minerals in surface conditions. The primary objective is to

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document how natural processes work. The second objective is to set out a method of practicing petrology of altered rocks and soils, since such a method is the most useful tool to characterize the physical and chemical properties of materials subjected to human activities.

This chapter is composed of four parts which it is hoped will give fundamentals as well as examples of profile studies. The first part is devoted to the description of the influence of the main parameters in terms of soil formation, water–rock interactions and dissolution–crystallization processes. It includes an introduction to a general method of reasoning with chemical and mineralogical data using different types of phase diagrams. The second part is devoted to a detailed presentation of the formation of soils and weathered profiles on a chosen parent rock: the granite. The aim is to give an example of the changes in mineralogy, chemical composition and structures which effect a hard rock at the surface horizon under vegetation in temperate conditions. The third part presents the effects of the mineralogical and chemical compositions of rocks on the formation of a weathered profile. Several examples of profiles developed on magmatic, metamorphic and sedimentary rocks are presented. Mineral reactions are interpreted using phase diagrams. The fourth part is devoted to the description of the major categories of soils which can be observed in different climatic conditions.

3.2 Weathered Rocks and Soils: The Major Factors in Their Development

3.2.1 General Organization: Soil and Weathered Rock Domains

Weathering profiles and soils often show a polarity between the organic horizons at the surface and the rock underneath (Fig. 3.1). Although it is totally artificial to draw a line between the weathered rock and the soil overlaying it, such a separation must be made for practical reasons. As a limit must be put somewhere it will be considered that the lower limit of soil is reached where the original structure of the rock is still preserved. In other words, the soil is considered as the unconsolidated, restructured material built with materials derived from the weathered rock. Moreover, the soil structure may change seasonally through physical processes such as drying and wetting cycles or biological activity. In contrast, the weathered formation is generally characterized by a permanent structure inherited from the parent rock.

Other features make soil different from weathered rock and allow one to consider it as an original body:

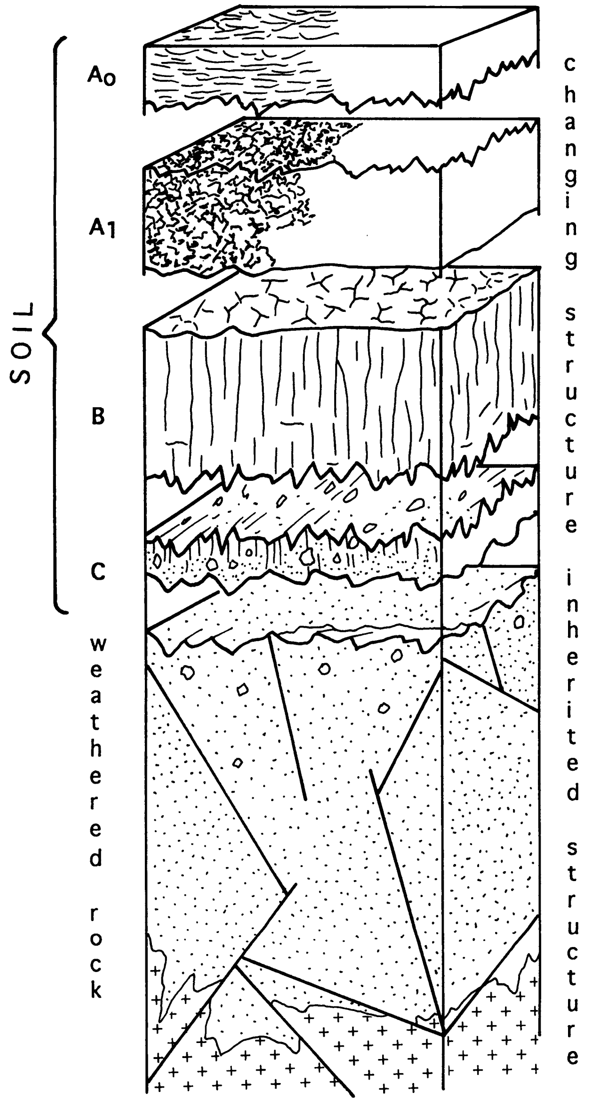


Fig. 3.1. Representation of the different horizons in a soil and weathered rock sequence

1. Soil is the place where the transformation of rock minerals into clays is most important. In some soils, all the original minerals have been transformed.
2. The upper soil layer is where plant roots and animals are living. After their death, organic matter from plants and animals in incorporated into soil material and intimately mixed with the mineral part of soil. After a complex course of transformations, including biological and chemical reactions, specific soil organics, the humic compounds, are formed. These humic compounds may contract close and strong associations with the mineral phase, especially with clay minerals. For most soils in the temperate zone, the

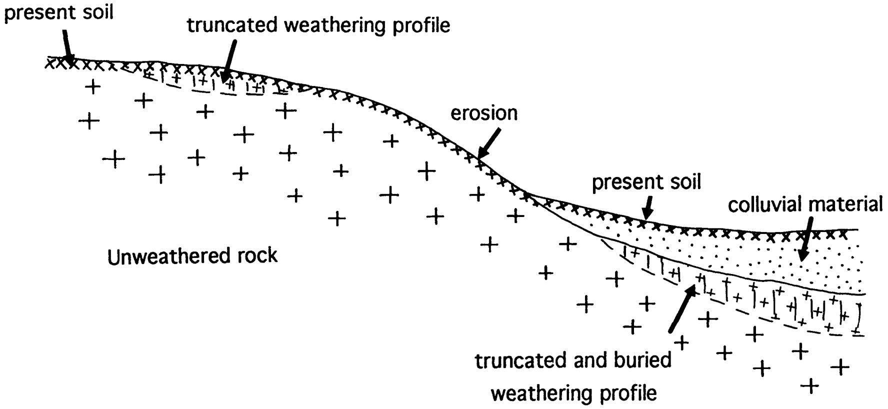


Fig. 3.2. Effects of erosion and colluviation on the ideal soil–rock weathering sequence

evolution of soil clays is related to that of organic compounds and the associations that they are able to form (Macias and Chesworth 1992).

In nature, the theoretical sequence from fresh to weathered rock and soils can be observed only at a few particular sites. These are in very stable landscapes where erosion is minimised. Usually, the sequence is disturbed by erosion and colluviation events; consequently the soil may develop from allochtonous materials, in regards to the rock underneath (Fig. 3.2). The present soil may also develop from a truncated weathering profile of which the upper part has been removed by erosion. This is typical for weathering profiles and soils developed in temperate and cold areas that were affected by glacial and periglacial erosion during the Quaternary period. Where ice fields were present, the whole soil and weathered rock would have been disturbed and removed, leaving either the fresh hard rock or thick glacial tills as surface materials. The present-day soils developed directly from the rock or glacial material. Periglacial disturbance was less drastic, generally preserving the lower layers of the weathering profiles. The present soil develops from this previously weathered material; however, in this case, the soil and the weathered rock underneath are of different ages and have not developed under the same climatic conditions.

3.2.2 Basic Factors in Weathering and Soil Formation

Weathering and soil formation do not lead to the formation of a homogeneous mantle over the Earth's surface. Several factors determine the transformation of rocks into soils of different types. These factors are climate, rock type (or parent material), vegetation, age and topography (FitzPatrick 1980; Duchaufour 1991).

3.2.2.1 Climate and Water Regime Within the Soil Mantle

Transformation of rock minerals into clays occurs through chemical reactions between the minerals and water which comes from rainfall. Therefore, rainfall is essential for weathering and soil formation. The amount of rainfall and its distribution over the year, determine the type of weathering and the type of soil that is formed. Temperature increases the kinetics of chemical reactions. Moreover, hot and humid conditions favour biological activity and, thereby, the transformation of organic matter. Temperature and rainfall define a climate; therefore it must be expected for soils to be of different types within the different climatic zones of the world.

Atmospheric and soil-temperature variations are the most important manifestations of the solar energy reaching the surface of the Earth. The main effect of temperature on soils is to influence the rates of reactions; for every 10 °C rise in temperature the rate of a chemical reaction increases by a factor of 2. The rate of biological breakdown of organic matter and the amount of moisture evaporating from the soil are also increased by a rise in temperature. Since most climates are seasonal, the rate of chemical and biological activity will vary during the year. In the warm season chemical weathering and biological activity are greater, providing there is an adequate supply of water. In the cool or dry season the speed of reactions is reduced. Thus, the rate of soil formation may vary seasonally. Soils have well-marked daily and annual temperate cycles. The daily variations extend to a depth of about 50 cm whereas the annual cycles extend to a depth of 2 m, below which the temperature is more or less uniform. During the daily cycle heat moves downwards during the day from the surface, which is warmed by solar radiation, and upwards during the night as the surface cools. During the annual cycle, in countries with contrasting seasonal climates, the soil is warmer during the summer and cooler during the winter.

Heat moves very slowly down through the soil so that the temperature fluctuations within the soil are greater at the surface than in the lower horizons. Daily fluctuations are strongly reduced at a depth of 25 cm as shown in Fig. 3.3 and, furthermore, the maximum temperature at depth occurs many hours later. The annual fluctuations of the temperature penetrate much deeper than the daily fluctuations. During summer, the diurnal mean surface temperature is higher than that in underlying layers, but in winter the reverse is true as shown in Fig. 3.4. The mean temperature at 2 m depth is approximately the same as the annual mean of the temperature of the air above the surface.

Soil temperature is mainly under the influence of two factors; latitude and slope orientation. Land surfaces normal to the rays of the sun are warmer than those at smaller angles. This is the case in tropical areas where the distance traveled by the sun's rays through the atmosphere is also shorter. To the north and south of the tropics, surfaces normal to the sun's rays are also warmer but, as the distance from the equator increases, the mean annual temperature of

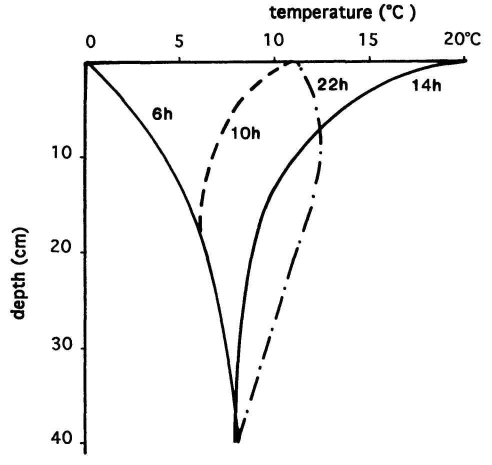


Fig. 3.3. Soil temperature at different depths at 6:00, 10:00, 14:00 and 22:00 h for a temperate climate

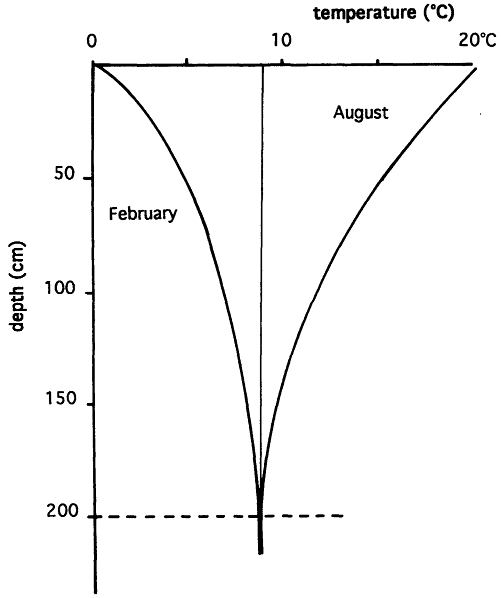


Fig. 3.4. Soil temperature at different depths in February and August under temperate climatic conditions

such surfaces steadily decreases. Differences in temperature between surfaces are particularly important in the middle latitudes where sloping land surfaces facing the equator generally have a warmer and drier climate than lands facing towards the poles. Altitude also influences climate. In the middle latitudes, mean annual temperature decreases at about 0.8 °C for each 100 m rise in elevation. Fluctuations of the soil temperature are strongly buffered by the vegetation cover. During the day, a large proportion of the radiant energy is adsorbed or reflected by vegetation. At night, vegetation reflects the heat radiated from the warm soil to the cooler atmosphere. The buffering effect of

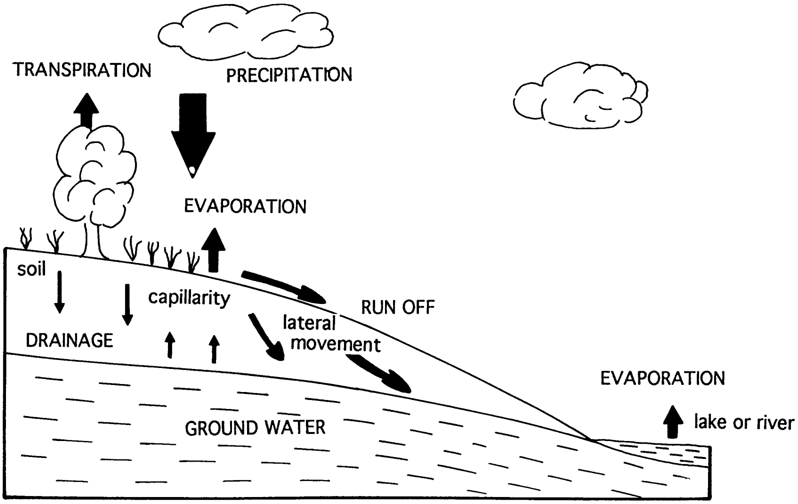


Fig. 3.5. Moisture cycle

vegetation is of particular importance in the middle latitudes where it prevents rapid heat loss during the winter and reduces the penetration of frost into the ground.

Not all of the water from rainfall enters the soil (Fig. 3.5). Depending on the slope and the state of the soil surface, a more or less important part of the rainfall water goes as runoff to streams and rivers. The other part enters the soil porosity. Depending on climatic parameters such as temperature, wind, and the density of the vegetation cover, part of the soil water evaporates and returns to the atmosphere: this process is called evapotranspiration. Soil water which is not evaporated moves downwards and finally joins the water table: this volume of water is accounted for as drainage.

For a particular site the annual balance of water may be written as:

$P = R + E + D$ (see Fig. 3.6),

where: P is rainfall (precipitation), R is runoff, E is evapotranspiration and D is drainage.

The amount of drainage is a very important parameter in rock weathering and soil formation. Large volumes of drainage water mean large volumes of water in contact with rock which results in large amounts of matter being lost through dissolution in rather diluted solutions. Conversely, a small volume of drainage water indicates that most of the soil water is evaporated. Losses of matter are reduced and soil solutions are concentrated through evaporation at some period of the year.

Such a balance may be computed for a year or for shorter periods of time, such as 1 month or 10 days. For the last two cases it is necessary to introduce the concept of field water capacity of soils. Soils are able to hold water in their

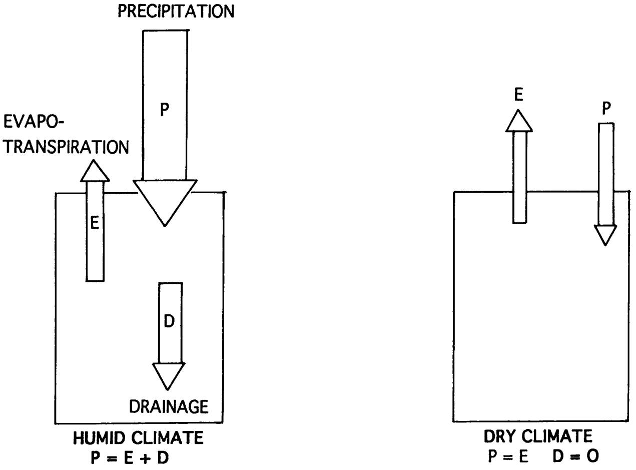


Fig. 3.6. Annual mass balance of water for humid and dry conditions. *P* Precipitation; *D* drainage; *E* evapotranspiration

pores, which does not immediately move downwards: this amount of water is called the field capacity and it is available for plant growth or evaporation after the rainfall period. A soil water regime is therefore defined by the variations of the volume of water held at the field capacity and the amount of drainage.

Two major soil water regimes can be distinguished. In one regime the amount of precipitation exceeds evapotranspiration, and some water moves down through the soil to the ground water at some time during the year. In the other regime water moves into the soil but is withdrawn by evapotranspiration, leaving behind precipitated carbonates and more soluble salts. For general considerations regarding losses of soluble materials or their accumulation in part of the weathering profile, this broad distinction is adequate. For the understanding of chemical and biological processes in soils and weathered rocks much more detail is needed. For example, a soil can be saturated with water and subjected to leaching in the winter when it is too cold for optimum chemical and biological activity. In the summer it can be too dry for any significant soil–solution reaction, even if the temperature is high.

Some typical water regimes are given as examples in Fig. 3.7. The first diagram illustrates the water regime in a soil in an *arid climate*. Evapotranspiration exceeds precipitation in all months of most years. The soil is dry for more than half of the year, and there is no leaching. In contrast, the second diagram illustrates the water balance in a soil in a *humid climate*. Precipitation exceeds evapotranspiration in all months of the year. The soil is permanently moist and water moves through the soil throughout the year. The third example typifies the soil water regime in a *temperate humid climate* with the rainy season in the spring and summer. There is enough rain during the summer such that the amount of stored water in the soil plus the rainfall is equal to the amount of evapotranspiration. The soil never dries for a long period and limited leaching occurs at the end of the winter and in early spring. The last

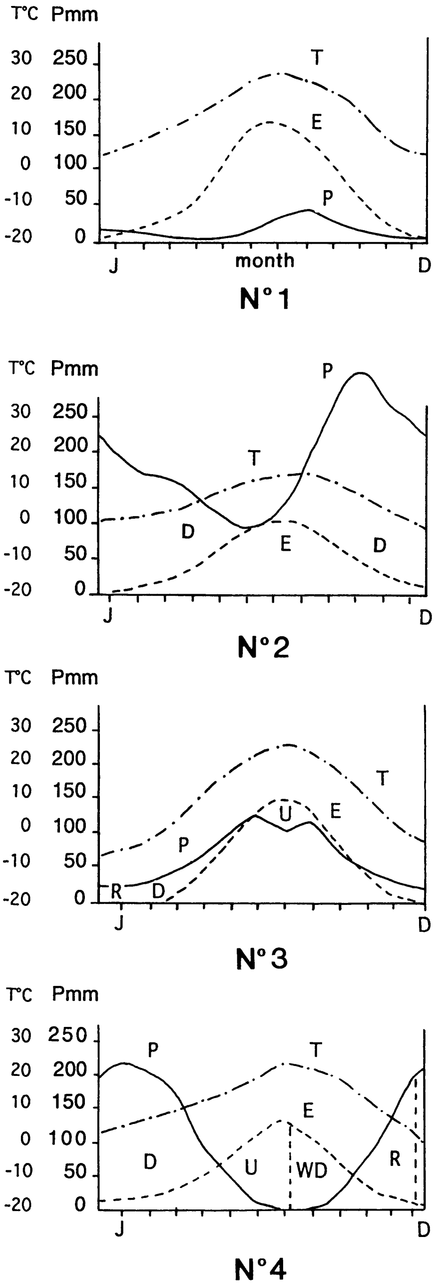


Fig. 3.7. Climatic data and soil water balance in some typical regions. *1* Arid; *2* humid; *3* temperate humid; *4* cool moist winter, warm dry summer. *T* Temperature; *P* precipitation; *E* evapotranspiration; *D* drainage; *R* soil water reserve; *U* utilization of water reserve; *WD* water deficit

example illustrates a water regime in a climate where *winters are cool and moist* and *summers warm and dry*. The moisture input in winter, when evapotranspiration is at minimum, is particularly effective for leaching. In summer, the stored moisture is used but is not enough to prevent the soil from drying out for two or three months. Because atmospheric climatic data do not always properly reflect the climatic conditions within the soil, soil scientists have produced classifications of soil climates.

The classification of soil moisture regimes used in the US Soil Taxonomy (USDA 1975) is given below as an example:

Aquic moisture regime. The soil is generally saturated with water and more or less free of oxygen so that reduction can take place.

Aridic moisture regime. The soil is dry for more than 50 percent of the growing season or never moist for more than 90 consecutive days during the growing season. There is little leaching in this regime and soluble salts usually accumulate.

Udic moisture regime. The soil is not dry for as long as 90 consecutive days. These soils occurs in humid climates with well distributed rainfall with enough during the growing season and leaching in most years.

Ustic moisture regime. The soil has a limited amount of moisture but it is present in sufficient quantity during the growing season. In the tropics this moisture regime occurs in monsoon climates.

Xeric moisture regime. The soil is dry for 45 consecutive days in summer and moist during winter. This soil moisture regime is found in Mediterranean climates.

3.2.2.2 Rock Composition

Soil formation is strongly dependent of rock composition. Soils with contrasting properties develop in granitic areas and areas of calcareous sediments. In spite of these very different soil features and properties, the clay minerals in the soils are not so different. Indeed, all the soils in the temperate zone contain a mixture of kaolinite and vermiculite as their dominant clay minerals. This situation is enhanced in equatorial climates where the rock composition does not control the clay mineral type that forms: basalt, as well as granitic rocks, produce soils which contain the same kaolinite + oxides assemblage. So long as a sufficient time has elapsed, the mineralogical composition of soils depends more on climatic conditions than on the chemical composition of the parent rock. Conversely, the rock composition is a determinative parameter for clay chemistry in the early stages of weathering, whatever the climate may be. This will be extensively discussed in Section 3.5.

3.2.2.3 Biological Factor: Vegetation and Soil Organic Matter

Organic matter is added to the soil system is by vegetation. The amounts of organic matter entering the soil is dependent on the vegetation cover. The

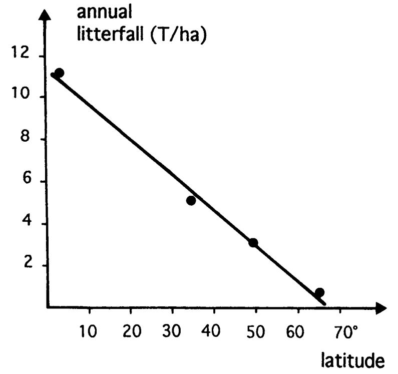


Fig. 3.8. Distribution of annual litter fall as a function of latitude

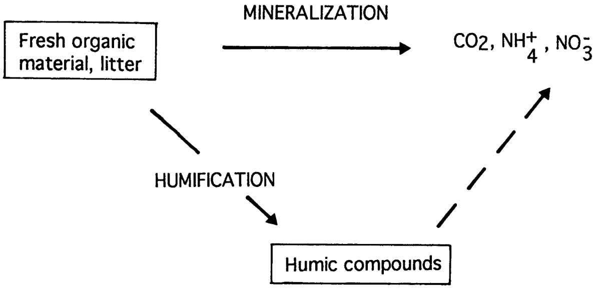


Fig. 3.9. Biological and chemical transformations of organic material in soils

organic compounds reaching the soils differ according to their origin and their resistance to biodegradation. Their persistence in soil and reactivity are highly variable. Therefore the type of vegetation may influence soil formation.

Most soil organic matter comes from the remains of dead plants falling on the soil. The quantity of vegetable material produced, and subsequently returned to the soil, can range from a trace, in arid and Arctic regions, to several tons per hectare in warm and humid climates where plant growth occurs throughout the year (Fig. 3.8).

Organic compounds from plant remains may be involved in two major processes: mineralization and humification (Fig. 3.9; Stevenson 1982). Mineralization is the transformation of organic molecules by microbes into CO_2, NH_4 and H_2O. Humification leads to more complex organic polymers, typical of the soil medium, so-called humic compounds. Humification is a slow process in which both biological and physico-chemical reactions are involved. The rate of humification versus mineralization determines, for an equal input of organic residues, the organic-matter content of the soil and, therefore, some important physico-chemical properties of the soil medium in which the clay minerals are formed and react. In response to factors such as climate, type of vegetation, and soil pH, the amount and types of humic substances that are formed may be very different. It is well known for instance that soils of the warmer climatic zones generally have low organic-matter content, despite the large quantity of plant material produced and returned to the soil. This is attributed to the high activity of microorganisms in the warmer temperatures. In contrast, in areas with cold climates, poorly transformed plant residues accumulate at the soil surface as a consequence of restricted biological activity. The highest levels of soil-organic matter are found in grassland soils of continental climates. The frequent wetting and drying cycles occurring in these soils are thought to be the best conditions for the synthesis and preservation of soil-organic matter.

The chemical composition of the mineral part of the soil may also strongly influence the processes of decomposition of plant remains and incorporation of stable organic compounds into the mineral soil. Parent materials which provide sufficient amounts of nutrients (calcium, phosphorus) through weathering favor biological activity and consequently a rapid and complete transformation of organic residues. Association with the clay fraction of the soil may also protect organic molecules against attack by micro-organisms and thereby contribute to the preservation of soil-organic matter.

Because humic substances are very complex and include many components, there is not yet a single and clear theory of humification. However, there is general agreement for two major processes. The first process gives great importance to the degradation of lignin (a component of vegetal cell wall) as a source for humic substances. The second process promotes microbial synthesis of aromatic substances which polymerize to form humic compounds. There is evidence that both processes are active, even in the same soil; however, certain soil conditions like acidity, excess of water, favor one or the other of these mechanisms (Fig. 3.10).

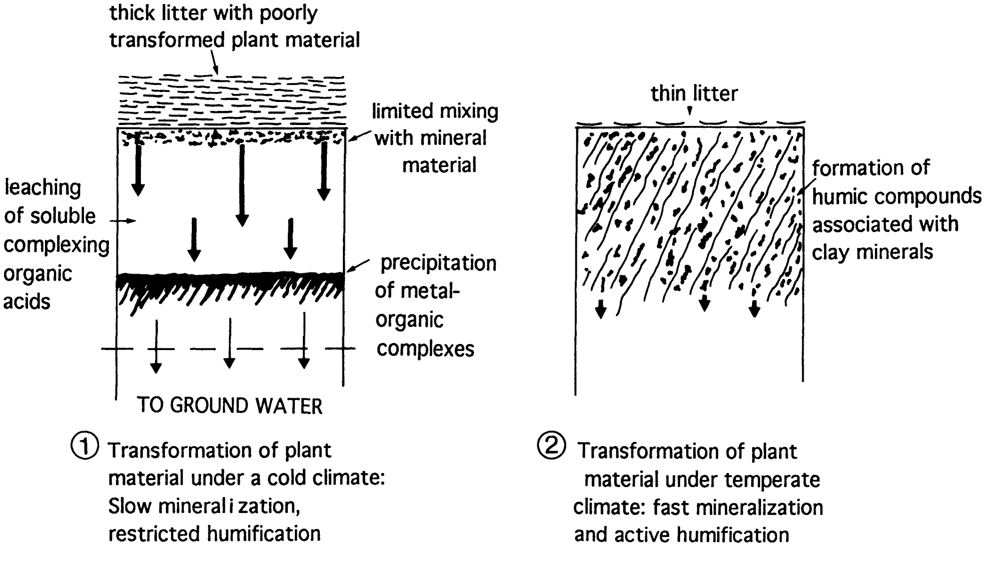


Fig. 3.10. Transformation of organic material in soils

When slow decomposition of plant remains is induced by cold climates or cation deficient parent materials, low-molecular-weight organic compounds are formed. These are complexing acids able to dissolve minerals and form organic complexes with metals such as Al and Fe. These organic complexes are soluble and promote exportation of the complexed metals out of the weathering system. In such conditions, transformation of initial minerals into clays is strongly disturbed as less Al or Fe is available for the formation of new clay minerals. Conversely, in a mild climate, an abundant clay fraction and a neutral pH promote the stabilization of humic compounds which contract close associations with the surfaces of clay minerals. As a consequence, no water soluble organic components are present in soil solutions. In this case contribution of organic matter to weathering is achieved through production of CO_2 which reacts with water to give carbonic acid.

3.2.2.4 Age and Soil History

Weathering of rocks, and the formation of soils and clay are slow processes that require hundreds, thousands and even millions of years. Moreover, periodic changes of climate and vegetation have often occurred which have changed the original pathways of soil development, and not all soils have been developing for the same length of time. Even in a single soil, some layers differentiate more rapidly than others. Incorporation of organic residues into the surface layer of a soil developed from unconsolidated rocks takes only a few decades, but translocation of a noticeable amount of clay from the top to the medium part of the soil profile may require 5000 years. The complete weathering of rocks to form the several meter thick kaolinitic layer in tropical soils is thought to take more than one million years (Tardy and Roquin 1992).

In most cases the interpretation of soil features, such as the type of clay present, as being the result of interactions under present-day environmental conditions would be erroneous. Due to climatic changes at a scale below that of soil formation, it is evident that most soils have experienced a succession of different climates which have induced changes in pedogenesis. Therefore, soils are not developed by a single set of processes, but undergo successive waves of formation. Furthermore, each wave imparts certain features that are inherited by the succeeding phases. In some cases their properties are so strongly expressed that they remain observable thousands and even million of years after their formation. Consequently, soils should be regarded as the result of a developmental sequence which exhibits not only the present-day factors and processes of soil formation, but also many preceding phases.

The oldest land surfaces, such as those in parts of west Africa, developed in the mid-Tertiary period. The soils on these surfaces are very old. At that time tropical conditions existed in many of the same areas where they are found today, as well as in many of the present subtropical and arid areas. These warm conditions caused the rock to undergo profound weathering.

Considerable erosion also took place during this prolonged period, to form the characteristic flat surfaces associated with old landscapes, but great thicknesses of soil and weathered rocks were maintained. The processes of weathering were so complete in many places that rocks of all types were transformed into kaolinite, and hydroxides and oxides of iron and aluminium. The warm, humid conditions were maintained in tropical areas but became cooler in higher latitude areas. This cooling of the climate culminated in the Pleistocene period leading to repeated glaciations in Eurasia and North America (Fig. 3.11). Glaciations and associated periglacial conditions effectively removed most of the deep soils and weathered rock that formed during the Tertiary period. Consequently, the formation of soils in Western Europe

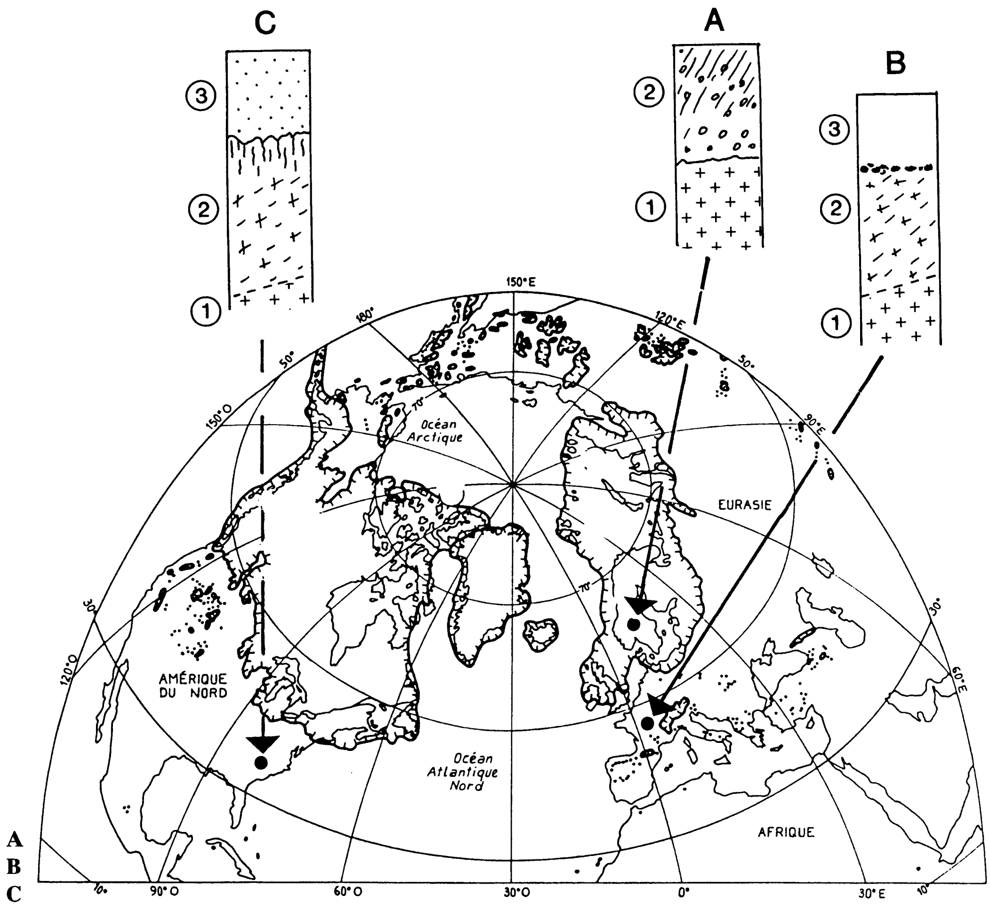


Fig. 3.11. The extension of the ice field during the last Quaternary glaciation *Heavy line* shows ice cap. Soil profiles. **A** Recent soil (<5000 years) from *2* glacial till; *1* eroded fresh rock; **B** recent soil (<10000 years) from *3* reworked material, overlaying *2* an old saprolite, *1* eroded fresh rock; **C** strongly developed soil *3* produced by a long weathering period

and North America has been achieved in the relatively short period of 10000 years. Thus, it must be expected that the transformation into clay of the primary minerals is far less advanced in these soils than in soils from the tropical zone.

3.2.2.5 Topographic Effects: Translocations and Accumulations

Climate and vegetation are relevant to the distribution of soil at the world scale, but within a smaller area topography strongly disturbs spatial distribution of soils. Topography (slope) changes the direction of the water flow which may be not only vertical, but also lateral along slope. Lateral transfers of matter through solution or suspension may occur from the higher to the lower part of the slope: soils at the higher parts become impoverished in clays whereas soils lower down are enriched.

Nearly all material in soils may be moved by one process or another. In fact, many of the processes of soil formation are concerned primarily with the reorganization and redistribution of material within the upper layers of the weathering profile. Translocation may be performed in solution or suspension.

In a humid environment, part of the water which migrates through the soil is lost as drainage water. Water–soil interactions lead to dissolution of materials which are lost from the soil as the solution moves downward. The highly soluble simple salts, including nitrates and chlorides, are completely removed, whereas carbonates usually precipitate in lower layers of the soil where the solution becomes concentrated. If lateral movement of water occurs along a slope, soluble products of weathering can migrate laterally downslope (Fig. 3.12). Enrichment in basic cations is generally observed in the lower

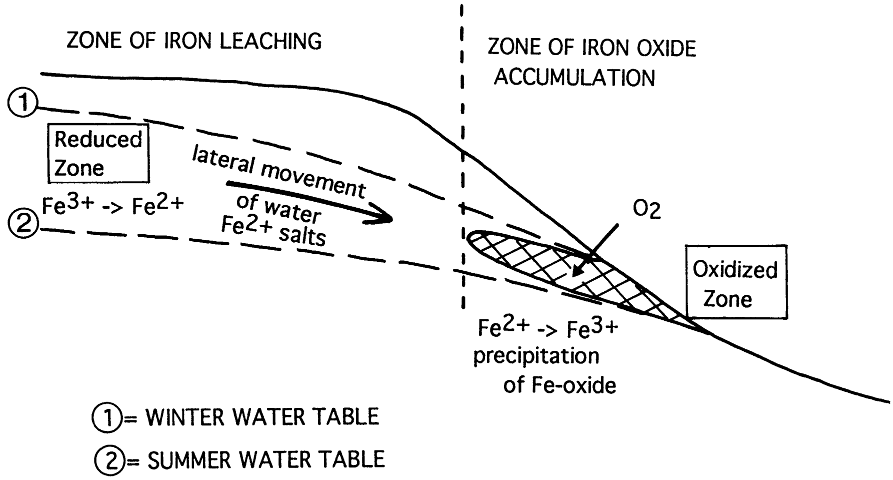


Fig. 3.12. Lateral translocation of ions along a slope with a shallow water table

positions of the landscape. Such a high-base environment (high pH) favours the formation of smectite.

The progressive leaching of divalent cations by drainage water, induces a partial desaturation of the exchange complex of clay minerals with respect to these cations. This allows colloidal clays to disperse as a stable suspension. Through this process clays are transported from the upper layers to the medium part of the soil profile. This is one of the most important process that affects clay minerals in soils. This process is called *clay illuviation.* Clays produced by weathering and soil formation do not stay in place, but frequently move to another place, even over long distances (hundreds of meters). Impoverishment in clays, observed in surface layers of soil developed from poorly permeable materials, is attributed to translocation of clays moving laterally with seepage water over poorly permeable subsurface soil layers.

Another important material that can migrate in soils is organic matter. Usually, organic compounds produced during humification are fixed on clay surfaces, and therefore are unable to move except with the clay suspension. However, in acid soils with low clay content, a more or less important fraction of the organic compounds is translocated in solution or as colloidal suspension. These mobile organics contain complexing organic acids which fix Al, Fe or other metals. In this way, elements such as Al and Fe can move, even under pH and Eh conditions where they are not expected to be soluble. Dissolved organic compounds and organo-Al and Fe complexes, are generally precipitated at depth in the soil profile, forming cemented layers. Some of the dissolved organic compounds may escape precipitation and enter rivers and lakes, giving typical brown waters such as those of the Rio Negro in the Amazon.

Considering now the "normal" evolution of a soil in a humid climate, the first process one may expect is the leaching of cations. Consequently, the ionic concentration of the soil solution decreases and clays are able to disperse and move from the upper soil layers. When a definite stage of clay impoverishment is reached, organic compounds can no longer be totally fixed and some move. To summarize, the succession of mobile materials in soils under humid climate is: cations (Mg, Ca), clays and finally organic matter (Fig. 3.13).

By contrast, in an arid climate, where evapotranspiration largely exceeds precipitation, there is only a short period following rainfall during which some of the most soluble materials are dissolved and are able to move. Since the rainfall under these conditions is small, any downward movement is quickly reversed by intense evaporation which induces upward movement of the soil solution and a deposition of salts at, or near, the surface.

