

Clays and Climate – Clay Assemblages Formed under Extreme Humidity Conditions

Introduction

Generally when one considers alteration sequences one thinks of climates and conditions common to one's environment; i.e. inhabited, agricultural areas. However some climatic conditions create special chemical systems where specific minerals form due to the climate, i.e. variations of total rainfall and rainfall distribution throughout a yearly cycle. Of course one can consider glacial conditions as a climate. But given that very little of the yearly interaction with rock and atmosphere occurs under conditions of liquid water/rock interaction, this climatic possibility is ignored here. Very cold, tundra, climates tend to be more assimilable to those of temperate climate systems but these systems operate only part of the year and biological activity is weak. The alteration rate is thus hindered but the quality of the minerals present and their specificity is not significantly modified compared to those of more clement temperate climate soils.

Climate extremes can create special mineral assemblages through very abundant, constant rainfall in tropical forest conditions or very sparse and concentrated rainfall experienced under desert conditions. We will consider here the cases of too much rainfall (tropical and near tropical conditions) and too little rainfall, concentrated in short periods (desert conditions). The two extremes show very different clay mineral formation patterns.

6.1 Impact of High Rainfall on Clay Mineralogy

6.1.1 Soil Development as a Function of Rainfall

One of the major factors in alteration (water/rock interaction) is that of rainfall and hence the ionic concentrations in solutions in alteration profiles. The lower the rainfall, the more influence a rock and its chemistry will have on the clays formed. The chemical potential of ionic species will tend to be controlled by the rock and the silicates present. Under such circumstances one tends to have multi-mineral clay assemblages forming at the expense of unstable high temperature minerals. The more water present in an alteration system, the more dilute the solutions will be throughout and the more the initial chemistry of the aqueous solutions will weigh on the clays stable. An infinite amount of water will cause the total disappearance of a rock. It will dissolve entirely. As the ratio of water to rock or silicates tends to one or less, the less soluble elements will tend to form solid phases. Iron and alumina are the least soluble

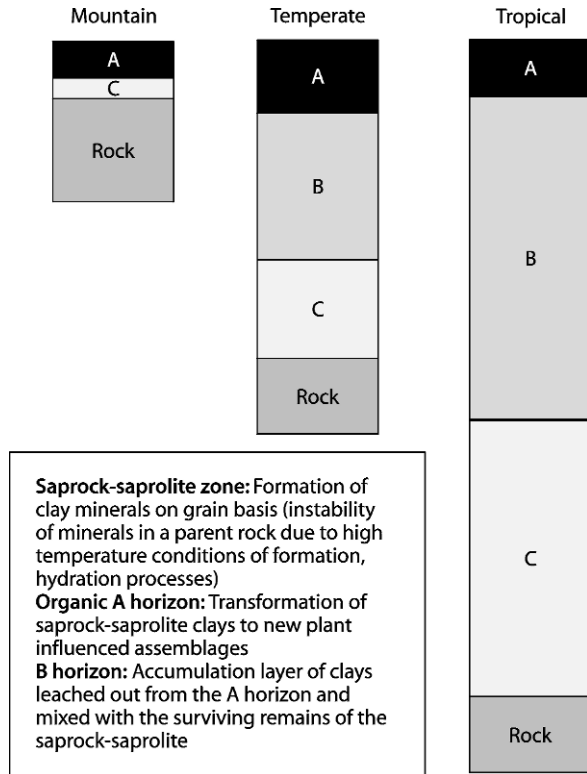
elements in major abundance in surface rocks. Next silica will combine with the insoluble elements to form clays and eventually incorporate potassium, calcium and some magnesium into these phases. Basically clay minerals and stable minerals in alteration zones are formed for the most part of iron, alumina and silica.

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

The major chemical difference between tropical humid soil situations and those typical of temperate climates is one of rainfall. The throughput of water is much higher and constant in humid tropical climates than in temperate ones. Therefore the altering fluids contain much less dissolved material than do those in temperate climate soils and alteration profiles. The importance of climate can be seen in the thickness of different portions of an alteration profile. This is outlined in Fig. 6.1. The differences in thickness of the different zones is essentially one of water availability.

