The Place of Clay Mineral Species in Soils and Alterites

Introduction

Throughout the book thus far one can find the crystallo-chemical descriptions of clay minerals, their specific chemical properties as well as the probable reasons for their formation and lack of crystal size development. The transformation of unstable high temperature minerals into clays by the interaction of meteoric water and rock silicate minerals producing fine-grained crystallites is given in detail. These are the classical accounts of clay mineral formation under the influence of surface water-rock interaction. They depend essentially on the ratio of water to rock or altering mineral during the reaction period. Clay minerals formed at the rock interface are present in the saprock and eventually saprolite zone, and they are eventually submitted to the direct interaction of meteoric water at the soil surface in the context of plant/silicate interaction chemistry. Attention has been drawn to the importance of plants on clay mineral stabilities and occurrences. Observing the literature one can see that different clay mineral assemblages are found in the soil zone, compared to the zone just below, C horizon and saprolite. The relations of the clays in the plant/silicate interaction zone do not always follow a sequence of alkali loss and silica loss which should be the case for continued water/silicate interaction under non-organic chemically controlled conditions. This observation leads us to a non-conventional and usual approach to understanding clay mineral origin and occurrence in soils and alteration profiles. Hence we will summarize and develop here the observations which have been made on the interactions which concern the major clay mineral forming factors: water/rock interaction compared to climate and vegetation.

First we must recall our nomenclature of the transition between rock and soil. We divide the profile that one might obtain by digging a hole into the ground into three major parts: (1) rock/water interaction zone, (2) alterite zone (saprolite) and C horizon where one finds altered rock and alteration products as dominant phases, mostly clay minerals and (3) the soil horizon where the effects of plant and silicate are predominant in forming the type of clay mineral present. This is the part of clay mineralogy which affects mankind the most today, that of agriculture and the biosphere.

8.1
Where Clay Mineral Types Occur in Alterites and Soils

In the previous chapters we have indicated the ways in which clays form and how they form. The demonstrations have dealt with different chemical environments which produce clay mineral assemblages. The initial motor of formation is the inherent in-

stability of high temperature minerals, those forming rocks, which are not at equilibrium under surface conditions in the presence of meteoric water. This action forms clay minerals and a large portion of dissolved matter carried away in aqueous solution. It is very important to remember that clays, for the most part in situations of surface alteration, form groups of minerals occurring together. Most often the initial clay assemblages formed by water/rock interaction are multiphase when one considers a sample of several grams. One finds assemblages of clay minerals the composition of which depends upon the climate, position in the alteration profile (soil zone, alterite zone or interaction zone) length of time of alteration and interaction, as well as the composition of the materials which are being altered. It is very rare to find a mono-mineral clay deposit in surface reaction zones due to rock/water interaction. As one moves upward in an alteration profile, clay assemblages become less complex.

This being the case, it is evident that the interpretation of the importance of a given clay mineral will depend upon its neighbors, i.e. the clay assemblage. However, clay mineral types do occur under certain general conditions and their strong concentration is due to specific conditions of the chemical environment. In general, the forces of alteration (interaction of rainwater with silicates) tend to reduce the alkali and alkaline earth content of the assemblages with a loss of Na, Ca, K and Mg roughly in that order. Concomitantly, but to a lesser extent, there is a loss of silica in the early stages of alteration. Eventually the surface, clay material will be composed of aluminum hydroxy and iron oxyhydroxide minerals given enough time and interaction with meteoric water. Such material is of course infertile to plant life, i.e. organisms with roots.

However, often one finds 2:1 clay minerals at the surface, and often with kaolinite (1:1 mineral) in the B and C horizons. This would seem to be a contradiction to the normal trend of weathering via silica loss and alkali loss. It seems useful to summarize where one finds the different types of clay minerals under alteration conditions.

Below we give a general summary of the conditions under which one is likely to find different clay mineral types.

8.1.1
The 2:1 Minerals

The 2:1 minerals tend to dominate the clay mineral assemblages of the soil zone in latitudes other than those of tropical rain forests. As suggested in the introductory Chap. 1, it is possible to consider several of the 2:1 clay mineral types found in soils as variations on a theme. That theme is a charged 2:1 layer structure with various cations present in the interlayer space. These phases are called HI minerals with partially filled sites and dioctahedral chlorite when Al-OH polymeric complexes are found in the interlayer site. Expanding minerals (smectites) with exchangeable hydrated cations in the interlayer sites having a high charge are usually called vermiculite and those with a low charge are called smectites. Finally, illite is the 2:1 mineral with anhydrous potassium as the interlayer ion. This mineral sequence of different interlayer ion occupancy is determined by layer charge and the site of the charge. The mineral names traditionally given to the different clay types are based upon the interlayer cation occupancy: illite with potassium, HI with aluminum ion complexes and smectites with exchangeable hydrated cations. The different types of 2:1 minerals are:

HI minerals. Here the interlayer ion is based upon an $Al(OH)_2^+$ or $Al(OH)_3$ interlayer structure. In order for such a mineral to form, the activity of alumina must be relatively high. At pH values above 4 low amounts of free alumina (near 6 ppm) will precipitate to form gibbsite or the more hydrous form of alumina and silica, allophane. However at these conditions enough silica is present to form other minerals (silicates). In fact one often finds gibbsite occurring along with HI minerals (Harris et al. 1989; Burkins et al. 1999; Soller and Owens 1991 for example) in the soil zones or in the alterite portion of the profile at pH below 4, where alumina solubility increases dramatically. The availability of alumina depends upon two factors: low pH which puts alumina into solution without precipitating gibbsite and a lack of complexing organic matter which allows the movement of alumina into the clay structures. Thus acid soils are instrumental in forming HI minerals. Such acid soils are often associated, at least in the minds of pedologists, with organic matter. The HI and gibbsite can be found together in different parts of the horizon. Gibbsite indicates a maximum of alumina activity in solution. However, pH is not the only factor in that many acid soils do not form HI minerals. This is undoubtedly due to the complexation of Al by organic acids and other organic molecules which fix alumina and restrict the formation of HI minerals at low pH.

HI minerals also seem to be a product of the initial stages of alteration of high temperature phyllosilicates, either trioctahedral or dioctahedral. The trioctahedral forms are less resistant to the chemistry of soil weathering and they generally are transformed into other minerals (see the demonstration by Righi et al. 1999). HI minerals are frequently considered to be a transient stage of transformation of phyllosilicates (biotite, chlorite and muscovite) towards a final smectite mineral. However, HI minerals have been observed to form in the soil zone (plant/silicate interaction) from other phyllosilicates (Sect. 3.4.1).

HI minerals are most often associated with acid soils, forest soils in temperate climates to tundra climates. This is especially true for coniferous forests. HI minerals are defined by the presence of hydroxyl alumina complexes. Such complexes are to be found in acid soil solutions. High alumina content of soil solutions is often a limitation of plant survival. Wolt (1994, p. 235) indicates the toxicity thresholds for some common plants, crops and trees. It is clear that agricultural field plants are highly susceptible to high alumina contents with thresholds 100 times or less than those for many species of trees, especially conifers. Thus the presence of HI minerals is a sign of potential crop plant toxicity. Common practice in converting forest soil to crop culture involved in the pioneering past of the Unites States "sweetening" the soil, either through the burning and distribution of tree alkali ashes or by liming which lowers the pH and thus diminishes the alumina content of the soil solutions. This action essentially destabilizes the HI minerals which become more common 2:1 forms, smectites or in the case of high charge HI minerals they can convert to illite.

In general one can expect to find HI minerals in young soils where they represent the initial stages of mineral transformation of high temperature phyllosilicates such as chlorite, muscovite or biotite formed under acidic conditions especially in conifer forest soils. The conditions of formation are a high activity of alumina in solution which is controlled by the pH due to the presence of organic material which does not complex the alumina.

Illite. This mineral is a high charge, potassic clay mineral which can be formed through the weathering of muscovite or formed through mineral reaction during mineral weathering. The occurrence of illite in the coarse clay fractions seems to indicate a detrital mineral origin, coming from muscovite or diagenetic-metamorphic illite material. However, it would seem that a significant part of illite in soils can be relatively easily transformed into smectite (or a mineral having a smectite behavior) and perhaps *vice versa* (see Sect. 3.4.1). Most likely then soil illite has different sources and probably different compositions. The amount of charge and charge site in soil illite are not known. Illite is commonly reported in almost all types of soils and alteration zones except those formed upon basic rocks (basalts, diabases, serpentines, etc.) and glassy eruptive rocks. Illite is rarely reported in tropical forest soil and alterite zones nor does it seem to be present in laterites. To a certain extent there is an antithesis between illite and kaolinite, at least when large amounts of kaolinite are present in soils.

Illite is commonly a component of smectite-illite mixed layer minerals in soils. This type of mineralogy is specifically common in prairie soils. It is also common in deciduous forest soils (see Sect. 3.4.1). Relations between illite-smectite proportions is agricultural soils can change dramatically (Sect. 5.2). Hence there is a strong inter-relation between illite and smectite in soils mineralogies. It is highly probable that illite can be" transformed" into smectite or a mineral with a smectite behavior quite easily under the action of plants.

Thus illite can have an origin in the weathering cycle (water/rock interaction) and be strongly affected by plant activity. It occurs in water/rock alteration and soil environments of temperate to cold climates on rocks containing abundant aluminum and potassium. The parent material such as granite, and acid intrusive rocks, metamorphosed pelites and most common sedimentary rocks are conducive to the formation of illite. These conditions are in fact those of most of the fertile agricultural zones today. Illite can be closely associated with agricultural fertility.

Smectite. This mineral is a variation of the theme of charge and charge site under conditions of low potassium or aluminum availability. Higher charge smectites (vermiculite) can form either illite or HI minerals when significant amounts of the requisite cations are present in solution, either K or Al. Smectite minerals are most frequent in temperate climate soils and in the rock/water interaction stages of alteration. Smectites can be either di- or trioctahedral and contain either Al or Fe ions. For the most part such minerals can form HI minerals but only aluminous dioctahedral smectite seem susceptible to form or be associated with illite.

In fact pure smectite behavior (expandability) is extremely rare in soil clay mineral assemblages. It is usually interstratified with another 2:1 mineral or, more rarely, with kaolinite. Smectites form the basis of soil clay mineralogy in vertisols, which are usually formed under dry prairie conditions. High altitude prairies form smectite-rich clay mineral assemblages also under humic, cool conditions which favor low pH soil solutions. However, smectites are found as precursor assemblages in high intensity alteration such as laterites and tropical forests. They are found in acid and basic soils and alterites. Most alteration assemblages of crystalline rocks contain smectite minerals. In general, smectites are found in most alteration zones.