A major consequence of translocation of soil material from one place to another is the change of soil structure. As soil structure greatly determines the pattern of water flow within soils, any translocation of material will lead to the disturbance of water flow. As water flow strongly influences weathering of initial minerals and clay formation, any translocation will change the local physico-chemical parameters of weathering. In other words, even with stable

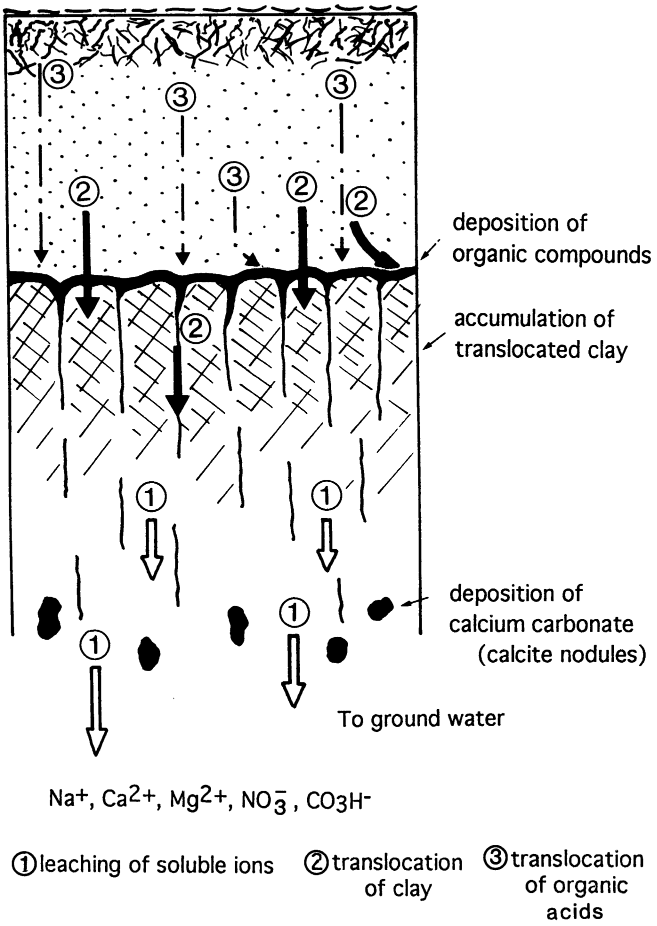


Fig. 3.13. Theoretical soil profile showing the successive translocations of cations, clay minerals and organic compounds in a wet climate

conditions of climate, rock chemistry etc., soil forming conditions are permanently changed by the process of soil formation itself.

One of the best examples that illustrates this process are Luvisols, i.e. soils where clay translocation occurs. It will be described in detail later on (Sect. 3.4), but can be summarized as follows. Clays move from the upper to the medium soil layer (the B horizon) where they accumulate. The increase in the clay content of the B horizon progressively reduces its permeability in such a way that an intermittent perched water table occurs above it during the rainy season. Such a waterlogging induces low redox conditions. Iron (from oxyhydroxides) is reduced to the ferrous state, becomes more soluble and moves, leaving iron-free materials. The clay assemblage shifts from a clay-oxide complex to essentially clay minerals.

3.2.3 Distribution of Major Soil Types at the Surface of the World

Soil classification has been a matter of debate between pedologists for years. The idea now is that soils cannot be classified as has been done for plants or animals. However, large groups of soils with common features and properties may be defined with general agreement among specialists. These major groups are used for the legend of a soil map at the world scale (Pédro 1985; Fig. 3.14).

The first observation is that the major soil units roughly reproduce the extension of major climatic zones: equatorial, tropical, arid, temperate, cold

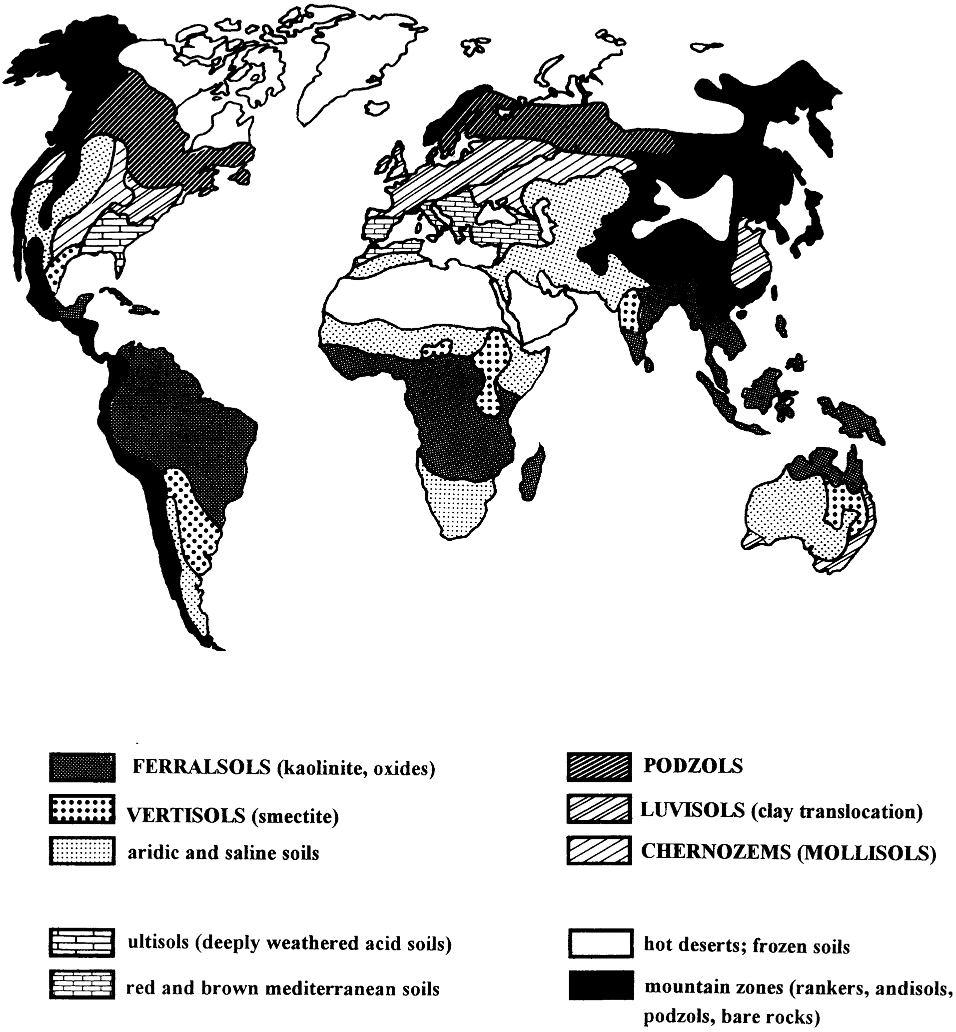


Fig. 3.14. Soil map of the world. (After Pédro 1985)

etc.. The large unit centered on the equator is that of *Ferralsols* which are thick soils (15 m) with a yellow to red colour. The mineral part of Ferralsols is almost exclusively clays. These clays are dominantly kaolinite associated with a more, or less, important fraction of Fe and Al oxides and hydroxides (goethite, hematite, gibbsite). CEC of the whole soil is very low (10 to 15 meq/100 g soil) due to the dominant fraction of kaolinite clay. The pH is about 5 throughout the soil profile. Organic-matter content is very low because organic components are quickly biodegraded by an active microflora under a wet and hot climate. The area covered by ferralsols is about 30% of the Earth's surface.

At the northern and southern edges of the Ferralsol unit one finds large areas of arid soils and deserts. Within these areas soils are not more than sand or an accumulation of stones. At some places accumulation of soluble salts occurs (Na-chloride, Na-carbonate). Between the Ferralsol and arid soil units one can see a soil unit of lesser extension. It is the area of *Vertisols* which are clay-rich soils, as are ferralsols. These clays are of a different type, typically smectites. Vertisols are far less thick than ferralsols, 1 to 2 m, with a very dark colour (black). The pH is in the range of 6.5 to 8.5. CEC (cation exchange capacity) is rather high; up to 80 meq/100 g dry soil (Chap. 2; Sect. 2.2.3.4). The best-known property of Vertisol is the large clay fraction dominated by smectites, which causes these soils to shrink greatly and crack upon drying.

In the Eurasian northern hemisphere, a latitudinal zonation of soils can be seen from the North to the South of the continents. In the southern part of the northern areas, where permanently frozen soils occurs, one finds the area of *Podzols*. Podzols are characterized by a slow and incomplete transformation of organic residues, and the production of large amounts of complexing organic acids. Initial minerals are strongly attacked by these acidic organic compounds, and the formation of clay minerals is weak. The fine mineral fraction of a Podzol is dominated by amorphous organo-mineral compounds that move in the soil profile and accumulate in a specific horizon. Podzols are acid soils with a low CEC. Going further south, the next area is that of *Luvisols*. The climate is milder and allows a rather good decomposition of organic residues. However, weathering of initial minerals is far from complete and most of the clay fraction is derived from the transformation of pre-existing phyllosilicates. Clays are typically vermiculite and clays with mixed layers of illite, chlorite and smectite. Luvisols are also characterized by the illuviation of clays. The pH of Luvisols is usually close to neutral.

South of the Luvisol area, where climate is continental, Luvisols are replaced by *Chernozems* which are characterized by an accumulation of humic compounds over a great depth (1 m). Calcium carbonate accumulations are frequent at the lower part of the soil. As in luvisols, clays are mainly derived from pre-existing phyllosilicates. They are dominated by smectite and illitic mixed layers. The pH is about 7 and increases up to 8.5 when calcium carbonate is present. Further to the south, arid soils are found.

The distribution of the great groups of soils also gives the distribution of some great groups of clay minerals: kaolinite is the dominant clay in the wet tropics, a dry tropical climate produces smectite, and temperate zones have mixtures of vermiculite and complex mixed layers (Pédro 1968). However, relating clay type too closely to the current climate is dangerous. Even at the world scale, the time of evolution and rock chemistry also control the soils and clays that form. Ferralsols are generally old soils developed from various rock types, but vertisols are restricted to calcium-rich rocks or occur in depressions where calcium-rich solutions concentrate. Podzols are young soils that develop, most often, in sandy or gravely materials such glacial tills. Luvisols are typically developed from loess, a fine-grained, well-sorted, recent material, in which clay movement appears to have been favoured. Clays and soils are dependent on climate but they are also conditioned by the their source material, the bed rock.

3.2.4 Structure of Weathered Rocks and Soils

3.2.4.1 Weathered Rocks: Inheritance of the Rock Structure

Under temperate climates, because of erosion, creep on slopes, and subsequent redeposition, the weathered rock and the soil are generally not in continuity, the boundary being marked by a stone line. Weathered and unweathered rock structures are typically in continuity. Most often, the macroscopic features of the unweathered rock (fractures, diaclases, dikes, veins, etc.) are still recognizable even in the highly weathered zones.

The structural differences between rock and its weathered products are mainly observable at the microscopic scale. Primary minerals are replaced by a porous fine-grained material which is composed of clays and tiny debris of the parent crystals. The initial fabric is conserved as long as the volume of altered zones in each primary crystal, do not reach a yield value beyond which the mechanical resistance of the rock collapses. In more intensely altered zones, the framework of parent minerals is destroyed and the original rock fabric locally disappears. Moreover, in some cases, the rock structure totally vanishes, giving place to a clay-rich horizon. This is observed in Fe, Mg-rich crystalline rocks (gabbros, amphibolites, serpentinites) where a clayey restructured horizon represents a transition zone between the weathered rock and the soil. In summary, the weathered rock domain is considered here, to be limited to the presence of observable macroscopic parent rock features.

3.2.4.2 Soil Structures: Importance of Aggregation

In most soils the individual particles do not exist as discrete entities, but are grouped into aggregates with fairly distinctive shape and size. The degree and type of aggregation determine aeration and permeability, and therefore, the infiltration capacity and extent of moisture movement. Structure also influ-

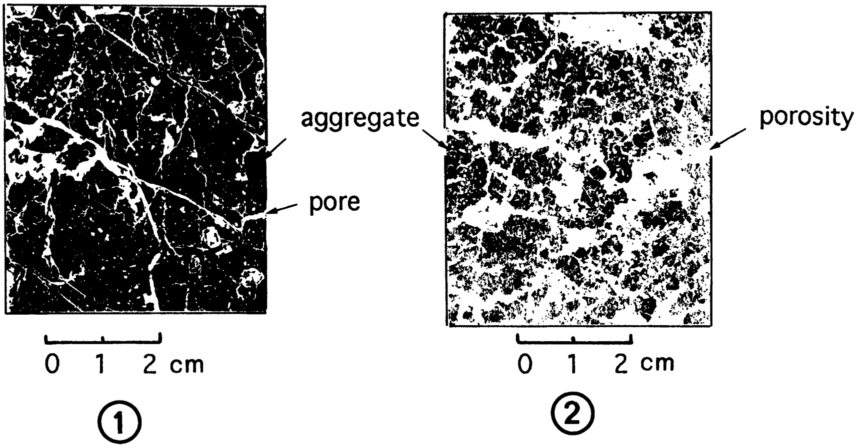


Fig. 3.15. Two typical soil structures. *1* Angular blocky structure formed by shrinkage and cracking of clay-rich soil materials; *2* crumb structure produced by burrowing animals

ences the erosive potential, since the presence of surface horizons with massive structure may reduce infiltration, which increases runoff thereby increasing the erosion hazard. Figure 3.15 shows two typical soil structures.

The genesis of soil structure involves, at least, three main processes. One of these is the expansion and contraction of clay-rich materials in response to wetting and drying. As the soil dries, its volume decreases; high tensions are created which are released by cracks opening in the soil material. Polygonal bodies are formed of different shapes and sizes, according to the importance of the retraction of the soil material. The fine granular structure of the upper layers of Vertisols is a typical result of this process.

A second origin for soil structure is physico-chemical. During the course of weathering of Fe–Mg phyllosilicates, Fe is exuded from the mineral, is oxidized, and precipitates as poorly crystalline, strongly hydrated oxy-hydroxides, which form bridges between, and covering, the remnants of weathered minerals (Fig. 3.16). As a result, small (100 μm) stable aggregates are formed, which leads to high soil porosity. Figure 3.17 shows how such a structure develops in a soil formed from a weathered micaschist (Righi and Lorphelin 1987).

A third origin for soil structure is the biological one. Animals, especially earthworms, strongly disturb the soil material and produce rounded aggregates as dejections. The structure of Chernozem soils is made essentially by earthworm galleries and dejections.

A major property of the soil structures is their possible evolution with time. For instance, clay-rich soil materials change their structure according to wetting and drying cycles. When dry, these materials are strongly aggregated, which leads to the development of numerous large pores in which water moves rapidly. As the soil is wetted and absorbs water, aggregates expand and

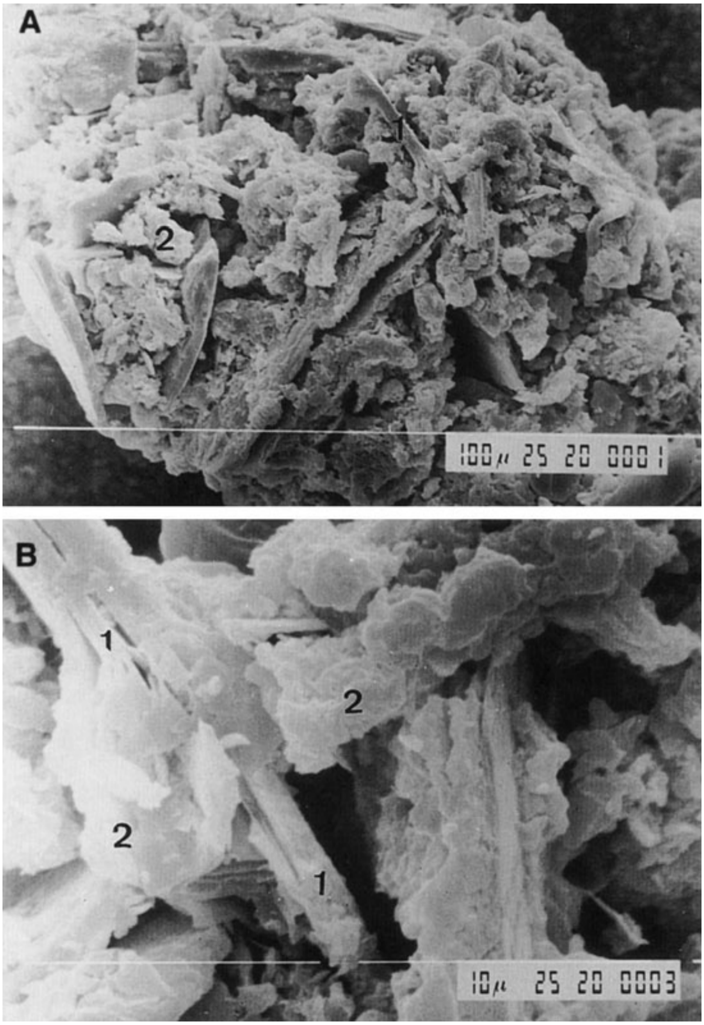


Fig. 3.16. Scanning electron microscope observation of a soil aggregate. **A** General view; **B** detail showing the edge–face association of the weathered inherited phyllosilicates and bridges of amorphous weathering products. *1* Inherited phyllosilicates; *2* iron-rich amorphous material

porosity is progressively reduced to very fine pores; water transfer becomes very slow. In such soils, moisture movement may follow two contrasting regimes. If rain falls on the dry soil, water flows directly to depth, by-passing interactions with soil material (Fig. 3.18). Conversely, if the soil has been previously wetted, water enters and moves slowly, allowing a close contact of solutions with the soil material for long periods. Another important point to be stressed is that the soil structure can be very different from one layer to another. Thus water circulation in soils changes greatly with time and space.

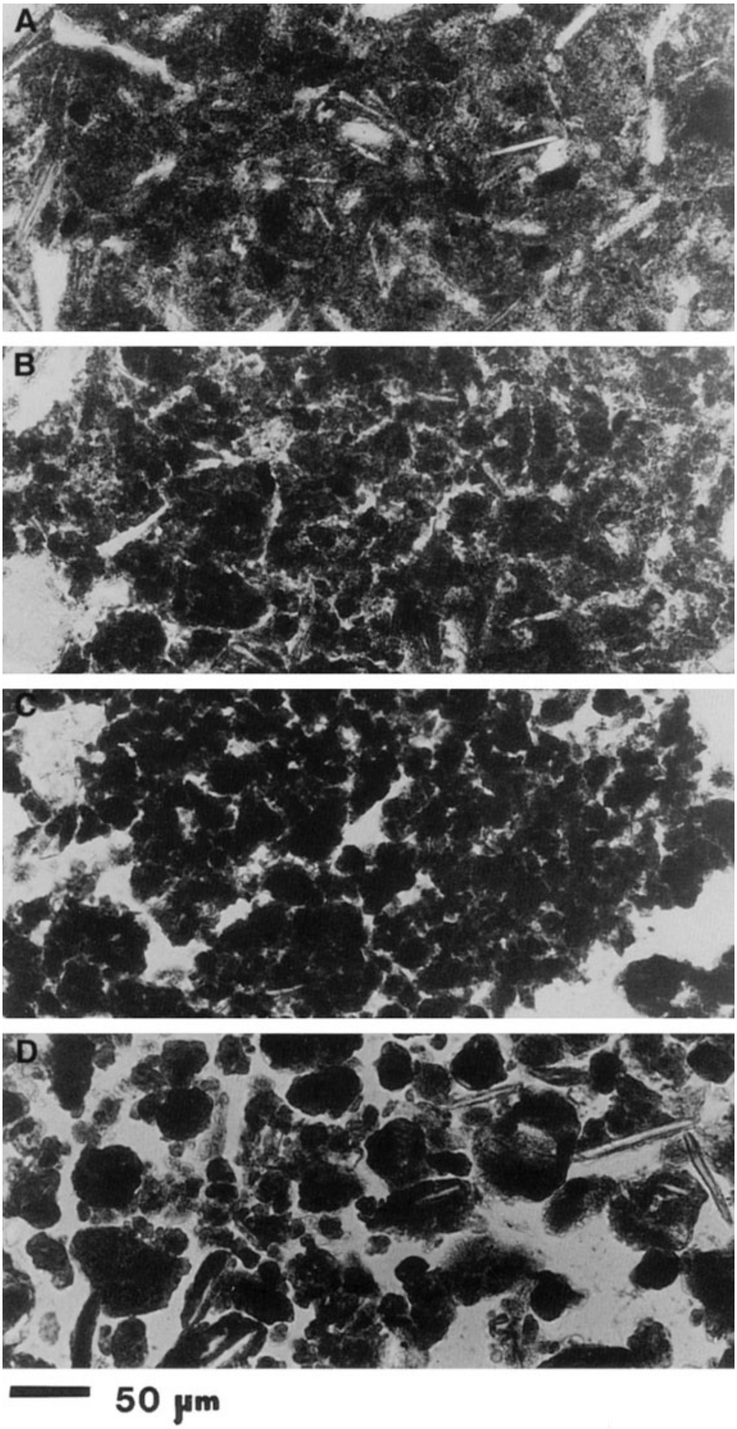


Fig. 3.17. Development of a fine granular structure from a chlorite-micaschist saprolite. $A \rightarrow B \rightarrow C \rightarrow D$ from the bottom to the top of the soil profile

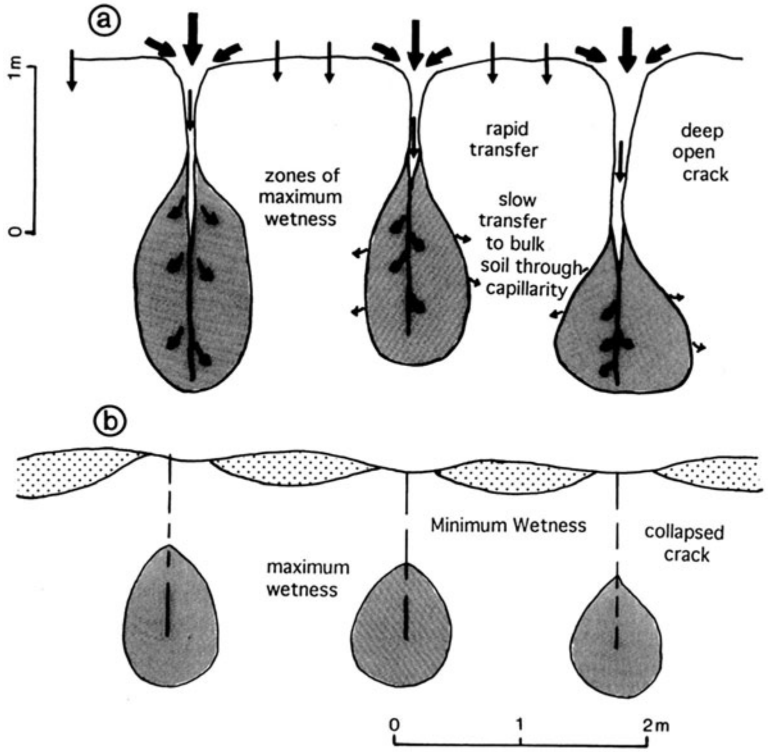


Fig. 3.18. Non-uniform distribution of wetness in a clay-rich soil. **a** Rainfall on the dry soil; **b** after a certain time of desiccation after saturation

This may explain why different clay minerals may be found in different soil layers.

Why put such an emphasis on the structural aspect rather than the chemical or mineralogical properties of these complex materials? The basic reason is that the circulation of water is the decisive parameter which controls mineral reactions. Dissolution of pre-existing minerals, as well as precipitation of new ones, depends on the local chemical composition of the solutions which, in turn, depends on the flow rate of water. Usually, the solutions are diluted in the larger pores, where water circulation is fast, and they are more concentrated in dissolved elements in narrow pores in which water moves slowly. In summary, the way that water penetrates into the soil depends on the structure, but the soil structure changes with wetness as the seasons change.

3.2.5 Soil Structure–Porosity Relationship

Soils, as well as weathered rocks, are discontinuous materials in which the solids (minerals, aggregates) are separated by voids. The spatial distribution of

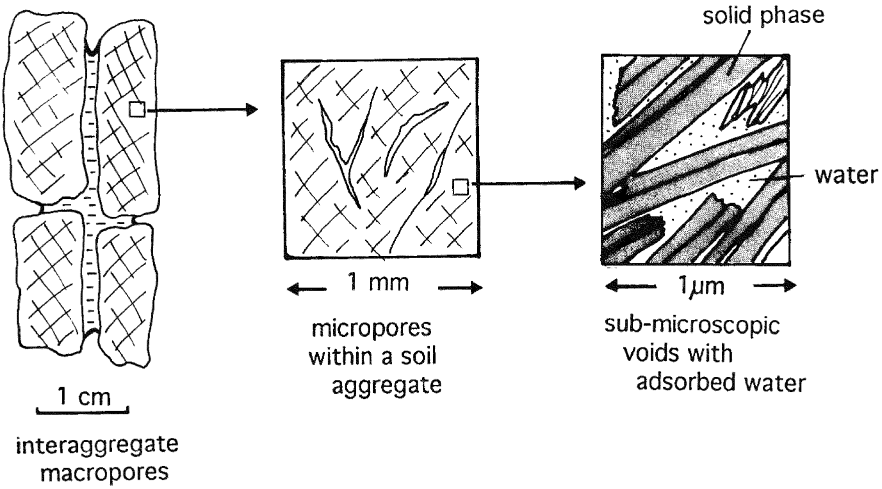


Fig. 3.19. Soil structure and porosity at different scales of observation

these voids depends on the structure of the rock or the soil. At a given time, in spite of structural discontinuities, the soil horizons and the weathered rock are interconnected by a complex void network. The largest interconnected voids form a fast-water pathway from the soil surface, through the weathered rocks, to the groundwater table and springs. Such interconnections may change with the seasons, because the soil structure is controlled by wetness and biological processes, wheras the weathered structure remains stable through the year.

In the smaller pores (Fig. 3.19) on the microscopic scale, capillary forces become important. Soil scientists consider that the competition between gravity and capillary forces arises in voids with diameter less than 200 μm. Below 0.2 μm in diameter, voids are not accessible to root hairs. Thus, the total volume of the voids with a diameter between 200 and 0.2 μm, represents the available (for plant growth) water capacity of the soil. Below the 0.2 μm boudary, voids are considered to belong to a sub-microscopic class. In such pores the fluids are retained on surfaces of solid particles by electrostatic forces. The chemical composition of these waters depends on the dissolution–precipitation phenomenon occurring at the interface.

3.2.6 Changes in Rock Density and Mechanical Properties

One of the major effects of the weathering processes is the transformation of a massive rock into a porous friable material. The increase of porosity and its consequence, the decrease of density, were discovered very early in the nineteenth century (Ebelmen 1847 for example). Considering the case where the structure of the parent rock is conserved, the volume balance of a given alteration reaction can be calculated as follows:

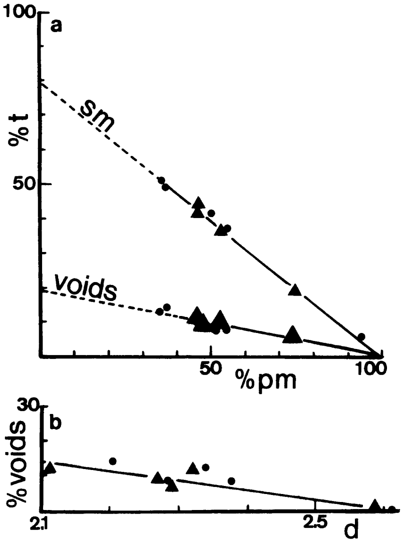


Fig. 3.20a,b. Variation of the relative volume of **a** secondary minerals and **b** dissolution voids (% t) and density (d) as a function of % unaltered primary minerals in the zones of two weathered profiles in which the initial structures of the granitic rocks are conserved . *Dots* La Pagerie profile; *triangles* La Rayrie profile; *sm* secondary minerals; *voids* dissolution voids. (Data from meunier 1980)

$$x\% \text{ vol primary mineral} \rightarrow y\% \text{ vol secondary minerals} + z\% \text{ vol voids}$$

where: $x = y + z$.

The majority of documented physical analyses are found in studies of granite weathering. This is because granitic rocks are the dominant outcrop at continental surfaces. Modal analysis (microscope observation) of samples from two altered granite profiles in western France, confirm the above equation: y and z increase linearly as x decreases (Fig. 3.20a). As a consequence, density is inversely proportional to porosity (Fig. 3.20b). This relation is not applicable in zones where the initial structure of the rock has disappeared. The question therefore is, why is the conservative alteration process limited to a maximum porosity of 12–15% in granite weathering?

A possible answer to this question can be found in studying the change in mechanical properties of rock during the alteration process. Baudracco et al. (1982) showed that the resistance of an altered granite to uniaxial strain, and the Young modulus, are strongly reduced in the early stages of weathering (Fig. 3.21). This means that the initial rock structure collapses when an alteration threshold is reached. The decrease in the Young modulus indicates that the rock progressively changes from a brittle to a ductile material.

In summary, the mechanical resistance markedly decreases at the beginning of the weathering process, giving rise to modification of the parent rock by different processes near the surface: collapse under gravity, penetration by roots. In this way, the parent rock is transformed into a new material whose physical and chemical properties are different from those of the saprock. In some cases, a clay-rich horizon (30–50% in weight) is formed; the density of the horizon increases while the porosity decreases. This is frequently observed in the weathered profiles developed on basic rocks (Ildefonse 1980; Proust

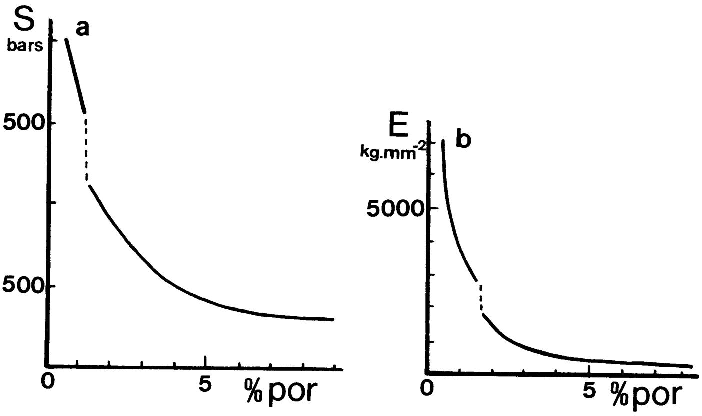


Fig. 3.21a,b. Relation ship between mechanical properties and the porosity of an altered granite from Sidobre, France (data from Baudracco et al. 1982). **a** Variation of the uniaxial stress (*S*); **b** variation of the Young modulus (*E*)

1983). The structure of these clay-rich materials is governed by the swelling power of expandable clays. The seasonal drying–wetting cycle induces local stresses which provoke the formation of new fractures and gives rise to the transfer of solids.

3.2.7 Water in Soils: Content and Chemical Potential

The variable amount of water contained in a volume of soil is an important factor affecting the chemical state and reactivity of the soil. In addition to this amount, which characterizes the soil wetness, soil water must be characterized in terms of physico-chemical condition or state. The energy state of soil water, i.e. the *potential*, is characterized by its free energy per unit mass. The most important components of the total potential of soil water are described below (Hillel 1980; Chamayou and Legros 1989).

Gravitational potential (physical): the gravitational potential of soil water at each point is determined by the elevation of that point relative to some arbitrary reference level (for instance the ground water level or the soil surface). All of the categories of soil water are affected by gravity, independently of the chemical and pressure conditions.

Osmotic potential (chemical): the presence of solutes in soil water affects its thermodynamic properties and lowers its potential energy.

Pressure potential (physical): in a soil saturated with water, the pressure potential originates from the pressure caused by the water column above the considered point.

Matrix potential (chemical): this potential results from the capillary and adsorptive forces due to the soil matrix. These forces attract and bind water in the soil and lower its potential energy below that of free water. The matrix potential is developed only in unsaturated soil (three-phase system: solid, liquid, gas). Capillarity results from the surface tension of water and its contact angle with the solid particles. The matrix potential can be described as a negative pressure potential, the so-called water suction or tension: consequently matrix potential and water suction have opposite signs.

The various potentials can be expressed in terms of an equivalent head of water, which is the height of a liquid column corresponding to the given pressure. The state of soil water is characterized in terms of a hydraulic head (H) which is the sum of (omitting the osmotic potential) the gravitational (z) and the pressure (Hp), or the matrix (Hm), potential heads: $H = z + H\mathrm{p}$ (saturated soil) or $H = z + H\mathrm{m}$ (unsaturated soil).

The energy state of water in soils can also be expressed by the following relations:

$$\Delta\mu_{\mathrm{w}} = \mu_{\mathrm{sw}} - \mu_{\mathrm{fw}} = \mathrm{RT}\log(P_{\mathrm{sv}}/P_{\mathrm{fv}}) = -2\sigma V/r = -\rho g V h_{\mathrm{c}}$$

where:

$\Delta\mu_{\mathrm{w}}$: energy of water in voids,
μ_{sw}: chemical potential of water in voids,
μ_{fw}: chemical potential of free water,
P_{sv}: vapor pressure in the void
P_{fv}: vapor pressure of free water in the standard conditions
σ = surface tension, r = radius of capillary meniscus,
V = molar volume of water,
ρ = water density, g = gravitational field, h_{c} = capillary height.

These equations indicate that the energy state of water, or its potential, decreases with the radius of the capillary pore (Table 3.1).

3.2.7.1 Soil-Moisture Retention Curve

If a slight suction is applied to a saturated soil, no outflow will occur until this suction reaches a value exceeding that applied by the soil matrix on water in the largest pores. Remembering that water is more strongly retained by soil as pore radius decreases, a gradual increase of the suction applied to the soil leads to a progressive removal of water from pores of decreasing sizes. Increasing suction is thus associated with decreasing soil wetness. This function is measured experimentally and it is represented by a curve, known as the soil-moisture retention curve (Fig. 3.22). The shape of this curve is controlled by the pore-size distribution and thus, strongly affected by the soil texture and structure.

3.2.7.2 Flow of Water in Soils and Weathered Rocks

Before discussing flow of water in soils and weathered rocks, it is necessary to distinguish between saturated and unsaturated soils. In saturated soils all the

Table 3.1. Energy state of water in soils. The relationship between suction pressure (bars) and pore diameter

Water suction (bars)	Chemical potential (J/Kg)	Water activity	Maximum size of pores (μm)
0.01	1	0.999993	150
0.10	10	0.999927	15
1	100	0.99927	1.5
10	1000	0.9927	0.15
15.8	1580	0.9888	
100	10000	0.927	0.015
500	50000	0.695	
1000	100000	0.485	0.0015

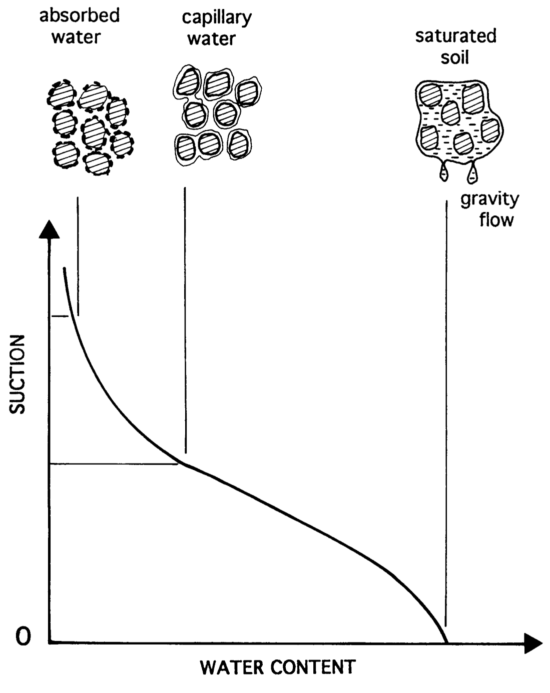


Fig. 3.22. Soil-water retention curve

pores are filled with water whereas in unsaturated soils some pores are filled with water and the other ones (generally the largest) are filled with air. Laws that govern flow of water are more complex in unsaturated soils.

Flow of Water in Saturated Soils

Figure 3.23 shows a horizontal, uniform, saturated soil body through which a steady of water flows from an upper reservoir to a lower one; each reservoir

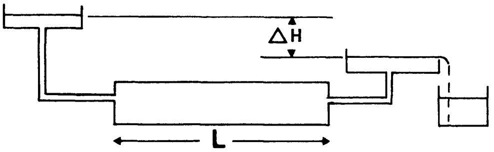


Fig. 3.23. Water flow in a horizontal soil column. L Length, ΔH hydraulic head drop

has a constant water level. The volume of water V, flowing through the column per unit time is proportional to the area of the cross section of the column and to the dropin hydraulic head ΔH, and inversely proportional to the length of the column L. Obviously, no flow occurs in the absence of a hydraulic head difference, i.e. when $\Delta H = 0$. The head drop by unit of distance in the direction of flow is the hydraulic gradient ($\Delta H/L$), which is, in fact, the driving force. The specific discharge (volume of water flowing through a unit cross-sectional area per unit time) is called the flux and is indicated by q. Thus, the flux is proportional to the hydraulic gradient: $q = \mathrm{K}\Delta H/L$. In this equation, known as Darcy's law, K is designated as the *hydraulic conductivity*. A more exact and generalized expression of Darcy's law is in differential form: in a one-dimensional system it is

$$q = -\mathrm{K}\,\mathrm{d}H/\mathrm{d}x.$$

Water flow in a horizontal column occurs in response to a hydrostatic-pressure gradient. Flow in a vertical column is caused by gravitation as well as pressure. At any point, a gravitational head, designated by z, can be determined as the elevation of the point above an arbitrary reference plane, in which case the pressure head ($H\mathrm{p}$) is the height of the water column resting on that point. The total hydraulic head is the sum of these two:

$$H = z + H\mathrm{p}.$$

K, the hydraulic conductivity, is obviously affected by structure and texture, being greater if a soil is highly porous, fractured, or aggregated than if it is compact and dense. Hydraulic conductivity depends not only on total porosity, but also, and primarily, on the size of the conducting pores. For example, a gravely or sandy soil with large pores can have a conductivity much greater than that of a clay soil with many narrow pores, even though the total porosity of a clay is generally greater than that of a sandy soil. In a saturated soil with a rigid structure the hydraulic conductivity is characteristically constant. Its value ranges from 10^{-2}cm sec^{-1} in a sandy soil to 10^{-7}cm sec^{-1} in a clayey soil.