In very cold or very dry climates, water is not active for the largest portion of the year with the effect that plant growth is very minimal and the rate of rock alteration is small also. Ice sequesters water from both plants and silicates and lack of water slows alteration processes as well. Temperate climates have a balanced situation where there is an interaction between plant growth and alteration reaction times for rock/water interaction. The plant-alteration portion of the profile, soil horizon, is usually well developed, being several tens of centimeters thick. A lower horizon of clay accumulation (along with some of the soil horizon organic matter) is often developed below the soil horizon. This zone contains soil derived clay minerals and water/rock interaction clay minerals. Below the B-C horizons and the saprolite lies the zone of altered rock or saprock horizon which is again reasonably well developed under temperate conditions. In all horizons one finds a rather high rate of water flow in cracks and open pores while more chemically bonded water is found in capillary zones. The capillary water comes towards chemical equilibrium with the minerals present whereas the pore and crack water is not in equilibrium but under saturated with respect to the component elements in the clays of the profile.

Fig. 6.1. Schematic representation of soil profiles according to climate



Therefore one can look for strong differences in profile segments as a function of rainfall. However, the availability of under-saturated aqueous solutions also has a strong effect on the clay minerals present in the alteration and soils. We return to our initial definition of soils – surface environments affected by plant activity – which keeps us from considerations of abiotic situations such as barren rocks in glacial areas or entirely dry desert areas. Even though such situations can have materials present in the fine size fraction, they are normally not affected, or little affected by water/silicate or plant/silicate interactions. Hence they are unlikely to contain soil clay minerals. They are based upon the internal constraints of a rock induced by differential thermal expansion.

We consider below two major environments – those of abundant, and continuous rainfall and those of low rainfall where sudden storms bring large amounts of water at rare intervals.

6.1.2

Very High Rainfall

The tropics are areas of abundant, almost constant water saturation of surface materials. A glance at daily world weather maps shows that each day it rains in the equatorial zones and adjacent areas. The situation where there is no dry season is one of con-

stant water input and high alteration by silicate/water interaction. The normal geographic definitions of tropical rain forest areas include the Amazon River basin, the Congo River basin and the southeast Asian island arc of Indonesia and other islands. In the first two areas the tropical rain forest is bounded by a savanna of high rainfall but contrasted seasons. These two climatic zones produce specific weathering facies and soil clays which characterize their climates.

Tropical Rain Forests

When water is in excess of plant/rock interaction, as in the case of tropical (wet) climates where there is an excess due to high rainfall one finds a great amount of alteration in the rock/water interaction zone where alkali and alkaline earth ions as well as magnesium enter into rainwater solution due to the high undersaturation of these fluids. There is little conservation of elements other than some silica, alumina and iron. In such alteration profiles, the alterite is highly developed. The clay minerals present are in general equilibrium with water of low alkali, alkaline earth and magnesium ion content. As these elements are in low abundance, one finds a predominance of kaolinite (or its hydrated form halloysite) and oxyhydroxides of aluminum and iron. The presence of low silica clays indicates that not only is there a lack of alkalis but also silica is of low abundance. The 2:1 soil clay minerals are of a higher silica content than is kaolinite.

The soil horizon, zone where organic matter accumulates, is very thin owing to the lack of 2:1 clay minerals and low K, Na, Ca and Mg ion concentrations. One must be careful in assessing tropical climate alteration profiles. Those that are the deepest are the product of not only high rainfall inputs but also long periods of formation in that they are found in flat, tectonically inactive areas. Not only are these soils highly weathered due to high water input but also they have experienced weathering for longer times than other soils.