The different types of 2:1 minerals in alteration products are responses to the constraints of chemical composition imposed by the environment (potassium for illite,

available aluminum in solution for HI minerals, more "neutral" pH conditions for smectite types). The mineralogical range is unstable, different plant regimes can change the clay mineral type, maintaining the 2:1 structure basically intact. Mixed layer minerals of the different interlayer types, illite/smectites, HI/illite, HI/smectites are responses to the cation activity in the solutions saturating the 2:1 clays.

8.1.2
Kaolinite and Kaolinite/Smectite Mixed Layer Minerals

The 1:1 almost exclusively aluminous mineral kaolinite is ubiquitous in soils. It is present in the early stages of most weathering in crystalline rocks, at least in minor amounts. Hence it is found in alterites and eventually in most soils. Under conditions of intense weathering, tropical contrasted season climates, kaolinite can be seen to become predominant in alterites. It is often dominant in portions of tropical forest soils also. Kaolinite is replaced by aluminum hydroxide (gibbsite) in laterite formation. Thus kaolinite is found to form and persist in most soil climates and under most conditions of alteration.

The overall tendency in alteration sequences is to lose silica compared to alumina in soil clay assemblages. Then alumina in its turn is lost (Pedro 1966). The loss of silica relative to alumina marks the difference between temperate climate soils and humid tropical alteration. This change in overall chemistry is applicable to the clay minerals, phyllosilicates and hydroxyl-oxides. It does not include quartz. In fact Lelong (1969) demonstrates that in tropical rain forest soils based upon granite, the quartz (and hence silica) content increases in many cases towards the surface while kaolinite content decreases. However on basalts, the clays show a decrease in aluminum hydroxides in favor of iron oxy-hydroxides. As a result humid tropical soils do not show much smectite content. Most commonly one finds kaolinite as the clay mineral present for several meters depth in such soils (Schultz and Ruhiyat 1998). In general, it is apparent that soils under high rainfall tend to contain kaolinite at the expense of 2:1 minerals. Kaolinite and muscovite have the same Si/Al ratios (near one) whereas smectite has a higher relative silica content than kaolinite. In fact if one considers the phyllosilicate transformations from micas and chlorite (high temperature minerals) to soil clays under temperate climate conditions, the initial equilibrium is towards more silica-rich phase, smectite in most cases. One can contrast then the clay assemblages in temperate climate to humic tropical soils as being more silica-rich than those formed under high rainfall.

8.1.3
Gibbsite

The hydroxyl aluminum mineral is restricted to two conditions of formation: one where highly acid conditions produce the precipitation of the mineral indicating the destruction of other alumino-silicate minerals, with loss of silica. It is the buffer to aluminum exportation. Gibbsite is also found in the early stages of granite alteration under temperate climates. Braga et al. (1989) have made some very interesting observations on the presence of gibbsite in the early stages of granite alteration, the arenite facies. They find a zonation from north to south in Europe, through temperature and climatic zones

essentially. In the non-glaciated regions (Norway, Sweden, Scotland to western France) the dominant alterite minerals are 2:1 types with kaolinite. Gibbsite becomes apparent in the more clement climatic areas which have not been glaciated and hence are older alteration profiles. One can equate the low mountain regions of France (Vosges) with the Scandinavian type of alteration in their analysis. In the older alteration zones of Spain and Portugal (equally at higher temperatures) gibbsite is more apparent and can become dominant. Gibbsite is however rare in soil clay assemblages based on these altered rocks. As one moves upward in the alteration profiles more 1:1 and then 2:1 minerals are present.

One reason that gibbsite is rare in the plant/silicate interaction zone is that the amount of soluble alumina necessary to produce this phase is sufficiently high that it will poison many plant species (Wolt 1994). High concentrations of alumina cannot be tolerated by plants. However, if the plants send roots to sufficient depths, they can probably extract silica that is the product of mineral dissolution and bring it into their biotic sphere as phytoliths. This silica, in the form of phytoliths, will be recombined with gibbsite to form kaolinite and probably smectites (becoming HI mineral in most cases) in the soil zone.

One must remember that the water which reaches the water/rock alteration zone at the base of alteration profiles is probably often present because of rapid drainage along major fracture or pore systems. It is not charged with ions from dissolution or equilibration of clays with the aqueous solution. Thus the presence of gibbsite in the early stages of weathering is due to a structural cause in the geometry of weathering. However, in the cases of tropical weathering, the great influx of unsaturated aqueous solution induces the dissolution of most minerals and only the most insoluble ionic species, Al and Fe, remain, forming gibbsite and hydrated iron oxides. Of course this analysis is valid for aluminous rock types, shales, gneiss and granite. More basic or calcareous types will not lead to the formation of gibbsite.

8.1.4
Iron Oxyhydroxides

Iron oxides are ubiquitous in soils. They are present in most types, showing a color in the reds under low pH and high weathering intensity, yellow under higher pH and lower water flux and brown to black under conditions of interaction with organic matter. However, iron oxide and hydroxide is present everywhere. Under conditions of high weathering intensity, laterite formation occurs with a strong concentrations of iron forming a semi-impermeable crust near the surface of an alteration profile.

8.1.5
Imogolite and Allophane

These minerals are often precursor phases to others. They are formed through the rapid precipitation of Si-Al allophane of various Si/Al ratios and Si-Al imogolite with Al = Si during the alteration of vitreous rocks or under conditions of alteration under high pH control (Farmer and Lumsdon 2001; Farmer 1999). Imogolite can also be strongly fixed to organic material in acid soils, especially the E horizon of podzols. In such situations the soil chemistry is of low pH and silica is exported. Since imogolite has a high alumina to silica ratio, it is the result of low silica activity in solution under these con-

ditions. The key to the presence of both imogolite and allophane is a continous humid condition. Under conditions of contrasted climate they are no longer present and are probably transformed into smectite for allophane and kaolinite for imogolite. They represent humid alteration conditions, and the presence of highly reactive substances, for the most part. The allophane and especially imogolite minerals are most likely very important in processes of chemical transfer from surface to lower horizons in acid soils under temperate climate conditions.

For the most part one thinks of imogolite and allophane as alteration products of glassy volcanic rocks. These rocks and their alterite and soils need to be kept humid in order to maintain the hydrous, amorphous or nearly amorphous materials.

8.1.6
Chlorites

Soil chlorites are found in two different types of situations, one dependent on source rock and the other on plant activity. To a large extent they indicate special chemical conditions of the source rock, either a strong iron content in the absence of alumina or a situation of low alumina activity with minimal alkali activities. Basalts and especially ultrabasic rocks are found to form trioctahedral iron chlorite in the weathering process (Velde et al. 1976). Magnesian trioctahedral soil chlorites are probably rarer, due probably to the same conditions but in the absence of iron activity. These chlorites are unstable at low pH values, but since magnesian and iron-rich rocks are "basic", i.e. weathering to form high pH soils, these minerals are the result of high Mg and Fe activity in solution. The trioctahedral chlorites are dependent on the presence of a basic (Fe- and Mg-rich) source rock.

A second situation for the formation of soil chlorite is that of a soil (zone of plant/silicate interaction) where the activity of alumina in solution is very high and this situation has pertained sufficiently for the formation of a completely hydroxyl aluminous interlayer in 2:1 mineral structures. These minerals are di-octahedral in composition, and hence largely aluminous. Dioctahedral, aluminous chlorites are a type of end member of the 2:1 minerals where no alkali ions are present. They are of low silica content. This represents situations in soils where silica is lost with the resultant formation of an aluminous 2:1 mineral. Usually such soils are found to have a very low pH and are formed under coniferous tree cover.

8.1.7
Palygorskite, Sepiolite

These magnesian minerals formed in deserts where capillary action precipitates saturated solution material to form magnesian silicates. They are not stable at the surface, in the soil zone (Paquet 1977). Hence they are most likely to disappear in many soil formation processes. They are relegated to areas of very low water activity at the surface where rainwater is not likely to be saturated with Mg, Al and other ions which form these minerals. In fact much of their presence is due to highly concentrated solutions, desert lake and other closed basin sedimentation in the presence of carbonates or sulfates (see Velde 1985, ch. 7). Hence these minerals are in fact present in the C horizon, usually in sediments where soil is little developed at the surface.

Summary

In this section we have attempted to outline the conditions under which the various components of clay assemblages formed in the alterite and soil zone will occur as a function of climate and hence plant regime. The predominance of 2:1 clay minerals (HI, vermiculite, smectites and illite with their cortege of interlayered minerals) is typical of temperate climate situations. They occur in young soils and mature ones in regions of reasonable rainfall and temperature variations from alpine to Atlantic or mid-Continent ranges. In areas of high rainfall and high temperatures, those climates where it never freezes in the winter, there is an increase in the presence of kaolinite at the expense of the 2:1 minerals. Eventually gibbsite and iron oxide minerals dominate under conditions of high and constant rainfall. These minerals lead eventually to a very low fertility of the soil zone for plant growth. As long as plants can maintain a biotope, especially the forest system, a fertile surface can be artificially maintained. If this system is destroyed, plants have difficulty in maintaining the artificial balance of silica and alkalies in the soil zone. Cutting a rain forest will lead rapidly to a loss of Si, K and other nutrients in the surface layer which cannot be maintained by crops which tend to exhaust these nutrients instead of re-enforcing their presence.

When gibbsite $[Al(OH)_3]$ and iron oxides are present it is difficult to maintain a reasonable plant biotope. Plants cannot grow well on such impoverished soils (tropical and laterite), needing essential alkali and alkaline earth cation nutrients. The smectite-illite clay minerals are potassium and cation-rich, chemical attributes which contribute to plant growth and fertility (Black 1968 for example, pp. 238–272).

8.2
Clay Minerals Present in Soils as a Response to Climate

8.2.1
Physical Factors and Their Effect on Alteration and Soil Clay Mineral Facies

Dry climates (arctic or desert), either by lack of water or lack of liquid water produce fine grained material which is most often little reacted chemically. Soil forming processes are largely mechanical due to differential thermal expansion properties of materials, either individual grains in a rock or the difference between rock and water. This material becomes fine grained but often is composed of the unstable high temperature minerals of which it is made. If the source rock is composed of sedimentary rock minerals, as is often the case on continents, the clay sized fraction will be one of diagenetic or low grade metamorphic phyllosilicates such as aluminous mica (illite) and chlorite with varying amounts of diagenetic mixed layer smectite/illite minerals. Other rocks, such as granites or higher grade metamorphic rocks will produce micaceous materials in the fine fraction and the sand fraction will be composed to a large extent of tectosilicates and other minerals in more minor quantities. These are the surface materials of arctic climates or dry deserts. This material cannot rightfully be considered to contain clay minerals in that the phyllosilicates have not come into chemical equilibrium with atmospheric aqueous solutions at low temperatures. However one of the early mineral transformations in desert zones is one of oxidation and

the production of a red coloring due to the formation of hematite. Usually this iron oxide is not abundant.