Flow of Water in Unsaturated Soil

Most of the processes involving soil-water interactions in the field occur while the soil is in an unsaturated condition. As we have seen, the moving force in saturated soil is the gradient of hydraulic potential which is the sum of the pressure potential and gravitational potential. When the same reasoning is applied to an unsaturated soil, flow takes place in the direction of decreasing potential, the potential gradient being the driving force. However, in an unsaturated soil, the pressure potential is replaced by the matrix potential. Matrix potential is often changed by water suction or water tension which is a negative pressure in unsaturated soils. Suction is due to the physical affinity of water for soil-particle surfaces and capillary pores. Water tends to be drawn from a zone where the hydration envelopes surrounding the soil particles are thicker, to zones where they are thinner, and from a zone where the capillary menisci are less curved (larger radius) to zones where they are more highly curved (smaller radius).

Water flows spontaneously from zones where suction is lower to where it is higher. This is especially true when the moving force is large, such as at a wetting front zone where water enters into an originally dry soil. In this zone, the suction gradient can be many bars greater than the gravitational force, and water can move “uphill”.

The most important difference between unsaturated and saturated flow is in the hydraulic conductivity. When the soil is saturated all the pores are water filled and conducting, so that hydraulic conductivity is at a maximum. When the soil becomes de-saturated, some of the pores (the larger ones) become air-filled and the conductive portion of the soil decreases. As suction develops, the first pores to be emptied are the largest ones, which are the most conductive, thus leaving water to flow only in the smaller pores. For these reasons, the transition from saturation to unsaturation is generally characterized by a large reduction in hydraulic conductivity which may be lowered by several orders of magnitude (Fig. 3.24). At saturation, the most conductive soils are those in which the overall pore volume is consists of large and continuous pores, wheras the least conductive are those soils with numerous micropores. For example, a saturated sandy soil conducts water more rapidly than a clayey one. The opposite may be true when the soils are unsaturated. Large pores are quickly empty and become non-conductive as suction, even weak suction, is applied, and the conductivity rapidly decreases. Small pores retain water, even at rather high suction, thus the conductivity does not decrease as rapidly and it may be greater than that of a soil with large pores subjected to the same suction (Fig. 3.25). Figure 3.26 illustrates how conductivity (K) increases and suction decreases as soil wetness increases.

3.2.8 Dissolution and Recrystallization Processes

3.2.8.1 General Statements

The energy state of water varies from place to place in a soil or a weathered rock, between a minimum value, in the absorbed layer on the solid surfaces, to

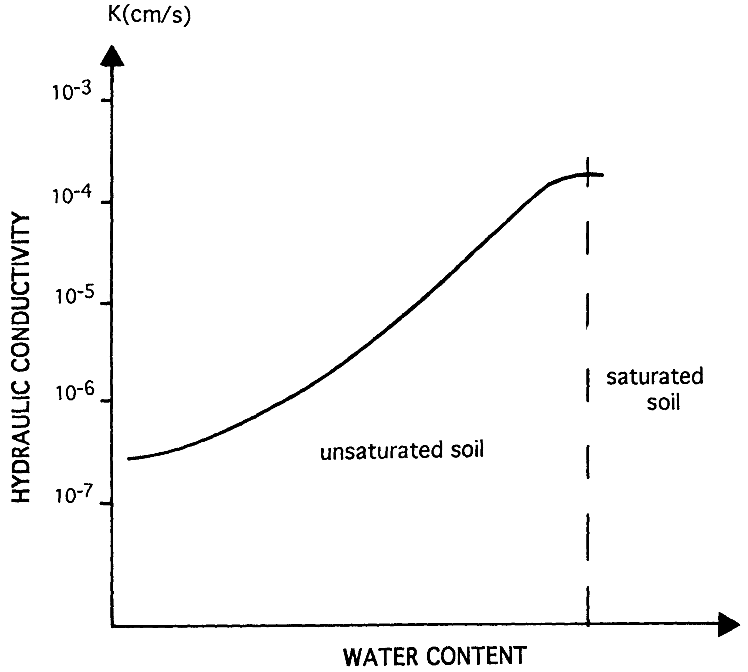


Fig. 3.24. Dependence of hydraulic conductivity on soil wetness

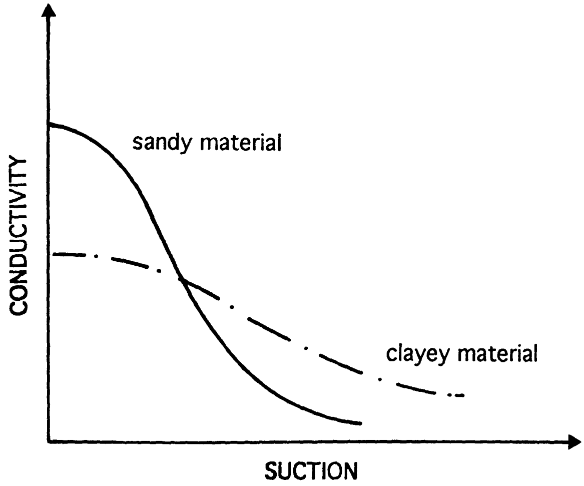


Fig. 3.25. Decrease in hydraulic conductivity as suction pressure increaces, for two materials with different textures

a maximum value which is that of free water in large voids. This is of importance for chemical reactions at the solid–fluid interface. These reactions could be regarded as two opposing processes: the growth and the dissolution of crystalline phases. During dissolution of silicates, cations will (1) detach from the oxygen bonds, (2) diffuse away from their site in the crystalline lattice, (3)

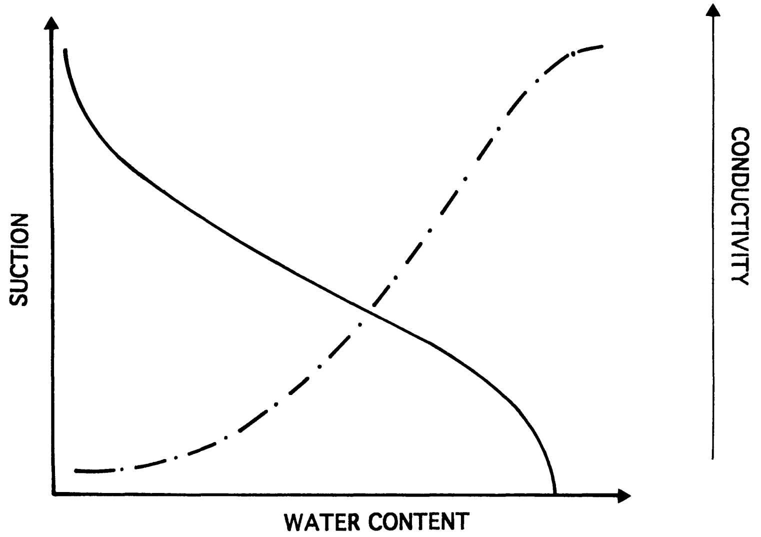


Fig. 3.26. Variation of wetness, suction pressure and hydraulic conductivity in an unsaturated soil

desorb from the crystal surface and (4) diffuse into the bulk solution (Hochella and White 1990). From a chemical point of view, growth as well as dissolution processes, could be reduced by the effects of ion concentration gradients at the crystal surface.

Dissolution of pre-existing mineral phases as well as nucleation and growth of secondary ones are controlled by the differences in chemical concentrations of the solutions far away and adjacent to the surface of the solids (C_α and C_{eq} respectively). A crystal is dissolved if the solution at the interface is maintained in an undersaturation state (i.e. C_α–C_{eq} is negative); on the other hand, a crystal will grow if the solution is oversaturated (C_α–C_{eq} is positive). Both phenomena occur in weathering processes in which the preexisting minerals are seen to be replaced by new ones.

The rate at which these processes occur is controlled either by transport of ions, reactions at the surface, or by a combination of both. These phenomena were formalized by Berner (1980) and are summarized in Fig. 3.27. In spite of the fact that the mechanisms of growth or dissolution are complex, an approximate value of the rate can be calculated using the following equation:

$$dr_c/dt = \nu D_s(C_\alpha - C_{eq})/r_c,$$

where:

r_c = average radius of crystals,
V = molar volume of the crystalline substance,
D_s = coefficient of molecular diffusion in aqueous solution,
C_α = concentration in solution away from the crystal surface,
C_{eq} = equilibrium concentration adjacent to the crystal surface,
t = time.

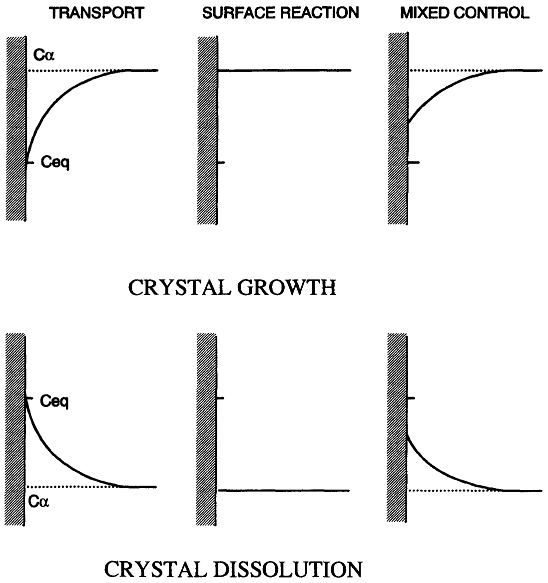


Fig. 3.27. Schematic representation of the concentration gradients of a given chemical component at the fluid-solid interface during growth or dissolution stages. (Berner 1980)

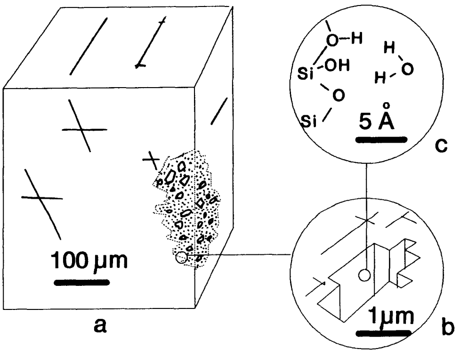


Fig. 3.28. Alteration features of a silicate at different scales. **a** Formation of the "alteroplasma" in place of the parent crystal. Most often, the alteration process is volume conservative. The alteroplasma is composed of parent mineral debris mixed with neogenic clay and/or oxide minerals; **b** view of an etch pit at the corroded surface. Etch pits frequently have geometrical shapes due to preferential dissolution along some crystallographic directions; **c** the Si–O or Al–O bonds are broken at the solid–fluid interface; cations are replaced by H^+

3.2.8.2 The Proton–Cation Exchange

The dissolution of primary minerals in aqueous solutions implies the rupture of inter-atomic bonds in the crystalline lattice (Fig. 3.28). Most often, the first step of the reaction is the exchange of alkali and alkaline earth cations in the crystal with proton in the solution. For example, the attack of feldspars by H^+

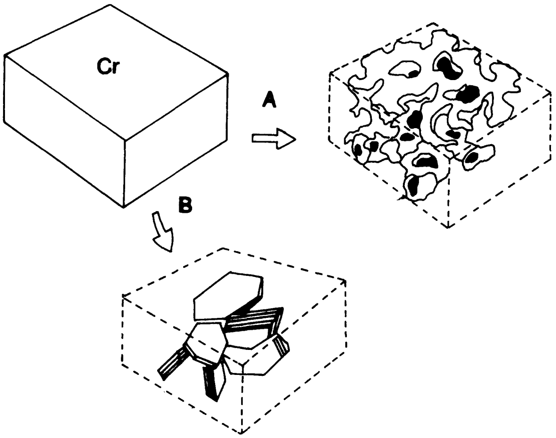


Fig. 3.29. The two alteration pathways for a crystal *Cr*. **A** Incongruent dissolution: the parent crystal becomes porous but no secondary phases are observed. The original crystalline framework is conserved; **B** dissolution–precipitation: the parent crystal is replaced by a microporous assemblage of secondary minerals

will lead to a surface which has lost the alkali cations; it is composed of SiOH or $SiOH_2^+$ groups. Further attack by H^+ or by H_2O will hydrolyze the Si–O–Al and Si–O–Si bridging bonds as shown in the reaction

$$Si{-}O{-}Si + H_2O \rightarrow Si{-}OH + OH{-}Si.$$

This process is affected by the diffusion of H^+, H_3O^+ and molecular water into the crystalline surface from the mineral–solution interface (Petit et al. 1987). The diffusion layer is several tens of nanometers thick. Mogk and Locke (1988) showed that cation diffusion occurs at the same scale changing the mineral composition near the interface. The size and properties of this intermediate layer at the interface are still a controversial subject. Nevertheless, except for phyllosilicates (micas, chlorites), the dissolution of silicates in natural rocks appears to be congruent at the micrometer scale. In other words there is no solid residue with a different chemical composition, and the solids which replace the pre-existing crystal are neo-formed secondary phases (Fig. 3.29). Phyllosilicates must be considered separately because their crystalline structure is similar to that of the clay minerals which replace them. The question is how to distinguish between those which are strictly neo-formed and those which could be considered as resulting from an incongruent dissolution. This will be discussed in more details in the chapter “Clays in soils from granite saprolite in the temperate zone” (Sect. 3.3.2).

Dissolution and growth are locally activated at excess energy sites such as lattice defects emerging on crystalline faces, edges or corners of crystals, twin boundaries, and micro cracks. Dissolution smoothes the angles and produces etch pits which become deeper and finally coalesce with time. This process results in a very irregular shaped interface showing corrosion gulfs. Usually the corrosion gulfs created by the dissolution of primary silicates are partially filled by the remains of the primary minerals and by secondary minerals. In other words, the continuous solid is replaced by a porous polyphase mineral assemblage (Fig. 3.28).

Secondary minerals formed in the corroded zones of primary ones can originate from two different processes: precipitation from solutions enriched in dissolved components (nucleation and growth), and transformation of the parent crystal lattice by diffusion. The latter is typical of phyllosilicate alteration (mica, chlorite) but it is also observed in non-phyllosilicate alteration. Indeed, olivine, pyroxene and amphiboles, weather in a biopyribole-sequence type (Veblen and Busek 1980; Eggleton and Boland 1982). In this case, the secondary phases grow in structural coherence with the parent crystal lattice; the coalescence of silica chains produces 2:1 layer silicates with minimum disruption of the pre-existing mineral structure. Nevertheless, the nucleation-growth process is the most common process involved in the crystallization of clay and oxide minerals in weathering or soil conditions. Nucleation is activated by the catalytic effect of defects on the dissolved surface of primary minerals (heterogeneous nucleation). In summary, the dissolution–recrystallization processes which occur at the mineral–aqueous solution interface can be reduced to an exchange of protons for soluble cations (hydrolysis). For example:

$$\text{K-feldspar} + H^+ \rightarrow \text{kaolinite} + K^+ + Si^{4+}$$

The alkali bearing mineral (feldspar) is replaced by a hydrogen bearing one. These hydrolysis reactions can be used to determine the relative stabilities of mineral species.

3.2.9 Basic Factors for Phase Relation Analysis in Rock Weathering

3.2.9.1 From Microsites to Microsystems

The striking fact when observing altered rock at different scales is the great variation in physical properties (color, hardness, porosity, etc.) from place to place. At the thin-section scale, alteration reactions can be observed in numerous microsites where the pre-existing minerals are corroded. However, in spite of their apparent diversity, these microsites belong to just a few different types according to their location (intergranular joints, intracrystalline microcracks, transcrystalline fractures, porous secondary assemblages).

The dissolution–recrystallization processes occurring in each microsite are controlled by local chemical equilibria. Reactions are made possible by the presence of aqueous solutions which, unfortunately, are not analyzable at this scale. Nevertheless, these fluids must be taken into account as they exchange

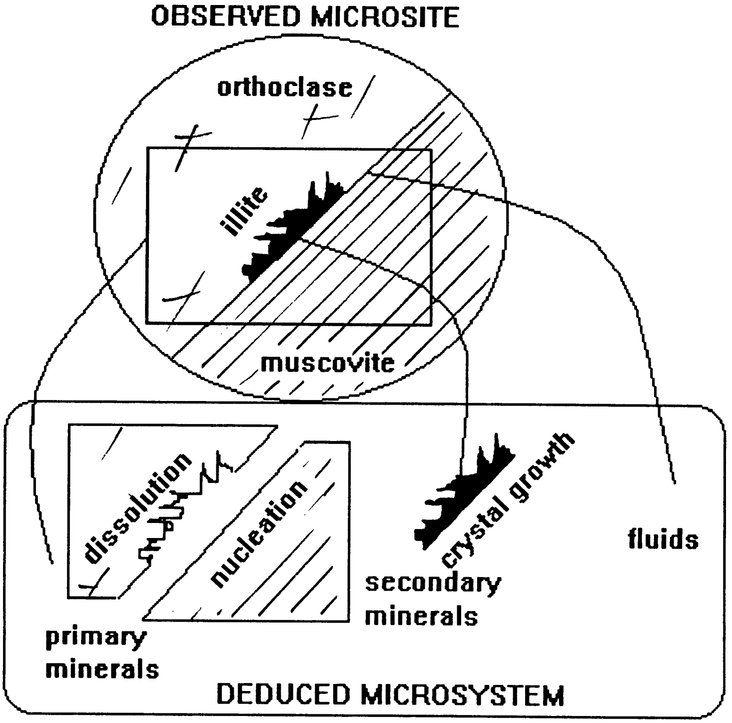


Fig. 3.30. Schematic representation of the different components of a microsystem. The example chosen is from a weathered granite where the observed mineral reaction takes place in the orthoclase–muscovite intergranular joint

energy and chemical components with the surrounding solids. Each microsite can be considered as a microsystem composed of three parts: primary minerals, secondary minerals and fluids (Thompson 1955; Korzhinskii 1959) (Fig. 3.30).

The microsystem concept is a useful tool to express mineralogical observations and chemical analyses in terms of phase equilibrium. It allows one to apply easily the Gibbs' phase rule and the classical laws governing the construction of phase diagrams. At this point, it is necessary to remember some basic definitions. A *phase* in thermodynamics is defined as a "pure substance, or mixture of pure substances, wherein the intensive properties do not vary with position" (Sposito 1981, p. 4). In fact, natural minerals are rarely homogeneous (zonations, inclusions etc.); nevertheless, they could be considered as phases in the Gibb's definition until their reacting interface with fluids becomes homogeneous. An *intensive variable* (V_{int}) does not depend upon the size of the system: for example temperature (T), pressure (P), density (ρ) and chemical potential (μ_x). *Extensive variables* (V_{ext}) depend on the size of the system: weight, enthalpy etc. The Gibbs' phase rule was extended to a more general expression by Korzhinskii (1959): $F = V_{ext} + V_{int} - P$ where F is the variability of the system (or *degree of freedom*) and P the number of phases. This expression is used here.

For example, in the mineral reaction: K-feldspar + $H^+ \rightarrow$ kaolinite + K^+ + Si^{4+} described above, the composition of the solution depends on the concentration of three mobile components: H^+, K^+ and Si^{4+} while Al remains fixed in solid phases (inert component). According to Korzhinskii (1959), the chemical potential of the three "mobile" components may act as intensive variables, if they are controlled by the external environment of the system. This is the case in water dominated systems. In contrast, Al whose concentration determines the quantities of solid phases involved in the reaction, is typically an extensive variable.

The quantities and the energy state of fluids involved in each microsystem vary with the dimensions and the interconnection of voids. Three types of microsystems are active in rock weathering (Meunier and Velde 1979):

Contact Microsystem. The earliest weathering reactions in macrocrystalline rocks, whatever their composition, have been observed in intergranular joints. Generally, the secondary phases nucleate on the surface of one of the parent crystals and grow into the other one. The microsystem is dominated by the chemical compositions of pre-existing phases; it is roughly closed.

Plasmic Microsystems. "Plasma" is the term describing the porous material composed of a primary mineral debris mixed with secondary minerals. In the saprock (in which the primary rock structure is conserved), the plasmic microsystems appear inside the primary minerals along internal microcracks, cleavages or twin boundaries (alteroplasma). In the saprolite, the primary rock structure disappears. Here another type of plasmic microsystem is observed in the restructured zones in which clay minerals, and the remaining debris of pre-existing minerals, are physically intermixed (pedoplasma). New clay minerals form from old ones due to local changes in chemical composition, caused by physical mixing. As the pores are in the microscopic class, the fluids cannot circulate quickly. Fluids control the chemical potential of the more soluble components of the rock in all the microsystems through which they percolates. Thus, in a given plasmic microsystem, the new phases will depend on the local chemical composition and the value of the chemical potential of the more soluble species.

Fissural Microsystems. Coatings on the walls of fractures and large pores are composed of identical secondary mineral assemblages, whatever the size and the position of the open fractures in the weathering profile. The sedimentary features observed in the coatings are interpreted as microstratigraphic formations in which each deposition stage corresponds to seasonal variations in fluid dynamics. The size of these voids is large enough to reduce the capillary effect to negligible values. Consequently, the fluids circulate under gravity and are quickly renewed. In this situation, the stability of the mineral phases which constitute the coatings is controlled by the chemical composition of the fluids; the microsystem can be considered as totally open.

3.2.9.2 Construction of Phase Diagrams

The Different Types of Phase Diagrams

Several types of phase diagrams can be used in rock weathering studies. Considering that the effects of P, pressure, and T, temperature, variations are negligible for the formation of mineral phases at Earth surface conditions, it is possible to reduce the number of intensive variables to the chemical potentials of elements which are active in the different microsystems. According to Prigogine and Defay (1954), the chemical potential μ_i of a component i, can be defined by the following equation:

$$\mu_i = \mu\theta_i(P,T) + RT \ln \gamma_{ixi} + g^E{}_i - \mu^\theta{}_i.$$

The terms are defined as follows:

$\mu^\theta{}_i$: This term refers to a pure substance. In a given system, the variation in chemical potential is a function of the intensive variables, pressure (P) and temperature (T).

$RT \ln \gamma_{ixi}$: This term refers to the effect of variable composition of a phase upon the chemical potential of component i; γ_{ixi} is the activity of i; R is the gas constant (1.987×10^{-1} kcal °C^{-1}mol^{-1}) and T is the temperature on the Kelvin scale. This is the function of mixing.

$g^E{}_i$: This term refers to the effect of structural configuration of a phase upon the chemical potential of component i which gives an excess function of mixing.

When two or more phases coexist at equilibrium, the chemical potential of all the components in the system must be identical in each phase.

Phase diagrams can be used to describe the changes of mineral assemblages induced by weathering processes at the scale of microsystems. If the microsystem considered is strictly closed (water is strongly retained on the mineral surfaces and the submicroscopic pores), there is no intensive variable acting in the formation of new phases. The components of primary mineral chemicals are recombined inside the microsystem without any exchange with its environment. Generally, the secondary minerals produced are polyphase minerals. If the microsystem is partially open (water can move in microscopic pores), the chemical potential of the more soluble component becomes an intensive variable. The dissolution–precipitation reactions modify the chemical composition of the microsystem; the number of secondary phases is reduced compared to the closed microsystem. Finally, if the microsystem is totally open (free water circulating under gravity in macroscopic pores and fractures), several chemical components become totally soluble; their chemical potentials act as distinct intensive variables. Figure 3.31 summarizes the different possibilities in a three-component system.

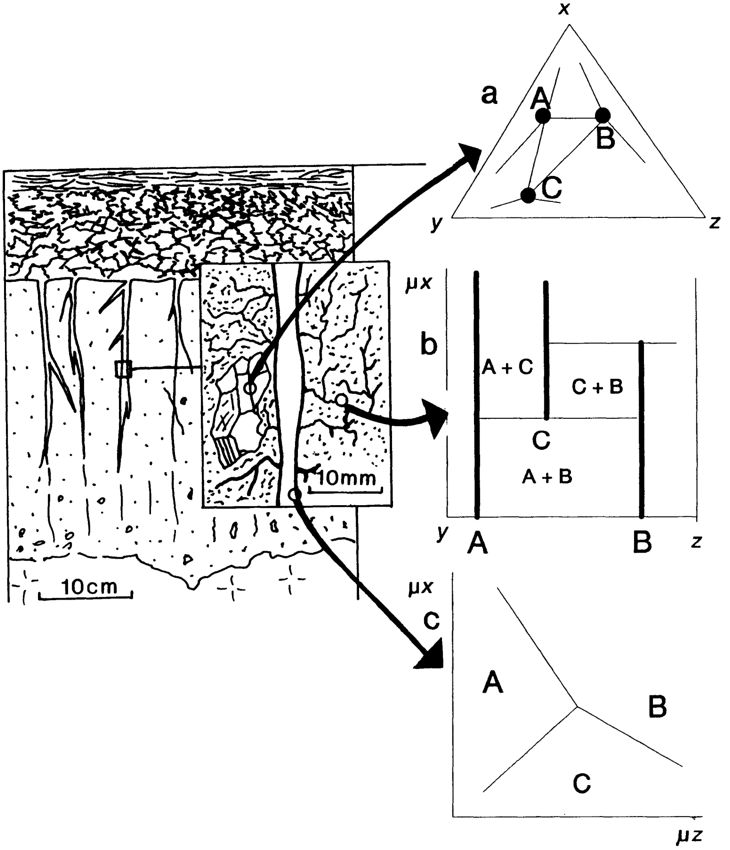


Fig. 3.31. Sketch showing the positions of the different microsystems in a soil. The adapted phase diagrams are related by the *arrows*; phase relations are depicted in a three–component chemical system (x-y-z). **a** Closed system (crystal microfissures or intergranular joints), the chemical components are inert; phases A, B and C are determined by the relative concentrations of x, y and z (*triangle*); **b** semi-open microsystem (altero or pedoplasma); one component (x) becomes an intensive variable; phase relations are controlled by the chemical potential of this component (μx-y-z system); **c** open microsystem (mineral coatings in fissures where fluids circulate under gravity); phase relations are controlled by the chemical potential of two mobile components, only one component remains inert (μx-μz-y system)

In summary, phase relationships in contact, plasmic and fissural microsystems can be graphically studied using triangular composition, potential–composition and potential–potential diagrams respectively.

How can one construct the correct phase diagram?

First Step. It is necessary to define a simplified chemical space in which the composition fields of the mineral phases which have been identified, are represented in the different microsystems (identification controlled by X-ray diffraction; composition given by microprobe analysis). Usually, in spite of the fact that natural rocks are composed of ten major elements, it is possible to

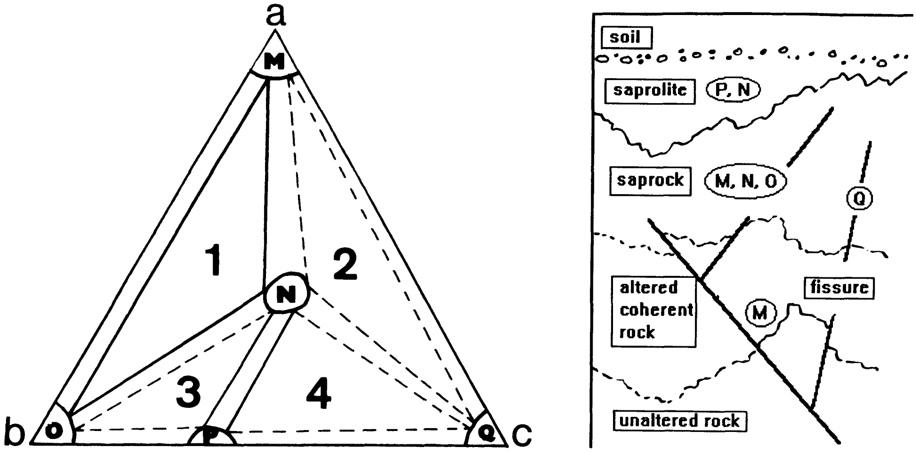


Fig. 3.32. Theoretical representation of a weathered profile in which the secondary phases are the following: M; $M + N + O$; $P + N$ and Q, in the altered coherent rock, the saprock, the saprolite and the fissures respectively. Composition fields of these phases are projected in the *a-b-c* chemical system. Observed and deduced mineral assemblages are represented by *heavy* and *dotted* tie-lines respectively

reduce the chemical system to a few groups of elements which react, chemically, in the same way. Indeed, some elements can be neglected because they are not decisive in the crystallization of clays and oxides or hydroxides phases (titanium for example); others can be grouped because of two reasons:

1. They are not independent in crystalline structure of these phases (for example, in the silicate group, the number of O^{2-} and $(OH)^{-}$ anions is fixed in a given crystalline structure);
2. They exhibit quite similar chemical behavior in the crystallization processes of the secondary phases (for example, Mg^{2+}, Mn^{2+} and Fe^{2+} cations are interchangeable in the octahedral layer of phyllosilicates). Thus, one can attempt to simplify the representative chemical systems in order to select three elements, or groups of elements, which determine the presence of phases. For example, the composition fields of phases M, N, O, P and Q identified in a weathering profile are projected in the triangular chemical system *a-b-c* as shown in Fig. 3.32.

Second Step. The mineral assemblages are determined by microscope observations, and are represented in the *a-b-c* triangle by tie-lines joining the phases which coexist. Coexistence means co-precipitation or replacement. The Gibbs' phase rule indicates that the maximum number of coexisting phases is only 3 in a three component system:

$$F = V_{ext} + V_{int} - P$$

as $V_{int} = 0$ in a closed system in the surface conditions, the equation becomes

$$F = 3 - P$$

if F = 0, the maximum number of coexisting phases is P = 3; three phase assemblages are represented by sub-triangles in the *a-b-c* system. Of course, not all the assemblages depicted in the diagram are observed in the weathered profile, because the chemical composition of the unaltered rock is represented by a limited field in the three-component system; nevertheless, when a sufficient number of tie-lines are known, there is only one solution to draw the missing ones. For example, in Fig. 3.32, the identified assemblages M + N + O; P + N; Q and M are represented by heavy lines. The presence of the N–O phase tie-line excludes M–P from coexisting (tie-lines must not cross, Niggli 1938). Consequently, the O–P, P–Q, N–Q and M–Q tie-lines (stippled lines) are necessary in order to respect the phase-rule relations (subtriangles).

Third Step. The secondary mineral assemblages change throughout the weathering profile from the nearly closed microsystems, which are numerous in the altered coherent rock, to the totally open systems in fractures (Fig. 3.32). These changes are due to variations of the chemical potential of one or two components. For example, if component *a* becomes an intensive variable, the succession of mineral assemblages in the profile is controlled by the variation of μ_a from high values in the closed microsystems to low values in the open ones. Thus, a sequence of μ_a equipotentials can be determined which depicts the mineral succession in the profile. The total number of equipotentials (N) necessary to describe all the mineral assemblages represented in the *a-b-c* system is given the following relation: $N = N_{tri} + 2$ where N_{tri} is the number of three-phase assemblages represented in the triangular diagram (Meunier and Velde 1979). A μ_a-*b*-*c* phase diagram can be derived from the triangular one (Fig. 3.32).

Fourth Step. In totally open microsystems such as fractures in the rock, mineral reactions are controlled by the chemical potentials of two elements. For example, if component *b* remains inert while components *a* and *c* become active, the best adapted diagram will be the μ_a–μ_b–*c* one. Such a diagram can be constructed in combining the μ_a–*b*–*c* and μ_c–*a*–*b* diagrams derived from the *a-b-c* one (Figs. 3.33 and 3.34) as shown in Fig. 3.35.

3.2.10 Summary and Conclusions

Soils and weathered rocks appear to be complex materials in which different physical, chemical and biological processes continuously transform organic and non-organic substances. The most important facts which must be kept in mind through out this chapter are the following:

1. The soil structure may change seasonally, whereas the weathered rock structure is permanent and inherited from the parent rock.
2. Although many parameters act in the formation of soils and weathered rocks (climate, age, topography, vegetation etc.), it seems that the most important parameter is the quantity of water which flows through.

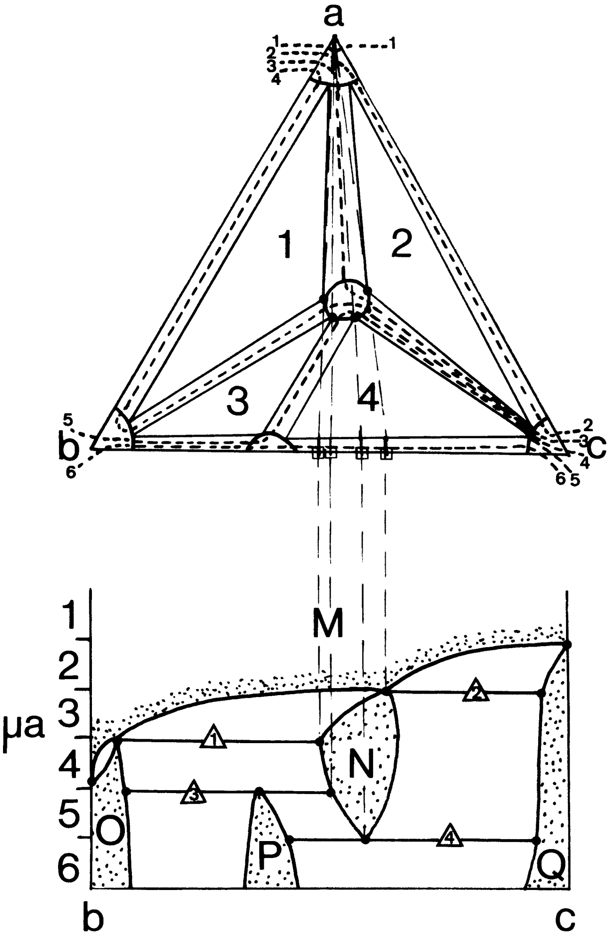


Fig. 3.33. Derivation of a potential-composition diagram from the composition diagram; assuming that component *a* becomes an intensive variable, all the mineral assemblages defined in Fig. 3.31 are depicted by a sequence of 6 equipotentials. A μ_a–b–c diagram is derived as shown. The triphased assemblages are formed for some fixed values of μ_a; they are indexed by the same numbers as in Fig. 3.31. The composition fields of *O*, *P*, *N*, *Q* are shown by areas; the stability field of phase *M* is represented by a *stippled area* (see text for details)

3. In spite of the fact that soils as well as weathered rocks seems to be dramatically complex at the microscopic scale, mineral reactions proceed in a few types of chemical microsystems.

Whatever the apparent complexity, an accurate observation of minerals and structures at different scales is the best tool we have, to determine the mechanisms of such continuous transformations. Thus, a general method for the study of soils or weathered rocks can be proposed:

1. As far as it is possible, observations must be made at different scales in order to determine the geometrical properties of the structure.

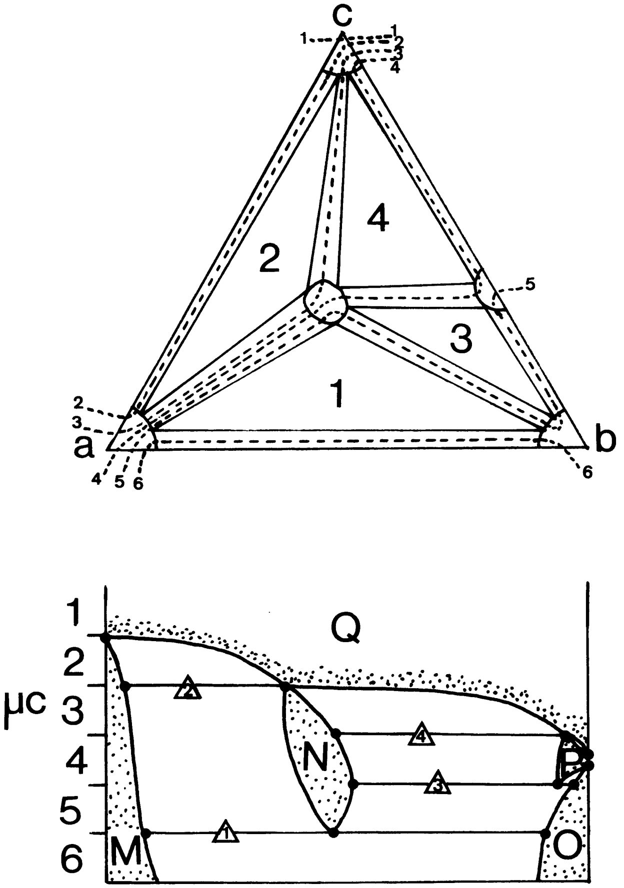


Fig. 3.34. Derivation of a μ_c-a-b diagram. The procedure is identical to that given in Fig. 3.32; the mobile component is *c*

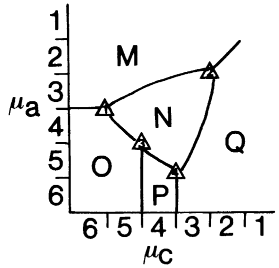


Fig. 3.35. Construction of a μ_a-μ_c-b diagram depicting the phase relations when two components (*a* and *c*) behave as intensive variables. Triphased assemblages are formed only for fixed values of μ_a and μ_c (no degrees of freedom); they are represented by *small triangles*; *numbers* are identical as in Figs. 3.31, 3.32, and 3.33

2. Then, mineral identification (X-ray diffraction) must be accurate enough to recognize the location of the phases or assemblages in the structure at the microscopic scale.
3. The chemical compositions of the different primary and secondary minerals involved in the reactions must be measured at the scale of the microsystems (electron microprobe).
4. Finally, petrographic observations, chemical data (microprobe) and mineral identification (XRD analyses) must be linked together by means of phase diagrams, in order to determine the mechanisms of the mineral reactions.