In the initial approach of this book, we have considered temperate climate conditions where one tends to find clay mineral assemblages developed from high temperature minerals which give a majority of 2:1 minerals accompanied by kaolinite (1:1 mineral) in the clay fraction. These clay minerals are due to water/rock interactions at the rock/altered rock interface which continue until all of the unstable, high temperature minerals are consumed (some 1 Ma or so). However, under conditions of higher water activity due to continuous rainfall which is evacuated from the alteration zones i.e. not in lakes or ponds, one has a situation where eventually the dissolution of clays becomes a factor in their stability. For the most part under temperate conditions, the major mineral-forming reactions occur under conditions where the silicate clays determine the silica and alumina content of the pore solutions. There is a re-adjustment of the 2:1 clay mineralogy to chemical conditions of the soil and alteration solutions which tends to favor the presence of 2:1 minerals.

Under conditions of high influx of rainwater, one finds that the 2:1 minerals are no longer stable with the result as a decrease in the silica content of the clays (see Pedro 1996). In humid tropical alteration profiles one finds that kaolinite becomes dominant towards the bottom of the profile where granitic or pelitic rocks are the parent material. When basic rocks are present, gibbsite and goethite dominate (Lelong 1969). Towards the surface one finds more quartz for pelitic rocks parent materials and more

goethite for basalts. Compared to temperate climate alteration of similar materials (see Chap. 4) there is a strong tendency to go beyond the initial rock/water microsystem mineral transformations.

In humid tropical alteration profiles there is clearly a new chemical equilibrium which produces more silica-poor clays under water/silicate alteration conditions. Given the low chemical activity of tropical surface clays, kaolinite, gibbsite and oxides, one can expect that the plant/soil clay mineral interaction will be reduced. In fact the humic horizon in humid tropical soils, typically forests, is particularly thin and apparently there is little plant soil interaction as far as one can gather from the rare studies of soil clay mineralogy. Plants must reach very deeply, up to tens of meters, to find unaltered alkali and alkaline earth ion material.

The general schema presented by Lelong (1969, p. 81) indicates that as a function of rock type, granite or basic, the sequence of clays is different. Granite weathers to kaolinite at the rock/water interaction interface with some goethite and gibbsite. Quartz is strongly present. By contrast basic rocks transform primarily to gibbsite and form increasing quantities of goethite towards the surface. The lack of kaolinite in basic rock alteration is most likely due to the relatively low content of silica in the rock material which leads to a direct formation of gibbsite instead of kaolinite as is the case in granitic rocks alteration.

Laterites and Red Soils

A special case of alteration under tropical conditions is the formation of laterites. These alterations are found in the savanna areas bounding the tropical rain forests of Africa and South America. The difference in the two alteration types is climatic, in the savannas the season is contrasted, with high rainfall during one season and a contrasting dry season. The vegetation is of course different, rain forests are tree dominated and the savannas are grass dominated. However, Ségalen (1995) believes that true laterites (crusts of iron oxide above gibbsite layers) are relict soils having formed under climates no longer existing where the laterites are now found.

Intense weathering can lead to the formation of concentrations of aluminum in the form of gibbsite or boehmite, hydrous and anhydrous alumina, and iron in the form of oxyhydroxides. Such soil concentrations are called laterites. Much work has been done on these soils or soil residua due to their economic importance as resources of aluminum. Their striking feature is a zone of accumulation of oxides and hydroxides below the soil zone. This accumulation zone is considered to be one due to intense leaching and transport of fine grained material (Aleva 1994). Laterites are complex, showing the formation of concretions and nodules which indicate local, intense migration of ions to form specific mineral concentrations (Boulangé 1984, p. 136–149). In certain, typical or ideal, cases the alumina is separated from the iron oxides into two layers, the iron forming a top crust or duricrust (Millot 1964, Lelong 1969). These cases are due to formation in tropical contrasted season climates under savanna vegetal cover (see review by Temgoua 2002, p. 4–6). These soil sequences were formed under conditions of intense rainfall for a part of the year and a more dry regime for the other part of the year. This is the contrasted season climate of the tropics.