Temperate climates have contrasted seasons (wet and dry) and contrasted temperature regimes. Under such conditions forests can prosper and when rainfall is not sufficient, prairies prosper. One can see such situations in going from north to south on the Eurasian continent or east to west in North America. The same changes can be observed on many oceanic islands of modest dimension (Hawaii, Azores, Galapagos, etc). Much work has been done to characterize the soils in regions of contrasting climate as summarized in Jenny (1994) and Birkeland (1984).

Rainfall is very important, of course, in that it controls the saturation of dissolved elements in soil solutions and hence the tendency for silicates to dissolve in order to come into equilibrium with the aqueous solution. For example Jenny (1994, p. 132) indicates that the clay content of soils based upon loess is three times greater with three times the rainfall at roughly constant temperature. Hence dissolution and reaction to form clays is greater under conditions of abundant rainfall. Demonstrations concerning the effect of temperature are somewhat more scarce. Nevertheless Jenny (1994, p. 172) proposes convincingly a relation between rainfall and temperature which indicates the rate of rock weathering and soil formation from granites and gneisss (pelitic or alumious rocks which contain micas as a major phase). The demonstration of muscovite-chlorite mineral conversion to illite-smectites mixed layer minerals in (see Sect. 3.4.1) indicates that a change in average temperature from mountain to temperate climate in grass-dominated soils can change the reaction time in soil clay mineral transformation by a factor of 10^3. This suggests that a serious estimation of average temperature is necessary in assessing the rate of alteration and soil clay mineral formation. These comparisons of course involve both temperature and plant activity which may not follow the same reaction rates and hence the effect of plants can be greater than would be seen in the water/rock interaction zone as a result of temperature differences.

One factor which has not been taken into consideration sufficiently in many cases is that of the plant regime which pertains in the soil environment. Biological activity is strongly governed by rainfall and hence such values as nitrogen, organic carbon, pH and so forth are determined by this factor. The impact of biologic variables on clay mineralogy is less well documented (see Birkeland 1984, chapter 10 for example). In general, forests favor a lower soil pH, a stronger dissolution of silicate materials and the formation of a sandy horizon (E horizon) almost devoid of clay minerals which lies under the surface, humic layer. Clay accumulation occurs below the E horizon with the formation of a clay-organic horizon. By contrast prairies favor the accumulation of clay minerals in the humic horizon with some clay accumulation in the lower B horizon. One can imagine that the plants will have a greater effect than climate alone concerning the type of clays in the soil horizon.

One very important relation in temperate climates, at least in the northern hemisphere, is the non-correlation between change in temperature and rainfall. Much work has been done and reported by Jenny (1994) and Birkeland (1984) on the different effects of these two variables concerning the major characteristics of soils such as pH, carbon, nitrogen and clay content of the soil horizons. If we consider that the influence of temperature on clay reactions is an exponential function of temperature and

that of rainfall a linear function, it is clear that the relations of climate in such situations, as measured by temperature and rainfall will be complex. Further, as showed by Jenny (1994, chapter 6), the relations of rainfall and temperature are not necessarily correlated. For example in North America, temperature is essentially a north/south variable whereas rainfall varies from east to west yet most soil chemical trends are east to west. Overall, if one looks at plant biotopes they follow rainfall for the most part. The amount of reaction between clays and plants will depend upon the thermal input which drives the intensity of the chemistry imposed by plants (and other biological action by bacteria and other organisms in the soils). However, variations of rainfall within a yearly cycle can change the plant regime. For example, the north Moroccan plains have a similar annual rainfall to that of western France. The plant regime is very different in the two areas. If rainfall comes in concentrated periods followed by long dry spells (contrasted climate) the overall effect is to reduce plant growth. Hence plant growth regime is perhaps more important in many cases concerning the effect on clay mineralogy. This is a very important factor in the development of clays, especially in the soil (plant/silicate interaction) zone. Therefore we can consider that there are three factors which will affect the development of clay minerals in soils; temperature, rainfall and above all plant regime. Plant regime is an integrator of the temperature and distribution of rainfall over a yearly cycle.

Tropical climates, especially those of tropical rain forests are dominated by unsaturated aqueous solutions and luxuriant plant growth. Six to seven meters of rainfall is quite a lot. These aqueous solutions will attempt to come into equilibrium with silicates or, by default, aluminous minerals. In doing so the alkali and silica content of the solids is diminished. The 1:1 clays (kaolinite and its hydrous equivalent halloysite) are dominant and eventually in older alteration sequences, hydrous aluminum and iron oxides (allophane and goethite) are the only survivors of the initial silicate rocks which have been altered. However, if the rainfall is alternated with periods of low water influx, contrasted tropical climates, the effect is to dry out the clays and produce gibbsite and hematite. Here the clay mineral types follow the seasons as well as total water input.

The generally accepted ideas on clay formation in alteration are that rainfall and temperature are the major variables which continue to change clay minerals in soils as a function of reaction progress or time. These relations are indicated in Fig. 8.1.

Overall, we would suspect that climate and hence plant regime are very strongly inter-related in the formation of clays in the surface layers of the alteration zone. One should probably look first at the type of plants forming the soil first before considering the clay mineralogy of a soil profile. The alteration zone (water/rock interaction) is surely less dependent upon plants and should respond to temperature and water influx in a more regular and predictable manner.

8.2.2
### Weathering Trend (Water/Silicate Chemical Trends)

What happens when rainwater enters a soil? If rainfall is moderate, the capillary water composition would be more dominated by solids than under high rain input. White et al. (2005) indicate that potassium is more abundant in macro pore water at the surface of a soil profile. Ranger (2002) gives data for coniferous forest soils under moderate climatic conditions in France where capillary and macro-pore water has been

analyzed (Fig. 8.2). When comparing Si and Al concentrations in these solutions it is clear that the capillary solutions contain more silica compared to the macro-pore water and that the Al concentrations are nearly the same, i.e. in equilibrium. Under such conditions, the soil clays reflect stability of a silica-rich mineral, smectite (Si/Al 3 to 5.5), whereas the macro-pore water would tend to be in equilibrium with kaolinite (Si/Al 1.2–3.5). In this example of a temperate climate soil, there seems to be a stability of the more silica rich minerals determined by the solids in the capillary water which is in close contact with the clay minerals. However, the larger, macropores contain water which contains less dissolved silica. This material would be more likely to form a silica-poor mineral such as kaolinite. The macropore water undersaturated with silica is that which finds its way downward in the alteration profile and which eventually interacts with the unstable minerals in the alteration profile and in the altering rock.

As we know (see Chap. 4) not only silica and alumina are involved in the formation of new clay minerals in alteration systems. The activity of alkalis, Ca, Na and especially K are fundamental parameters in mineral stability. Also one must consider hydrogen ions, which can temporarily replace K and Na ions in silicate structures causing de-stabilization and re-crystallization. The major motor for mineral change from high temperature, anhydrous minerals to hydrous clays is alkali/H exchange. The lower the activity of potassium for example, the lower the K/H ratio and hence on sees the transformation of potassium feldspar, into mica, and then mica into smectite, and so forth. In our case of macro-pore water and capillary water, one can compare the K/H ratios of the two fluids. In Fig. 8.2 it is apparent that the two values are similar for each of the samples, and hence one can assume equilibrium for these elements in both waters. The chemical pressure for change into clay minerals is the same.

Hence, using the major parameters of clay stability with respect to alkali-bearing minerals, the water analyses show that most elements are in equilibrium between capillary and macropore water in this example of a temperate climate soil with the exception of silica.

Fig. 8.1. Schematic representation of the clay mineral types as a function of climate considered as rainfall and temperature and alteration time. *2:1* = three structural layer clay minerals
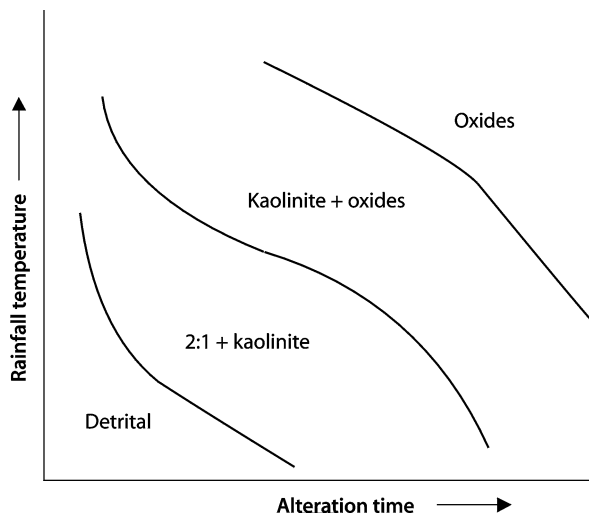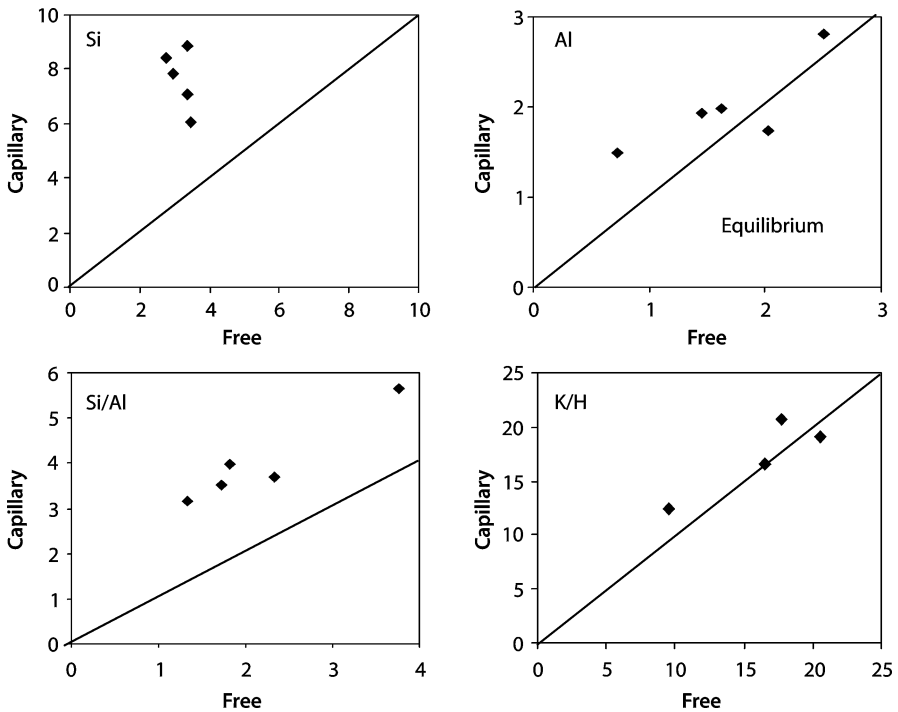
Fig. 8.2. Abundance of dissolved elements in free (macro pore = free) and capillary water in a forest soil (Ranger 2002); *points above the diagonal line* show enrichment in the capillary water, and those *below* enrichment of the element in the macro pore water; *points near the line* represent a near equilibration between the two types of soil water

This has potential importance for differences between tropical humid and temperate alteration mineralogies. If we can assume that macropore water is similar to that found in humid tropical profiles, the lower silica content would favor the formation of kaolinite compared to the more equilibrated water in temperate climate alterations which is more silica-rich and will favor the formation of 2:1 minerals such as smectites, illites and mixed layer minerals.