This four-step method is essentially applied to the study of weathered profile. It needs to be modified for soil study because microsystems are more complex and more difficult to observe directly under optical microscope. This will be explained later on.

3.3 From Rock to Soil: The Granite Example

The guide lines for phase analysis and the determination of the influences of the physical parameters on rock weathering and soil formation have been outlined above. However, a demonstration of their applicability has not been made, yet. We would like to demonstrate the analysis method described above as applied to a real case of the alteration of a rock type under a given climate at the Earth's surface. In doing this, a careful analysis is made to illustrate the use of the methods. The conclusions are drawn and the influences of structure, chemistry and the physical parameters are assessed as a function of their relative importance. In doing this it is hoped that the analysis method can be understood and that the subsequent analyses of soils and rock weathering which are presented will become clearer to the reader. The method proposed is that shown above applied to soil formation and the weathering processes developed on a granite. Why granites? They are among the most widespread rocks found at the surface of continents; thus, soils derived from granites, as well as weathered rocks, are well represented in large areas of many countries. The detailed study which is proposed in this section aims to describe the mechanisms which govern the transformation of a hard rock into a friable sandy material and then into a soil. It appears that soil properties depend more on the water regime than on the mineralogical and chemical properties of the parent rock. The formation of more or less horizontal layers (horizons) indicates that the governing mechanisms are chemical transfers and particle translocation from the atmosphere interface. In contrast, weathering produces a friable rock in which the structural, mineralogical and chemical characteristics are strongly dependent on that of the parent rock. Usually, the transition between soils and weathered rocks is sharp. Both can be considered at first glance as independent environments. Soils and weathered rocks will be studied separately. As the first secondary minerals form from the primary granitic minerals, it seems more logical to begin with the weathering reactions.

3.3.1 Clay Formation in Weathered Granite Under Atlantic Climatic Conditions

3.3.1.1 Weathered Profiles on Granitic Rocks: The First Stages of Weathering

The weathering intensity is classically considered to regularly increase from the freshest rock at the bottom of the profile to the most altered zones at the top. Thus, the profile is composed of a vertical sequence of horizons: fresh rock, coherent slightly altered rock, saprock and saprolite. This is usually an oversimplification, since such a vertical sequence is rarely observed. In particular, weathering does not produce a regular and continuous coat above the granitic massifs. Erosion, as well as preferential alteration in the fractured zones, greatly modify the theoretical vertical distribution of the different horizons. It is common to observe weakly altered zones above deeply altered ones. Besides, heterogeneities are commonly observed in a given zone at the centimeter scale: for example, small volumes of coherent rocks are often seen in a friable zone. Figure 3.36 shows the most common occurrence of weathered profiles developed under an Atlantic climate in the Armorican Massif (Meunier and Velde 1979). It is composed of the following zones: fresh rock, coherent slightly altered rock, saprock (structure conservative friable material) and saprolite (restructured clayey zone).

The Coherent Slightly Altered Rock

This zone is not systematically found at the bottom of the profile: for example, it is seen in the right part of the La Rayrie profile as large blocks outcropping through the soil cover (Fig. 3.36). The granite remains coherent, representing the initial stages of alteration via the weathering process. New phyllosilicate phases are found along the microcracks and discontinuities of the rock structure. These are grain boundaries, internal microcracks in grains and polycrystalline microfissures. Consequently, the energy state of water is high; the microsystems can be considered as closed. Two stages are noted:

1. The first new mineral to be formed is illite which grows on the (001) faces of muscovite or biotite found in grain to grain contact with potassium feldspar (Fig. 3.37a). At a slightly later point in stage 1, dioctahedral and trioctahedral vermiculite are found along the muscovite–biotite interfaces

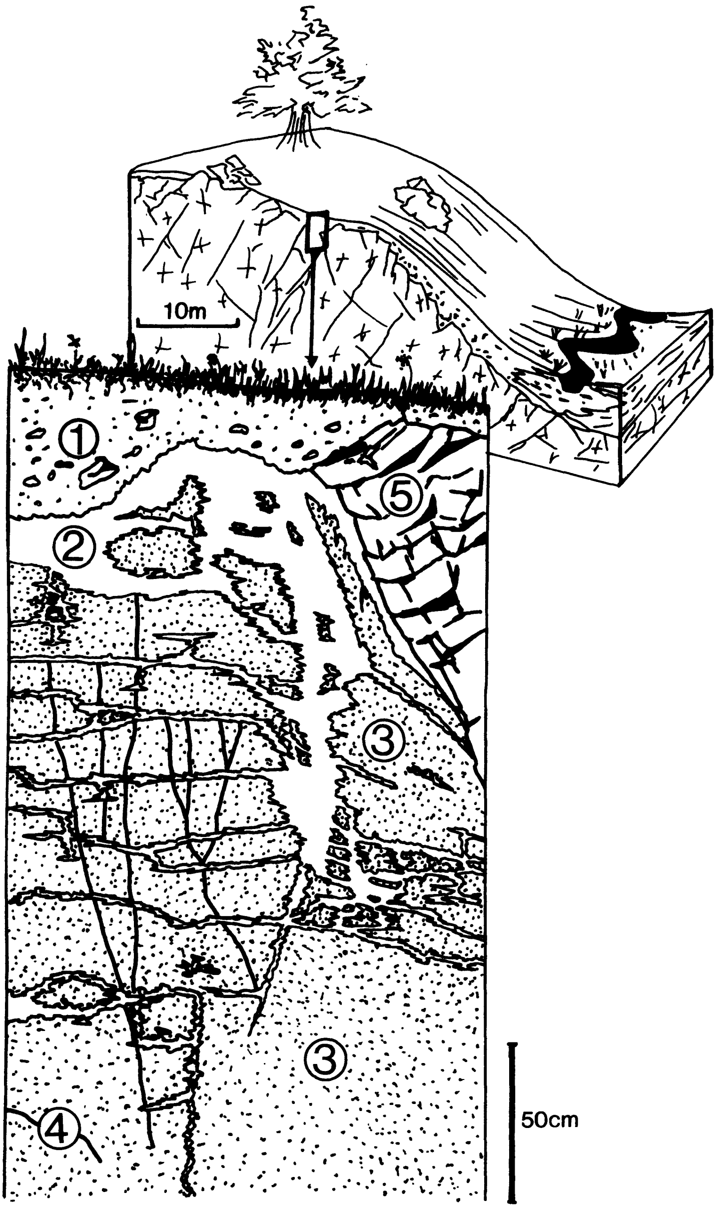


Fig. 3.36. The La Rayrie weathering profile on a granitic rock (Meunier 1980). *1* Colluvial soil; *2* white zone in which the initial granitic structure is modified; *3* saprock; *4* fissures filled by a reddish deposit; *5* altered coherent rock

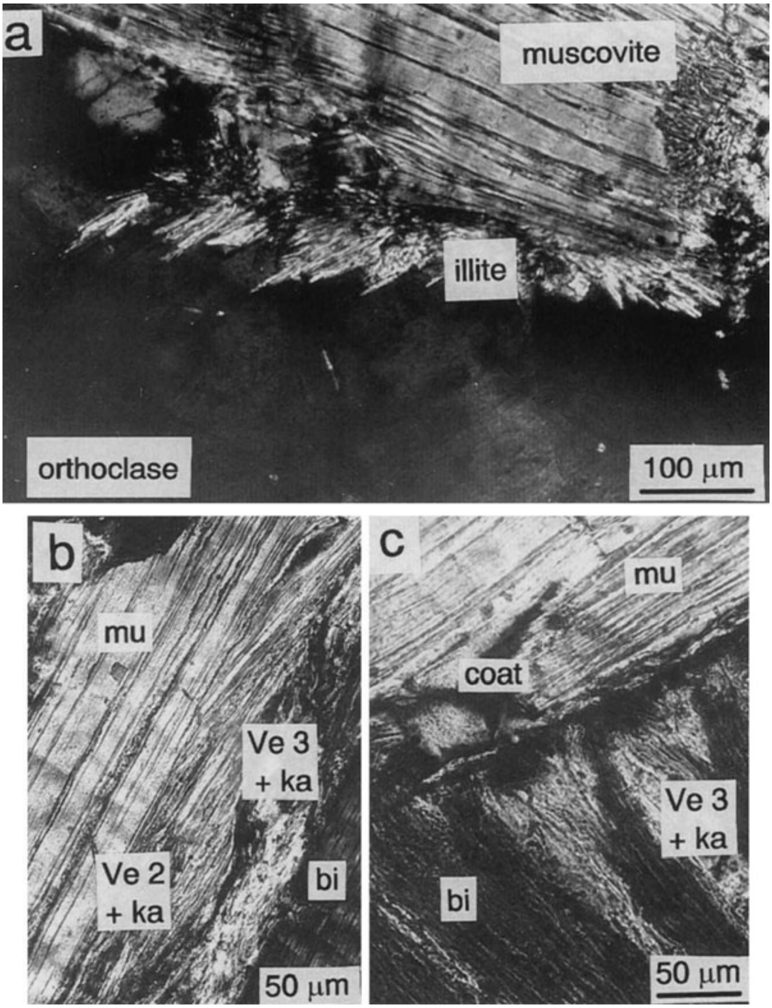


Fig. 3.37. Microphotographs of some weathering microsites in the La Rayrie profile. **a** Illite growth on a muscovite–orthoclase intergranular joint. This microsite can be considered as a closed microsystem; **b** alteration zones at a muscovite–biotite intergranular joint (parallel to the 001 crystal faces). Muscovite *mu* and biotite *bi* are replaced by a dioctahedral vermiculite *Ve 2* + kaolinite *ka* and a trioctahedral vermicilite *Ve 3* + kaolinite secondary mineral assemblage; **c** microfissure outlined by a clay coating *coat* at the muscovite–biotite intergranular joint (orthogonal to the 001 crystal faces); the coating is composed of kaolinite + Fe-hydroxides

(Fig. 3.37b). These minerals are the only ones to be found at grain contacts where two preexisting phases participate in the formation of a weathering mineral (contact microsystems).

2. The primary minerals destabilize internally. Kaolinite is found in microcracks in plagioclases. Beidellite–montmorillonite (smectite) zones are

apparent in potassium feldspars in more altered grains of the slightly altered rock. Kaolinite is at times also present. It should be noted that there is no evidence of new mineral growth along quartz grain boundaries, nor is there evidence of dissolution even though these zones are quite permeable (Parneix and Meunier 1983). The accessibility of water to minerals is obviously the more important factor in the early stages of alteration. This accessibility is strongly dependent on the initial microfissuration as shown by coloration techniques (Rassineux et al. 1987).

The Saprock

The altered rock becomes friable (i.e., individual grains are loosened with one's fingers) in hand specimen but the structure of the crystalline granite is still visible, i.e. initial feldspars can be distinguished with respect to quartz and mica grains, even though their color and general aspect is greatly modified. In this zone, all primary minerals except quartz are internally destabilized (alteroplasma) showing single or multi-mineral assemblages of phyllosilicates. Biotite produces a trioctahedral vermiculite + kaolinite + iron oxide assemblage. Muscovite forms a dioctahedral vermiculite + kaolinite assemblage (Fig. 3.37c). Plagioclase recrystallizes into single-phase kaolinite zones. Orthoclase is seen to recrystallize into alteroplasma zones sometimes with sericite (largely due to deuteric alteration in the late stages of the magmatic evolution) but more often with vermiculite or beidellite and kaolinite. In all cases, the initial magmatic minerals form a new alteroplasma which wholly or partially replaces the initial grains without changing the dimension of the grain zone. Thus, the mineral transformations observed depend upon the original chemistry of the minerals which were destabilized by the altering solutions. In other words, several chemical components are extensive variables of the system (inert components: Fe, Al) while others are intensive (mobile: alkalis, Ca and Mg) variables. The rock structure becomes one of the mosaic of microsystems (Korzhinskii 1959) which are in internal equilibrium with an altering fluid.

The Saprolite

The altered rock becomes very friable and porous. The granitic structure is destroyed. In temperate climates, the saprolite zones do not form continuous horizons, as is the case in tropical climates (Nahon 1991). Instead, white patches or bands are found which cut the saprock mass. Parental minerals are largely destroyed, except quartz, and one finds a general plasma (pedoplasma) structure in thin section. The reorganization of old and new phyllosilicate phases in the pedoplasma creates new chemical potentials which crystallize new minerals. In this zone, the assemblage illite + kaolinite has been identified, it replaces such minerals as dioctahedral vermiculites and smectites, mixed with remaining debris of orthoclase.

Fissures

Micro- and macrofissures (from micrometer to centimeter widths) are found throughout the alteration profile. They are always coated with clay deposits which have been transported by the aqueous flow in the system. Thus, at any point in the profile (slightly altered rock, saprock, saprolite) the only minerals found in fissures or on fissure walls are kaolinite and iron oxides (Fig. 3.37c). If the altering fluid in a profile is collected, i.e. that fluid which flows easily in the profile through the large fissures, it will be in equilibrium with kaolinite (Feth et al. 1964). This indicates that the other clay minerals which are also transported (vermiculite, smectite) are not stable in such diluted solutions. Their absence must not be taken as an effect of a selective translocation but rather as a result of their dissolution.

In summary, the following key mineral assemblages in the different zones of alteration will be:

1. veins: kaolinite + iron oxides (deposit after transportation: coatings)
2. saprolite pedoplasma zones; illite + kaolinite
3. saprock alteroplasma zones: beidellite (smectite) + kaolinite
4. altered rock grain contacts: illite + orthoclase
5. initial rock grain contacts: orthoclase + muscovite.

The above table was constructed from the data of Meunier (1980) and Dudoignon (1983) for the profile of La Rayrie. Mineralogical observations are given in the studies of Harriss and Adams (1966), Bisdom (1967), Wolff (1967), Sikora and Stoch (1972), Gilkes et al. (1973), Rice (1973), Eswaran and Bin (1978) and Boulangé (1984) from other profiles. These assemblages do not include biotite or its reaction products which contain magnesium and iron. This phase has been left out in order to simplify the chemical system under consideration. It appears that there is little interaction of the biotite with the other minerals in the altered rock, saprock or saprolite zones. Since the mineralogy of the altered biotite is similar to that of altered muscovite (vermiculite + kaolinite), it will be assumed that the exclusion of this mineral will not greatly change the interpretation which follows.

The problem of plagioclase must be considered here. It has been noted in the La Rayrie profile, as well as in others, that the plagioclase is replaced in the early stages of alteration by kaolinite (or halloysite). This introduces the phase which is typical of the latest stage of alteration into the early parts of the alteration sequence. Essentially, the assemblage is one of kaolinite plus silica in solution, which cannot crystallize a phase which would form at silica saturation. Possibly, one can propose that the sodium and the calcium of plagioclase do not seem to play the role of potassium. Neither mica or smectite replace the plagioclase. The only micaceous mineral to form under surface conditions is a potassic one. Neither paragonite nor margarite have been found to crystallize in natural surface environments (Velde 1985). Hence, Na–Ca plagioclases do not form micas. A second observation critical to an understanding of phase relations is the lack of albite found as surface mineral. The Na and Ca tectosilicates observed at surface conditions are normally zeolites (Velde 1985). Since high pH and silica activity is needed to form these minerals, it is possible that lack of silica in solution and the low pH reduces a kaolinite + plagioclase + zeolite field to an aqueous solution–kaolinite tie-line. Silica activity would not be high enough to establish a smectite mineral in the local plagioclase alteroplasma environment. At the early stages of alteration, the alkali potential (sodium and calcium in this case) is still too high to form a smectite, but the potential of Si released into solution is too low to produce a zeolite. The kaolinite forms as a metastable mineral, relative to the others, forming at the same level of alkali (potassium) potential in the sequence. In the alteroplasma environment of the plagioclase grains, the ratio Na + Ca to K is such that the system is no longer one of K + Na but of Ca + Na, and the phase relations change in that there is no mica phase present (see Helgeson et al. 1969).

3.3.1.2 Construction of Phase Diagrams

Composition Diagram

Initially, one must proceed to place the mineral compositions of the phases observed into a chemical framework. Given the phases which occur in weathering as a result of the basic granite composition, it is possible to restrict the chemical parameters necessary to describe the reaction observed. Three components are used: silica, alumina and alkalis. This simplification has been used for quite some time (Garrels and Christ 1965). The assimilation of calcium with alkalis is possible because no calcic silicate (zeolite or margarite) forms during granite weathering. Magnesium has a minor role in the system. Iron is initially present in the granite primary minerals, but it quickly becomes an unreactive element as far as the silicates are concerned because it forms an insoluble oxide Fe_2O_3. In using the three components of Si, Al and alkalis (Na + K), we then automatically ignore the existence and evolution of biotite, if it occurs in the granite. As it turns out, this phase does not appear to react with the aluminous minerals to a great extent in the weathering process, and its exclusion should not greatly affect the phase relations described (Meunier 1980). In fact, the biotite forms the silicate phases, as do the muscovites in the granite. The presence and chemical activity of quartz poses a problem to the interpretation of phase diagrams at low temperature. As has been pointed out by Velde (1985), the very low reactivity of quartz at surface conditions excludes it from the active components in most silicate systems. Silica saturation of a solution normally gives a solid phase in the form of a precipitate of amorphous material. This occurrence has not been noted in the weathering of granites, at least in temperate and tropical climates. Thus, in the system studied, the solutions behave as if they were undersaturated with respect to

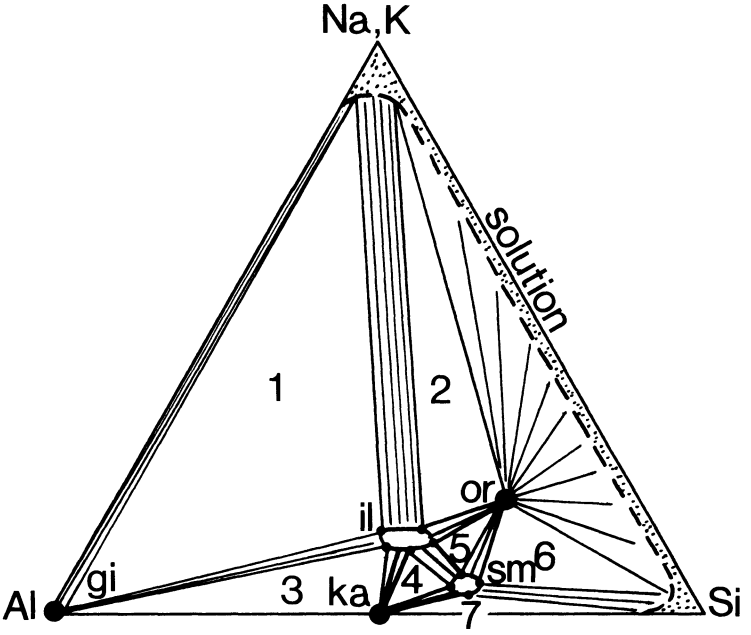


Fig. 3.38. Phase diagram representing the mineral relations in surface conditions in the Si-Al-K,Na system (see text for detailed explanation). *il* Illite; *or* orthoclase; *sm* smectite (expandable minerals including vermiculite); *ka* kaolinite; *gi* gibbsite. Triphased assemblages are indexed from *1* to *7*. *Heavy* tie-lines represent the mineral assemblages observed in the La Rayrie profile

Table 3.2. Mineral assemblages in weathered granite classified according to the microsystem under which they formed

	Mineral. Assemblages	Microsystems
1	Illite + K-feldspar	Contact microsystems
2	Illite + Expandable minerals	Contact microsystems
3	Kaolinite + Expandable minerals	Alteroplasma microsystems
4	Illite + Kaolinite	Pedoplasma microsystems
5	Kaolinite (+ Fe-oxides)	Fissural microsystems
6	Kaolinite + Gibbsite or Gibbsite (+ Fe-oxides)	Residual microsystems (Tropical climate)

amorphous silica in their SiO_2-rich portion. The low reactivity of the stable form of silica (quartz) will have a consequence on the phase diagram derived from the observation of the natural assemblages: since silica is not found as a mineral phase, the assemblages will be buffered by the next most stable siliceous mineral. Gibbsite, which is commonly found in weathered rocks under tropical climates, was not seen in the studied profile. Thus, it represents a boundary phase only.

Figure 3.38 shows the compositions of the mineral phases found in Table 3.2 as projected into the Si–Al–Na,K system. The petrographic observations made above allow one to place the tie-lines between the minerals to form the basic mineral assemblages. The mineral pairs illite + kaolinite, kaolinite + smectite and orthoclase + illite are thus established. This excludes the destabilization of plagioclase (see explanations above).

The relations between illite, orthoclase and quartz in the alkali–silica–alumina system are not established. Since, as has been mentioned previously, the reactivity of quartz is very low and the solutions are never saturated with SiO_2 it is probable that the mineral equilibria in solution will be controlled by another mineral, such as the smectite instead of quartz. In this way, one establishes the active or effective tie-line orthoclase–smectite instead of the illite–quartz tie-line which might represent a more stable mineral pair. The illite–smectite tie-line is based upon reports in literature (cited above) of the coexistence of these minerals. Its justification by our petrographic observations will follow in the section concerning the chemical potential–composition diagrams.

It is useful at this stage to establish the lines of equipotential for the elements which are likely to become mobile or intensive variables in the system of chemical weathering (Korzhinskii 1959; Spear et al. 1982; Meunier and Velde 1986). These lines should be based upon the observations of relative mineral instability at a given level of alteration intensity. In other words, when one sees illite forming with smectite, do other phases form at the same time, or after this mineral assemblage? Such an analysis is a cross-check on the use of a given representation of mineral assemblages. In the composition diagram of Fig. 3.38, the key equipotential is number 7 which includes the illite–kaolinite tie-line and the illite–smectite tie-line assemblages. This is justified by the observed destabilization reaction, illite → kaolinite + smectite (vermiculite), found at level 8. This reaction implies that the two-phase field or tie-line occurs below the illite stability or the equipotential line number 7. This renders an orthoclase–kaolinite tie-line impossible. Such a situation can be found in Helgeson et al. (1969) whereas the illite–smectite tie-line which intersects the orthoclase–kaolinite tie-line can be found in Garrels (1984). The problems of the geometric configuration as a function of the tie-lines in the illite–orthoclase–kaolinite–smectite quadrilateral is discussed at length in Drever (1982). The observation that the alteroplasma of muscovite is made up of smectite and kaolinite, substantiates the illite–smectite tie-line. It should be noted that there is no evidence of a continuous solid solution of the smectite–illite series, such is found in mixed layering of the two components, in the weathering minerals. The I/S mixed layered minerals are typical of diagenesis.

Composition–Chemical Potential Diagrams

In our weathering system, it is evident that the rock is affected by a loss of material. In general, two elements have been considered in the past as mobile species: Si and alkalis (Na, K). This is the classic approach given by Garrels and Howard (1957). If one considers both elements to be intensive variables of the system, i.e. their chemical potential to be variable, the phase diagram which results presents large mono-mineral fields with two or three phase assemblages found at very restricted conditions of the variable chosen. One can say that the system is buffered by the solutions present. In our granite, it was found that there are usually two-phase clay mineral assemblages present. This suggests that there are not two but only one chemical element acting as a fully intensive variable. Such an eventuality leads to a chemical potential–composition diagram such as is represented in Fig. 3.39.

In the weathering of the surfaces of minerals, it has been noted that hydrogen is introduced into the solid phases. As a result, the chemical potential of H^+ (pH) should be considered in the weathering process, as was proposed many years ago. If the compositional representation of Fig. 3.39 is considered as a combination of Si–Al–(Na + K)/H^+, the use of aqueous equilibria is much easier. In this way, one can conceive of an aqueous solution which dissolves orthoclase by adding $(OH)^-$ to the silica and alumina components, so that all species are dissolved. One can then approach natural conditions of alkali and hydrogen ion concentration as independent variables; one must assume that all reaction boundaries are orthogonal to the projection of the chemical system, i.e. there are no field boundaries which can exist over a range of K^+ to H^+ ratios. Also, the solids, such as SiO_2 and Al_2O_3 must not be destabilized by a change in pH alone, such as is known at extreme values of pH. In our representation of the chemical phase relations we will use the representation of μ_x–X, as proposed by Korzhinskii (1959). In fact, the weathering sequence produced in granites is strongly buffered by the minerals present and the initial pH of the rain water which is introduced into the rock–clay system. The pH could vary by two or three whereas the concentration of alkalis reduces to an infinitely small quantity in the upper zones of weathering. Therefore, the variable of greatest interest is the activity of the alkalis, which will have a greater effective range than that of hydrogen ions.

Here, we have chosen to represent the silica and alumina as extensive variables and the alkalis (less hydrogen-ion activity) as the intensive parameter, where their chemical potential is the variable to be considered. The equipotential lines traced in Fig. 3.39 use the alkali chemical potentials which occur between the values where major mineral transformations take place. The important feature of the diagrams is the compression of the three-phase fields of the triangular diagram into a single equipotential (Korzhinskii 1959; Spear et al. 1982). We cannot distinguish, at present, between the relative positions of certain phase reactions as a function of chemical potential on either side of a single phase in Al–Si dimensions; i.e. the position of the illite–gibbsite–solution line with respect to the illite–smectite–orthoclase line because our data do not sufficiently cover the aluminous assemblages. Gibbsite has been reported in early stages of granite weathering (Velde 1985) but was not found in this example. Because the phase associations have not been determined, the mineral occurrence will not be discussed further. Several of

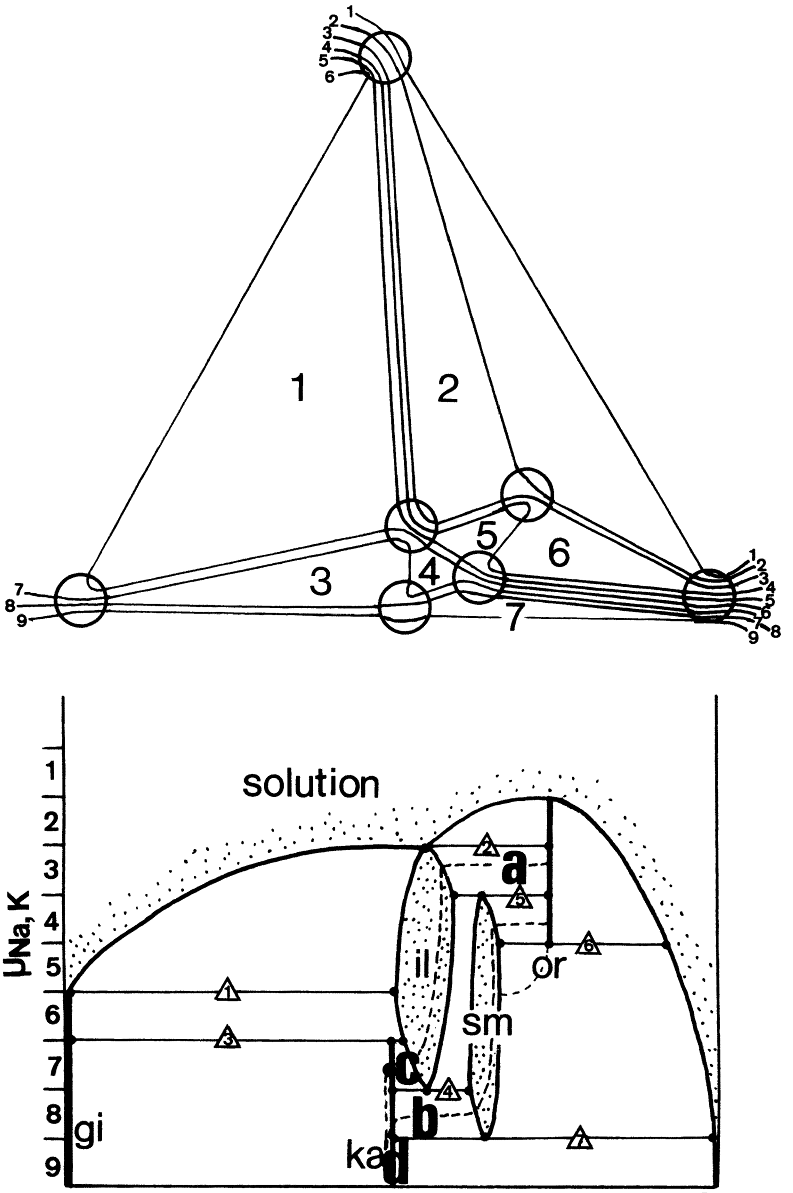


Fig. 3.39. Derivation of the $\mu_{Na,K}$–Si–Al phase diagram using the 9 equipotentials (see text for detailed explanation). *Abbreviations* are identical to those used in Fig. 3.38. Triphased assemblages are indexed by *numbers in triangles*; compositions of phases in triphased assemblages are indicated by *dots*. Solutions and solid solutions are represented by *dotted areas*. The chemical domains of the different microsystems are indicated by letters: *a* contact; *b* alteroplasma; *c* pedoplasma; *d* clay deposits on fracture walls. Alteration processes are indicated by downward trajectories, *stippled lines*, which converge toward a monophased kaolinite assemblage

the reactions do not necessarily occur at the same equipotential but they will be near one another. Thus the general relations of the diagram are the probably correct, but some of the details are not established.

In the potential–composition representation we can fix the position of illite in the presence of orthoclase as a function of Si–Al content from the chemical data (electron microprobe analyses). Also the existence of illite in contact with kaolinite is known. Therefore, the illite–smectite boundary is fixed by the smectite composition. The composition of the smectite at the illite–smectite–orthoclase boundary is fixed by the maximum Si content of illite found in this assemblage. The extension of the smectite composition to the silica-rich side of the diagram is not established, nor is the alumina content of illite in the presence of gibbsite. However, it is clear that the compositions of both illite and smectite become more aluminous as the chemical potential of alkalis decreases.

If we assume the phase diagram to be correct, it is possible to make a certain number of general deductions concerning the behavior of minerals and solutions in which they occur. In the instance of the first stages of alteration, i.e. where the solution just penetrates the magmatic minerals and is therefore almost in equilibrium with the previously formed clay minerals present, the composition of the solution is alumina-rich with respect to the mineral. This is seen in the series of solution–solid curves in the upper part of the diagram. The muscovite–orthoclase contacts are active because the muscovite buffers the K^+ to H^+ ratio of the solution at a level where orthoclase is no longer stable. Illite, the siliceous low-temperature equivalent of muscovite, crystallizes. The quartz–orthoclase contacts are not active because the buffering effect of muscovite does not exist. The solution reaches equilibrium with orthoclase.

Once the solution is buffered by the active clay minerals, the change in the Si/Al content is less important, but there is still a tendency to lose silica. The active part of the system, excluding quartz, becomes one in which the clay minerals illite, smectite (vermiculite) and kaolinite control the Al/Si content of the solution. In this zone, the chemical potential of alkalis is at an intermediate value. If we assume that the system is in the late stages of weathering, the initial solutions are dilute in the content of all dissolved solids. If quartz remains inactive, the tendency for the system will be to produce the next more siliceous mineral from the assemblage illite–smectite–kaolinite which is present. In the zone of lowest chemical potential of alkalis, this phase is kaolinite. If one recalls the mineralogy of the fracture zones in the rock, one finds that kaolinite is the only clay mineral present. Thus, in the situation of dilute solutions, one finds a monomineral assemblage. However, this might simply be due to the fact that the quartz will not react rapidly enough to buffer the assemblage.

The fact that the saprolite pedoplasma contains the assemblage illite + kaolinite, indicates that there is a general loss of silica in the weathering sequence, since the bulk composition of the granite should initially lie somewhere in the area between orthoclase and muscovite, excluding the inactive quartz component. Thus it is evident that the loss of silica is gradual but persistent throughout the process of granite alteration in a temperate climate.

As a counter proof of the correct choice of the alkali chemical potential as the chemical component which is an intensive variable, we can attempt to construct the phase diagram using the Si component as the intensive variable, keeping the alkalis as extensive variables. This analysis is presented in Fig. 3.40.

It can be seen immediately that the first phase to be found in such a situation, at maximum silica chemical potential in solution, will be the smectite mineral. As one will remember, the first mineral to form was seen to be the illite mica. Thus the representation of silica as the intensive variable is not correct.

Chemical Potential–Chemical Potential Representation

The most conventional method of representing the clay mineral assemblages found to be modified by aqueous solutions, is one of chemical potential against chemical potential (or the ratios of these values in some cases). The arguments for the use of potential–composition diagrams in the case of the granite weathering in temperate climate conditions have been given. However, other conditions prevail for surface alteration processes in the tropics where soils and altered rocks tend to form mono-mineral zones as horizons instead of veins, as in temperate climates. The most intense weathering, forms concentrations of gibbsite at the surface which grades into kaolinitic zones (Nahon 1991). Boulangé (1984) has further identified a smectite-rich zone at the base of the kaolinite zone. This horizon is much smaller in extent, centimeters, compared to the normally plurimetric sequences of kaolinite. Here, there is a good evidence that the system is guided by a multi-chemical potential variability where probably only the alumina is an inert, extensive variable. If we transpose the diagram of alkali potential–composition into coordinates of silica potential and alkali potential, we obtain the result as given in Fig. 3.41.

Again, it is assumed that all of the phases are stable over the common ranges of pH found in granite weathering. In the figure, the reaction boundaries are shown as curved lines. It is certain that phase reactions between minerals of variable composition will produce curved phase boundaries (Garrels 1984; Meunier and Velde 1986). However, those presented here could not be calculated due to a lack of chemical data, since not all of the mineral compositions are known for the different reaction boundaries in the granite system under study. It seems reasonable to omit the details for the time being. The topology is correct, respecting the interdiction of a phase-boundary intersection of an invariant point at a sector angle of more than 180°. The applicability of the diagram to weathering in tropical zones has been mentioned. In the case of the weathering in a temperate climate, only the open fissure zones found throughout the profile will be adequately described by such a diagram.

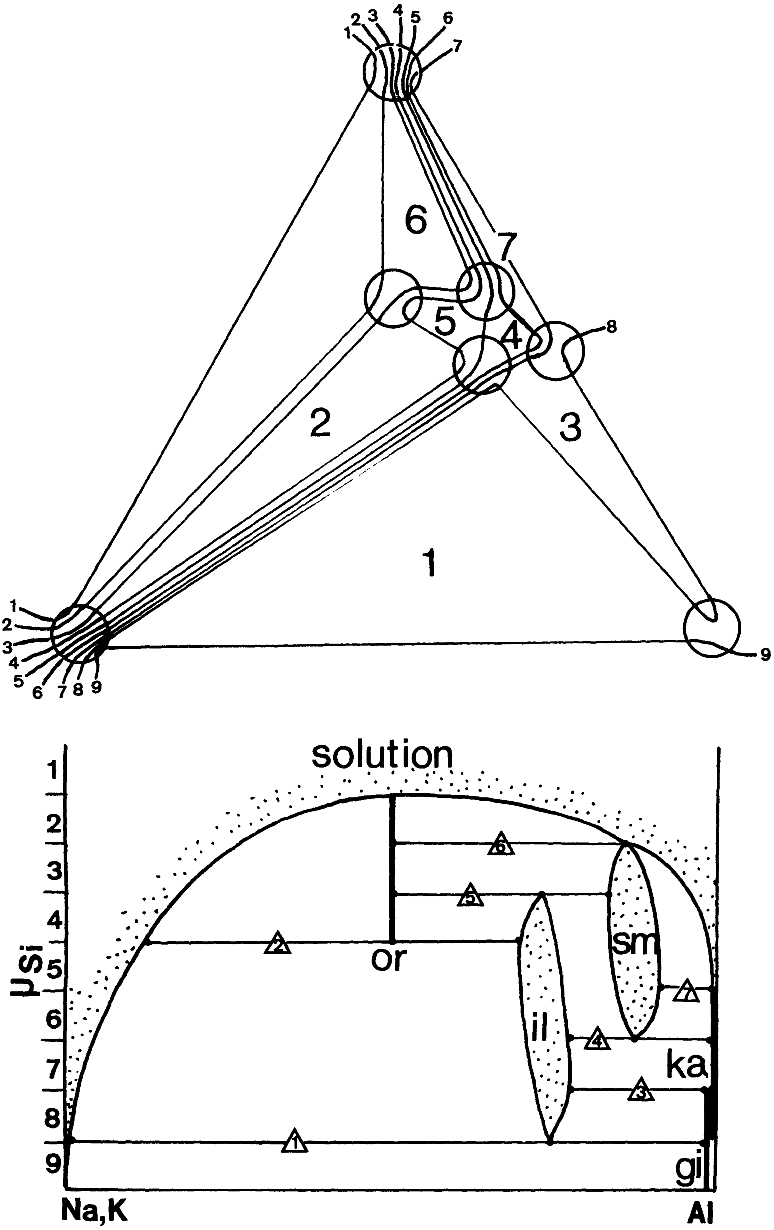


Fig. 3.40. Derivation of the µSi–Al–Na,K phase diagram using the 9 equipotentials (see text for detailed explantion). Abbreviations are identical to those used in Fig. 3.39. Triphase assemblages are indexed by *numbers in triangles*; composition of phases in triphase assemblages are indicated by *dots*

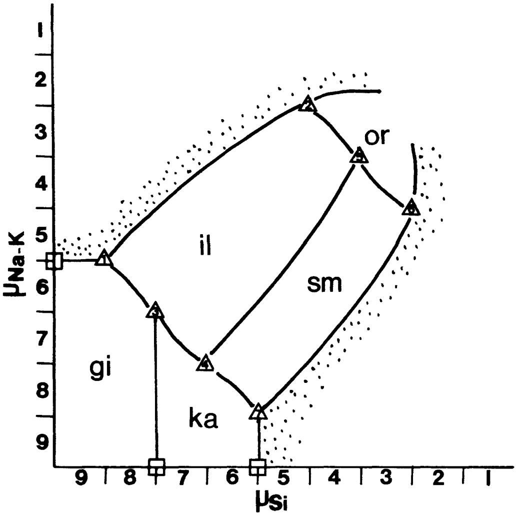


Fig. 3.41. Construction of the μ_{Si}–$\mu_{Na,K}$–Al phase diagram by combination of the $\mu_{Na,K}$–Si–Al and μ_{Si}–Al–Na,K phase diagrams represented in Figs. 3.39 and 3.40 respectively. Triphase assemblages are indexed by *numbers in triangles*. The shape of the curved tie-lines is hypothetical

Reaction paths for tropical weathering will be as follows: the unsaturated water which enters the upper profile will form either kaolinite or gibbsite, depending on which minerals are present in the soil, illite or smectite. If silica activity is very low, illite could transform into gibbsite. However, the normal succession is from kaolinite to gibbsite. Thus the initial minerals must be in equilibrium with a solution which is richer in silica. In the initial stages of weathering, in the rocks at points of microfracturing, the first reaction upon dilution of a solution in equilibrium with orthoclase will be to form either mica (illite) or smectite. Exact reaction paths can only be determined with more information concerning the precise mineral assemblages. The final product of granite weathering in tropical conditions is a soil composed of Al and Fe oxides and hydroxides; Al and F^{3+} being the remaining inert components in the system. This new material was shown to be sensitive to water activity by Trolard and Tardy (1989). The variation of compositions of oxides and hydroxides was calculated and presented in a μ_{H_2O}–Al–Fe^{3+} diagram.