Since such intense concentration and segregation of elements in a soil context is likely to be a lengthy process, one can assume that laterites are the products of long

periods of alteration which must have persisted over at least tens of thousands of years to millions (Aleva 1994, p. 73). Thus one can assume that the formation of laterites necessitates a stable climate or at least one that has not changed drastically as did those in the northern hemisphere. Most places where they are now found the oxide crusts appear to be unstable and can be seen to be breaking up.

The saprock zone (recent water/rock interaction) usually has kaolinite and smectite along with iron oxides (goethite). Gibbsite and goethite-hematite become important in the bauxitic and duricrust zones. Quartz is present in most horizons indicating its low reactivity to chemical constraints.

Temgoua (2002, p. 7) indicates that the laterite structures formed in contrasted season tropical conditions are not stable under tropical forest conditions, where the concentration zones tend to be ruptured by climatic change. Thus the formation of mono-elemental zone concentrations of Al and Fe depends upon wet and dry seasons, not those of a humid tropical forest.

According to Boulangé (1984) the initial stages of alteration or mineral transformation in the rock/water interaction zone produces kaolinite and gibbsite and biotite-HI phases in granites. Quartz and goethite are present as are white micas. As one moves up the alteration profile, gibbsite is more abundant at the expense of kaolinite. More basic rocks (amphibolite) produce gibbsite and goethite with less kaolinite. Hence the major change is a decrease in the silica content of the clay assemblages. This shows the impact of the high input of the unsaturated rainwater on the mineral stabilities.

Pion (1979, p. 190) gives a general scheme for the occurrence of different clay minerals formed from basic rocks under climates of relatively low rainfall (400–1 100 mm yr⁻¹) to moderate (850–1 400 mm yr⁻¹) to high rainfall (1 200–2 200 mm yr⁻¹). Under high rainfall one can find vermiculite type minerals at the rock/alterite interface whereas above this zone gibbsite and kaolinite (plus iron hydroxides) are dominant. The alteration minerals in profiles formed under less rainfall show the strong presence of more siliceous 2:1 soil clay minerals.

One can consider red oxisols to be the product of contrasted season alterations. Here strong dissolution occurs during the rainy season and strong evaporative movement and dehydration of oxyhydroxides occurs during the dry season. This process is slow to occur and hence much of what one sees today as laterite material is frequently being degraded by forces of new climatic actions.

6.2

Rainfall and Vitreous Rocks (Andosols)

6.2.1

Andosol Characteristics

Andosols represent a combination of two specific variables which produces very characteristic, and unusual soils. Andosols are noted for their high water content, high content of organic matter in the A horizon (15–30%), high capacity to fix phosphorous, and moderate to low CEC often related to the amount of amorphous or extractable alumina present (Shoji et al. 1993, p. 2; Garcia-Rodeja et al. 2004). Although fresh or immature andosols usually select Ca over K in cation exchange reactions, it has been noted in several instances that slightly more mature andosols (containing 1:1 miner-

als) can strongly select potassium (Ndayiragije and Delvaux 2004). In general andosols are very fertile. This fertility is most likely due to a continued high weathering rate of glassy materials which furnishes plant nutrients such as K and P (Shoji et al. 1993, p. 210). As an example, the volcanic context of central and southern Italy and the development of andosols undoubtedly attracted populations from regions with less fertile soils, such as the limestone Aegean area, and as a result the Italian peninsula became an area of constant population movement from the early times of human agricultural practice.

Andosols occur under various latitudes from tropical Africa and Oceanic Pacific regions to mid continent areas such as Italy, Germany (Kleber et al. 2004) or France (Quantin 2004) to northern climates such as Iceland (Arnalds 2004). Temperature is obviously not a significant variable in the formation of andosols (see *Catena*, vol. 56, 2004).