Bulk Chemical Effect of Unsaturated Aqueous Solutions

The chemistry of weathering (interaction of rainwater with continental rocks which are essentially silicate mineral assemblages) is an age old process which has been investigated for quite some time (Ebelmen 1847). The overall trends have been noted to be an initial loss of alkali and alkaline-earth cations and then silica, with a resultant concentration of hydrated alumina and iron oxides. More intense weathering shows loss of both alkalis and silica with a clear change in clay mineralogy from temperate to tropical to laterite soil types (Pedro 1966). The sequence can be indicated by the clay mineral relations:

Rock → illite-smectite → kaolinite → gibbsite

|	Si/Al > 1	Si/Al = 1	Al
	temperate	tropical	laterite
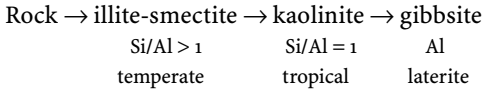
As discussed in Chap. 4, weathering is the result of two reactions engendered by the interaction of rocks and aqueous solution (1) the initial integral dissolution of minerals and (2) the hydration of others (i.e. exchange of hydrogen for cations) which leaves a clay mineral residue. These reactions are activated by slightly acid rainwater and in the surface soil zone one assumes acid products of plant growth (root exudates) as well as decomposition of plant material (Jenny 1980 for example) which in principle impoverish soils and eventually leads to their inevitable infertility (Mohr and Van Baren 1959).

Chemographic Analysis

In order to understand the reaction sequence in soils it is important to understand the chemical relations of atmospheric alteration processes and the chemical relations between the basic forms of clay mineral.

Weathering (water/rock) reactions. One demonstrative initial weathering reaction involves the high temperature 2:1 silicate mineral muscovite, used here as an example. It represents what should be a very common mineral reaction in the initial stages of weathering in the lower portions of alteration profiles (water/rock interaction) or in the upper portions of young soils.

Hydrolysis (cation exchange) of muscovite to kaolinite (loss of K)

$$2KAl_3Si_3O_{10}(OH)_2 + 3H_2O + 2H^+ = 3Al_2Si_2O_5(OH)_4 + 2K^+$$

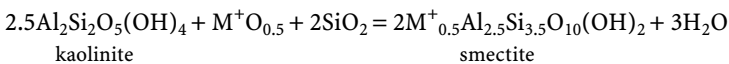   muscovite   kaolinite
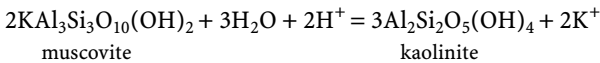
A second reaction step, that of intense weathering, would be the loss of the alkali-free kaolinite to the ultimate stages of weathering, the formation of bauxite.
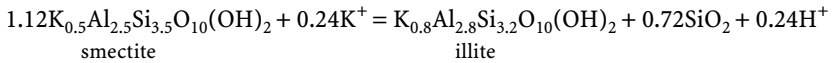
Transformation of kaolnite to gibbsite (loss of Si)

$$Al_2Si_2O_5(OH)_4 + H_2O = 2Al(OH)_3 + 2SiO_2$$

    kaolinite   gibbsite
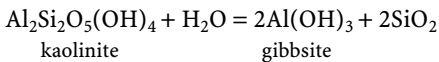
Soil (plant/silicate) reactions. Despite these weathering reactions, which are essentially rock/water interactions with their loss of alkalis and silica, we know that many soils tend to form smectite in the plant/silicate interaction zone (Righi et al. 1999) and probably illite (Reichenbach and Rich 1975). This process is can be envisioned in simple expressions such as:
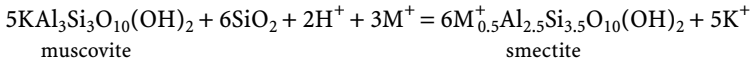
$$2.5Al_2Si_2O_5(OH)_4 + M^+O_{0.5} + 2SiO_2 = 2M^+_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + 3H_2O$$

    kaolinite   smectite

Transformation of smectite to illite (gain of K, loss of Si)

$$1.12K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + 0.24K^+ = K_{0.8}Al_{2.8}Si_{3.2}O_{10}(OH)_2 + 0.72SiO_2 + 0.24H^+$$
$$\qquad\qquad \text{smectite} \qquad\qquad\qquad\qquad\qquad\qquad \text{illite}$$
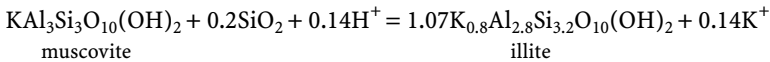
To complete the soil clay mineral transformations it is possible to directly form smectites or illite from high temperature muscovite:

Hydrolysis of muscovite to smectite, via vermiculite (gain of Si, loss of K)

$$5KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2H^+ + 3M^+ = 6M_{0.5}^+Al_{2.5}Si_{3.5}O_{10}(OH)_2 + 5K^+$$
$$\qquad \text{muscovite} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{smectite}$$

Hydrolysis of muscovite to illite (gain of Si, loss of K)

$$KAl_3Si_3O_{10}(OH)_2 + 0.2SiO_2 + 0.14H^+ = 1.07K_{0.8}Al_{2.8}Si_{3.2}O_{10}(OH)_2 + 0.14K^+$$
$$\qquad \text{muscovite} \qquad\qquad\qquad\qquad\qquad\qquad \text{illite}$$

We can represent these relations in a simplified version of chemical activity of Si and K with alumina considered as constant in its chemical activity in the system shown in Fig. 8.3 which involves the major clay minerals concerned. Here we can see that the loss of alkali will form kaolinite from muscovite or illite (arrow 1) and that the desilicification of kaolinite (arrow 2) will form gibbsite (aluminum hydroxide).

8.3
The Impact of Plant Regime on Clay Minerals in Soils

(This section is largely inspired from the PhD thesis of Pierre Barré, Ecole Normale Supérieure)

Normal weathering should give rise to a sequence of silica and alkali impoverishment as one moves from source rock at the bottom of an alteration profile upward to the surface. Older alteration profiles should show this tendency more than younger alteration sequences. This is the general idea given in most introductory texts which describe soil formation. This would mean that 2:1 minerals would be found at the rock/water interface and the base of the alterite portion of profiles and kaolinite or eventually gibbsite in the upper portions of soil profiles. Our observations in Chaps. 3 and 5 based upon published studies seem to invalidate this concept to a large extent, especially under conditions of temperate climate alteration where plants are abundant in the upper, soil portion of an alteration profile. Basically, one finds the 1:1 mineral kaolinite dominant only in regimes of high and continuous rainfall. What is the problem?

8.3.1
Reactivity of Clay Minerals in Ecosystems

It has been noted in several places in the text that mixed layer minerals are almost exclusively found in the soil horizon and that these minerals are dominantly of the

Fig. 8.3. Effect of water–rock type interaction of mineral dissolution and loss of silica and alkali (potassium); μ = chemical potential of the elements concerned
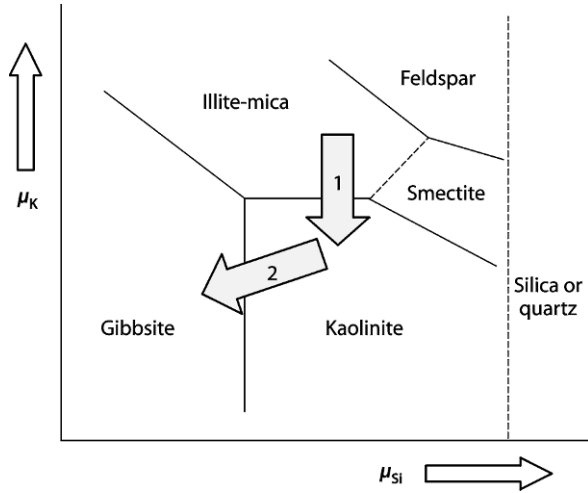
2:1 type, either illites or smectite/illite MLM typical of prairies or HI minerals typical of forests. How can one explain the strong presence of 2:1 minerals, which are the highest in silica content of the clays, in the soil horizons where the impact of unsaturated rainwater is the greatest? In order to do this one must compare the relations of normal water/rock interaction and the presence of clay types in the soil horizons.

It is known that plant ecosytems appear to affect the chemistry and clay mineralogy at or near the soil surface. Lucas (2001) has argued in favor of a stabilization of kaolinite in the place of aluminum hydroxide (gibbsite) at the soil surface under tropical forest cover due to siliceous plant phytoliths. Berner et al. (2005) have summarized this and other data which indicate the same influences. Hajek and Zelazny, (1985) summarize published data indicating that in old, strongly weathered largely forest soils in the Southeastern United States, the silica-rich minerals HI vermiculite and illite typically occur in the soil zone (plant/silicate interaction horizon) while kaolinite and gibbsite are found below this zone indicating that severe weathering occurs at depth. A sort of "chemical uplift" (Jobaggy and Jackson 2004; Reichenbach and Rich 1975, p. 81) or chemical translocation has also been invoked to explain that essential cations (K, Mg, Ca) are enriched as exchangeable elements in soil surfaces due to plant action in temperate climate soils. Birkeland et al. (2003), Velde (2001) and Reichenbach and Rich (1975, p. 81) have argued in favor of a stabilization and growth of the silica-rich clay minerals smectite and illite in prairie soils as a general feature. Thus various plant regimes appear to enrich the surface zone in silica-rich clays containing vital cations, especially potassium. Such effects are pointed out by White et al. (2005).

The clay minerals forming in the soil zone where plants determine the chemistry to a large extent must be a function of the type of plants present. This is due to the fact that plants are chemical agents in that they grow and decay in the soil, they exude various organic substances into the soil and their dead matter falls onto the soil and is incorporated in it through the action of bacteria and other living agents. Each plant regime has different types of organic material in it and thus influences the soils in different ways through the chemical controls engendered by its evolution.