3.3.1.3 Summary

It is apparent that a complete sequence of phase diagrams can be constructed on the basis of the mineral compositions found in the active part of an alteration sequence. The relative order, in the altering sequence, in which each reaction takes place will determine the position of the phases in a hierarchy of equipotential lines. Observed mineral assemblages will relate the phases in compositional space. The equipotential lines must follow the tie-lines between the minerals. Such tie-lines are established by petrographic observation aided by X-ray micro-diffraction (Rassineux et al. 1988).

It has been seen that the weathering reactions of granite under temperate climate are best represented in the alkali chemical potential versus Si–Al composition coordinates. The potential–potential type of diagram is best employed in cases of weathering in tropical zones or highly drained areas where mono-mineral horizons (or nearly so) are encountered. In the case of weathering under temperate conditions, the lateral inhomogeneity gives various assemblages which indicate local control of the solutions by the silicates present.

3.3.2 Soil Clays Developed on Granite Saprolite in the Temperate Zone

Because they are young soils in which the transformation of initial minerals into clays is far from complete, clay transformation in soils of the temperate zone is certainly a difficult case to study. Moreover, granite (but also sedimentary rocks or superficial deposits) contains phyllosilicates such as mica and chlorite, the structures of which are very similar to those of clay minerals. Thus, it is often very difficult to distinguish inherited fine-grained phyllosilicates from clay minerals that formed in place. However, it is a frequent case encountered in Europe and North America. In these areas soils have been intensively cultivated for centuries and are subjected to pollution from farming or industrial activities. Studies of the nature and properties of clays from these soils should be done to answer properly the environmental problems facing the industrialized countries, even if the clay mineralogist would have preferred more academic examples.

The methodology presented above for studying weathering must be modified for the study of soils. Indeed, if the aim is the same (how mineral reactions proceed?), the particular structure of the soils and the very small size of most of the minerals (less than 10 μm) do not allow us to apply exactly the same sequence of analytical procedures. Direct observation of reaction sites under microscope is nearly impossible. Thus, the basic technique to employ is the fractionation of the material in different size classes. Each class is composed of polyphase mineral assemblages which can be accurately determined using mathematical decomposition of the complex bands of X-ray diffraction diagrams.

3.3.2.1 Methodology

Clay formation in the temperate zone will be exemplified by a detailed study of clays from a soil developed from granite saprolite in the western part of the Massif Central, France (Righi and Meunier 1991). The soil is a typical Cambisol i.e. a soil with slight morphological differentiation, it is a good example of those encountered in granitic areas and, can be described as follow:

Soil Description

0–8 cm: *A12*, very dark greyish-brown sandy loam, strong, very fine-granular structure, friable, many medium and fine roots, bleached sand grains, few granite gravels, diffuse smooth boundary.

8–15 cm: *A2*, dark yellowish-brown sandy loam, weak, fine-granular structure, friable, common fine roots, few granite gravels, clear smooth boundary.

15–25 cm: *Bw*, dark yellowish-brown sandy loam, weak, subangular blocky structure, friable, few medium roots, granite gravels, diffuse wavy boundary.

> 25 cm: *C*, yellowish-brown sandy loam, weak, subangular blocky structure, friable, gravely, few roots.

The soil pH is about 5, cation exchange capacity (CEC) is low, ranging from 8 to 18 $\mathrm{cmol_c kg^{-1}}$ (1 $\mathrm{cmol_c kg^{-1}}$ = 1 meq/100 g), organic carbon content is rather high, up to 6% in the A1 horizon. The clay content (2 μm) increases upward from 5 to 13% from the C to the A1 horizon. This clearly shows that clay is formed in the soil, other sources of clays, such as wind deposition or colluviation being negligible. Moreover, Fig. 3.42 shows that the clays that formed are predominantly fine sized clays (<0.2 μm).

Another interesting point is the increase in citrate-bicarbonate-dithionite (CBD) extractable iron, which represents iron as oxy-hydroxides. In the soil and parent rock (granite) iron is mainly present in silicates. The weathering of these iron-bearing primary minerals produces amorphous (short-range ordered) Fe-oxy-hydroxides which generally occur adsorbed onto the clay particle surfaces, and which are extractable by the CBD treatment. Therefore, an increase in the amount of CBD extractable Fe measures the increase in weathering of Fe-bearing silicates.

Extraction and Preparation of Soil-Clay Samples

The clay fraction (<2 μm) is separated from the bulk soil sample by sedimentation following destruction of organic matter with hydrogen peroxide and removal of the Fe-oxyhydroxides with CBD. The whole clay fraction is then

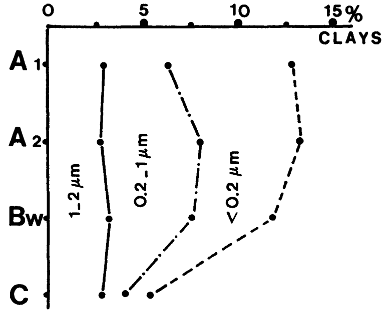


Fig. 3.42. Proportion of total clay in the 1–2 μm, 0.2–1.0 μm and <0.2 μm fractions in the different horizons of a soil

subjected to size fractionation according to the following sizes: <0.1 μm, 0.1–0.2 μm, 0.2–1.0 μm, and 1–2 μm. Size fractionation allows one to separate newly formed soil clays, generally very fine, from their precursors which have larger sizes. The 2–5 μm and 10–20 μm silt fractions are also investigated as characteristic of the inherited minerals.

Moreover, within the coarse fractions, magnetic separation allows the separation of Fe-bearing phyllosilicates, such as biotite and chlorite, from quartz, feldspars and muscovite. The combination of particle-size fractionation with magnetic separation, leads to fractions that contain only phyllosilicates; this is an important step for their further study. For example, a soil sample that contains quartz, feldspars, muscovite, chlorite and clay minerals can be separated in a fine fraction (<0.2 μm) that contains only the clay minerals. Quartz, feldspars, muscovite and chlorite (inherited from the rock) are collected in a coarse fraction. From this coarse fraction, chlorite can be isolated by magnetic separation and subjected to specific investigations.

X-Ray Diffraction: Identification of Minerals

In the silt and coarse-clay (1–2 μm) sub-fractions, the phyllosilicates inherited from the granite saprolite are identified by X-ray diffraction. These minerals are mica, chlorite, vermiculite and interstratified mica/vermiculite and chlorite/vermiculite. Vermiculite and interstratified minerals originate from early stages of the alteration of biotite (a granite-forming mineral).

A series of X-ray diffraction diagrams obtained from subfractions of decreasing size is given in Fig. 3.43. For the finest subfractions, X-ray diffraction produces broad and overlapping bands instead of sharp and separated peaks found in the coarse fractions. Thus, a special treatment of the diffraction signal must be used to improve the reading of the diagrams. The broad bands are decomposed into elementary curves, using a microcomputer program (DecompXR, Lanson and Besson 1992). When the decomposition program is used, it is evident that the soil clays studied here are a complex mixture of three to five individual phases. However, a clear trend of evolution can be seen.

3.3.2.2 Observations

A complete description of decomposed XRD diagrams from the A1 clay subfractions is now given in order to illustrate how one can work with this complex material.

Coarse Clays. in the range of 4–11° 2θ, only two major reflections are obtained from the 1–2 μm subfractions. They are attributed to mica (1 nm) and vermiculite (1.4 nm) respectively, these two minerals being inherited from the saprolite. The peak of mica is decomposed into two curves, one very sharp, indicative of a well-crystallized mineral, the second, broader and less

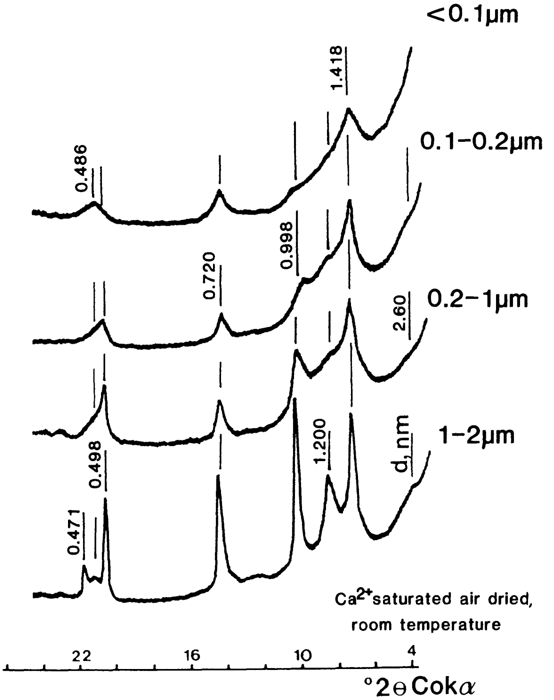


Fig. 3.43. X-ray diffraction diagrams for clay fractions of decreasing particle size for the top horizon of the soil studied. Smectites are found at 1.42 nm, mica or illite at 0.99 nm, mica/vermiculite mixed layers at 1.20 nm, and kaolinite at 0.72 nm

intense, indicating less material and some interstratification of vermiculite with mica.

Fine Clays. compared to the coarse-clay fraction, the pattern of the XRD diagrams from the fine fractions (<1 µm) are different. These diagrams give four or five basic curves instead of two. From the 0.2–1 to the <0.1 µm subfractions the following changes are observed (Fig. 3.44):

1. The sharp peak at about 1 nm, still present in the 0.2–1 µm subfractions, disappears from the finer fractions. Only the second broad mica band, present as a smaller band in the coarse fraction, persists, but its position is shifted toward 1.02 to 1.07 nm and its width is increased;
2. A peak at about 1.20 nm shows increased intensity and decreased width from the 0.2–1 to the <0.1 µm subfractions;
3. A peak at about 1.40 nm becomes the most intense peak in the finest fractions. In the 0.2–1 and 0.1–0.2 µm subfractions, the 1.40 nm reflection is made of two basic curves with either a large or a small width. This indicates the presence of two types of vermiculite particles, one with few layers in the stacking sequence (large width) the other with a better ordered stacking (small width);
4. Smectite layers, or interstratified minerals with a smectitic component (basic curve with a maximum of intensity at about 1.60 nm), are observed in the <0.1 µm subfraction only;

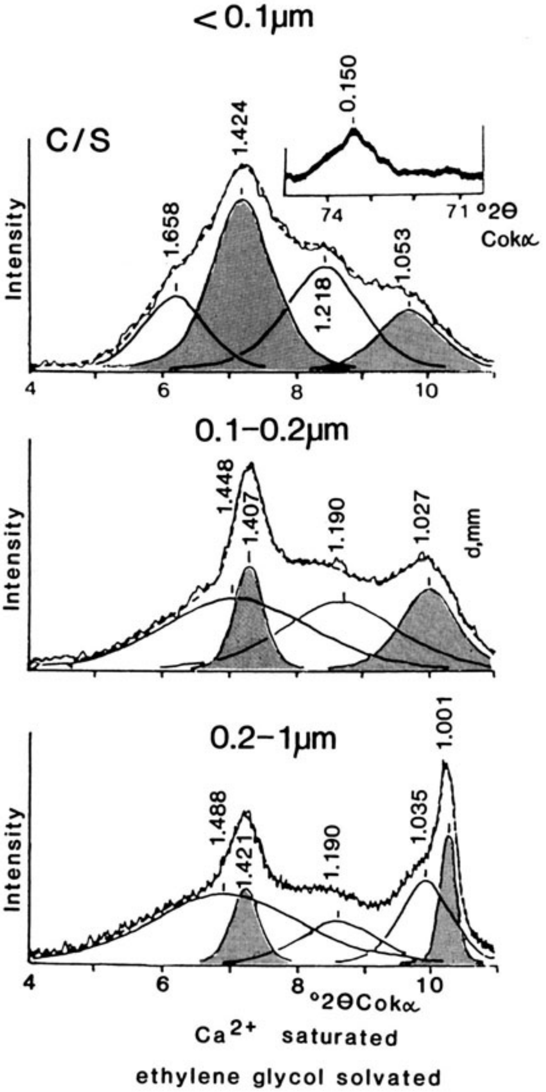


Fig. 3.44. X-ray diffraction patterns of the fine clay fractions. Diagrams show decomposition peaks for the multiphase assemblage. Smectites are found at 1.658 nm, vermiculite at 1.424 nm, illite/vermiculite mixed layers at 1.218 nm and illite at 1.027 nm, < 0.1 µm subfraction: 060 band at 0.150 nm for dioctahedral minerals

5. A rather strong peak at 2.38 nm is present in the <0.1 µm subfraction indicating the presence of an ordered interstratified mica/vermiculite (first-order reflection).

The same general trend is observed for the sub-fractions from the A2 and Bw horizons, except for the finest subfractions from the Bw horizon in which the relative intensity of the peak at 1.40 nm is greater than for the equivalent A1 horizon sample (less smectite and more vermiculite layers in the Bw sample than in the A1 sample). All the <0.1 µm subfractions contain mainly dioctahedral minerals as indicated by a broad reflection near 0.150 nm.

3.3.2.3 Clay Genesis in Temperate Acid Soils

The silt and clay fractions from the C horizon contain chlorite as individual particles, or clustered or separated layers, within interstratified minerals. Compared to the C horizon, the proportion of chlorite layers in the A1 horizon is much reduced in the fine-silt fraction (2-15 μm). Moreover, chlorite has totally disappeared from the coarse clay of that horizon (1–2 μm), but it is found in the finer-clay subfractions (<1 μm). The same remark can be made for the mica/vermiculite-interstratified and vermiculite layers. These are present in the fine-silt fractions but have disappeared from the coarse clays of the A1 horizon. The distribution pattern of the mica layers in the different subfractions is quite the opposite: as they are the major component of the A1, 1–2 μm subfractions, their proportion progressively decreases with the subfraction size. Thus, it is deduced that the large particles of chlorite, mica/vermiculite and vermiculite layers are preferentially affected by mechanical fragmentation and dissolution. This results in the concentration of more resistant mica layers in the coarse clay subfractions. Weathered residues of chlorite, mica/vermiculite and vermiculite are accumulated in the fine clays.

This can be seen at the scale of a single clay particle using high resolution microscopy. Figure 3.45 shows a complex clay particle made of mica layers associated with vermiculite and chlorite mixed layers. The mica core is apparently unweathered, whereas the chloritic and vermiculitic mixed layers are partly dissolved, leaving smaller residual particles which were analyzed in the fine clay fraction by X-ray diffraction. Mica cores are recovered mainly in the coarse clay fraction.

Within the fine-clay fraction, if one makes the assumption that the finest subfractions are also the most weathered, the changes from the 0.2–1 μm to the <0.1 μm subfractions indicate that weathering proceeds via the transformation of mica layers through mica/vermiculite and vermiculite layers. Smectite layers are finally formed in the finest subfraction as end products of the mineralogical evolution.

3.3.2.4 Composition and Properties of the Subfractions

Cation Exchange Capacity

CEC varies from 8.5 $\mathrm{cmol_c kg^{-1}}$ to 34.4 $\mathrm{cmol_c kg^{-1}}$ and increases from the large to the fine fractions (Fig. 3.46). A good agreement is found between the mineralogy of the subfractions, their K_2O content and CEC values. XRD shows a decrease in the proportion of mica layers, from the large to the fine subfractions, whereas the proportion of interstratified, vermiculite or smectite layers increases. This is consistent with the decrease in the K_2O content and the increase in the CEC. Thus, soil evolution induces the formation of fine clays with an increased CEC.

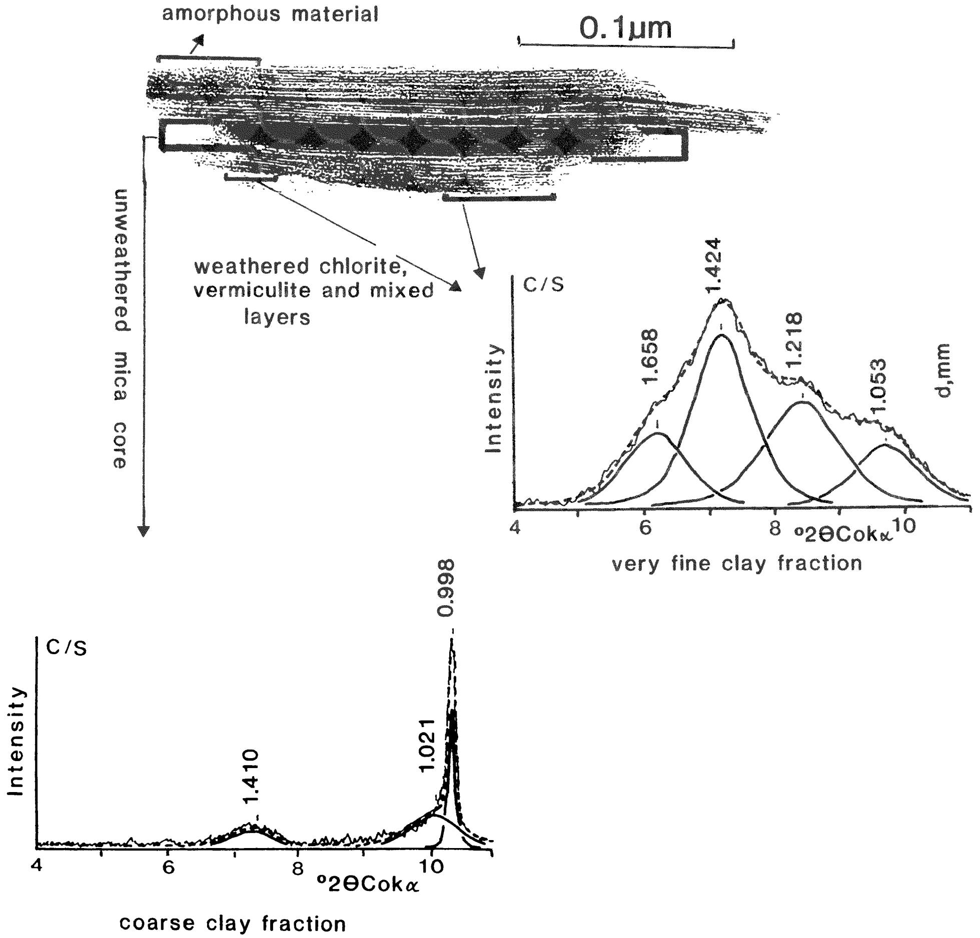


Fig. 3.45. Preferential weathering and fragmentation of chlorite, vermiculite and mica/vermiculite or mica/chlorite mixed layer minerals in a complex particle. Smectites found at 1.658 nm, vermiculite and/or chlorite at 1.424 nm, illite/vermiculite(or chlorite) mixed layers at 1.218 nm, illite at 1.053 nm (broad band) and mica at 0.998 nm (sharp band)

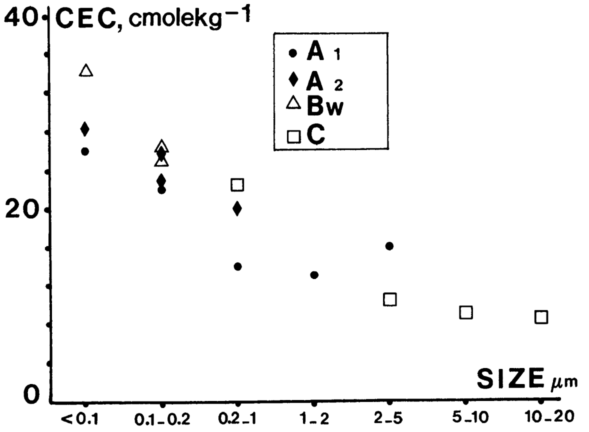


Fig. 3.46. Cation exchange capacity (CEC) for clay and silt fractions in different horizons of a soil profile

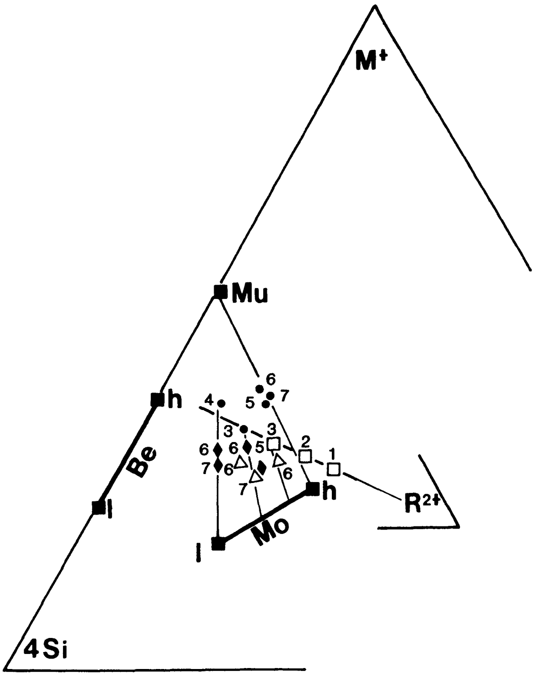


Fig. 3.47. Chemical composition of the separated fractions of different horizons in a soil profile, as plotted in a ternary system MR^+–4Si–R^{2+}. *Squares* C horizon; *triangles* Bw horizon; *diamonds* A_2 horizon; *dots* A_1 horizon. *Numbers* represent size fractions: *1* 10–20 M, *2* 5–10 µm, *3* 2–5 µm, *4* 1–2 µm, *5* 0.2–1 µm, *6* 0.1–0.2 µm, *7* <0.1 µm

Chemical Composition

The chemical analyses of the silt and clay fractions are plotted in the M^+–4Si–R^{2+} ternary system (Fig. 3.47) but, because XRD shows that both the coarse and the fine fractions constit of more than one phyllosilicate species, the chemical analysis of such a fraction represents the bulk composition of the mixture. In the diagram, the chemical analyses of the silt and coarse-clay fractions are distributed along a line joining the R^{2+} pole at one side and the composition of a high–charge beidellite at the other side. However, the high-charge beidellitic pole is not reached. Interpretation of Fig. 3.47 confirms the mechanism of preferential dissolution of the vermiculite and chlorite layers, leaving a residue consisting of K-depleted, charge-reduced mica layers with essentiall Al in the octahedral sheet, seen as the sharp 0.99 nm peak in Fig. 3.45.

The chemical compositions of the fine clay subfractions from the Bw and A2 horizons are distributed along several lines joining the composition of montmorillonite in the M^+–4Si–R^{2+} diagram, indicating a change in the weathering pathway. The decrease in the layer charge and increase in the Si atom content are the new directions involved. Each transformed coarse mineral seems to produce a montmorillonite with a layer charge dependent upon its composition. The composition of the fine clays from the A1 horizon are different from the others. They are on a line joining muscovite and high-charge montmorillonite. This could be due to a greater contribution of weathered dioctahedral micas in these fractions.

Evidence for Hydroxy-Interlayered Minerals

In acid soils, the interlayers of vermiculite or smectite are often occupied by non-exchangeable contaminants, these being hydroxy-Al, Fe or Mg polycations. Such clays are known as intergrade or hydroxy-interlayered minerals (Jackson 1963; Barnhisel and Bertsch 1989). Evidence for interlayered contaminants is generally obtained by heating the K-saturated clay sample to increasing temperatures: 110, 300, 550 °C. In response to the heat treatment, interlayered contaminants induce a progressive and incomplete collapse of the interlayers. This results in an asymmetric XRD peak enlarged toward the small 2θ angles. This is observed with the clays in this study; the collapse of the interlayers is progressive and, even after heating to 550 °C, incomplete for all the samples. An improved identification can be done using decomposition of the diagrams, as shown in Fig. 3.48.

For the coarse clay (1–2 µm) subfractions, decomposition of the diagrams gives a sharp curve, with its maximum intensity at about 1 nm, attributed to completely collapsed interlayers. A broad curve with its maximum at about 1.04 nm is associated with the 1.00 nm sharp curve. The intensity of this broad curve increases from the coarse to the fine fractions where it is prominent. Moreover, a third curve, centered at slightly higher *d*-spacings (1.08 to 1.11 nm), is an important component of the XRD diagrams of the finest subfractions. These curves are attributed to interstratification of minerals having either collapsed or uncollapsed interlayers with hydroxy-contaminants. These appears to be more abundant in the finest subfractions.

A chemical treatment (Na-citrate) can be performed to extract interlayered hydroxy-Al (or Fe) contaminants. XRD diagrams of the treated samples are compared to those of the corresponding untreated sample. If interlayered materials are extracted, the collapse of the mineral is greatly improved. The composition of the extract can be analyzed, giving information about the nature of the interlayered materials. When this done on the Bw, <0.1 µm subfraction (Fig. 3.48) only a small decrease in the relative intensity of the 1.09 nm peak is observed and the diagram for the sample which was K-saturated and heated to 550 °C is still strongly asymmetrical: the interlayered material is poorly extracted. For the A1, <0.1 µm subfraction an improvement of the collapse is observed, but the diagram is still asymmetrical (Fig. 3.49). However, compared to the Bw, <0.1 µm subfraction, the effect of the treatment is greater for the A1, < 0.1 µm subfraction. Moreover, the XRD behavior of the glycolated samples from either the A1 or Bw, <0.1 µm subfractions is different. Compared to the untreated sample, the proportion of swelling layers (1.65 nm) is strongly increased in the A1, <0.1 µm subfraction. This is an indication that most of the interlayered material is extracted by the treatment.

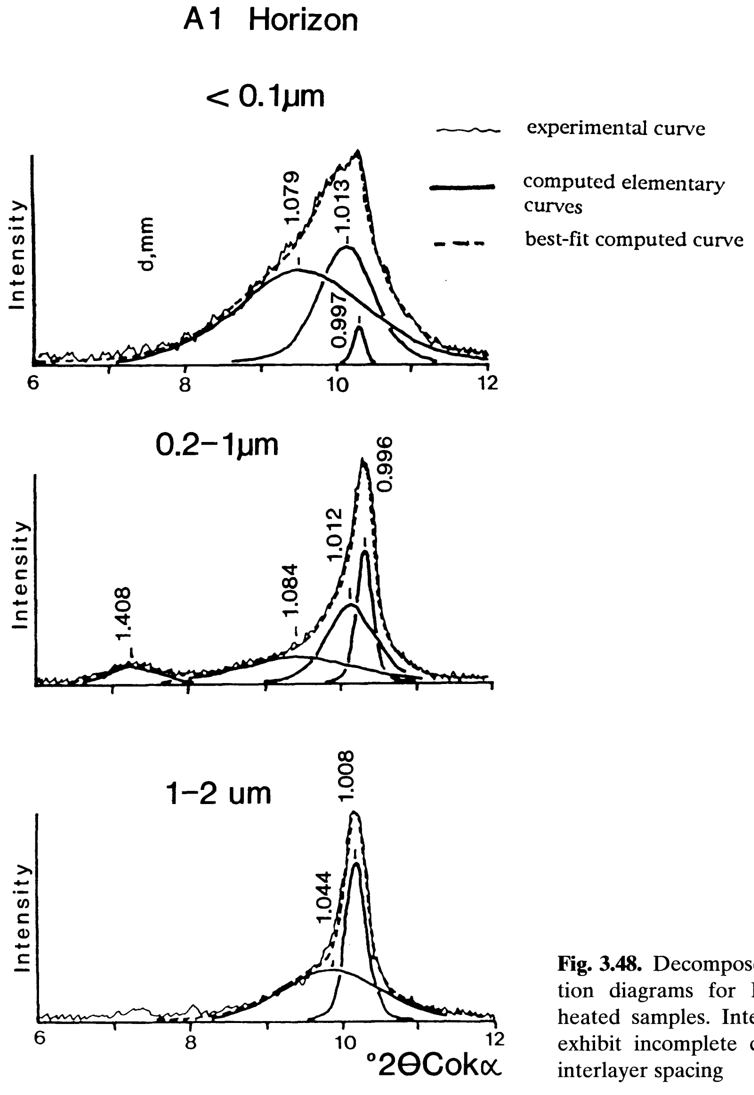
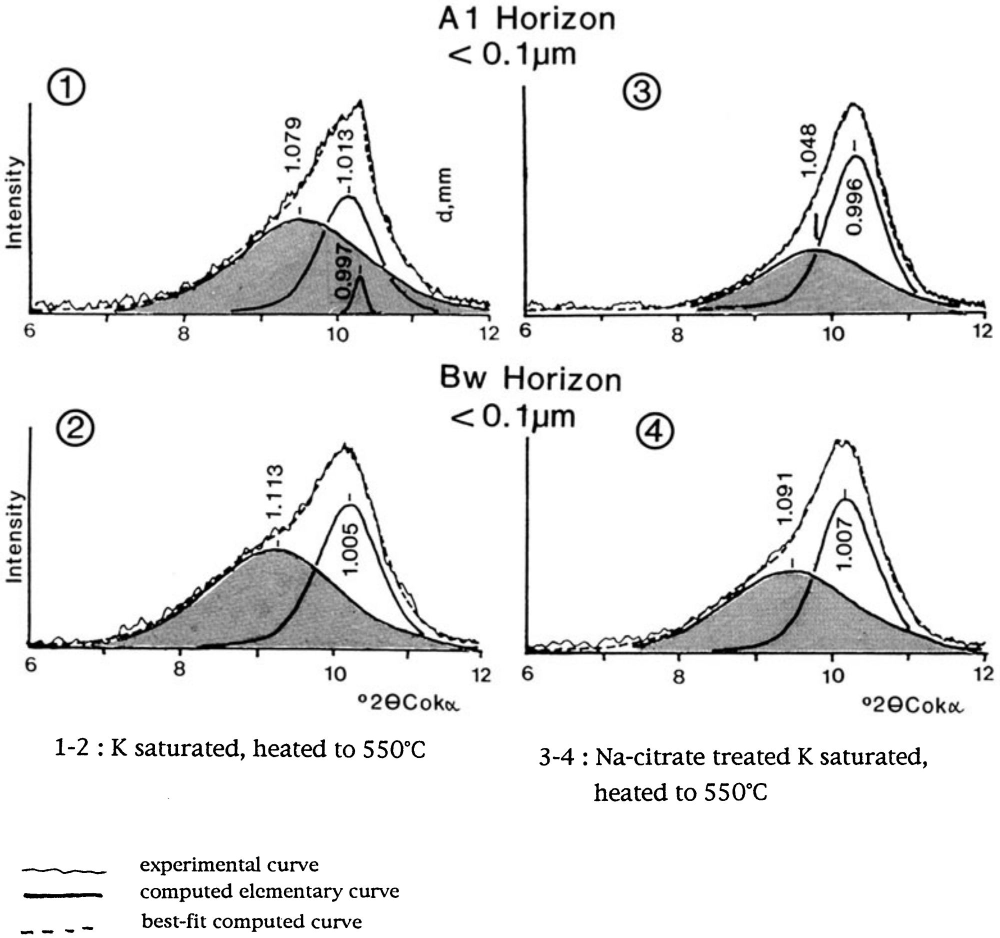


Fig. 3.48. Decomposed X-ray diffraction diagrams for K-saturated and heated samples. Intergrade minerals exhibit incomplete collapse to 1 nm interlayer spacing

The composition of the extract is also different according to the sample from which it is obtained. From the Bw, <0.1 µm subfractions large amounts of MgO (30% of total MgO) are extracted together with Al_2O_3 and Fe_2O_3. Conversely, only small amounts of MgO are extracted from the A1 subfraction. As the interlayered material is quite well extracted from the A1 sample and, as the extract contains almost exclusively Al and Fe, it is presumed that hydroxyl-Al and Fe are the interlayered materials in this sample. Despite the fact that Fe and Al are extracted from the Bw horizon at the same levels as from the A1 horizon fraction, only slight changes are observed in the XRD behavior of the treated Bw sample. A large part of the interlayered



1-2 : K saturated, heated to 550°C

3-4 : Na-citrate treated K saturated, heated to 550°C

experimental curve
computed elementary curve
best-fit computed curve

Fig. 3.49. Decomposed X-ray diffraction diagrams for K-saturated and heated samples before and after Na-citrate treatment which extracts the interlayer hydroxy-Al contaminants

compounds is apparently not extracted. Compared to the A1 fraction, far larger amounts of Mg are extracted from the Bw fraction by the Na-citrate treatment. This is the result of partial dissolution of chlorite layers. The poorly crystalline parts of the minerals are dissolved by the treatment which, however, does not result in its conversion to vermiculite. Therefore, it is likely that a chloritic mineral with a more or less stable brucite interlayer is a component of the Bw fine-clay fraction. As the Na-citrate treatment does not selectively dissolve the interlayered hydroxide sheet, the remaining undissolved minerals may contribute to the XRD intergrade behavior still observed for the treated sample.

In conclusion, the origin of the intergrade minerals in the finest subfractions, either from the A1 or the Bw horizons, appears to be quite

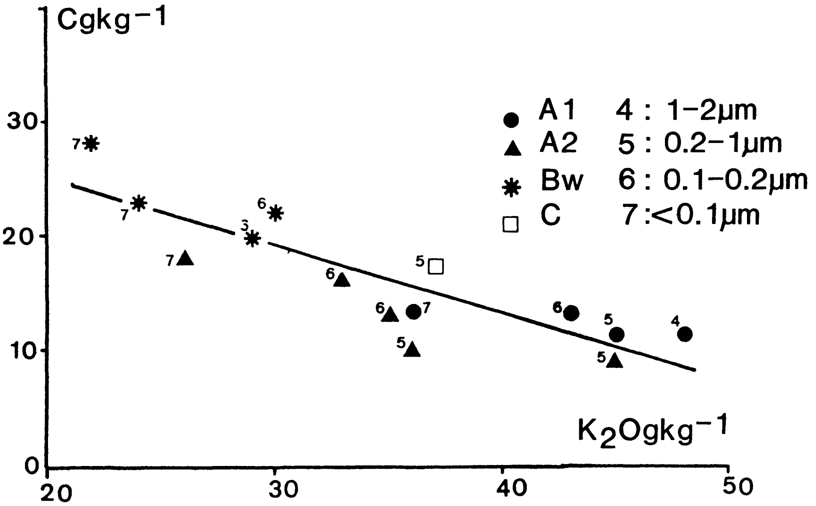


Fig. 3.50. Organic carbon resistant to peroxidation vs non-exchangeable K_2O for separated size fractions. *Cgkg*$^{-1}$ organic carbon per kg soil

different. In the A1 horizon this fraction is identified mainly as a hydroxy-Al (Fe) intergrade smectite that may have been derived from the weathering of mica layers. In the Bw horizon, the major component is an intergrade vermiculite originating, at least in part, from chlorite layers. These differences are likely to be linked to the physico-chemical conditions which prevail in the horizons; the A1 horizon being more acid and richer in organic matter than the Bw horizon. In strongly acid and organic soils, chlorite may be completely dissolved, whereas when soil is weakly acid and poor in organic matter it transforms to vermiculite.

Evidence for Clay-Organic Complexes

Even after extended treatment with hydrogen peroxide, soil clay samples may still contain rather large amounts of organic carbon (Theng et al. 1986; Schnitzer et al. 1988). For example, organic carbon was found in the clay sample described above. There is a clear negative correlation between the K_2O and organic carbon content (Fig. 3.50). As shown by the XRD study, these clays are a mixture of mica (illite) and vermiculite or smectite, i.e. minerals with no K in the interlayers but hydrated exchangeable cations. So, the decrease in K_2O content means a decrease of the proportion of mica (illite) layers and an increase in vermiculite or smectite layers. The fact that the organic carbon content increases as the K_2O content decreases is a strong indication that organic carbon is associated with vermiculite and smectite and is probably located in the interlayers of these minerals.

3.3.2.5 Conclusion

Clays in a soil which has developed from a granite saprolite under temperate climate originated largely from the mechanical fragmentation of pre-existing phyllosilicates, the clays produced from weathering of feldspars being far less abundant in soils than in the weathered granite. Phyllosilicates are granite forming minerals (e.g. muscovite, biotite) or are produced by alteration. Vermiculite was produced by weathering of biotite in the saprock. Chlorite was formed at an early stage by hydrothermal alteration of biotite. Kaolinite produced by granite weathering is found in the soil but only as a minor component of the clay mineral assemblage.

In the soil, the mechanical fragmentation of inherited phyllosilicates preferentially affects chlorite and vermiculite (Fe-bearing minerals). Consequently, chlorite residues, with a typical XRD pattern of intergrade minerals, are the major component of the fine clays in the deeper soil horizon (Bw). In the surface horizon (Al), where weathering is more aggressive, a greater contribution of pre-existing dioctahedral micas is observed in the formation of fine-clay soils. These micas are mica/vermiculite, mica/smectite or vermiculite/smectite interstratified minerals. These clays also contain interlayered materials that would not be residual brucite layers, such as is found in the Bw horizon but hydroxy Al (or Fe) polycations. Figure 3.51 illustrates schematically the evolution of muscovite, vermiculite and chlorite in an acid soil.

3.3.3 Summary of Weathering Effects

Mineral reactions in weathered profiles and soils occur within a few types of microsystems: grain contacts, alteroplasma, pedoplasma, fissures and soil aggregates. In these microsystems the local water/rock ratio and the chemical composition of primary mineral both control the clay phases that are formed by weathering. Contact and plasmic microsystems are rather closed systems with low water/rock ratios. Thus, the formation of the new clays is essentially controlled by the local chemical conditions which are dictated by the altering mineral chemistry: for instance, illite grows at the mica-orthoclase grain contacts, a high-potassium medium. Given the importance of rock chemistry, we will look in detail at the clays formed in weathering profiles of several rock types (Sect. 3.4). The profiles to be studied are all in the same temperate climates. Soil microsystems are totally open. They are directly exposed to climatic wetness fluctuations and the clay minerals formed are largely controlled by local water/rock ratios. Consequently it will be more convenient to describe clays of pedogenetic formation in various climatic conditions later (Sect. 3.5).

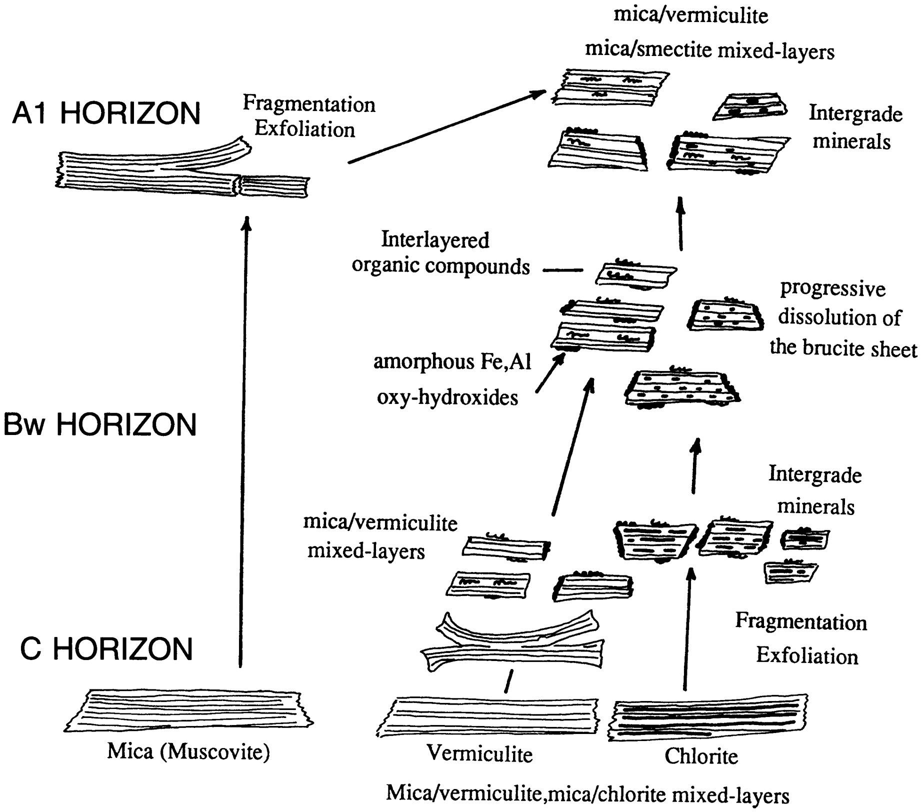


Fig. 3.51. Schematic evolution of primary phyllosilicates in an acid soil

3.4 Clays Formed During Rock Weathering

The granite example has provided a pattern of the weathering mechanism. The question is to know if this pattern is applicable to any rock whatever its particularities. Several profiles of magmatic, metamorphic and sedimentary rocks will be presented here, in order to show the effects of the chemical and mineralogical properties of the parent rock on the formation of the weathered profiles. Some examples were chosen because of their high contrast in chemical or mineralogical compositions with granites: e.g. Fe, Mg-rich crystalline rocks and clay-bearing sedimentary rocks.

3.4.1 Weathering of Basic and Ultrabasic Rocks

3.4.1.1 Weathering Profiles

In temperate climates, the weathering profiles which have developed on basic (amphibolite, gabbro) and ultrabasic rocks (serpentinite, peridotite) normally

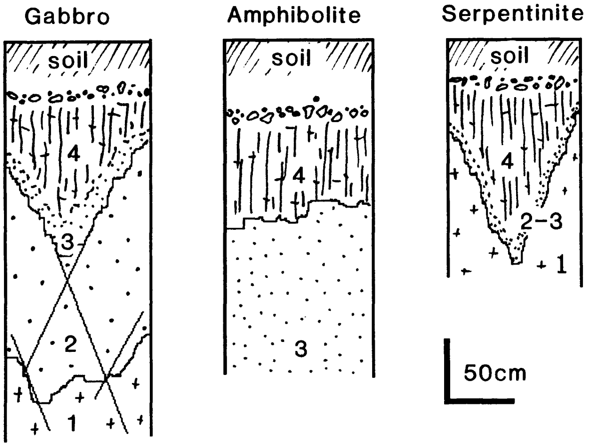


Fig. 3.52. Schematic representation of weathering profiles developed on basic to ultrabasic rocks. *1* Unaltered rock; *2* saprock; *3* saprolite; *4* clay-rich horizon with prismatic structure. (Ducloux et al. 1976; Ildefonse 1980; Proust 1983)

show four distinct zones: *1* altered coherent rock; *2* saprock; *3* saprolite; *4* prismatic level (which is a neo-structured clay-rich level under the soil) (Ducloux et al. 1976; Proust and Velde 1978; Ildefonse 1980; Fontanaud 1982; Proust 1983). These profiles are usually 1 to 3m thick (Fig. 3.52).

In tropical countries, such profiles frequently reach several tens of meters in thickness and produce large oxide and hydroxide deposits (Trescases 1973; Nahon and Colin 1982; Nahon et al. 1982; Delvigne 1983; Colin 1984; Boukili et al. 1983). Excepting amphiboles (hornblende), the major primary minerals, in such rocks are anhydrous; e.g. calcic plagioclase, pyroxenes (CPx and OPx), olivine and magnetite. However, most of these minerals are partialy or totally transformed during hydrothermal alteration or low-grade metamorphism events into hydrated phases; e.g. chlorite, antigorite, talc. Both hydrous and anhydrous phases react under weathering conditions to produce clay minerals associated with oxides or hydroxides.

The weathering processes appear to be strongly dependent on the initial structure of basic to ultrabasic rocks. Altered profiles of macrocrystalline rocks (gabbros, amphibolites, lherzolites) have a similar organization to the granite profile, but those developed on serpentinite are obviously different. We shall distinguish these two kinds of rocks in spite of the fact that their chemical compositions are quite similar from the alteration view point.

3.4.1.2 Weathered Macrocrystalline Basic Rocks

As is the case for granitic rocks, the weathering process of basic rocks operates in microsystems. Contact microsystems dominate in the altered coherent rock level, producing saponite (hornblende–chlorite contact) or Fe-beidellite (plagioclase–actinolite contact). In the saprock, the great contrast in composition between the coarse-grained primary phases leads to the juxtaposition of different microsystems, producing the alteroplasma inside the primary minerals. The secondary phases which crystallize are controlled by the chemical composition of the mineral host: aluminous clays are found in plagioclase (dioctahedral vermiculite, beidellite, halloysite); Al–Fe–Mg clays in amphiboles (trioctahedral vermiculite, saponite); Mg–Fe clays in pyroxenes and olivines (talc, saponite, Mg-rich gels). In the saprolite, the collapse of the original rock structure induces the reorganization of mineral assemblages. As a consequence, the local contrasts of chemical composition tend to be reduced. New secondary clay phases appear (di- and trioctahedral vermiculites) while the pre-existing ones such as saponite or chlorite/vermiculite mixed-layer change in chemical composition. The clay content becomes high enough to provoke the formation of prismatic structure. New clay minerals crystallize: Al and Fe^{3+}-rich smectites + kaolinite in the saprolite of weathered aluminous amphibolite profiles; Mg-trioctahedral vermiculite or Mg gels + nontronite in saprolites developed on magnesian rocks (gabbro, peridotite).

In open fractures which are found everywhere in the profiles (fissural microsystems), no magnesian clay phases are observed. Whatever the chemical composition of the parent rock, the secondary phases produced are nontronite or Fe-beidellite associated with large amounts of Fe-oxide. Weathering parageneses are summarized in Table 3.3 (as the parental chlorite weathers to chlorite/vermiculite mixed layer, the secondary product is considered to be vermiculite for simplification of phase analysis).

3.4.1.3 Weathered Macrocrystalline Ultrabasic Rocks

The weathered profiles developed on ultrabasic rocks are organized differently according to the size and crystalline structure of the parent minerals. In the case of a macrocrystalline rock which is partly or not serpentinized, such as the lherzolite studied by Fontanaud and Meunier (1983), the saprock represents about half of the profile thickness (decimeters). The early alteration stages are controlled by chemical microsystems. The initial serpentinized lherzolite is composed of clinopyroxene, calcite, chrysotile, spinel and some orthopyroxene relicts. Two alteration stages can be distinguished in the saprock. The first weathering reaction is: pyroxene → talc + Fe-oxide + Si and Ca in aqueous species. Talc is a highly siliceous and magnesian low-temperature phase. At this stage, chrysotile and calcite remain unweathered. The second weathering reaction is the formation of saponite at the expense of pyroxene, talc and chrysotile. Calcite is dissolved and spinel is oxidized, but the initial structure of the rock is still conserved. Saponite is highly magnesian and Fe-rich. The new assemblage shows a bulk composition poorer in R^{2+} ions than the previous one. There is a tendency to form a single-silicate phase assemblage in the saprock, because most of the Fe ions remain in the ferrous state and behave similarly to magnesium; Fe^{3+} is fixed in oxides.

Table 3.3. Weathering reactions in different macrocrystalline basic rocks. These examples all contain hydrous, high-temperature minerals, as is commonly the case. The minerals which react and their reaction products are indicated

	Amphibolite	Amphibolitized gabbro	Serp. lherzolite	Serpentinite
Altered coherent rock (contact microsystems)	Horn + Chl → Sap And + Chl → Kaol	Labr + Act → Fe-Beid		
Saprock (alteroplasma microsystems)	Horn → Sap And → Kaol (Halloy) Chl → Chl/Verm3	Labr → Verm2 + Zeol Act → Ta + Nont + Ox	OPX + CPX → Ta + Ox Ta + Chry → Fe-Sap Spinel → Ox	Chl1 + Antig + Talc → Nont + Chl2
Saprolite (pedoplasma microsystems)	Horn → Verm2 + Verm3 And → Kaol (Halloy) Chl → Chl/Verm3	Act → Verm3 Labr → Verm2 + Fe-Beid Plasma → Verm3	OPX + CPX → Fe-Sap	Chl1 + Antig + Talc → Nont + Chl2
Prismatic clay-rich Horizon (solifluxed pedoplasma microsystems)	Horn → Verm2 + Fe-Beid And → Kaol (Halloy) Chl → Verm3 Plasma → Verm3	Plasma + Verm3 → Fe-Beid + Ox	Plasma → Al-Sap + Nont	Chl2 + Nont → Corr
Fissure coatings (fissural microsystems)	Nont + Fe-Beid	Fe-Beid + Ox	Nont (Fe-Gel) + Ox	

In the upper neo-structured clay-rich zone, a new assemblage appears. It is composed of aluminous saponite and nontronite which form big flakes. As oxidation of Fe progresses, a bi-phased clay mineral assemblage crystallizes in which each phase fixes preferentially one or other of the two inert components (Al and Fe^{3+}). Fissures in the saprock and the restructured zones are filled by a Mg–Fe^{3+}–Si gel and Fe-oxides; saponite becomes unstable. At this stage, the oxidation of Fe ions is total and the Mg loss is at its maximum. It is highly probable that aluminous saponite recrystallizes into nontronite via a concentrated solution phase in which the gel precipitates. Nontronite can then be formed as Harder (1976) showed. For simplification, because the gel is a metastable phase, nontronite will be considered here as the stable one (Table 3.3).

In summary, the important parameters which control the mineral reactions occurring during the weathering of ultrabasic rocks are μ_{Mg} and the oxidation of Fe^{2+} ions. Their individual effects are difficult to distinguish since the decreasing of μ_{Mg} is concomitant with the oxidation increase during the weathering process. Nevertheless, these parameters are independent: μ_{Mg} is an intensive variable wheras the oxidation modifies the Fe^{3+} composition of the microsystems (inert components).

3.4.1.4 Phase Diagrams

The bulk chemical composition of basic to ultrabasic rocks depends on the relative proportions of five major elements; Si, Al, Mg, Ca and on Fe (whose valence state changes with oxidation). Chemical mass balance calculated for each weathering profile shows that the variation in silica content is quite low from unweathered rock to the prismatic level and that the less soluble elements (Al and Fe, when in the Fe^{3+} state) are concentrated in the solid phases. Calcium and magnesium are the most exported elements in surface waters (Barnes et al. 1967, 1978; Tardy 1969; Barnes and O'Neil 1971; Nesbitt 1974; Pfeiffer 1977). However, there is an important difference between calcium and magnesium. Indeed, they can both fill the exchangeable sites in the interlayer of expandable secondary phases but only Mg is fixed in the crystalline lattice of most of the secondary phases (talc, saponite, vermiculite). As a consequence, the Mg activity in solution and the oxidation of Fe^{2+} ions are the determinant variables for the crystallization of the dioctachedral or trioctahedral clay phases. Therefore, it is possible to reduce the chemical composition of the solution-rock system to a three component one: Mg–Al–Fe.

When plotted in the Mg–Al–Fe system, the chemical composition domains of the weathering minerals do not overlap in spite of extended solid solutions. For simplification, it should be noted that, kaolinite and iron oxides, which have very low Fe for Al substitutions, are represented by the Al-pole and the Fe-pole of the diagram respectively. Taking the amphibolitized gabbro

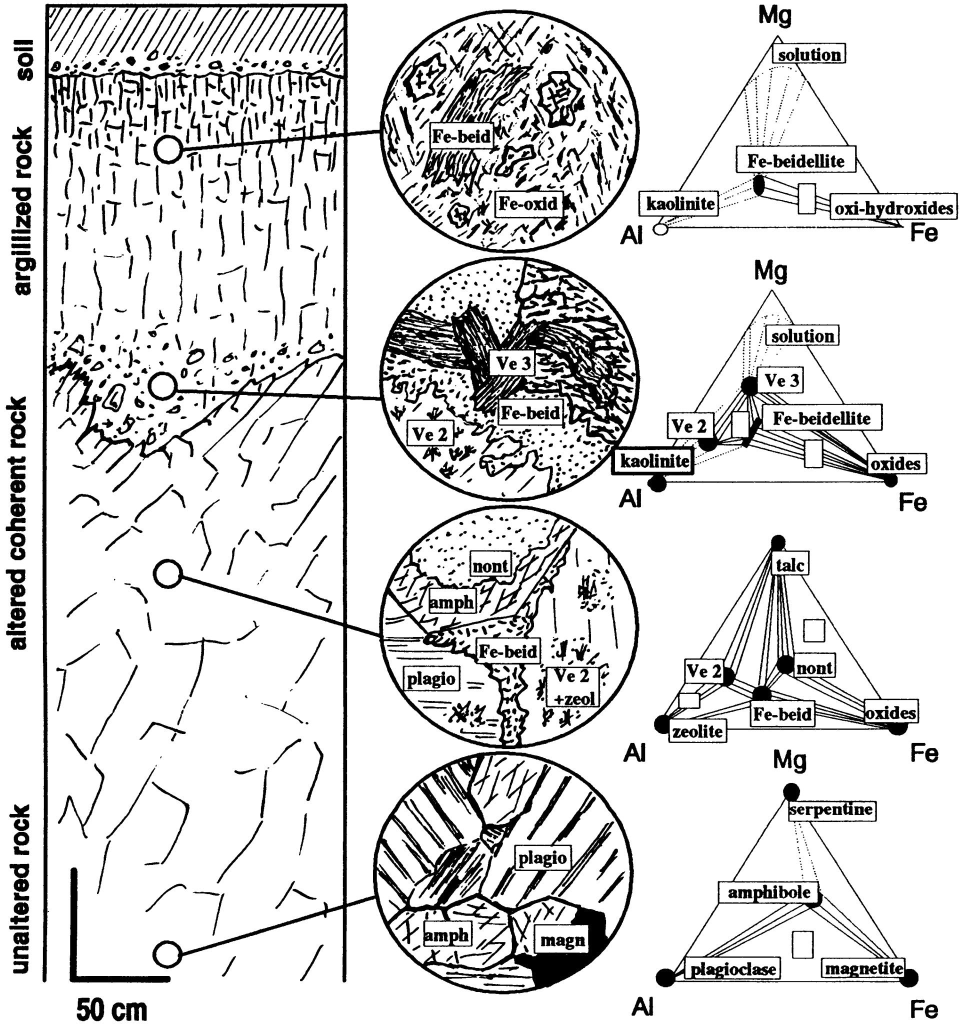


Fig. 3.53. Weathering profile on a gabbroic rock (Ildefonse 1980). Detailed petrographic views were drawn from microphotographs; the diameter represents 400 µm. Primary and secondary mineral assemblages are represented by *open rectangles* in phase diagrams (the choice of the Mg–Al–Fe system is explained in the text). No purely magnesian solid phase was identified in the argillized horizon; the Mg-pole is represented by solutions

from Le Pallet (Ildefonse 1980) as an example, the sequence of alteration minerals is represented in Fig. 3.53.

A general phase diagram (no mobile components) can be drawn considering the stability or instability relationships between phases as observed in thin sections from different weathering profiles developed on macrocrystalline rock (Table 3.3; Fig. 3.54). Applying the phase rule for a three-inert-component system, the maximum number of coexisting phases will be three; conse-

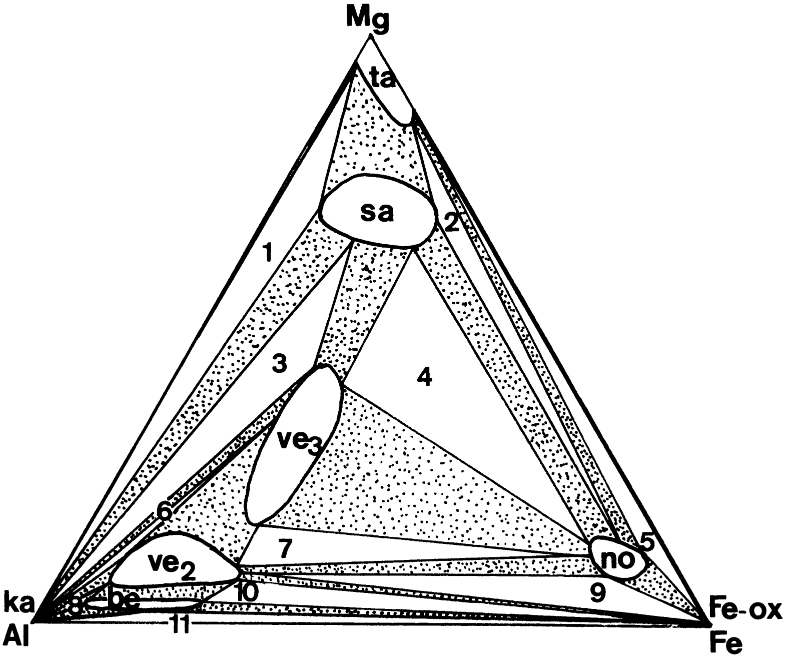


Fig. 3.54. Phase diagram depicting the relationships between secondary minerals crystallizing in weathered basic to ultrabasic rocks in the Mg–Al–Fe chemical system. Triphase assemblages are indexed from *1 to 11*. Biphase assemblages are represented by *dotted areas*. *ta* talc; *sa* saponite; *ve_3* trioctahedral vermiculite; *ve_2*: dioctahedral vermiculite; *be* beidellite; *no* nontronite; *ka* kaolinite; *Fe-ox* iron oxides or hydroxides

quently subdivisions of the Mg–Al–Fe diagram must be sub-triangles. These sub-triangles are limited by tie-lines joining the composition domains of two stable coexisting phases (stippled area in Fig. 3.54).

The degree of opening of the dominating microsystems increases from altered coherent rock (contact microsystems), through saprock and saprolite (plasmic microsystems) to open fractures (fissural microsytems). Magnesium, which could be considered as an inert component (acting by its concentration) in the most closed microsystems, becomes an intensive variable in the open ones (acting by its chemical potential). In the first case, Mg concentration determines the weight of Mg phases; in the second case, Mg chemical potential controls the stability fields of secondary phases. Consequently, the Mg–Al–Fe triangular system is no longer adapted and must be replaced by the μ_M–Al–Fe phase diagram, which can be derived from the former using μ_{Mg} equipotentials.

The chemical potential of Mg ions in solutions (μ_{Mg}) varies from high to low values as alteration intensity increases. This is represented by the sequence of equipotentials from the Mg-pole (higher possible value) to the Al-Fe line (lower possible value). Portions of some equipotentials are determined by the observed parageneses: for example saponite–talc, saponite–trioctahedral vermiculite, nontronite–Fe-oxide. When all the observed parageneses are represented, complete equipotentials can be established (Fig. 3.55a). Then, the set of equipotentials is completed in order to respect the phase rule corollaries, i.e. the number of equipotentials (N_{eq}) is given by the number of tri-phased assemblages (N_{Tr}) by the relation: $N_{eq} = N_{Tr} + 2$ (Meunier and Velde 1979). Finally, a chemical potential–composition phase diagram can be derived by positioning the weathering phases according to their relative inert element contents (Al and Fe) and the μ_{Mg} range in which they are stable (Fig. 3.55b). We must keep in mind that the stability fields of the different phases observed in the profile are established in relative coordinates in such a diagram. Indeed, it can be surprising at first glance to see talc represented as a complete solid solution between the Al and Fe poles. Do not forget that Al and Fe ions are highly diluted by Mg ions (talc is represented here as the phase stable in the highest μ_{Mg} conditions): Al and Fe are contained in talc as traces.

The different mono or bi-phased secondary mineral assemblages are described by the μ_{Mg} trajectories for each primary mineral and for the secondary plasmic systems in the neo-structured areas (Fig. 3.55b). The trajectories are clearly distinct for Al-rich amphibolites, amphibolitized gabbro and lherzolite. In Al-rich amphibolites (23% Al_2O_3), kaolinite (or its hydrated equivalent: halloysite) crystallizes in the very early alteration stages. Its presence in the alteration system buffers the amounts of Al in amphibole secondary products. The two trajectories converge toward the kaolinite + Fe-beidellite assemblage which composes the reacting portion of the neo-structured areas (pedoplasmic microsystems). This buffering effect disappears in fissural microsystems where the unique stable phyllosilicate is the Fe-beidellite associated with Fe-oxides. Kaolinite becomes unstable in the highly diluted and highly oxidizing solutions which flow in open fractures. Indeed, Barnes and O'Neil (1971) shown that spring waters in ultrabasic massifs are supersaturated with respect to magnesian phases.

Alteration reactions in the amphibolitized gabbro differ from those described above because the parent rock is less aluminous (16% Al_2O_3). The more aluminous secondary phase produced in the weathering profile is a Fe-beidellite which appears in the altered plagioclase; kaolinite or halloysite were not observed. The destabilization of actinolite first produces a talc + nontronite assemblage. Nontronite is stable until large amounts of aluminum are dissolved by the dissolution of plagioclase. Then, the next stable phase is a trioctahedral vermiculite. At this alteration stage, the mechanical resistance of the rock collapses, producing a new material. The pre-existing clay phases (primary as well as secondary) are involved in another set of reactions which produce the final Fe-beidellite + Fe-oxide assemblage. This assemblage is also stable in the fissural microsystems.

The third rock (lherzolite) is very Al-poor (3% Al_2O_3). The first phyllosilicate to form during the earlier alteration stages is talc associated with Fe-

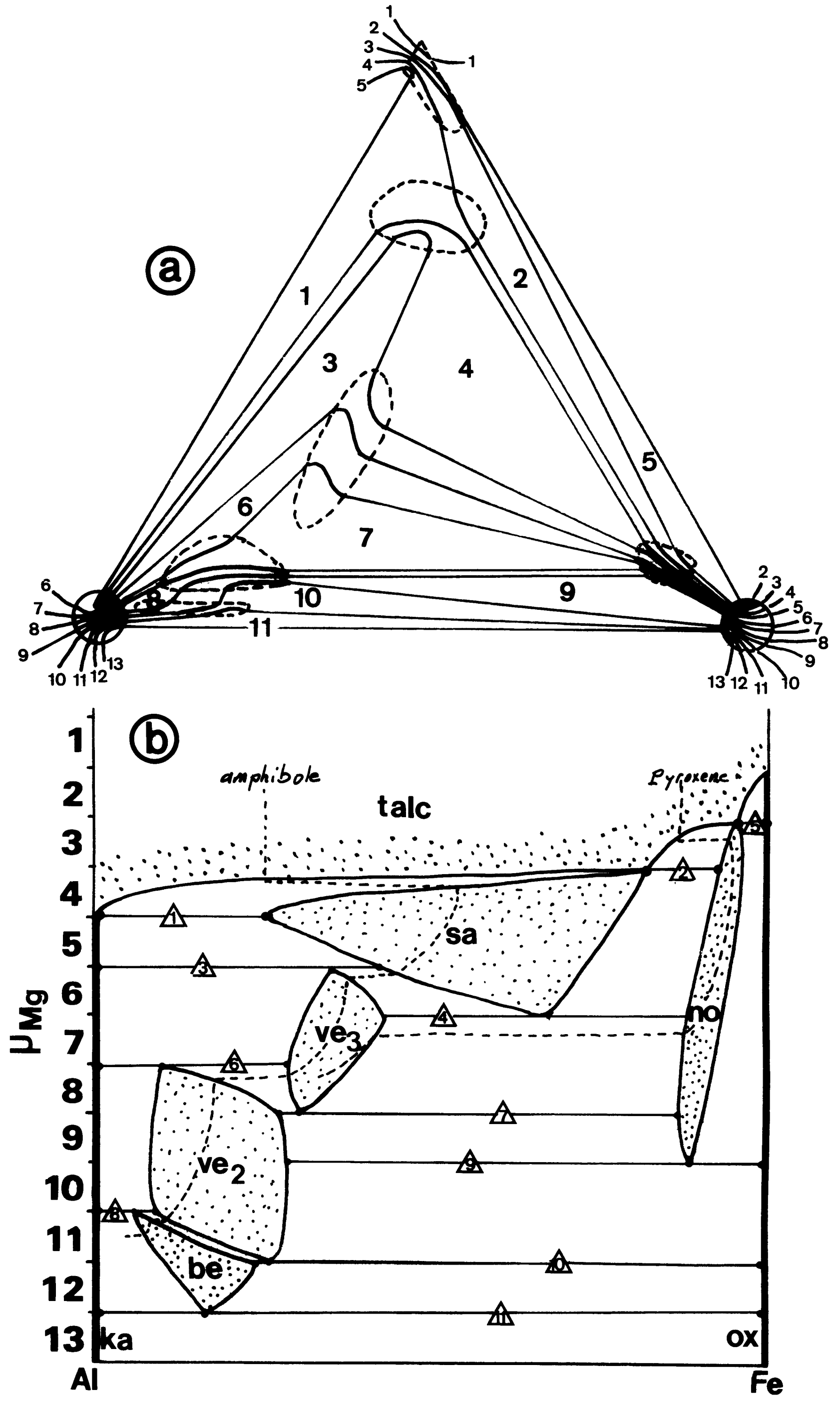


Fig. 3.55. Derivation of the Mg–Al–Fe phase diagram using the 13 equipotentials necessary to depict all the assemblages represented in Fig. 3.53. Triphase assemblages are indexed by *numbers in triangles*. Composition of minerals in the triphase assemblages are represented by *dots*. The sequence of mineral reactions due to amphibole and pyroxene are represented by trajectories in the μ_{Mg}–Al–Fe space (*stippled lines*)

oxides, because only the ortho-pyroxenes are reacting. Then, clino-pyroxenes are dissolved and saponite precipitates as the most aluminous secondary phase. The intense weathering in the upper horizons produces an abundant clay mineral fraction. The initial rock structure disappears. In these clay-rich levels, the iron oxidation increases with the dissolution of primary silicates and a new mineral assemblage is stable: saponite + nontronite. The Fe^{3+} bearing phases, nontronite (gel) + Fe-oxides, form the ultimate assemblage observed under temperate weathering conditions in the fissural microsystems.

3.4.1.5 Weathered Serpentinite

The serpentinite taken as an example here has a chemical composition close to that of the lherzolite: it is very poor in aluminum (less than 2% Al_2O_3). Nevertheless, in spite of such similarity, the weathering processes are completely different from that described above for two major reasons. First, the primary mineral size is frequently less to 1 mm. The minerals are intimately mixed and at a small volume scale (mm^3) the rock can be considered as homogeneous. Secondly, serpentinite is a phyllosilicate bearing rock which is composed of talc, serpentine, chlorite and chrysotile. Because of its homogeneity at small scale and the high reactivity of magnesian phyllosilicates in surface conditions, the rock appears to weather as a whole with no apparent microsystem effect at the thin-section scale (Fig. 3.56).

The rock is converted into a clay-rich horizon through a very narrow saprock of about 1–2 cm thick (Ducloux et al. 1976). A magnesian smectite (saponite) and a silica-rich secondary chlorite are produced in the thin zone

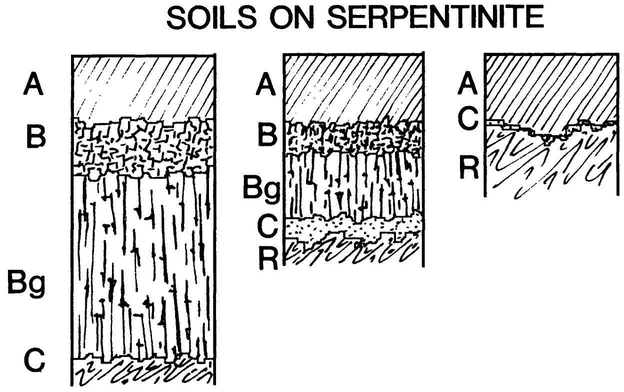


Fig. 3.56. Soil profiles observed on a weathered serpentinite (Ducloux et al. 1976). The illuvial horizon is composed of two parts showing a prismatic structure at the bottom (*Bg*) and a polyhedric one at the top (*B*). The thickest profile shown is formed on a fractured area; the two other profiles are formed on unfractured serpentinite at different slopes

where the internal destabilization of primary minerals does not change the parent structure (saprock). The saprolite is observed as a prismatic clay-rich horizon (about 50% day by weight). The magnesian saponite disappears and a ferric smectite (nontronite) becomes predominant in the <0.1 μm fraction. A secondary chlorite is still observed in the 0.1–2 μm fraction. In the upper part of the profile, the structure changes from prismatic to polyhedric (Fig. 3.56) and the clay fraction proportion decreases to about 30–40% in weight. The soil chlorite disappears and is replaced by a new Mg-rich and Al-poor phase, corrensite (ordered chlorite/vermiculite mixed-layer mineral). This suggests a reaction such as chlorite + smectite → corrensite + smectite, in which an overall balance in the Si–$3R^{2+}$–$2R^{3+}$ coordinates in maintained between the two pairs of alternate assemblages. Tie-lines between the two mineral pairs in Fig. 3.57 suggest this reciprocal relation.

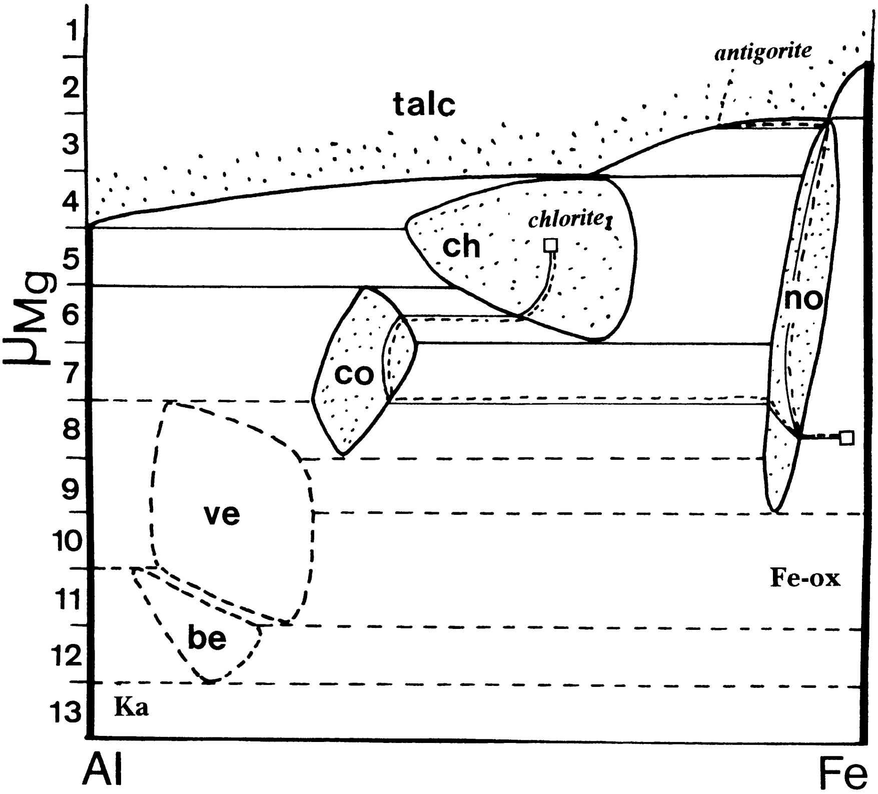


Fig. 3.57. Construction of a μ_{Mg}–Al–Fe phase diagram depicting the mineral relations in weathered profiles developed on serpentinite. *ch* Secondary chlorite; *co* corrensite (ordered chlorite/trioctahedral vermiculite mixed layer); *ve* dioctahedral vermiculite; *be* beidellite; *no* nontronite; *ka* kaolinite; *Fe-ox* iron oxides or hydroxides. The alteration process of the primary chlorite *chlorite I* and antigorite is controlled by two sequences of mineral reactions by which trajectories *continuous* and *stippled lines* in the phase diagram converge toward the nontronite + Fe-oxyhydroxide assemblage

The change in mineral assemblage in the polyhedric horizon is probably due to the decrease of Fe^{3+} content which stabilizes the corrensite at the expense of the pre-existing chlorite phase. The loss of iron is due to the presence of organic matter which reduces the Fe^{3+} ions to soluble Fe^{2+}. Weathering of serpentinite leads to an intense leaching of the dominant chemical components (Si and Mg) and to the oxidation of Fe^{2+} ions. The remarkable fact is the formation of Al–Fe^{3+} bearing secondary phyllosilicates in a rock which is very aluminum-poor (less than 2% Al_2O_3). Indeed, nontronite, as well as soil chlorite or corrensite, fix Al atoms in their crystalline lattice even when they are in such low concentrations in the system. Expandable magnesian clay phases (saponite and vermiculite) do not crystallize in the weathering profile because the chloritic phases (secondary-soil chlorite and corrensite) are stabilized by the high concentration of Mg ions in solutions. In spite of the fact that Si and Mg components are leached out from the profile, the reciprocal chemical balance between the iron-rich smectite and the chloritic phases suggests a relation which is found in chemical systems closed to chemical migration. Phase relations depicted in Fig. 3.55 must be modified as shown in Fig. 3.57.

In spite of the fact that it was impossible to observe directly the mineral reactions at the scale of a thin section, it is necessary to consider two different microsystems in order to depict the sequence of secondary parageneses as weathering increases: these are Al-depleted minerals (talc, serpentine, chrysotile) and Al-richer ones (chlorite). The reactions for both microsystems converge toward a final assemblage composed of nontronite + iron oxyhydroxides.

3.4.2 Weathering of Basaltic Rocks

Basaltic plateaus, tuff formations and ash deposits around volcanoes belong to the more fertile areas in the world because volcanic rocks are particularly unstable in surface conditions; glass is extremely reactive with water. Its dissolution is as intense as the reactivity surface is important: highly permeable ash deposits are much more rapidly transformed into soils compared to basalt flows. Soils on ash deposits are rich in organic matter; they belong to the Andosol class (Sect. 3.5). In spite of the high rate of their formation, andosols are never thicker than 2 m wheras soils on basalts are formed more slowly and become thicker (5–15 m). Because of the high reactivity of glass to ground solutions, there is no transition horizon between the fresh ash deposit and the soil. In contrast, weathering profiles on basaltic rock are frequently several meters thick and show an organization similar to those described on other crystalline rocks: saprock, saprolite and clay-rich zones (Fig. 3.58). There are however some differences due to the presence of glass and to the prismatic structure of basaltic flows (Ildefonse 1987).

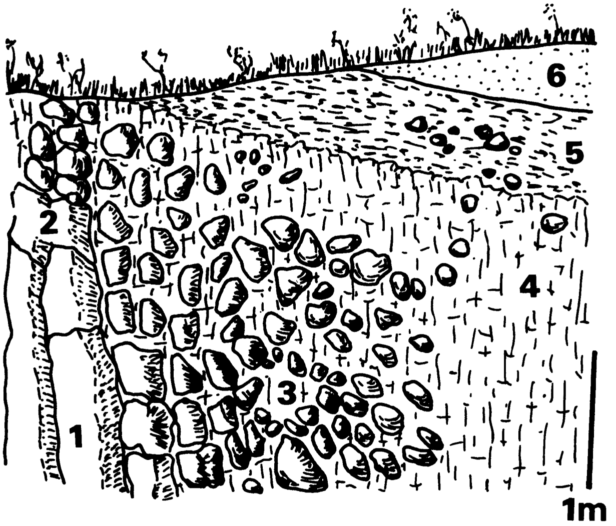


Fig. 3.58. Weathered profile on basaltic rocks at Belbex, France (Ildefonse 1987). *1* Unaltered prismatic basalt; *2* fractured basalt; *3* weathered basalt (ball-shaped coherent rock); *4* saprolite (polyhedral structure); *5* clay-rich horizon (lamellar structure); *6* allochthonous material

Usually, glass and olivine crystals in basaltic flows have been altered by hydrothermal alteration processes during the cooling period at the Earth's surface. They are partially or totally replaced by a microcrystalline clay mineral + Fe-oxide assemblage, classically identified as iddingsite (Eggleton 1984) Consequently, weathering reactions concern not only the primary minerals (unaltered olivine, pyroxenes and plagioclases) but also hydrated glass and hydrothermal alteration products. These components do not react at the same rate; some of them are transformed during the earliest stages of meteoric alteration, such as olivine, hydrated glass and hydrothermal products; others do not react until the rock becomes a saprolite (plagioclases and pyroxenes). Each primary component behaves as an individual microsystem, as it does in the case of macrocrystalline rocks. Chemical transfers operate between the different intracrystalline microsystems as early as the first alteration stages: for example, the weathering secondary products of olivine (saponite Fe-beidellite) contain Al ions which, of course, cannot be found in place but necessarily come from the neighbouring altered glass. Secondary parageneses are summarized in Table 3.4.