In a very general way, prairies, deciduous or conifer forests can be considered to be the major ecosystem types, at least in temperate climate regimes. This has been discussed in Chap. 5 and it has been understood, intuitively and from experience by farmers for the last 2 500 years or so. It is still useful to return to these ideas and ancestral uses in that they are probably the key to an understanding of the effects of human intervention on soils clay mineralogy. The age old methods of keeping soils fertile involved rotations of crop plants (de Serres 1600) designed to favor the retention and renewal of mineral nutrients, potassium and phosphorous as well as supplying nitrogen. Nitrogen comes from the air, through plant and other biological activity while potassium and phosphorous are derived from the destabilization of high temperature minerals in the alterite (saprolite) and soil environment. In Sect. 5.4 concerning the plant chemical translocation effect, it seems that plants have a general tendency to preserve certain characteristics of soil chemistry which favor the presence of 2:1 clay minerals and especially smectites and illite. This involves the potassium cycle in soils and alteration zones. The preservation of potassium depends upon the presence of 2:1 minerals which is dependent upon silica activity that stabilizes these minerals. One of the major characteristics of plants is the presence of silica in their tissue, which when decomposed releases this element to soil solutions. The installation of plants on altering materials tends to slow down the process of alkali and silica loss.

Prairies are of particular interest in the plant/soil relations in that prairie type soils were those used by agricultural man to develop his favorite foods, grains, which can be stored and transported with greater ease than other food stuffs. The maintenance of soil fertility for agricultural purposes is in most cases related to the chemical conditions favored by grasses. It seems that these plants tend to form potassium-rich clays; smectites interlayered smectite/illite and illite. Intensive cropping tends to exhaust these clays, releasing potassium and favoring smectites. These smectites can be regenerated into illites given enough potassium in their chemical environment. Plant uplift of potassium from deeper parts of an alteration profile where high temperature minerals are continually altering to clays releases potassium which is incorporated into plant tissue by roots and re-deposited on the surface of the profile. In the soil zone, one finds the greatest root activity (root mass) where the re-utilization of the uplifted potassium can occur. Since potassium is not highly favored by cation absorbers (usually the potassium content of exchangeable ions in soils is 10 to 15% of the ions available), the incorporation of potassium into high charge smectites to form soil illite is a critical source of potassium for plants. Prairie soils seem to be particularly rich in potassic clays and hence lead to a source of potassium for crops.

By contrast, it appears that conifers tend to form soil HI minerals which will not capture nor retain potassium. They are antithetic to crops. It is possible to modify some of the HI minerals into other forms such as illite using different plant regimes such as oak trees (Tice et al. 1996) or of course prairie growth. Thus it is likely that one can manipulate soil clays to form a fertile assemblage using proper crop or plant sequences. This is of course nothing but classic, pre-1950 agricultural "wisdom" dating in fact from ancient greek times, practices recorded by classical writers (Toutain 1927, part 1). Crop rotations are just that, manipulation of soil chemistry to favor potassium-bearing minerals. However, once the 2:1 clays are degraded into kaolinite by intense weathering conditions, the problem is much greater and probably some time will be neces-

sary to convert kaolinite to a 2:1 mineral by the addition of silica through phytolith incorporation into the soil zone. We have no specific data on this problem.

8.3.2
Convergence of Soil Clay Mineralogies

There is some indication (Birkeland 1984, p. 287 reporting data of Barshad 1966) that plants can even overcome to a large extent the imprint of initial rock composition in the formation and transformation of clay material into soil clay mineral assemblages. Figure 8.4 indicates the soil clay minerals in the 0–15 centimeter depth zones of soils formed in the California Coast Range. The plot is one of relative clay mineral species content of the clay fraction versus rainfall and hence plant regime. The low rainfall samples form under prairie-scrub vegetation while those above 100 cm precipitation are formed under forest (mostly conifer) cover. Either felsic or basic eruptive or intrusive rocks give a very similar clay mineral family grouping if one considers the 2:1 versus 1:1 clay types or kaolinite versus illite, smectitie and HI minerals. Smectite is more abundant under the prairie regime and becomes a minor phase compared to kaolinite in these soils formed on slopes. In fact one sees the formation of 2:1 minerals, aluminous for the most part, from alterite products and altered micas in felsic rocks. Certainly the presence of 2:1 minerals formed from basic rocks passed through a ferric smectite (nontronite) to a more aluminous phase before becoming an HI mineral.

Fig. 8.4. Clay minerals formed in soils on different substrates (Birkeland 1984). Precipitation in cm per year. Substrate rock composition does not influence the clay assemblage to a great extent except for the absence of illite on basic rocks
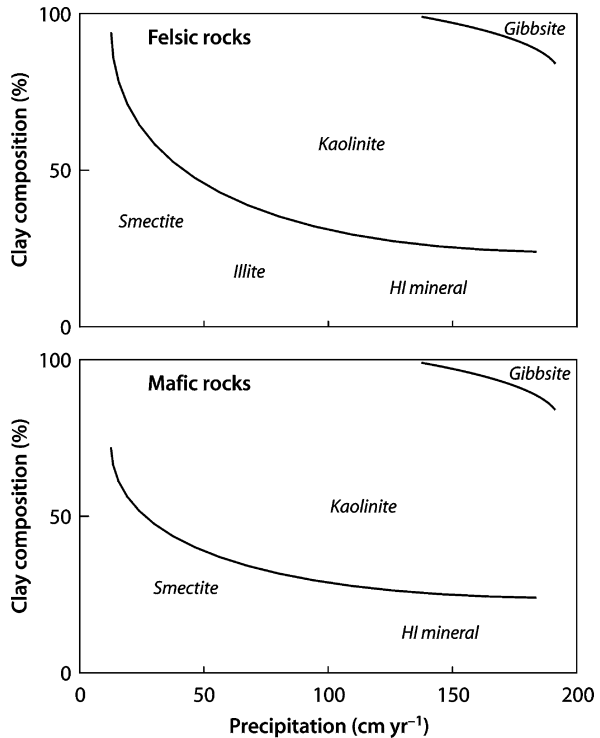
The alteration of prairies favors smectites in the surface zone while forests (conifer) favor the presence of HI minerals. This top soil mineralogy appears to be largely independent of the rock material which the alteration profile is based upon. This indicates that the plant regimes tend to efface the chemical differences of inherited clays to form a series which is beneficial to their survival. The fact is that one rarely finds trioctahedral minerals in the soil zone, they seem to converge on different types of aluminous 2:1 minerals, smectites, illite or HI minerals depending upon the plant regime concerned. The imprint of rock chemistry is left behind in the alterite (saprock) zone of alteration. It should be noted that in the zones of lower rainfall, one finds more 2:1 mineral content in the clay assemblage.

8.3.3
Effect of Chemical Translocation by Plants on Clay Mineral Stabilities

The observation by Meybeck (2005) that K and Si are of the lowest abundance in contemporaneous pristine river waters compared to Ca, Mg, Na, Cl, and S ions is of great importance. This suggests that K and Si are withheld during the processes of alteration since their elemental abundance in most rocks is closer to that of the other ions compared. This is especially the case for silica of course. If the sea is salty (with NaCl) one can explain the extraction of Ca by animal action to produce carbonate shells, and eventually Mg incorporation into these materials. However the low abundance of potassium, two orders of magnitude, below other common elements should provoke some thought.

If plants can be associated with fertile, silica and potassium-rich clay minerals such as smectite and illite, how can they stabilize these minerals in the face of the assumed normal trends of weathering (alkali and silica loss)? The question which can then be posed concerns in fact a mechanism whereby plants control or at least limit the effects of water/silicate interaction, K and Si loss, which destroys the fertile clay minerals.

Most plants contain silica in the form of phytoliths (Farmer et al. 2005; Derry et al. 2005) which, upon the decomposition of the plant material will enrich the soil in a very active form of silica. This material is highly reactive because it is in an essentially amorphous or possibly in a crystalline state of high reactivity such as cristobalite whereas the stable form of silica, quartz, is of low chemical reactivity. Thus the high activity phytolith silica is brought to the surface by plant transport.

Further, most plants contain significant amounts of potassium in their different parts (Gain 1895 for example). Plants then accumulate potassium at the surface in the same way that they enrich soils in silica. This overall chemical effect can be seen in the chemical profiles of certain rock types, especially those which are initially potassium-poor. Data presented by Dahlgren et al. (1991) for grass and oak forest soil solutions in Japan formed from volcanic rocks indicates that silica concentrations in the organic horizon are significantly higher than in the lower horizons, by a factor of five, and potassium content is ten times higher than in pore water below the surface zone. The clays at the surface are 2:1 hydroxy-vermiculites which disappear below the upper horizon. Bonifacio et al. (1997) and Pion (1979) give chemical data for soils formed on serpentines, and basic intrusive and metamorphic rocks which are potassium-poor where there is an increase in potassium in the uppermost levels of the alteration profile. The potassium translocation effect can also be seen for weathering profiles on basic

eruptive vitreous materials forming andosols and extrusive basic vitric materials (Meijer and Buurman 2003; Lorenzoni et al. 1995).

Plants then can move (translocate) material from the alterite (saprock) zone to the surface, plant/soil interface. This is indicated in Fig. 8.5 by an increase in silica and potassium activity in solutions. This action maintains and perhaps creates in some cases clay minerals of the 2:1 type which are the most silica-rich of the clay types found under weathering conditions. Silica is the key to their stability. Plants need the siliceous clay minerals smectite and illite to prosper. These are the clays that can furnish an abundance of potassium, calcium and magnesium to insure vigorous plant growth *via* cation exchange. Clays fix needed cations for use during the growing season of the plants. The normal trend of weathering (water/rock interaction) depletes the alteration zone of the elements essential for the stability of these clays (Si and K). Concentration of these elements in plant tissue by root action (chemical translocation) produces a surface layer in the soil horizons which favors the stability of these clays.

Of course each ecological system is more or less adapted to the soil type (substrate and alterite mineralogy) and the climate under which it prospers. These factors will influence the chemistry of the soil and the clay mineralogy independently of plant interaction. The evolution of each system depends upon the ability of soil minerals to conserve the specific ions extracting them from solution for their eventual incorporation either in plant tissue, to stock them in the clays or failing either, favorize their release to solutions and removal from the soil system.

Plants can only do so much against the forces of chemical dilution which engender the loss of silica and alkali ions. Although deeply weathered surfaces in the Eastern United States show high silica-rich clay content in the form of HI vermiculites (Hajek and Zelazny 1985; Norfleet and Smith 1989; Bryant and Dixon 1964) tropical rain forests appear to be devoid of fertile 2:1 clay minerals (Bravard and Righi 1988) and hence are significantly more fragile and less resilient to ecological changes such as de-forestation. This indicates that plants can arrange their surface soil chemical environment to a certain extent but eventually the dissolution of silicates, loss of silica and potas-

Fig. 8.5. Effect of chemical translocation by plants of Si and K which stabilizes the 2:1 minerals smectite and eventually illite. μ = chemical potential of the element in solution
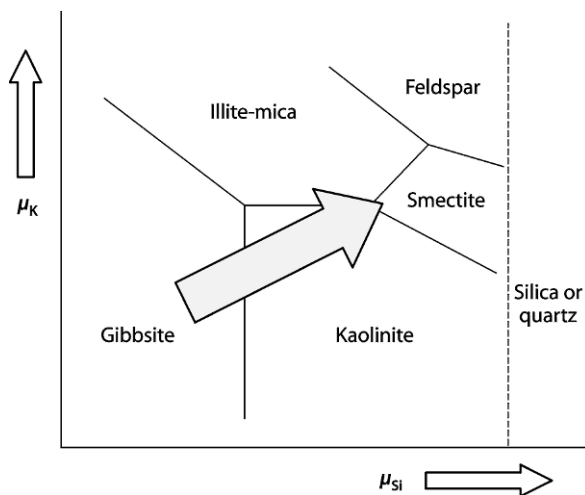
sium will impoverish the soil substrate. Just how much can plants do to counter act the normal trends of weathering by silicate/meteoric water interaction?