As happens in basic rocks, alkalis, silica and Mg ions are leached out during the weathering of basalts while Al and Fe^{3+} are concentrated in the upper intensely altered horizons. Celadonite, originating from hydrothermal alteration of glass, is replaced by a Fe-beidellite + halloysite assemblage through an intermediate series of celadonite/smectite mixed-layered minerals. The saponite–nontronite assemblage, originating from olivine hydrothermal alteration (iddingsite), is replaced by the Fe-beidellite + Fe-oxide assemblage.

Table 3.4. Weathering products in the alteration of basalt according to the alteration horizon. The host mineral and the associated weathering minerals are given

	Olivine	Hydr. Miner.	Glass	Labrador	Pyroxene	Fissures
Unweathered basalt	Iddingsite	Celadonite Fe-beidellite Halloysite	Hydrated glass	–	–	Calcite
Fractured basalt	Nontronite Fe-saponite Iddingsite	Fe-beidellite Halloysite Calcite	Hydrated glass Cryptocryst. minerals	–	–	Calcite
Saprock	Iddingsite Fe-beidellite Halloysite	Celadonite-smectite Fe-beidellite Halloysite	Hydrated glass Cryptocryst. minerals	Halloysite	Fe-beidellite Fe-oxides	Halloysite Fe-beidellite Fe-oxides
Saprolite	Fe-beidellite Halloysite	Halloysite	Halloysite	Halloysite	Fe-beidellite Fe-oxides	Fe-beidellite Halloysite Fe-Mn oxides
Clay-rich zones	Halloysite	+	Fe-beidellite	+	Fe-Mn oxides	

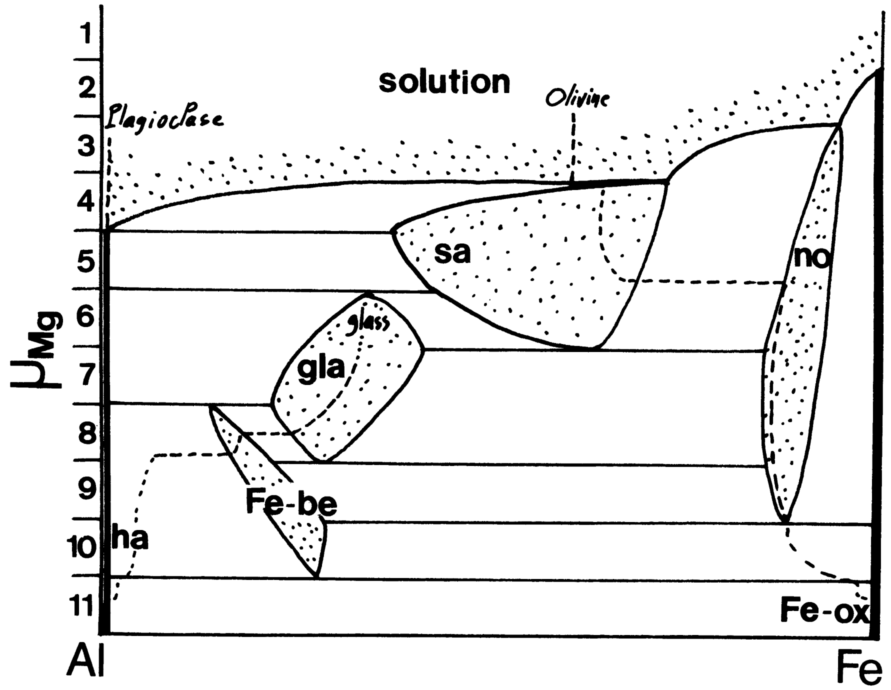


Fig. 3.59. μ_{Mg}–Al–Fe phase diagram depicting secondary mineral relationships in the weathered profile observed at Belbex, France (Ildefonse 1987). *sa* Saponite; *gla* glauconitic mixed layer; *Fe-be* iron-rich beidellite; *ha* halloysite; *Fe-ox* iron oxides or hydroxides. The alteration process of glass and olivine is controlled by a sequence of mineral reactions which end in a biphased halloysite + Fe-oxiyhydroxide (*stippled lines*)

The large homogenization of the rock operated in the neostructured clay-rich horizon leads to the formation of a triphased assemblage: Fe-beidellite + halloysite + Fe-oxides. The sequence of mineral assemblages from unweathered basalt to clay-rich horizons can be represented in a μ_{Mg}–Al–Fe phase diagram (Fig. 3.59). Trajectories are indicated for each individual microsystem; they converge downward to a triphase assemblage. Solutions flowing through fissural microsystems are diluted where μ_{Mg} reaches the lowest values in the profile. As a consequence of this, the stable assemblage is composed of only one phyllosilicate species which concentrates Al ions (halloysite) and an oxide phase which concentrates the Fe^{3+} ions.

3.4.3 Weathering of Clay-Bearing Rocks

3.4.3.1 Weathering of Glauconitic Sandstones

The weathering of glauconitic rocks was investigated by Loveland (1981) and Courbe et al. (1981) using petrographic techniques and, particularly,

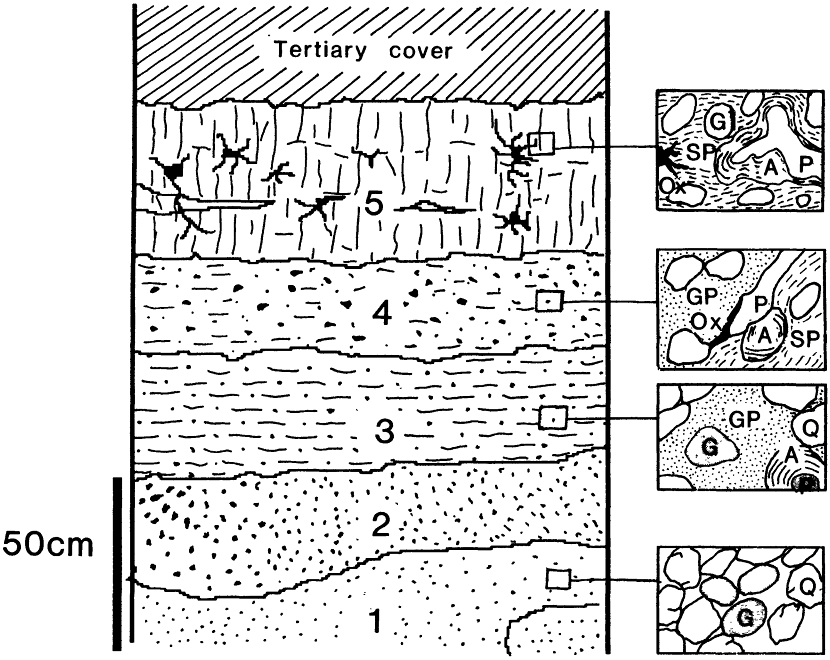


Fig. 3.60. Weathered profile developed on a glauconitic sandstone at Chacé, France (Courbe et al. 1981). *1* Unweathered green sandstone (30% glauconite); *2* reddish level (the initial structure of the sandstone is conserved); *3* transition zone where the sandstone structure disappears (about 10% clay minerals); *4* oxidized level (Fe-oxide concretions, 25% clay minerals); *5* clay-rich horizon (prismatic structure; 35% clay minerals)

microprobe analysis. In spite of the fact that profiles could be differently developed on limestones or sandstones because of large differences in porosity, the glauconite transformation under weathering conditions seems to be identical in all the cases. The weathering profile of Chacé, near Saumur (Maine-et-Loire, France) is taken as a representative example (Fig. 3.60).

The parent rock is a green fine-grained sandstone with 77.3% of the grains between 100 and 200 μm in diameter; glauconite, in rounded grains, represents about 30% in volume of the sand. In the earliest alteration stage, the rock appearance does not change but some of the glauconitic grains are replaced by a green plasma. On moving up the profile, the amounts of quartz and glauconite grains gradually diminish whereas the clay fraction increases and the color becomes reddish. Several active microsystems can be identified: altero-plasmic (internal destabilization of glauconite grains), pedoplasmic (formation of clay-rich areas in place of altered glauconites) and fissural (cutanes). Mineralogical investigations (XRD and electron microprobe microanalyses) show that glauconites are progressively transformed into a smectite + Fe-oxyhydroxide assemblage through illite/smectite mixed-layered minerals. The K_2O amount regularly decreases from unaltered glauconite

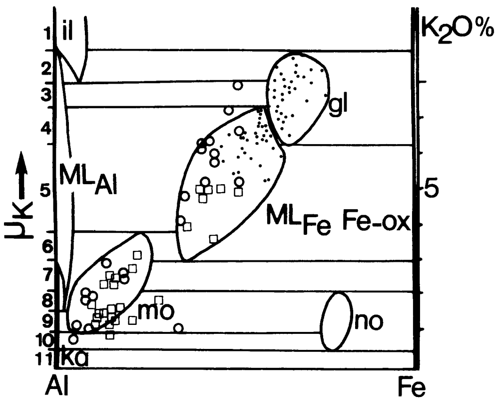


Fig. 3.61. Construction of a μ_K–Al–Fe phase diagram depicting the relations between secondary minerals in the weathered profile of Chacé. The correspondence between relative values of μ_K and K_2O in % weight is given by scales on the left and the right sides respectively. The position of analytical points (microprobe analyses) is indicated by *dots* (green glauconite grains in zone 1); *squares* (glauconitic plasma and cutans, zone 4); *circles* (glauconitic plasma and cutans, zone 5). *il* illite; *gl* glauconite; ML_{Fe} iron-rich mixed-layered phase; ML_{Al} Al-rich mixed-layered phase; *mo* montmorillonite; *no* nontronite; *ka* kaolinite; *Fe-ox* iron oxides or hydroxides

grains to coatings which are composed of kaolinite + Fe-oxide. This is shown in the μ_K–Al–Fe diagram (Fig. 3.61).

The clay fraction formed in the pedoplasmic microsystems is composed of a montmorillonite and nontronite, representing the aluminous and ferric poles respectively. In the highly permeable zones where cutans are observed, the smectites are no longer stable and are replaced by a kaolinite + Fe-oxyhydroxide assemblage. The mineral sequence observed in this profile is the reverse of glauconitization which operates at the seawater–sediment interface (Hower 1961; Velde 1976). This suggests that glauconitization is a reversible process under low-temperature conditions and thus should be considered as a stable reaction

The result of glauconite weathering is to release K and Fe ions into the altering solution. These solutions react to produce new mixed-layer minerals in a step-wise process which gives an iron-rich or aluminous trend depending upon the position in the rock fabric. Materials in close contact with glauconitic grains or plasma change into a montmorillonite–nontronite assemblage (some of the Fe ions are incorporated into clay minerals) while those near pores, in closer proximity to flowing diluted solutions, produce iron-poor phases (kaolinite) associated with Fe-oxyhydroxides.

3.4.3.2 Weathering of Marls

Marls are sedimentary rocks commonly composed of clay minerals intimately mixed with carbonates and sometimes pyrite. Their permeability is very low and the alteration effects are only detectable by a color change from black to ochre in the unaltered and altered levels respectively. The Roumazières profile (Charente, France) used here as an example is developed on a Toarcian age marl composed of detrital mica, quartz, pyrite, dolomite, illite and chlorite (Laffon and Meunier 1982). No modification of the rock structure is observed in the ochre weathered areas. Nevertheless, some mineralogical change occurs:

1. the large white mica flakes are almost unaltered;
2. pyrite crystals are oxidized;
3. dolomite, as well as calcite, grains are dissolved;
4. the initial illite + chlorite assemblage is partly replaced by a kaolinite + illite/smectite mixed layer + Fe-oxide assemblage.

Because of the oxidation of pyrite crystals, the solutions become more acidic and dissolve the Mg-rich trioctahedral phyllosilicates chlorites as well as the carbonates. Consequently, the solutions are locally strongly enriched in Ca, Mg, Si and Al. These new chemical conditions favour the formation of Si–Mg-rich dioctahedral clay minerals at the expense of illite which is replaced by illite-montmorillonite (I/S) mixed layer minerals. The excess Al ions are fixed into kaolinite. The change of the initial illite + chlorite clay assemblage to the I/S + kaolinite assemblage in the weathered zones is represented in Fig. 3.62. As the total loss of dissolved component is quite small and can be neglected, the major effect of weathering is the oxidation of Fe^{2+} ions which explains why the bulk rock composition (large dot) moves in the MR^3–$2R^3$–$3R^2$ coordinates from the right to the left side of the triangle. In summary, one can consider that weathering is the reverse process of the diagenesis which had transformed the initial sediment into the present marl (Velde 1985).

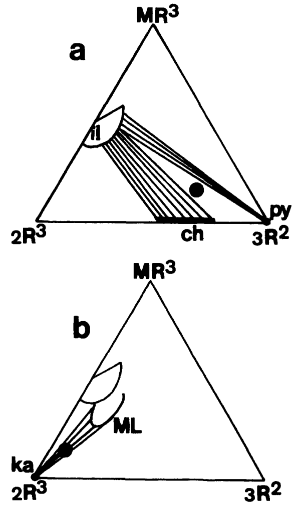


Fig. 3.62. Representation in the MR^3–$2R^3$–$3R^2$ phase diagram of the mineral assemblages of **a** the unweathered marl and **b** the oxidized zones. *il* illite; *py* pyrite; *ch* chorite; *ML* mixed-layered minerals; *ka* kaolinite. (Laffon and Meunier 1982)

It is remarkable that the weathering of sedimentary rocks, i.e. glauconitic sandstone and marl, follows the reverse step-wise pathway of glauconitization and diagenesis respectively. This could indicate that reactions involving clay minerals in low-temperature conditions are stable, or at least reversible metastable reactions.

3.4.4 Summary and Conclusions

Under weathering conditions, rocks, whatever their origin, are progressively transformed into a final assemblage of Fe and Al oxyhydroxides. This endpoint is a attained under tropical or equatorial climate where the reactions between minerals and meteoric water are intense and proceed for long periods of time. This confirms that Al and Fe are true inert components. In contrast, silica, alkalis, calcium and magnesium are dissolved. Their chemical potential can act as active intensive variables in permeable zones of the profile where they control the formation or the dissolution of mineral phases. Under temperate climates, where the weathering processes are less aggressive and where they have usually been active only since the last glaciation, one can observe a series of mineral reactions which progressively transforms the parent rock into a soil.

Weathering of rocks under temperate climate forms the soil saprolite–saprock–rock sequence which is found as one descends into the profile. Thickness and geometrical characteristics of each of these zones depend on chemical composition and structure of the parent rock, topography, permeability, and the age of the alteration. Whatever the profile, there are essentially two parts: (1) that where high temperature phase assemblages react with meteoric solutions and (2) that where clay minerals react with the solutions. Most of these reactions proceed inside microsystems in which local equilibria are reached. The new phase assemblages produced in these microsystems are in their turn destabilized, when local conditions change because of modifications of the structure of the weathered rock or the soil. In summary, one could say that, under temperate climates, weathering processes lead the primary phases to a kaolinite + Fe-oxyhydroxide assemblage via a sequence of reactions which depends on the local structural properties. The chemical transfers are controlled by this sequence, the steps of which are represented in chemical potential–composition phase diagrams.

In summary, the weathering processes under temperate climatic conditions depend on the chemical and mineralogical properties of the parent rock. The microsystem effects control the mineral reactions. Clay properties are highly variable from point to point in the profiles. This variability disappears when the weathering conditions are more aggressive, i.e. in tropical or equatorial climates. This introduces the major difference between soils and weathering profiles: soils are more sensitive to climate than to the chemical and mineralogical properties of the parent rocks. In contrast to weathered profiles, it is easier to present the great soil groups according to climatic conditions that to rock type. Such a presentations is proposed in Section 3.5 which devoted to clays in soil environments.

3.5 Clays Found in Soil Environments

There the chemical composition of the rock is of great importance in determining the clays which form in the early and intermediate stages of weathering. In soils, the importance of this compositional control is balanced by the effects of other parameters, climate, age, and topography, which are more determining controls. The discussion that follows gives an insight into the clay types formed in soil under various climates. The rate of clay formation, the influence of organic compounds, and the effect of mechanical transportation are also discussed for soils developed in cold or temperate climates. A short chapter is devoted to specific clays (short-range ordered minerals) formed in soils from volcanic ashes.

3.5.1 Clays in Soils from Cold and Temperate Climates

Because of the short time of evolution (<10 000 years) and the low temperatures that reduce the rates of weathering reactions, the formation of clay minerals in soils in the cold areas of the world is limited to very small amounts of change. The processes of weathering and soil formation are strongly influenced by complexing organic acids which are produced by slowly decaying plant residues. This process of weathering, in which organic compounds act not only as proton donors but also as complexing anions, is known as acido-complexolysis. It makes weathering in northern areas quite distinct from that which occurs in other parts of the world (Ugolini and Sletten 1991).

Acido-complexolysis is characterized by organic acidity, which generates a pH in the range of 3–5, and organic complexation of metals such as Al or Fe, which leads to the complete solubilization of all the minerals, except quartz, without any formation of clay. However, soil solutions contain mixtures of organic acids which have strong, weak, or even no tendency towards complexation. Therefore, depending on the type of acid which predominates, the weathering trends actually observed are intermediate between complete destruction by acido-complexolysis, and a less drastic attack on initial minerals leading to the formation of interstratified clays (illite/vermiculite, illite/smectite). Moreover, smectites (or illite/smectites) are the major clay minerals observed in the eluvial horizon of Podzols, which are the typical soils in northern areas.

3.5.1.1 Nature and Rate of Clay Mineral Formation

A very demonstrative study has been made of a sequence of soils of increasing age in the Hudson Bay area, Canada (Protz et al. 1984, 1988). Along the coast of Hudson Bay, periodic storms have built sequential beach ridges made of sand and fine gravel materials including up to about 50% carbonates. From these materials, a sequence of soils, with ages ranging from less than 100 years to about 5500 years, from the coast to the inner country, has developed. The morphology of the soils clearly indicates the development of podzolization: a typical Podzol profile is formed within 2000 years of soil development. The soil formation starts with the dissolution and leaching of calcium carbonate. The depth of complete leaching of $CaCO_3$ increases with time and reaches 30 cm after 5000 years as shown in Fig. 3.63. A parallel decrease in the soil pH from 8 to 4 is observed.

In the C-horizons of all soils, the clay mineralogy is practically the same, but changes in the clay mineralogy with time are observed in the surface (A) horizons. X-ray diffraction analysis indicates that chlorite and mica contents decrease with increasing age, whereas vermiculite content increases and after 4500 years becomes the only clay mineral present together with a small amount of smectite. The amount of vermiculite that has formed is well correlated with time of evolution as shown in Fig. 3.64. A diffraction peak at 0.150 nm indicates that vermiculite, as well as the associated smectite, are dioctahedral. Thus, the mineralogical evolution over 4500 years involves the destruction of chlorite and the transformation of mica to dioctahedral vermiculite. A few smectite layers are also formed.

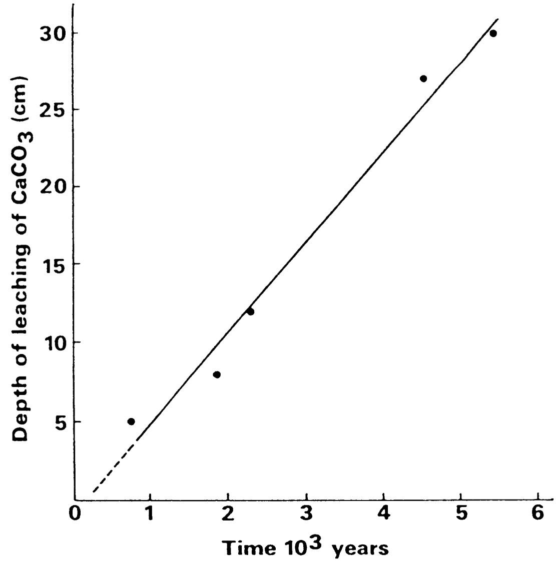


Fig. 3.63. Depth of leaching of $CaCO_3$ as related to time in the Hudson Bay area. (Data from Protz et al. 1984)

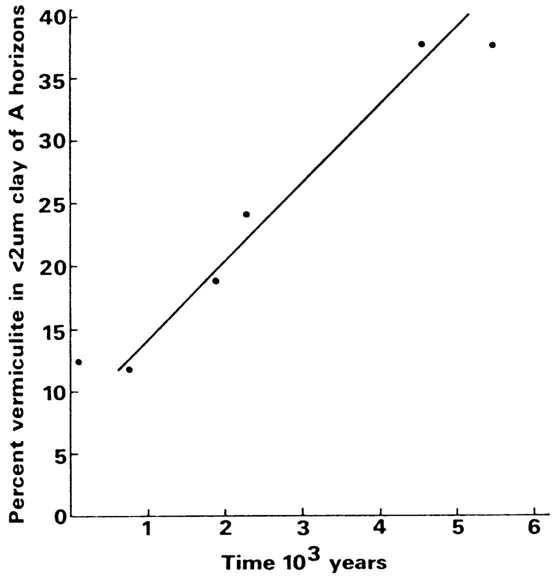


Fig. 3.64. Vermiculite formation related to time of soil formation in the Hudson Bay coastal area. (Data from Protz et al. 1984)

Another chronosequence developed on similar parent material was studied in the southern James Bay area where the mean annual air temperature is 5.5 °C higher than at Hudson Bay. In the C-horizons, the <2 µm fraction is dominated by mica and chlorite, and only minor or trace amounts of vermiculite are present. In contrast, the <2 µm fraction of the E-horizons of the older (>1200 yr) soil is dominated by vermiculite, whereas chlorite is absent. Again, the XRD patterns of the E-horizon clays show the destruction of chlorite and the transformation of mica to vermiculite and eventually smectite. The amount of vermiculite which has formed appears to be correlated with time of evolution, as given by the distance of the soil profile from the coast. Compared with the Hudson Bay coast, the rate of vermiculited formation at Bay James is twice as great (Fig. 3.65). That can be explained by wetter and warmer climatic conditions at this place.

The mean annual drainage is 180 mm of water at Hudson Bay, but 370 mm in the southern James Bay area. When coupled with the 5.5 °C higher annual temperature, an approximately two-fold increase in the rate of biological and chemical reactions in southern James Bay over the Hudson Bay coast may be expected. The mineralogical evolution in these young sandy sediments illustrates the early stages of the formation of soil clays. Chlorite is an easily weatherable mineral which is quickly destroyed or transformed. Transformation of mica to vermiculite is also an early process of soil-clay formation. The rate of these processes is strongly related to climatic factors. The wetter and warmer the climate, the greater is the rate of clay formation.

Another detailed study was done by Gjems (1967) on the clay minerals from more than 200 Podzols in Norway. The relative amounts of the different

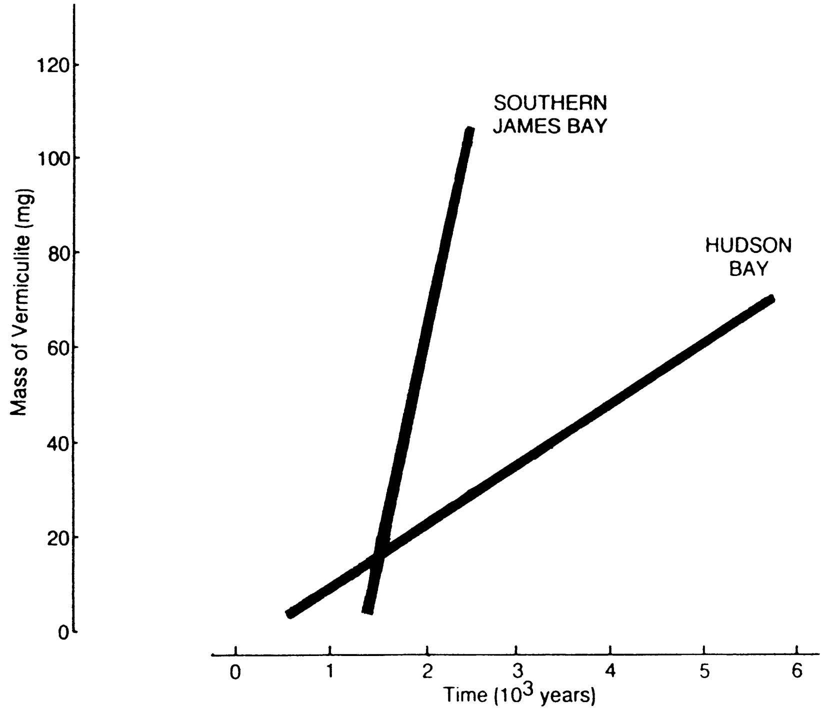


Fig. 3.65. Comparison of vermiculite accumulation, between Southern James Bay and the Hudson Bay coast. (Data from Protz et al. 1988)

mineral phases was estimated on the basis of XRD analyses. From the data obtained it was deduced that:

1. transformation of illite and chlorite to vermiculite occurs in the soil profiles;
2. smectites form in the E horizon of Podzols at the expense of chlorite and vermiculite;
3. in podzolized soils, mixed-layer minerals (mica/chlorite, chlorite/vermiculite) become less chloritic upwards in the profile;
4. the mixed-layer minerals are generally of a more regular interstratified type in the E compared with the B and C horizons.

Therefore, the profiles of the Norwegian Podzols are characterized by enrichment of smectites in the E horizon. Smectite, vermiculite and mica/vermiculite increases upwards in the profile inversely with trioctahedral mica, chlorite, mica/chlorite and mica/vermiculite interstratified minerals. The intensity of weathering in the E horizon of Podzol profiles, expressed as the content of expanding minerals, is related to the environmental factors as follows:

1. recognisable amounts of expanding minerals are formed after a few hundred years of soil formation;

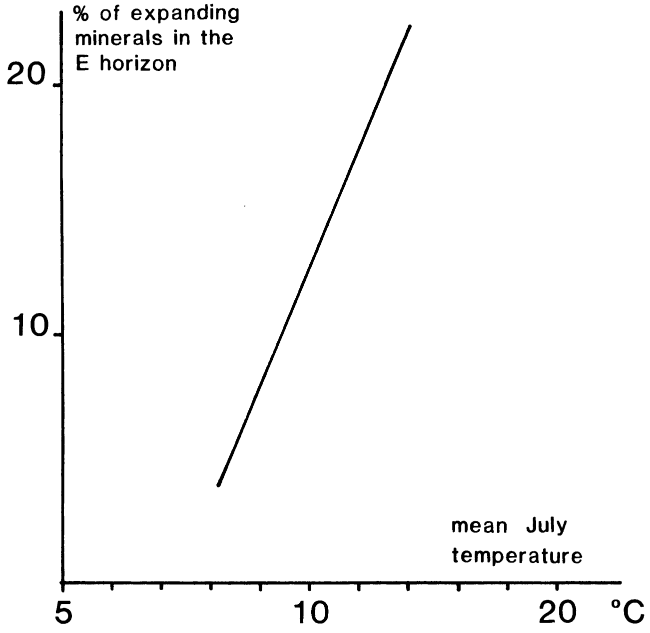


Fig. 3.66. Relationships between climate and rate of weathering in Norway. (Data from Gjems 1967)

2. weathering increases with a warmer climate; this is clearly shown by the relationships between the amount of smectite in soil and the mean July temperature at the place the soil come from (Fig. 3.66);
3. weathering increases with decreasing acidity of the parent material.

A far shorter period of time is needed here in Norway than in northern Canada to form smectite; once again the role of climate in the rate of clay formation is evidenced.

3.5.1.2 Podzolization and Clay Mineral Evolution in the Temperate Zone: Influence of Organic Matter

In the temperate zone, podzolization never affects the whole soil mantle, but only some specific sites characterized by acid, sandy parent materials. Usually Podzols are associated with acid Cambisols. The clay-mineral associations appear to be different in the two types of soil. Mineralogical transformations and their relation to soil-forming processes are studied in a short toposequence in the Landes du Medoc (France) (Righi et al. 1988). In this sequence (Fig. 3.67). Both Podzols and Cambisols are occur within a small area. Except for the dynamics of organic matter, all other factors are the same for the two types of soil. The parent material (a coarse quartzitic sand) contains few clay minerals: a mica phase, a vermiculite and a randomly interstratified chlorite–vermiculite mineral. In the Cambisol, the mica phase is transformed into a vermiculite mineral. After potassium saturation and

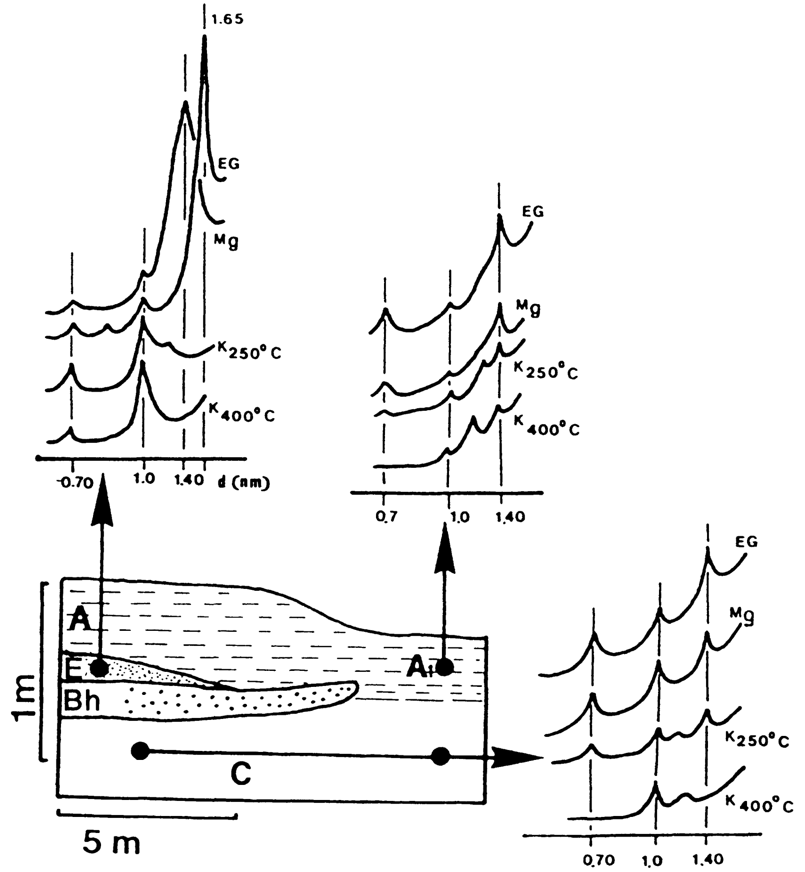


Fig. 3.67. Mineralogical changes of clay minerals in a podzol and in an acid brown soil from the same short toposequence (Médoc, France). *EG* Ethylene glycol saturated, *Mg* Mg-saturated, air dried, *K* heat treatment at different temperatures, as indicated. (Data from Righi et al. 1988)

heating this mineral exhibited a progressive and incomplete collapse. Such a behavior is generally that of intergrade minerals with an incomplete hydroxide interlayered sheet.

In the E horizon of the Podzol, the mica phase is transformed to a 1.4nm mineral. The 1.4nm reflection moved to 1.65nm after ethylene-glycol solvation, indicating the presence of smectitic layers. This example shows that in the temperate zone, an acidic and complexing medium favors the formation of smectitic minerals, with only small amounts of interlayered material being formed, whereas intergrade minerals, with a more developed interlayered hydroxide sheet, are found in acid soils where complexing organic acids are less aboundant. Exportation out of the weathering medium of Al and Fe as organic complexes is certainly the reason for a greater alteration of initial minerals in podzolized soils.

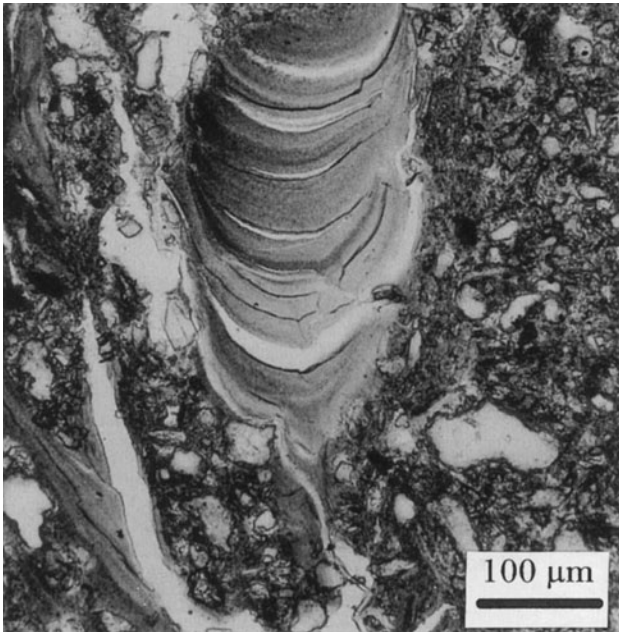


Fig. 3.68. Microphotograph of clay accumulations in soils under plain light

3.5.1.3 Clay Illuviation in Soils Developed from Glacial Loess Deposits: Movement by Transport of Solids

Loess is an aeolian deposit dominated by silt-sized particles (2-50 μm), which covers about 10% of the land surface. Because only glacial grinding can produce appreciable quantities of silt, most of the loess deposits are close to glaciated areas. Loess covers were built-up from silty material which was spread across the landscape by wind moving over barren areas. In northern Europe and North America thick loess deposits were spread over large areas during the Quaternary period. Soils developed from loess material exhibit very clear features of clay illuviation, such as clay coatings filling small pores (Fig. 3.68). Clay illuviation is the movement of clay particles by transport in suspension in the soil water. It is a major process that affects the clay fraction in soils: large amounts of the clay produced by weathering reactions may be lost from the surface horizon of soils through illuviation. On the other hand, redeposition of translocated clay causes the formation of clay-rich horizons at a certain depth in the soil profile. This process has been extensively studied, and so it is possible to form a general description in terms of a chronosequence of soil development, as illustrated in Fig. 3.69 (Jamagne and Begon 1984).

Because the loessic material is generally calcareous, the first weathering stage involves the dissolution of calcium carbonates which are leached out of the soil profile. A change to a more brownish colour, the development of a polyhedric soil structure and limited mechanical fragmentation of silt-sized

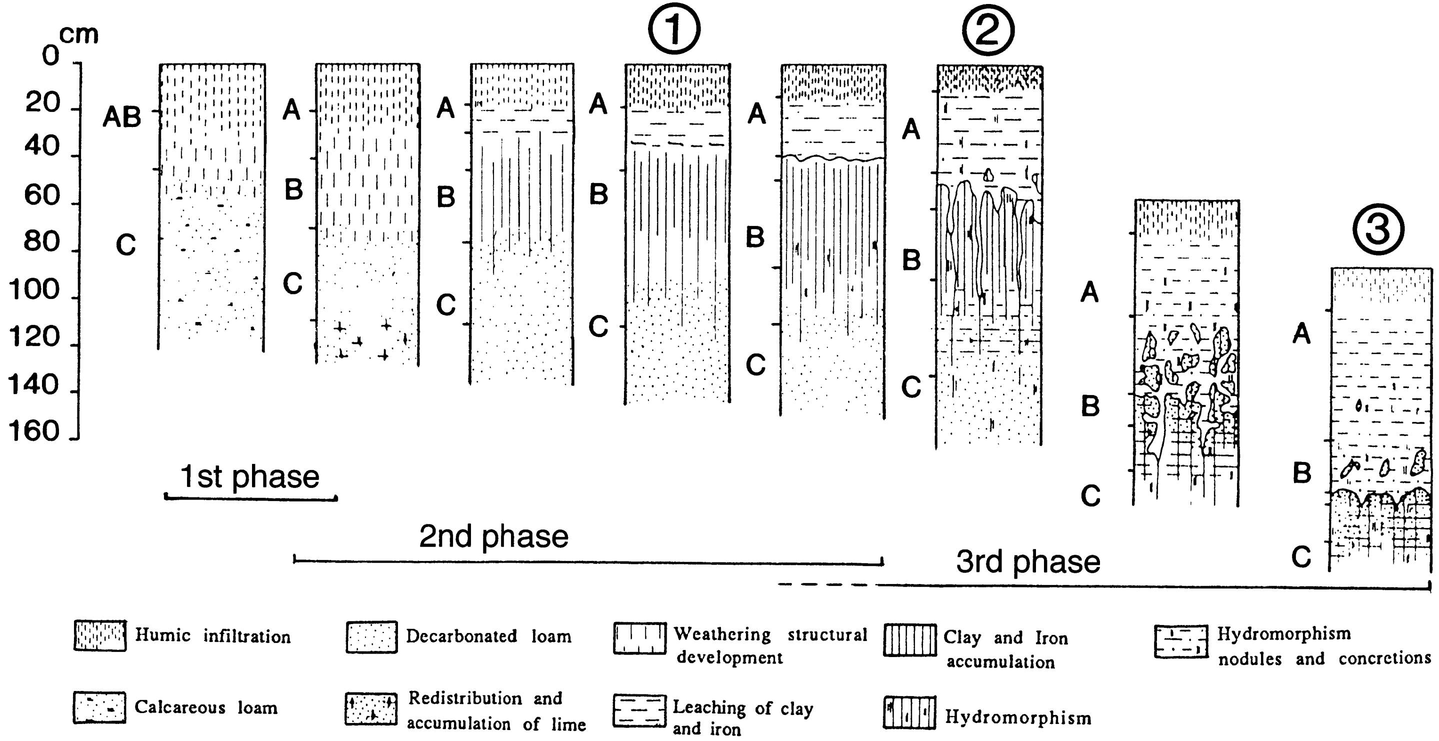
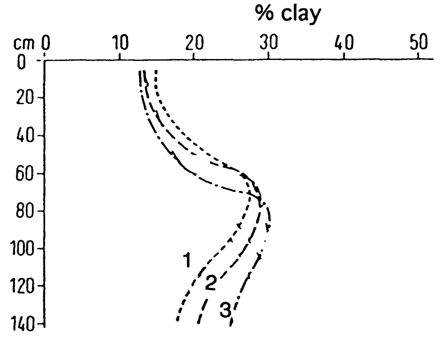
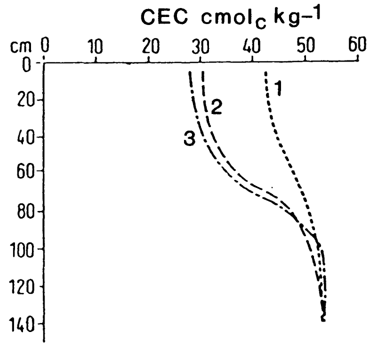


Fig. 3.69. Schematic evolution of soil-morphology sequence on loamy materials. (After Jamagne and Begon 1984)



Distribution of clay in the soil profile



Cationic exchange capacity of clay

Fig. 3.70. Distribution of clay and CEC of clay in three soil profiles with increasing clay illuviation. *1*, *2*, *3* refer to profiles in Fig. 3.69. (After Begon and Jamagne 1972)

phyllosilicates is associated with this stage. Decarbonation and a subsequent decrease of Ca concentration in the soil solution, favors the dispersion of clays and hence their suspension in solution. The movement of clays begins and their redeposition occurs deeper in the soil profile, producing the typical distribution of clay with depth shown in Fig. 3.70. The finest clay fraction (0.1 µm) is most affected by this dispersion and translocation wheras coarse clays are less mobile. Generally, for soils from the temperate zone, fine-clay fractions contain a higher proportion of expandable clay minerals (vermiculite, smectite) than coarse fractions, which are dominated by mica, kaolinite and quartz. This explains why the clay fractions in the B horizon have a higher CEC (Fig. 3.70).

Considering the spectacular evolution of soil morphology, surprisingly, only slight mineralogical changes are observed (Jamagne et al. 1984). Illite, chlorite, kaolinite and smectite are the phyllosilicates that generally constitute the clay fraction in the loess material. During soil formation, illite is transformed into illite/vermiculite interstratified minerals, while chlorite is quickly weathered to give smectite layers as weathering products. Kaolinite would be the most stable phyllosilicate. The most important change is certainly found in the interlayer spaces of vermiculite and smectite, which progressively desaturate, i.e. exchangeable basic cations (Ca, Mg) are removed and replaced by Al polycations; hydroxy-Al interlayered minerals are formed. This was demonstrated by the isotopic analysis of the clay minerals in two Luvisols from western Canada (Spiers et al. 1985). The parent material, a glacial till, contains smectite, kaolinite, dioctahedral mica and chlorite as initial phyllosilicates. The following changes were induced by pedogenesis in the mineral suite: kaolinite remains in the E horizons whereas mica and smectite are enriched in the B-horizon as the result of illuviation. In addition, smectites, which are a mixture of montmorillonite and beidellite in the parent material, are almost exclusively beidellite in the E horizon. A gradual increase of the beidellite proportion in the smectite mixture is observed from the parent material to the E-horizon. Thus, either neogenesis of beidellite in the E horizon or preferential illuviation of montmorillonite over beidellite are possible processes. As clays inherited from the parent material should be isotopically distinct from any neo-formed one, the hypothesis of beidellite neo-formation was tested using oxygen isotope analysis (^{18}O). Isotope data demonstrated that beidellite was not neo-formed in these soils. Therefore, only differences with regard to susceptibility upon translocation can explain the changes observed in clay mineral distribution between the different soil horizons.

A further stage of evolution is induced by the reduction in permeability as the result of clay illuviation. The accumulation of illuvial clays in a B horizon (medium part of the soil profile) causes a progressive filling of the pores in this horizon, so that it becomes more compact and less permeable. As a consequence, the amount of water percolating through the B-horizon is strongly reduced and a perched water table forms during the rainy season. The compact, clay-rich B horizon develops a typical coarse prismatic structure. Prismatic aggregates are separated by large and deep cracks which are progressively enlarged and deepened, forming a typical morphology called a glossic (tonguing) feature. These are the main pathways for water circulation. The clays in suspension are not pure clay minerals but, more exactly, particles comprising clay minerals and amorphous iron-oxyhydroxides, the later forming coatings on the clay mineral surfaces. The origin of these amorphous iron coatings is mainly in the weathering of the initial Fe-bearing phyllosilicates by means of oxidation of ferrous iron, exsudation out of the phyllosilicate structure, and subsequent precipitation on the surface of particles. The seasonal hydromorphic conditions in the upper part of the soil profile induce the reduction of ferric oxy-hydroxides. As iron is far more soluble in the ferrous state it can be removed, causing the dissociation of the iron-oxy-hydroxide–clay complex. Subject to large local changes in redox conditions, dissolved ferrous iron reoxidizes and precipitates forming iron nodules.

Clay minerals released by the dissociation of the iron-oxyhydroxide–clay complex are very dispersible, and so a secondary stage of clay illuviation is observed, leading to the accumulation of clay in the bottom of the tongues (DeConinck et al. 1976). The result is a strongly contrasted soil profile with an upper horizon, greatly impoverished in iron and clays, overlaying a lower compact clay-rich B-horizon. Water flow is strongly reduced in the vertical direction and water moves laterally over the impervious floor made by the B-horizon.

3.5.1.4 Clays in Soils from Heavy Clay Rocks: Selective Transport of Clays

In addition to loessic materials, other sedimentary clay rocks also have a large extension in northern Europe and America. Soils developed from these materials are initially clay-rich soils, and their clay minerals are mostly directly inherited from the parent material. Only slight mineralogical evolution occurs. Soil formation on these rocks generally induces a strong structure of the material within the first meter below the surface. This structure determines the pattern of water circulation in the soil. Although only slight mineralogical changes occur, soils developed from clay-rich sedimentary rocks often exhibit large differences in clay content between the upper and lower horizons of the soil profile, upper horizons having lower amounts of clays. Illuviation of clay fails to explain the contrasting depth function of clay content in these soils, as no absolute accumulation of clays in the deeper horizons can be proved.

Mass-balance studies show that the decrease of the fine-clay content in the upper horizons accounts for most of the matter which is lost. Losses as high as 400kg/hectare/year of fine clays have been measured in heavy clay soils in France (Nguyen Kha et al. 1976). Moreover, very stable suspensions of fine clays can be collected in drainage waters from these soils. This process is described as superficial and selective erosion. Loss of fine clays occurs both through runoff and seepage waters, according to rainfall intensity and the soil structure which can change with the season. During winter and early spring, water content of soils is close to field capacity and water moves slowly through micropores. Heavy rains cannot penetrate totally into the soil and runoff occurs. During summer and autumn, soil desiccation leads to the opening of large cracks. Rainwater enters these large cracks and mechanically disperses fine clays which finally join seepage waters and eventually streams and rivers. No redeposition of the dispersed clay occurs within the soil profile. As the different clay mineral species do not have the same ability to be dispersed, the change in their proportions in the soil profile occurs. Smectite and expandable minerals (vermiculite, interstratified minerals) are the most affected by selective transport. Kaolinite, mica, and also fine quartz accumulate relatively in the upper horizons.

3.5.1.5 Summary

Most of the soils in the temperate zone are developed from rocks which contain phyllosilicates. This is the case for soils formed on granite, sedimentary rocks and a great majority of those formed on metamorphic rocks. Fine-grained sediments like loess or glacial tills, which cover large areas in Europe and north America, also contain phyllosilicates similar to clay minerals such as muscovite, biotite and chlorite. In these soils the clay fraction is constituted of a mixture of relicts of the initial phyllosilicates, with the new clay minerals formed by weathering. However, not all of the initial phyllosilicates have the same stability: some are more easily weathered than others. For instance chlorite is certainly one of the most unstable phyllosilicates in the soil environment. Weathering of chlorite in soil conditions proceeds through intense physical fragmentation leaving clay-sized particles. Mineralogcial transformations of the chlorite remnants leads to the formation of complex chlorite/vermiculite and chlorite/smectite mixed layers. The brucite sheet of the chlorite is partially dissolved, and intergrade minerals between vermiculite and chlorite are formed. The end result is the formation of a fine clay fraction (<0.2 μm) with smectitic characteristics associated with coarser fractions (>0.5 μm) which are relicts of the initial biotite and muscovite.

Physical transport of clays from the surface to the B horizon is the other process that affects clay minerals in soils. This induces large changes in soil permeability at the depth at which clays are redeposited, and water flow from the soil surface to groundwater is strongly disturbed.

3.5.2 Clays in Soils on Volcanic Rocks: The Short-Range-Ordered Minerals, Allophane and Imogolite

Tephra deposits of rhyolitic, dacitic and andesitic composition form superficial formations in many parts of the world. Highly weatherable, they are of major importance as soil parent material. The presence of allophane and imogolite (short-range-ordered clay minerals) constitutes one of the specific features of soil derived from volcanic ash and pumice, and called Andisols. Thus, the geographical distribution of allophane and imogolite is associated with areas of recent volcanic activity: e.g. Pacific ring of volcanism, the West Indies, Africa, Italy and Australia. However, allophane and imogolite are also found in soils derived from rocks other than volcanic ash, specifically soils derived from basalts. Imogolite is a paracrystalline unique nesosilicate consisting of a tube unit with a diameter of about 2 nm (Fig. 3.71). Its structural formula is $(OH)SiO_3Al_2(OH)_2$. Allophane is X-ray amorphous and consists of hollow, irregular spherical particles with diameters of 3.5 to 5.0 nm and with compositions $(SiO_2)_{1-2}Al_2O_3(H_2O)^{+}{}_{2.5-3.0}$ (Wada 1989). The formation of imogolite and allophane occur during weathering of volcanic ash under humid, temperate or tropical climatic conditions. The large proportion of glass in the volcanic materials favors the formation of short-range-ordered minerals which are metastable phases and are characteristic of recent soils. Because of the high activity of glass, nearly all varieties of volcanic ash (basaltic, andesitic or rhyolitic) produce allophane–imogolite as weathering products. With time

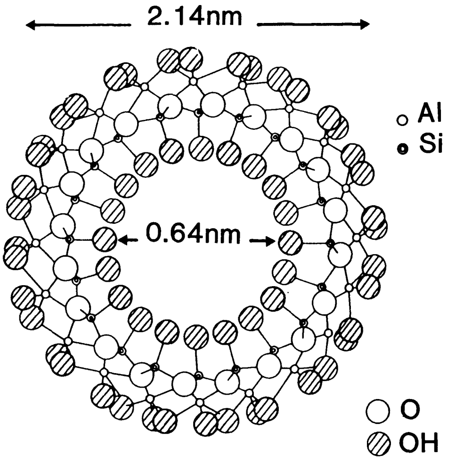


Fig. 3.71. Cross section of an imogolite tube. (After Cradwick et al. 1972)

allophane –imogolite transforms to gibbsite or halloysite, depending on whether the environment favors desilication or not. However, allophane–imogolite may persist in soil for long period of time if conditions are favorable. Their greatest stability occurs under a climate with constant humidity. A dry season induces soil desiccation and increases silica concentrations in the soil solution. This results in the formation of halloysite and cristobalite at the expense of allophane–imogolite minerals (Lowe 1986).

There are factors other than age and periodical dessication which contribute either to the persistence of allophane–imogolite or to its transformation into halloysite. Because rhyolitic material has a lower Al/Si ratio, it favors the transformation into halloysite, whereas andesitic material with a higher Al/Si ratio promotes allophane and imogolite stability. The accumulation of large amounts of humus in andisols is generally ascribed to its reaction with allophane, forming humus-allophane complexes. However, the absence of allophane–imogolite in horizons in which the accumulation of humus is very active, suggests that the formation of Al-humus complexes inhibits the formation of allophane–imogolite through competition for Al released by weathering of volcanic ash.

In contrast with 2/1 phyllosilicates (smectite, vermiculite) allophane and imogolite do not have a permanent CEC. They develop a variable electric charge on their surface. Sign and amount of charge are governed by pH and concentration of ions (anions and cations) in the soil solution. Cation exchange capacity or anion exchange capacity (AEC) can develop. Figure 3.72 shows that allophanic soil material has an increasing CEC and a decreasing AEC as pH increases from 4 to 8. At pH 4, CEC is nearly zero and an AEC of $20\,\mathrm{cmol_c kg^{-1}}$ has developed. At pH 8, AEC is strongly reduced and CEC is at its maximum ($30\,\mathrm{cmol_c kg^{-1}}$). Probable reactions for charge development on allophane–imogolite surfaces are given below:

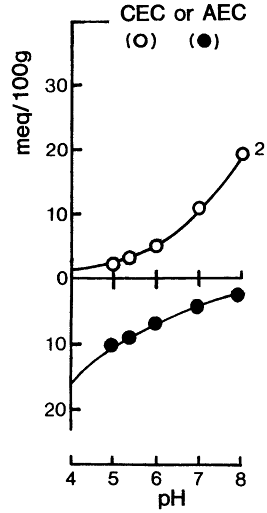


Fig. 3.72. Charge characteristic vs. pH of an allophanic material showing the strong variation of surface characteristics dependent on pH. (After Wada 1989)

high pH; $Si(OH) + OH^- = SiO^- + H_2O$

low pH; $Al^{VI}(OH)(H_2O) + H^+ = [Al^{VI}(H_2O)_2]^+$.

This has important implications on the status of plant nutrients in soils containing allophane and imogolite. Specific adsorption of anions such as phosphate occurs extensively on these materials. Organic anions such as citrate or acetate are also strongly adsorbed and thus protected against biological degradation.

3.5.3 Clays in Soils Formed Under Tropical Climate Conditions

Because of the higher mean annual temperature and the longer time of evolution, the formation of clay minerals in soils is generally more advanced in tropical areas than in temperate and cold regions. In tropical areas the tendency is to produce simple clay assemblages made of only one or two clay phases. The phases produced are controlled for a large part by the chemistry of the soil solution, which itself depends on the prevailing climatic conditions, especially the amount of rainfall and its distribution throughout the year. High rainfall, regularly distributed throughout the year induces soil solutions with low concentrations of silica and basic cations: this favors the formation kaolinite clay. Low rainfall, followed by dry periods with intense evaporation, induces soil solutions concentrated in silica and basic cations. In this latter environment smectite clays are formed. From the equator to the tropics a sequence of increasing dryness is observed. Clay minerals that have formed in

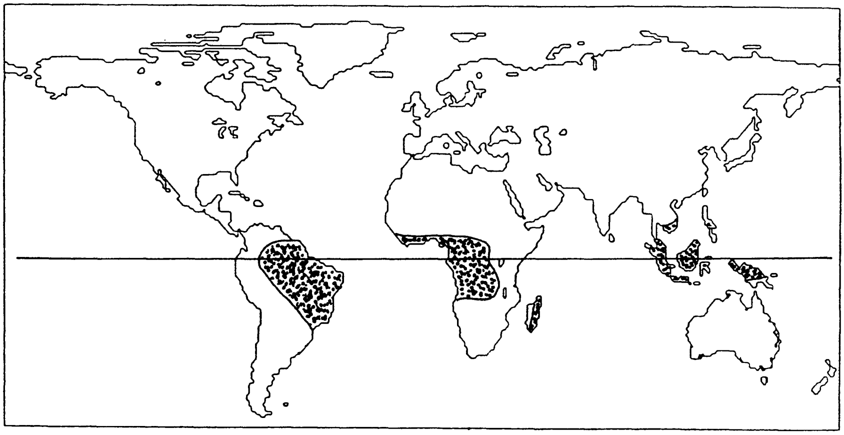


Fig. 3.73. Distribution of Ferralsols in the world. These are soils with kaolinite as the dominant clay mineral. (After FitzPatrick 1980)

soils reflect this change: kaolinite and Al,Fe-oxyhydroxides are found in Ferralsols of the wet equatorial zone, whereas smectites are found in Vertisols of the tropical dry zone. In arid areas with extreme evaporation, a fibrous caly mineral, palygorskite, can form.

3.5.3.1 Equatorial Wet Zone: Kaolinite and Al,Fe-Oxyhydroxides in Ferralsols

Humid tropical climatic zones in Africa, South America and Indonesia are covered by the so-called lateritic formations or Ferralsols (Fig. 3.73). When they have not been strongly eroded, lateritic soil profiles show an ordered succession of three main horizons from the bottom to the top (Fig. 3.74) (Bocquier et al. 1984; Muller and Bocquier 1986):

1. A lower weathering horizon (saprolite) is present, in which the weathering products maintain the structure of the original rock. The clays are mainly macrocrystalline kaolinite, hematite and goethite, associated with stable primary grains such as quartz or muscovite. This horizon is friable and very porous. In the upper part of the horizon, blocks of saprolite are isolated in a ferruginous clay material which is characterized by the disappearance of the original rock structure and is composed of poorly ordered microcrystalline kaolinite associated with iron oxides. A gradual transition may be observed between a discontinuous red and compact matrix which contains hematite, and a continuous and loose yellow matrix which contains goethite.
2. An intermediate nodular horizon occurs in which two types (coarse and fine) of indurated nodules are found. The coarser (20–80 mm in diameter)

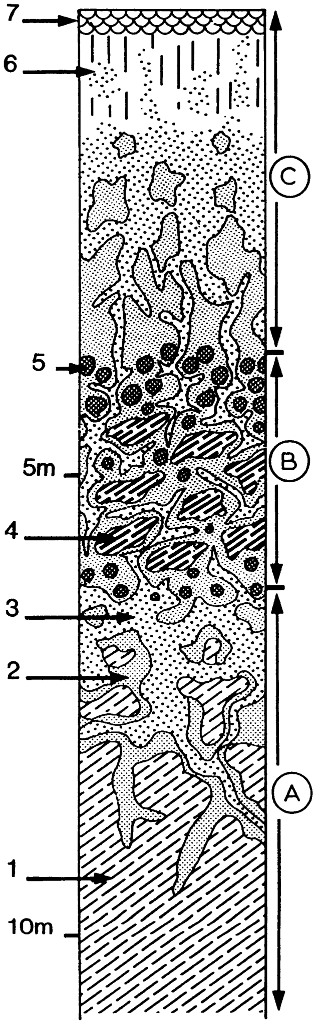


Fig. 3.74. Schematic representation of a Ferralsol profile (Muller and Bocquier 1986). *1* Saprolite, *2* red, compact matrix, *3* yellow friable matrix, *4* ferruginous lithorelict, *5* clay-rich nodules, *6* yellow, compact matrix, *7* zone of accumulation of organic matter. *Circled A, B, C* indicate major soil horizons

are irregular ferruginous relicts of the parent material and are characterized by a more or less preserved rock structure. They are mainly composed of macrocrystalline kaolinite associated with hematite. These nodules are more abundant in the central part of the horizon and display a gradual transition with their surrounding matrix. The finer nodules are sub rounded clayey nodules characterized by a total disappearance of the rock structure. They are mainly composed of microcrystalline kaolinite associated with hematite. These nodules are more abundant, and even occur exclusively, in the upper part of the horizon. Here the internodular matrix has the same characteristics as the ferruginous matrix in the underlying horizon, but the red hematitic matrix becomes the most abundant and is very compact.

3. An upper loose ferruginous clay horizon occurs. From the bottom to the top of the horizon the yellow matrix is again more abundant: the red matrix becomes progressively discontinuous and then disappears at about one meter depth. The upper part of this horizon is affected by organic matter accumulation.

From the brief description given above it appears that the weathering products are essentially kaolinite with Fe-oxides (hematite) and oxyhydroxides (goethite), plus some gibbsite found in the intermediate nodular horizon. Iron compounds concentrate in small soil volumes; the nodules. These are separated by internodular material which is constituted by kaolinite and smaller amounts of iron oxyhydroxides. Physical properties, especially permeability, in the upper loose horizon are attributed to the specific organization of kaolinite clays in that horizon. Indeed, in spite of a large clay content, the upper horizon remains highly permeable because the clays have built up microaggregates which are small rounded volumes of soil, 10 to 200 μm in diameter. The microaggregates (Fig. 3.75) are made up of kaolinite particles associated through edge–face contacts which are made very stable by thin coatings of iron oxides. They induce a large interaggregate porosity at the micrometer μm scale and also a large intra-aggregate microporosity at a submicron scale (0.1 μm).

These microaggregates are stable enough to behave like undissociable particles and they are often called pseudo-sand or pseudo-silt according to their size. For such microaggregated clays swelling–shrinking processes due to wetting–drying cycles are restricted: this material has quite a rigid behaviour. As the kaolinite crystal surfaces are covered to a large extent by iron-oxyhydroxide coatings, the surface properties of the kaolinite clay are partly hidden and inactive. For instance, CEC is far lower than for a reference or uncoated kaolinite. The specific association between kaolinite and iron-oxyhydroxides produces a material with a rigid structure and a low physico-chemical activity.

The critical role attributed to iron-oxyhydroxides in the inactivation of the kaolinite clay can be demonstrated by using a treatment that removes iron compounds from the soil sample (NH_4-oxalate in the dark). After this treatment the usual properties of the kaolinite clays are restored: the soil material swells and shrinks following wetting and drying, and the CEC is greatly improved, compared to the untreated initial material. Moreover, only a small fraction of the iron-oxyhydroxides (the fraction which is amorphous or poorly crystallized) is removed by the treatment; however, that is the crucial fraction which is actually responsible for the microaggregate stability (Pédro et al. 1976).

The dissociation of these microaggregates may occur in nature by any process that causes the removal of iron-oxyhydroxide coatings, as can be done experimentally. Any process that provokes the removal of amorphous iron-oxyhydroxides will cause the destruction of the microaggregates and thus

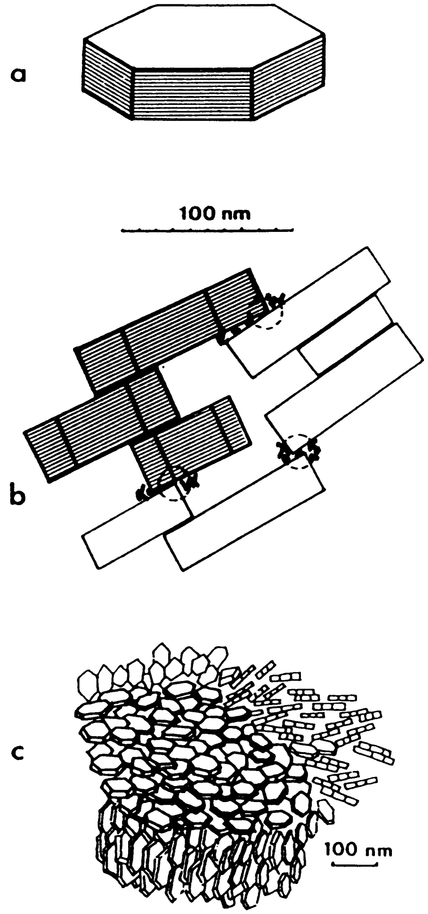


Fig. 3.75. Organization of kaolinitic material in a ferralsol. *a* Kaolinite crystal, *b* particle aggregate composed of kaolinite crystals connected at plate ends, *c* micro aggregate structure made of edge–face crystal associations. (After Robert and Herbillon 1990)

will completely change the soil structure and soil physical properties. Possible processes include, reduction and complexing of iron by organic acids; reduction of iron through water stagnation; and strong dessication. The latter process needs some explanation. In areas where a marked dry period occurs, Ferralsols with typical microaggregated structure show a progressive transformation of that structure to form soils with a compact and impervious horizon. This is attributed to the deep and strong desiccation of the soil that occurs during the dry season. The extreme hydric conditions generate constraints responsible for evacuation of water contained in the microsites and for breaking of interparticle bonds. Moreover, it has been shown that when the water films become increasingly thin, water molecules dissociat more than in free water generating a very low local pH (pH < 2). This strong surface acidity is responsible for the dissolution of iron-oxyhydroxides and consequently the disruption of the microaggregates. That irreversible change in the kaolinite–

iron relationship is induced when climate shifts from humid towards dry or arid as has been demonstrated in West Africa (Chauvel 1976).

The disruption and collapse of the microaggregates leads to a more compact and impervious new structure which restricts the vertical flow of water. Runoff and lateral water flow are favoured with possible mechanical translocation of the clay particles which can now be dispersed. The upper soil layers become impoverished in regards to clay and so become more sandy.

3.5.3.2 Tropical Dry Zone: Smectites in Vertisols

So called Vertisols are formed in areas with tropical wet–dry climates (climates with a marked dry season of 4 to 8 months). In this climate, drainage and consequently leaching of basic cations (Ca, Mg) are at a minimum. They accumulate in the soil, providing favorable conditions (pH, Ca, Mg concentrations) for the formation of smectites. However, the parent material from which the soil develops, must contain sufficient amounts of basic cations, therefore development of Vertisols is restricted to basalt, shale, limestone or volcanic-ash rocks. Cation deficiencies in the parent material can be made good by seepage and subsequent accumulation in lower parts of the landscape where soil water becomes concentrated by evaporation. The largest areas covered by Vertisols occur in India, Australia and the Sudan (Fig. 3.76).

Smectites from Vertisols show something of a continuum between montmorillonite–beidellite–nontronite with respect to octahedral composition and charge distribution, but these compositions clearly tend to cluster around that of the iron-rich beidellite (Wilson 1987; Bradaoui and Bloom 1990). The reason is that Vertisol smectites are derived directly or indirectly

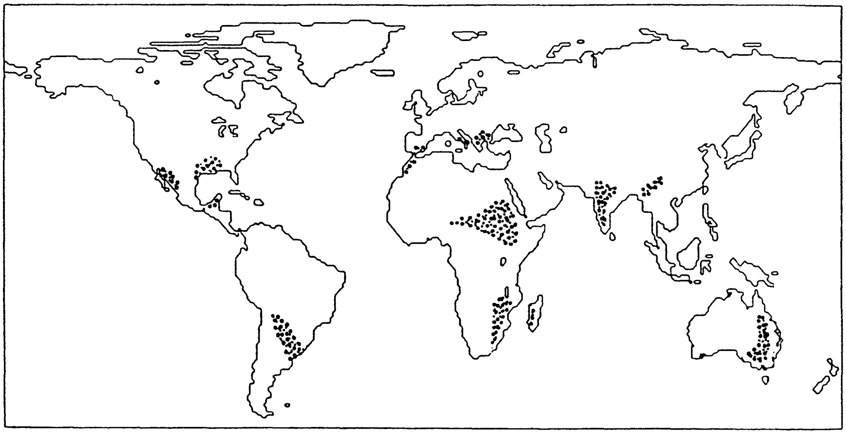


Fig. 3.76. World distribution of smectite-dominated soils (Vertisols). Compar with distribution of ferralsols, Fig. 3.73. (After FitzPatrick 1980)

from parent materials containing ferro-magnesian minerals. A positive correlation exists between the amount of structural iron in the smectite and the amount of iron in the parent rock, especially for Vertisols directly derived from weathering of basic parent rocks. Smectites in Vertisols are poorly ordered structures. They are rarely pure smectites. XRD diagrams most often exhibit features typical for interstratification and/or interlayering. In many Vertisols the smectites show higher basal spacings than might be expected from Ca-saturated montmorillonite. A spacing of 1.6 nm for material in the air-dry state and 1.8–2.0 nm after ethylene-glycol or glycerol treatment is common. Such values have been shown to be characteristic of Vertisols in many countries, such as Kenya, South Africa, Turkey and Uruguay (Rossignol 1983). This high spacing is thought to be the result of organic matter in the interlamellar space. Although evidence for smectite–organic complexes has been produced, this is only for clay minerals exhibiting normal spacings and normal swelling behavior. Most of the published XRD diagrams clearly show features that have patterns similar to randomly interstratified I/S. This indicates that at least a part of the smectitic clay in many Vertisols is inherited from the rock.

The coexistence of interstratified I/S minerals and clay-sized micas with high charge beidellite in Vertisols developed from sedimentary or alluvial materials, is often taken as an indication that bedeillite is a transformation product of mica. However, SEM (scanning electron microscope) pictures have shown very clearly that the growth of smectite layers occurs on the dissolved edges of mica (Kounestron et al. 1977). This indicates that the process of smectite formation from mica is more than a simple transformation through K-depletion, oxidation of octahedral Fe and subsequent lowering of the layer charge, but a process of dissolution–recrystallization. If chlorite is present in the initial material, it may also be a potential source mineral for smectite. In this case smectite seems to be montmorillonite rather than beidellite. Also, repeated wetting and drying cycles by K-rich solutions on high charge smectite may lead to interstratification of expanded and collapsed 2:1 layers. Moreover, interstratified I/S minerals can be obtained by wetting and drying montmorillonite samples placed initially in K-bicarbonate solutions. The presence of large amounts of smectitic clays induces the features and properties of Vertisols. Their main characteristic is a specific soil structure that develops as the result of swelling and shrinking of the soil material, which causes pressures and stresses. If the pore space is not sufficient to accommodate the increase of volume, internal movements of the soil material are induced which are demonstrated by shear planes. The combination of wide and deep cracks from the surface downward to a depth of 50 to 150 cm, and a loose, granular surface mulch that sloughs down into the cracks during the dry season, seems to start a process of mechanical pedoturbation. Surface soil reaches lower parts of the soil profile in the cracks. When the soil swells and the infilled cracks can no longer provide the volume required for swelling of adjoining soil bodies, subsurface soil is pushed upwards.

The specific soil structure of Vertisol, which changes according to the season, also induces a large degree of heterogeneity of water content in the soil. Rainwater coming on a dry, deeply cracked Vertisol percolates first through the wide open cracks leading to rewetting of deep soil layers, while the bulk volume of the surface soil layers remains dry. In spite of large gradients of water tension, homogenization of water content throughout the soil takes a long time, because water conductivity is low in the clayey material.

3.5.4 Arid and Semi-arid Zones: Palygorskite in Saline Soils and Calcareous Crust

Pedogenetic formation of palygorskite, a fibrous clay mineral, is reported from arid areas of the world (Fig. 3.77) in which saline or alkaline ground water frequently affect soil formation, such as the case of the flat, saline plains called sebkhas. Stability of palygorskite requires alkaline pH conditions and high activities of Si and Mg in solution. Palygorskite would not be stable under a pH of 8 at high Mg concentration, or under a pH of 9 at low Mg concentration. In soils, the required concentrations of Mg and Si are not commonly reached, except those affected by rising ground water and submitted to strong and continuous evaporation. This is the case in the saline sebkha soils (Singer 1989). In the absence of rising ground water supplying concentrated solutions, calcareous crusts are the other pedogenic environment which allows palygorskite formation. Calcareous crusts (horizons of calcite accumulation) are commonly associated with soil formation in arid and semi-arid zones. In the crust, local increase of pH levels to greater than 9 are observed. In such conditions, Si dissolution from quartz can be high. The destabilization of Mg-bearing primary minerals provides adequate Mg activity. The required condi-

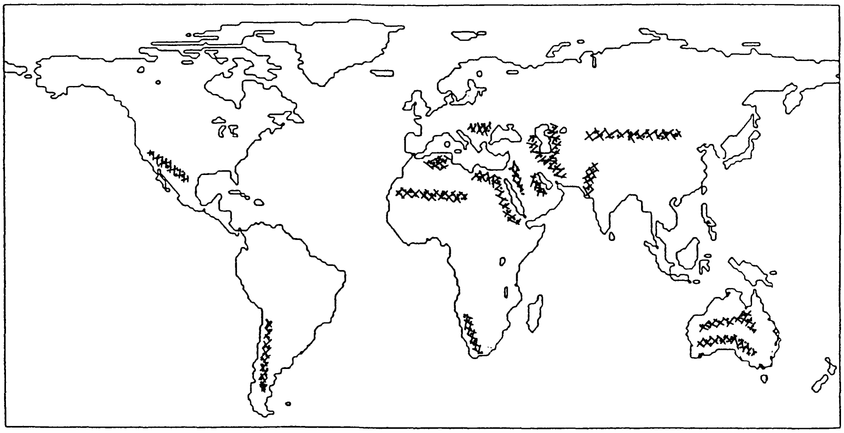


Fig. 3.77. World distribution of soils with palygorskite clays. (After FitzPatrick 1980)

tions of soil-solution chemistry are reached for palygorskite formation (Paquet 1983).

Smectite is the other clay mineral associated with palygorskite in these soils. The mutual stability relationships of these two clay minerals show that palygorskite formation is favored over smectite, by an increase in either pH, Mg or H_4SiO_4 activities. Accordingly, clay minerals which develope in calcareous crusts from Mg deficient parent materials, such as granites, are smectites and not palygorskite. In conclusion palygorskite has a wide distribution in soils of semi-arid and arid areas, where it appears in small to moderate amounts. Because this mineral rarely dominates the clay fraction, no specific soil properties are associated with its presence.

3.6 General Conclusions

Weathering of rocks and pedogenesis are major processes for clay mineral formation at the Earth's surface. They are essentially water–rock interaction processes. In this specific surface environment, only a limited number of variables govern the amount and the type of clays which form. These are *rock composition, water/rock ratio, temperature and time.* Water/rock ratio and rock composition are certainly the most important in determining the type of clay mineral which forms. Time and temperature are kinetic factors which determine the rate at which the chemical process proceeds. Basically, the water/rock ratio is determined by the amount of rainfall. Large amounts of rainfall produce high water/rock ratios and, in a freely drained system, solutions are diluted as they are rapidly renewed. This stands only as a general statement. Indeed, the effective water/rock ratio can be strongly modified by permeability and topographic effects. In the early stages of weathering, water penetrates the rock only through small fissures, permeability is low, water flow is slow and the residence time of solution in contact with rock is long: a low effective water/rock ratio is reached, even in regions with large rainfall. With increased weathering, porosity increases, leading to higher water/rock ratios. A maximum porosity is generally reached by which the soil is a totally open system.

In the soil system topographic effects are important. In addition to permeability, slope also controls the effective water/rock ratio. The displacement of the aqueous solution over the soil profile is more rapid if the slope is greater. This shortens the solution residence-time and prevents extensive water–rock interaction, thus the soil solution chemistry appears to be one of a high water/rock ratio. In flatter areas, the residence-time of solutions increases and low water/rock ratios are reached. Moreover, in lowland positions, under dry climate, evaporation may concentrate solutions and make them similar to those which circulate in the slightly weathered rock. Therefore, the importance of rock composition is greater in sites where the effective water/rock ratio is low, i.e. sites with either, low permeability, a flat topographic position or low rainfall. With reference to these variables (porosity, slope, climate) it is possible to explain schematically the occurrence of some major clay species. Although in variable quantities, *kaolinite* is found in most of the weathering and soil profiles. This mineral forms where solutions have low silica and alkali cation activities. This can be reached in the early stages of weathering by the destabilization of an individual aluminous primary mineral, such as plagioclase in granite or garnet in amphibolite. Increasing chemical weathering (progressive leaching of silica and alkali cations) and higher water/rock ratios also favor the formation of kaolinite: this clay mineral is found in the large fissures where the water flow is high, and also in soils on steep slopes in which the residence time of solutions is low. The thick mantle of kaolinite which covers the tropical wet zones is the result of very humid climatic conditions acting over a long period of time.

Except in tropical dry zones, *smectites*, either di- or trioctahedral, are found only in the lower parts of the weathering profiles, i.e. sites where the rock composition has a greater influence on the chemistry of the whole system. For example, saponite, a trioctahedral, highly magnesian smectite, is formed by destabilization of serpentine, pyroxene and talc in ultrabasic-rock saprocks. In the soil where magnesium is leached to a great extent, saponite is replaced by nontronite, indicating the greater stability of dioctahedral smectites in sites with higher water/rock ratios. In acid rocks, *beidellite–montmorillonite* (aluminous smectites) commonly forms by destabilization of orthoclase in the slightly weathered-rock zone. In tropical dry and arid climates, low water/rock ratios and high silica and alkali cation activities are the caused by low rainfall and the concentration of solutions through evaporation. Beidellite is the dominant clay mineral in soils in downslope and lowland areas.

Because most of soils in the temperate zone are developed from phyllosilicate-bearing rocks, they contain complex mixtures of inherited and partially transformed primary phyllosilicates. *Complex mixed layers and intergrade clay minerals* dominate the clay assemblage in temperate soils. Sediments like loess or glacial tills, from which many temperate soils have developed, contain large proportions of muscovite, biotite and chlorite. These phyllosilicates are unstable under the surface conditions but tend to remain in the soil-clay fraction as metastable relicts. The result is a mixture of primary minerals with newly formed clays which have a rather similar structure and chemistry. The primary phyllosilicates are destabilized in a stepwise process, the interlayer spaces being first affected. Biotite is progressively transformed into vermiculite through extraction of interlayered potassium. The brucite sheet of chlorite progressively dissolves and minerals with intergrade properties between vermiculite and chlorite are found as relicts of the initial chlorite. Because, in a single phyllosilicate particle, not all the layers are weathered, mixed layer minerals are formed; e.g. mica/vermiculite, illite/smectite, chlorite/vermiculite(smectite). These minerals are difficult to identify because several stages of change are found in the same soil clay sample. However, they are the dominant clays in temperate soils, which are the most concerned with agricultural and/or industrial pollution. Their chemical (exchange capacity, adsorption) and physical (swelling) properties must be established in order to assess their control on the environment.

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