It is possible to consider such relations, rainfall, plant growth and elemental translocation as they could affect clay mineral species in the soil (plant/alterite reaction zone). It is known that there is a general, if not precise, relation between plant production (biomass) and rainfall (Lieth 1975). At low rainfall, biomass production is low and the translocation factor would be low. This should be reflected in loss of silica through the sparse but periodic rainfall in deserts. For instance, Manizhnan et al. (2006) indicate that kaolinite can in fact form in very desertic environments in western Australia. The interesting observation on the relations presented as a curve in Fig. 8.6 is that at high rainfall, the biomass does not increase greatly, certainly not as much as in changes under lower changes in rainfall regimes. This suggests that the production of biomass is not at all linear as a function of rainfall but attains as one would suspect a maximum. Biomass is also rather variable depending upon climate, i.e. the periods and intensities of rainfall throughout the year. For example the rainfall in western Europe is similar to that in North Africa, but the vegetation and bioproductivity is not at all the same. Biomass is in fact an integrator of the climate variables. Hence it cannot be directly compared to mean annual rainfall except in a very general way. Biomass production is an indicator of climate, seasonal effects of rainfall.

Now if we consider that biomass does not produce only carbon, nitrogen and oxygen-bearing material (atmospheric material), but also contains significant amounts of potassium and silica (mineral components) as indicated above, one can postulate the effect of biomass on the chemical composition of the soil. Increased productivity will increase the K-Si in the upper portions of the soil. This will favor 2:1 minerals compared to 1:1 minerals, the normal product of water/rock interaction, such as indi-

Fig. 8.6. Schematic diagram representing the effect of rainfall on plant activity (biomass) which indicates the amount of material translocated from depth to the surface soil mineral zone. The biomass curve shows that at high rainfall, the plant regime will not exceed a certain amount of translocation effect and hence dissolution of alkalies and silica proceeds producing the kaolinite and eventually gibbsite soil clay assemblages. Lower rainfall shows great changes in biomass, due essentially to the variations of rainfall throughout the year. Steady rainfall gives higher biomass production that does irregular, contrasted season rainfall where biomass production is lower
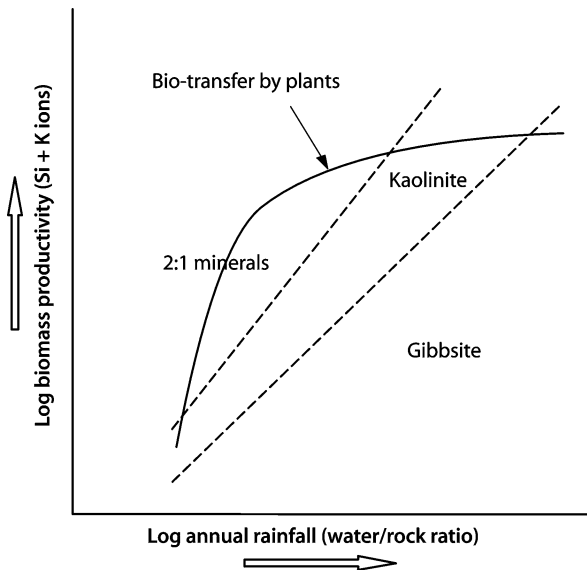
cated in Fig. 8.5 translocation by the arrows. Biomass increase shifts the equilibria to higher potassium activity and silica activity. However rainfall, the effect of diluting the solutions and hence transporting elements out of the system must be considered also. The important feature is that of the inevitable shift from 2:1 minerals towards kaolinite and gibbsite as a function of high rainfall even under high biomass production (tropical rain forest conditions). As rainfall increases, plants cannot keep up with the dissolution rate in soils due to rainfall. Here the influence of plants diminishes with rainfall. Moderate rainfall induces high plant input to the surface, favoring the stability of 2:1 minerals. As rainfall decreases, plant production decreases rapidly and the minimum stability of 2:1 minerals will be attained.

This schematic description of plant and clay mineral relations under different rainfall regimes is a potentially important tool which can be used to interpret different portions of soil sequences under different climate regimes. One very important point to consider is that such a diagram assumes maximum chemical equilibrium between water and clays. At each rainfall input, the silicates come to chemical equilibrium with the aqueous solution. One knows that in all soils there are macropore passages of high influx and capillary porosity which holds water for much longer periods of time. In the capillary situation one can expect chemical equilibrium whereas in the macropore situation this is less likely to obtain. The importance of macropores in a soil and alteration profile is a function, in general, of the clay mineral content. The more clay, the less macroporosity will occur during periods of humectation.

Another important point in considering rainfall averages is that they represent a yearly input. In climates of high seasonality, the rainfall can enter the system and leave without attaining chemical equilibrium with the clays. Such rainfall events will selectively affect the alteration profile in zones similar to those of the initial interaction of water and rock described in Sect. 6.3. Rainfall on a slope will move more rapidly leaving less time for chemical equilibration. These effects will exaggerate or magnify the effect of the amount of rain input into the system. Hence high rainfall, where biomass cannot over take the rainwater dilution factor will produce kaolinite and eventually gibbsite despite plant activity and translocation of Si and K. One should consider the case where plant activity and biomass input of Si and K are low due to low rainfall, and hence one could expect the presence of kaolinite and perhaps gibbsite in soil surfaces with low plant activity.

Overall one can propose a general schema for the change in clay mineralogy from top to bottom of an alteration profile. Alteration begins at the bottom, in the water/rock interaction zone. Here very local chemical forces come into play to form the individual clay minerals. In this process much matter is lost to solution, alkalies, alkaline earth elements and silica. The remnants of rock structure (saprock) keep the different new phases spatially separated which slows chemical interaction which would form new species. The loss of structure (saprolite) tends to form new clays which reflect the overall chemistry of the alterite. In these portions of the alteration profile, the minerals reflect local or more general chemical forces which are essentially determined by water/rock interaction (Fig. 8.7). The next zone of the profile (B) reflects the activity of the upper most part of the profile. This is the zone of physical displacement of clay particles associated with organic material fixed to these particles. Under conditions of high acidity (usually due to organic acids) the upper B is characterized by low clay content, and loss of these minerals. This is the E horizon of podzols.
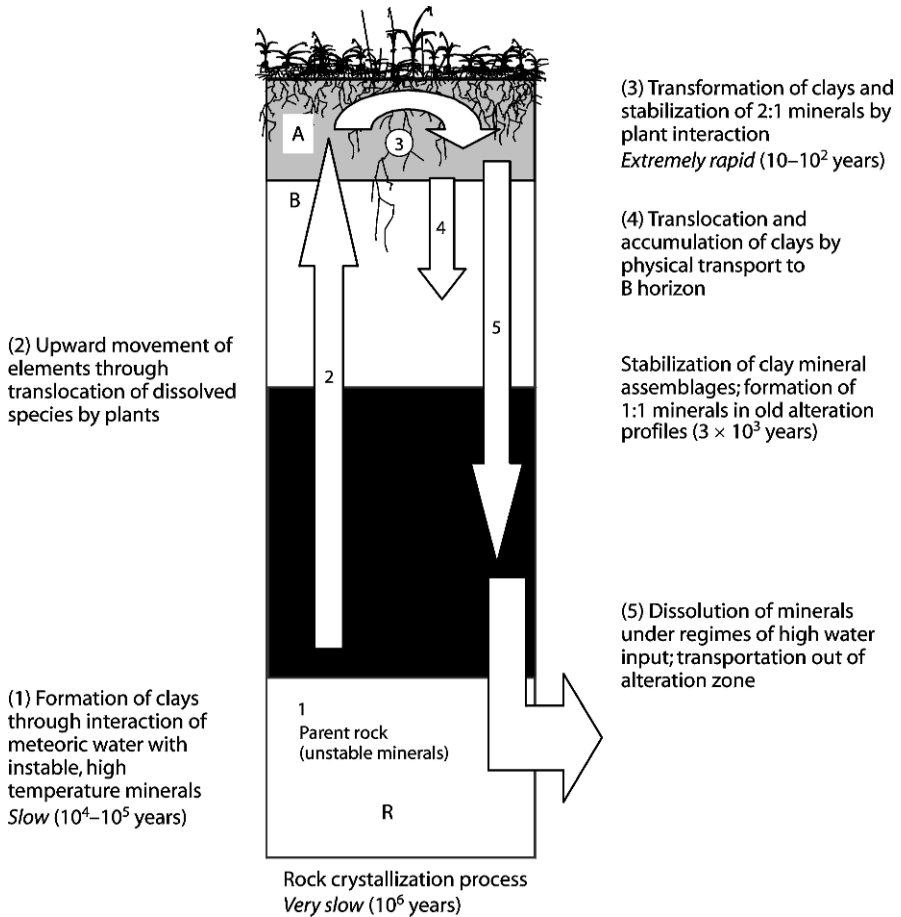
Fig. 8.7. Overall movement of material in alteration profiles. *Arrow 2* shows plant translocation vector, *arrow 3* the deposition of elements by plant decay, *arrow 4* shows the movement of clays by movement in pore water to the B horizon, and *arrow 5* shows the movement of dissolved elements in solution which leave the system to be concentrated, eventually, in sea water

The A horizon is one of plant/silicate interaction. Here the chemistry is largely determined by biological processes, be it input from plant material by chemical translocation or the production of organic molecules which can interact with the silicate material. Many of the reactions are controlled by bacterial activity which controls the rate of the processes. Hence one can find a change of 10^3 in reaction rates of chlorite transformation to interlayered illite/smectites for example as demonstrated in Sect. 7.2.2. This change in reaction rate can be described as being one of temperature, which of course determines the bacterial action and growth. Minerals in the soil zone tend to be 2:1 types, which can retain cations useful to plants, such as potassium.

8.3.4
Equilibrium and Disequilibrium of Soil Clays

The initial stages of clay formation under atmospheric conditions are the water/rock interaction. This relationship is one of disequilibrium. Most rock materials are strongly out of equilibrium with surface conditions. They have formed under higher temperature conditions and for the most part in systems where the silicate solids are by far greater in mass than the liquids, mostly aqueous. These minerals are not in thermodynamic equilibrium with surface conditions where slightly acid water is abundant and the average temperature is nearer 10 °C than 50 °C where diagenesis begins or near 200 °C where metamorphism begins (see Velde 1985; Gharrabi et al. 1998). The hydration (hydroxylization) of silicate minerals occurs in the water/rock interaction. The disequilibrium between high temperature minerals and slightly acidic aqueous solutions is the motor of such reactions. The initial equilibrium attained during these reactions which form clay minerals is that determined largely by local (individual mineral grain) systems or grain contact regions. These minerals gradually come to a certain equilibrium as more and more of the high temperature material is altered. As alteration proceeds to the ultimate transformation of all of the rock into clay, the amount of altering fluids increases with time and the proportion of most soluble elements decreases. Alkali and alkaline earth elements are lost then silica. By the time the rock is totally altered, a large part of the soluble elements have been transported out of the system. The resulting clay assemblage at near total transformation is dominated by kaolinite, oxides and eventually gibbsite. Total transformation takes on the order of hundreds of thousands of years. This is the basic equilibrium towards which alteration is driven.

However, plants cannot thrive on kaolinite and gibbsite. They wish to have potassium available as well as minor quantities of calcium, magnesium and other elements. This can be effected by providing a chemical climate conducive to the stability of 2:1 minerals. Hence the equilibrium in the soil zone is controlled first by the activity of silica in solution, which favors the siliceous clays, the 2:1 minerals. This is the basic equilibrium maintained as much as possible by plants. The prairie regimes tend to favor smectites or illite minerals while the forest plants, especially conifers, favor HI minerals.

Now one must consider the effects of human activity. Changing the plant regime, mainly by exhausting the potassium supply, can create a new less potassic clay assemblage in periods of tens of years. We have no information indicating a change in clay mineral type, i.e. the loss of 2:1 minerals in favor of kaolinite for example. The changes in clay mineralogy appear to be reversible (when 2:1 minerals are still present). The traditional remedy was to change the plant regime, essentially by planting prairie in place of cash crops (see Washington 1801). Cycles of five and five years, prairie to cash or food crops were gradually reduced to one in three in the 18th–19th centuries (Patullo 1758; Seltzenberger 1912) by the use of the most efficient part of the prairie plant population, usually luzern or clover. These cycles were aided by the use of prairies as pasture where manuring was automatic. This type of land use can lead to disequilibrium or equilibrium depending upon the type and cycle of plants used. Of course one can

substitute chemicals to replace those taken out by plants. Thus in general one would expect that a 2:1 mineral would be favored by potassium fertilizer application, assuming that it replaces roughly what is taken out by crop plants.

Cutting trees and replacing them with cash crops will not help maintain the chemical equilibrium established by plants. This is especially true in tropical forest areas. Careful change to prairie type plants can bring deciduous forest soils rich in HI minerals to a mineral equilibrium compatible with cropping (smectite-illite). This has been done for about 6 000 years with success in Western Europe (Clark 1955).

The above analysis assumes that the transport of fine clays is not a dominant factor in the structure of the soils considered. If one produces new minerals of small grain size which are transported out of the alteration profile by water flow, not much can be done except to favor intense root growth at the surface to favorize physical stabilization of clays. Again plants come into play in such a situation.

8.4
The Structure of Alteration and Clay Formation

The different chapters of this book have been devoted to a description of the different types of alteration mechanisms and the resulting products of chemical interaction at the Earth's surface. From this we can determine two major zones of interaction which pre-figure the chemistry and clay minerals produced. The first is the interaction of water and rock and the second is the interaction of plants and altered material, essentially clay minerals. The first interaction tends to produce multiphase clay assemblages while the second tends to produce more homogeneous clay assemblages. This effect is due to the nature of the chemical systems concerned.

8.4.1
Water/Rock Interaction

Chapter 4 describes the interactions which are active in the early stages of water/rock interaction. The chemical constraints and interaction are determined on a very small scale, microns to millimeters. The context is one of unstable high temperature minerals which are put into contact with relatively dilute rainwater which first tends to dissolve the old, high temperature phases. The initial reactions are those of rapid dissolution, usually rapidly forming a new mineral when the immediate solution is saturated with low solubility elements. Thus high solubility elements such as alkalis and alkaline earths are put into solution leaving behind less soluble elements such as alumina, iron (ferric) and silica to form new phases. The role of magnesium is important in many alteration systems where ferro-magnesian rocks are altered. The higher temperature of formation of the source rocks, the faster they will react. Also, the higher the temperature of formation the greater difference between the old and new mineral phases. The clays formed in granite or gabbro rock alteration are greatly different from the clays formed from the alteration of sedimentary rocks. Low grade metamorphic rocks and sedimentary rocks contain to a large extent phyllosilicate material, excluding carbonate and quartz minerals, which is very close in mineral character to that of clay minerals. In any event, the systems of alteration are quite localized in space with single or two minerals reacting in the presence of unsaturated aqueous solutions. The

special distribution and segregation of the new clays is maintained until the old rock structure is destroyed forming the alterite zone. Here the inherited new minerals are brought into contact and they begin to react with one another. In this alterite zone, some parts of the initial rock, as mineral grains or rock fragments, still are present and they gradually react with unsaturated aqueous solutions.

The process of water/rock interaction is slow, taking up to a million years to be accomplished. The vector of alteration is downward into the substrate. Hence we have a lower interaction zone in an alteration profile that is slowly producing a multi-phase clay assemblage.

Due to the small size of the chemical systems forming clay minerals, one can find a large variety in different parts of the altered rock, saprock and lower saprolite zones. These multi-species assemblages are gradually effaced as the percentage of clays increases and the old rock structure is effaced, leading to a more general chemical system extending over larger and larger volumes.

8.4.2
Source Rock and Clays

Of course the basic importance of bulk rock composition cannot be ignored. One can distinguish basically three types of rock which contain large quantities of silicate minerals – acid eruptive, basic eruptive and their metamorphic equivalents, and pelitic metamorphic and sedimentary rocks. Carbonates and sandstones do not produce much clay material.

The acid crystalline and pelitic metamorphic and sedimentary rocks form aluminous silicates as clay minerals; kaolinite, 2:1 clays and oxy-hydroxides (Al and Fe) in the soil horizons. Basic rocks (those dominated by ferro-magnesian phases) tend to form ferric smectites and in some instances talc and chlorites. Oxidation and loss of silica tend to form, eventually, more aluminous smectite minerals. Most rocks under conditions of contrasted climates form dioctahedral 2:1 minerals in the soil horizon whereas the types of clay minerals formed in the rock/silicate interaction zone depends more strongly on the composition of he altering rocks. In these regions one will find trioctahedral minerals which become rare or non-existent in the superficial plant/silicate interaction zone.

When the eruptive rocks are glassy, containing much non-crystalline material, poorly structured minerals such as imogolite and allophane form under conditions of constant humidity. Here chemistry is less important than the high instability of the silicate material.

The imprint of rock type is seen in both the water-rock interaction zone as well as the soil/plant interaction zone, although the convergence of mineralogy towards the 2:1 minerals tends to efface the specificity of the initial rock composition to a large extent.

8.4.3
Plant/Soil Interaction

The upper, organic-rich portion of a profile, defined as the A horizon, is where most of the plant interaction occurs. Here the chemistry is determined by the action of plants,

their decay products and transformations by living organisms. For the most part, in soils developed by abundant plant regimes under conditions of moderate rainfall, the clay mineralogy tends to be similar, i.e. based upon 2:1 minerals with more or less minor amounts of kaolinite. These 2:1 minerals tend to form interstratified complexes probably with only two dominant types of inter layer ion present, potassium, exchangeable bases or hydroxyl alumina. This represents a strong homogenization of the clay suites found in the water/rock interaction zone where 1:1, 2:1 and hydroxy-oxides are found. If the clays are more homogeneous, in special terms, on a horizon scale, they must be responding to more general chemical constraints which affect the silicates over several tens of centimeters depth in the soil zone.

Different plant regimes (conifer, deciduous forests and prairie) tend to favor different types of clay minerals in the soil zone. This is the result of plant and bacterial actions as well as the effects of rainfall and temperature regime on these living organisms. Acid soils, those where pH is below 5, are normally the combined product of siliceous rock source matter and the presence of conifer or evergreen trees. Here one finds the aluminous interlayered 2:1 clays, HI and soil vermiculite. The high acid regime tends to dissolve the clays below the humic zone giving rise to an E horizon, dominated by quartz sand. Why the soil horizon contains 2:1 minerals and that just below shows their dissolution is a mystery at the moment.

Deciduous forest and especially prairie ecosystems promote the potassic 2:1 minerals illite and interlayered illite/smectites. These minerals stock potassium for use by the plants growing in the soil/plant interaction zone.

The clays dominant in the soil horizon are of the 2:1 type, either as pure or homogeneous phases or as interlayered minerals with components of two or perhaps more types of interlayer behavior.

8.4.4
Clay Transport

Below the A horizon of plant/clay interaction one finds an accumulation of clay minerals coming from the humic, A horizon. This is the B horizon, developed by the physical transport of clay particles in percolating soil solutions. The vector of vertical displacement is not the only one possible. When the alteration profile is on a slope, some horizontal component of clay movement can be observed. In fact, even in areas of heavy vegetal cover, streams are known to be cloudy, and brown carrying fine clay particles after periods of heavy rain. This is not surface run off, but lateral transport of clays under percolation flow. The effect of mobilization of clay particles in suspension in moving fluids in the soil and alterite zones should not be under estimated. For example, clays are well know to carry absorbed charged molecules on their surfaces, such as exchangeable cations or more importantly charged organic molecules such as herbicide or insecticide metabolites. These vectors are not evident from surface observation, but it is well known that these potentially toxic organic molecules can be traced in ground water and especially in stream waters. For the most part they are not soluble but are attached to clay or other charged particles. This effect should be taken into account in studies of dispersion of industrial organic compounds.

8.4.5
Kinetics of Clay Change in the Soil Zone

In Chap. 6 one has seen the effect of agriculture on clay mineralogy of the soil zone. According to classical mineralogical definitions, new minerals such as illite can be formed or lost through agricultural processes. Transformation of chlorite to mixed layer minerals in illite-chlorite dominated source materials by plants can occur over periods of thousands or less than ten years. These reaction rates are very much greater than those for isolated silicate systems such as are found in diagenesis where temperature is the motor of mineral change. One can ascribe the differences in mineral reaction rate to the effect of biological action which will change the chemical intensity of the reactions by furnishing certain material at a great rate, which is in fact controlled by temperature also. However the impact of plants and bacteria seems to dominate in soil clay mineral stabilities.

One should take these observations as a function of their relative importance. If one considers most of the changes, they in fact occur between 2:1 minerals where the interlayer ion site changes occupancy giving a different X-ray diffraction characterization. In fact the difference between HI and illite is one of potassium availability in many instances as demonstrated by Tice et al. (1996) in field experiments and the observation on Arkansas agricultural soil clays (Chap. 5.5) with K-saturation in the laboratory. Shifts from smectites behavior to illite (closed layer, 10 Å spacings) can be effected by potassium saturation also. Reversal or this effect has been seen when corn is grown without fertilizer. Then one can form or lose HI, smectite and illite by manipulating the concentrations of ions in solution. This is not a true mineral change, in the sense that the different behaviors are due only to exchangeable ion site occupation. The interchangeable family of 2:1 mineral structures is in fact being manipulated by different plant regimes in the soil zone. This is a very important concept which should be kept in mind in studies of ecology and agricultural engineering. Rapid mineral change representing differences in the availability of potassium and other interlayer ions can be determinative concerning the productivity or in fact the presence of different plants in the soil zone.

8.4.6
Minerals Present and Their Change in the Soil/Plant Interaction Zone

If the rock/water interaction zone (saprock) is heterogeneous in its mineralogy from point to point, the mineralogy of the soil zone is mostly homogeneous as it is considered to be in a soil horizon by pedologists. This suggests that the plant regime tends to homogenize the chemistry of pore solutions in order to produce similar mineral phases from point to point in the horizon. The clay minerals present are dominated by 2:1 structural types of the aluminous, dioctahedral type such as the smectite/illite mixed layered minerals. Even HI minerals tend to become more aluminous with their evolution in the soil zone (Gillot et al. 2000). As far as we know the HI minerals in the evolved alteration sequences on various crystalline rocks in the south-eastern United States are also of an aluminous character (Rich 1960; Norfleet and Smith 1989; Bryant

and Dixon 1964; April et al. 2004). Hence it seems that there is a convergence of mineral type towards a dioctahedral 2:1 structure in the soil horizon. To a large extent, in reasonably mature soils one finds 2:1 minerals and kaolinite as the clay assemblage. Weathering intensity and time of interaction or low plant activity can favor the kaolinite over the 2:1 minerals. Thus one finds aluminous clays in the soil horizon in old soils of high rainfall.

The large portion of agricultural soils farmed today, for the most part in the northern hemisphere at least, is formed in reaction to rather recent climatic changes and effects, glaciation, loess deposits and river action. These soils are young, i.e. they have not reached an equilibrium with the plant regime and water influx that reigns. This is due to recent removal and transportation of surface materials and to the fact that the plant regime established today is rather recent. Here plants are the major actors in determining the chemistry of A horizon fluid compositions closely associated with the clays.

If plants control the local chemistry of soil solutions, this is the control of soil clay mineralogy. We have demonstrated that clay mineralogy can change (according to current mineral names) over periods of time that are much shorter than those necessary for mineral transformation and re-crystallization under conditions of diagenesis, those of higher average temperature than the surface. However, if one considers the changes observed, they concern mostly the 2:1 minerals. The changes involve soil vermiculite or HI minerals, smectite and illite. If one considers these minerals as a two layer TOT structure with different interlayer ions occupation, one can explain the "mineral" changes in a more simple manner. In fact, the "mineral" changes are due to changes in interlayer ion occupancy. The changes observed in the conversion of HI mineral to illite can be considered to be one of cation exchange of Al-OH material for potassium. Change of illite to HI mineral can be considered in the same light. Loss of illite to form smectites or interlayered minerals is simply one of loss of fixed potassium for a more easily exchangeable ion. These chemical changes can be effected by controls of the soil solution chemistry. Hence the apparent mineral conversions in the soil horizons are between members of a single 2:1 mineral family, for the most part dioctahedral and aluminous.

We propose the following schema then to account for the apparent rapid change (tens of years) in mineralogy:

- 2:1 mineral substrate – high charge
  - high alumina availability = HI mineral
  - high potassium availability = illite
  - low potassium availability = smectite
- 2:1 mineral substrate – low charge
  - smectites with exchangeable ions
  - high Al availability = Al exchanged smectites and HI minerals

At present we have little information on the possibility of change in the charge and ionic occupancy of the 2:1 mineral, but recent data (Bauer et al. 2006) indicates that internal ionic diffusion is possible at low temperatures (80 °C) which can modify the charge intensity in the interlayer site. It is quite possible that significant compositional change can be accounted for by internal diffusion as suggested by Gillot et al. (2000) for large crystals of phyllosilicates in soils.

Hence soil clays can be affected by changes in solution chemistry which changes the interlayer ion occupancy giving rise to differences in apparent mineralogy (tens of years), and on a longer time scale (perhaps hundreds of years) ionic diffusion can modify the charge intensity and charge site within the 2:1 structure. These time scales and reactivity contrast strongly with those found for the alteration of unstable rock minerals into clay minerals by water-rock interaction, occurring on the scale of thousands to hundreds of thousands of years.

8.4.7
Conclusions

The exercise given above in these pages attempts to emphasize the relations between the major actors in the alteration of rocks to clays at the surface of the Earth. Much study has been done on different aspects of the panorama of change and chemical interaction. For the most part previous workers have concentrated upon the mineral chemistry aspect of the problem, the interaction of rainwater with inherently unstable high temperature minerals in rocks. However, the importance of plants and their chemical control of the chemistry of surface waters in the plant/silicate interaction zone (A soil horizon) has been underestimated in many cases. This last aspect is perhaps the most striking in that the interaction and control of major mineral properties (to the point of giving specific physical and chemical characteristics which have led to mineral names) is evidently a major influence of clay minerals in the soil horizon. Control and observation of these properties can lead to a better use of natural fertility as it is involved in the plant/clay interaction processes.

8.5
Perspectives for Clay Mineral Science in Surface Environments: Challenges for the Future

8.5.1
Soils and Crops

The Cation Exchanger in Soils

As with many resources, we find today that supply is not infinitely elastic concerning the soil. There are limits as to how much substitution one can do using factory or industrial products to replace natural soil fertility. Soil structure is controlled to a large extent by the organic matter present at the surface, its type and interaction with clays. One cannot continue to count the carbon atoms in the soil as an index to its fertility. Methods of sequestration do not consider the type nor the function of the carbon-bearing matter buried and held in the soil. Organic/clay interactions are the key to understanding soil structure.

Further, there is a general feeling that clays play a somewhat minor role in the capture and release of cations captured and fixed by plants. However, only some 10 to 15% of exchangeable base cations in common soils are potassium, one of the major fertilizing agents. The anhydrous potassic layers in 2:1 clays (illite) contain more than enough potassium to cover the needs of plants in most soils in temperate climates.

The destruction of these 2:1 minerals can seriously compromise the long term fertility of an agricultural soil. Following and predicting illite-potassium availability is the key to understanding long term fertility of agricultural soils.

Are Soil Quality Criteria Important?

In the recent past the question was moot. It was, and still is in some circles, considered that modern chemical and mechanical manipulation of soils could be used to overcome weaknesses in soil characteristics. The development of crop plants dependent upon industrial nutrients was a strong goal for agro-industrialists. The cycle of higher productivity using more and more fertilizers, insecticides and phyto-sanitary products led us to the present state of affairs where much drinking water in many areas of the developed world are at the limits of normal sanitary consumption for well known chemicals or degradation products such as nitrates. We do not know about the many unknown products of biological degradation of the phyto-sanitary chemicals used in ever increasing amounts on the soils. Few controls are possible for molecules so powerful as to be effective at doses undetected by normal laboratory analysis of soils and water. Many people are beginning to think that more care should be taken in using modern chemical treatments of soils.

However, if one talks of reducing artificial treatments of soils, one must consider the alternatives. Can we go back to 30–40 bushel corn after the heady years of 80–100 bushels per acre? Can we reasonably reduce the productivity by 70% of the land in developed countries? It is hard to believe such a scenario. The challenge is then to understand the reactions and reversible processes inherent in crop rotation farming. We know that cycles of fertilizing and extracting crops maintained a balance in many agricultural lands. In France, much of the territory was first farmed 6 000 years ago and it did not lose its "natural" fertility until the post-War era. If one can make genetic strides in developing plants that need nitrogen and potassium to grow, cannot it be possible to develop ones that fix these elements in the soil? Such development must be accompanied by a careful study of the effects on clay mineralogy (illite-like behavior). In this way one can optimize the effects of plant selection.

Of course the corollary is to develop plants that can do with less nitrogen and can extract more potassium from the clay resource. In many cases one increases the illite (potassium) resource by the addition of potassium which, at least in part, is not plant extractable. Research must be done on the interaction of crop plants and different types of soil clay assemblages which form the basic soil clay types in agricultural areas. Each soil type will need a diagnosis as to what type of crop rotation is necessary with the varieties of crops planted. It is a multi variable problem, but one that can be solved with a little patience.

Soil/Plant Interactions: Soils and Ecology

The interaction of plants and soils should be a fundamental (and will be in the future) of the study of land use. What are the limitations in converting a prairie into agricultural use? What can be done to convert forest soils into agricultural soil? What are the best methods of using agricultural lands in a forest-crop or prairie rotation plan? Very much has been abandoned to non-farming use (prairies and forest) for tech-

nical reasons; tractors with 12 row planters have a hard time on hills. However, less intensive farming can be accomplished for crops that need different soil types. The future of bio-carburants might just yield some new landuse schemes, with $100 a barrel oil. Rotations of less profitable land abandoned under intensive farming techniques to different cropping methods can most likely free up some of the resources now neglected in many former farming areas.

Trees, grasses and agricultural plants are the basis of a new ecology of plant/soil interaction. Biotopes and their effects on the soil will need to be studied in order to develop the full potential of land use in the future. At present this is just a nascent field of endeavor. Ecological engineering must be studied from with a better knowledge of ecosystems as eco-engineers.

8.5.2
Soils as a Natural Safety Net for Modern Society

Contamination and accidental events are always going to occur, in one way or another. It is necessary now to study the natural capacity of soils to absorb and disperse high concentrations of anomalous chemical materials. Soils are in fact our natural barriers to disaster. Unfortunately little is known concerning the natural processes of fixing and dispersing elements which in high concentration are immediately harmful. Study should be done in understanding the natural processes of movement concerning for example Sr, Ni, U, As or other elements in a functioning soil system. When the basic systems are understood, one can commence working on methods to improve the capacity of fixation and dispersion over long periods of time for such elements. One can have an idea of the natural capacity of soils under stress and hence can estimate the limits and types of soils which will be most efficient to handle the problems that modern civilization will give them. Soils mean of course plant/silicate interactions, and hence ecosystem study is necessary to develop new soil types which can respond to the needs of society, another field of study to develop.

It is quite clear that many of the challenges of the future concerning clay science are those of developing a close relationship with biologists and ecologist in order to form a new science. One might call such an effort Geo–Ecology. Perhaps some young people with stars in their eyes will heed this call, and we can proceed into the 21st century on a better footing than when we left the 20th.

Suggested Reading

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