Several principal factors then are necessary to produce these special soils. Regular rainfall is necessary, equal to or less than the tropics but above what is normally considered to be necessary for temperate climates. The soils should be well drained. The second factor is a source rock which contains significant amounts of glassy material, usually volcanics. It appears that there is not much difference between basic, basaltic material and more acidic types as they form andosols except that the transformation or alteration rate for basalt is significantly higher than for acidic glass up to two times greater (Shoji et al. 1993, p. 38). The essential material for the formation of andosols appears to be a glassy, or highly alterable substrate.

A distinct problem in the study of the properties and the development of andosols is that they are normally found in active volcanic areas and hence subject to renewed accumulation of fresh material on the top of the profile. Andosol alteration profiles are frequently interrupted by paleosols, indicating renewal of material by ash flow or lava flows which buries and fixes the soil zone with a renewed starting material upon which soils are formed.

Major phases characteristic of andosols are (see summary by Shoji et al. 1993, p. 113–123):

- *Allophane* which contains a hydrated network of Si-Al-O atoms. Both H₂O and OH units are present. The stoichiometry is slightly variable but usually is between 1:1 to 1:2 Al/Si atoms,
- *Imogolite* a hydrated network of Si-Al-O atoms with a rather well organized tubular structure which is not detectable by XRD methods. The ratio of Si to Al is near 1,
- *Gibbsite* the hydroxyl form of aluminum,
- *Opaline silica*,
- *Halloysite*, the hydrated form of kaolinite,
- *Kaolinite/smectite* mixed layered minerals often occur in soils materials associated with andosols,
- *Iron hydroxy-oxides* are of course present in andosol materials,
- *Humic material* is extremely important for the stability of the hydrated phases as is of course a ready supply of rainwater.

Clay minerals which are not typical of andosols are:

- *Kaolinite* usually not in a true andosol material,
- *Vermiculite-smectites* also usually not found in andosol soils.

It is clear from this resume of the phases present in andosols that the initial rock materials have lost their alkalis and alkaline earths. Andosol minerals are dominated by Al, Si, Fe hydroxyl and oxide phases. Further, the ratio of silica to alumina and iron is much less than in the source rocks indicating a strong loss of silica. Such a loss is a key to the formation of the particular mineralogy of andosols. Elemental relations in andosols are clearly shown in the summary in Shoji et al. (1993, p. 148). Such material will not provide much transfer of nutrients by CEC or more tightly bound potassium as is the case for 2:1 minerals. Some data however suggest that the soil (plant/silicate interaction zone) can accumulate K and Si at the surface (Meijer and Buurman 2003). Cation exchange appears to come largely from the abundant organic material in the surface horizons.

Mohr and Van Baren (1959, p. 302) and Sifferman (1973, p. 150) indicate that there is a strong evolutionary trend in the development of andosol soils where an initial stage of “juvenile and virile” evolution produces a high vegetal cover which decreases strongly with time in the “senile” and lateritic stages of soil development on volcanic ash materials under tropical humid conditions. This indicates a natural exhaustion of the soils concerning plant activity. Thus the effects of high water influx and dissolution strongly affect the soils making them evolve rather rapidly towards concentrations of oxy-hydroxides.

The geographic situations in which andosols occur are very important as to their extension, longevity and relations with other soil types. In fact andosols depend upon the volcanic (glassy) substrate, high rainfall or constantly humid conditions and good drainage. If one is in the humid tropics, these conditions can be considered to be roughly general. However, the actual rainfall can depend upon geographic relief even there. In many instances where andosols occur, the volcanic material forms a mountain which affects the weather patterns, rainfall being higher on the summit. Ocean islands tend to accentuate this effect with rain shadow effects, such as the Hawaiian Islands, Azores, etc. Thus, on the same contiguous edifice, one can find soils developed under conditions of high rainfall and those under less humidity or one can see differences depending upon the climate of different islands (Bates 1962, p. 318). In these instances andosols will be present on one part of the edifice and other types around them (Delvaux et al. 2004; Fauzi and Stopes 2004; Sifferman 1973). This situation leads to the gradual change between andosol characteristics and those of other, more classical soil types. However, in some instances, other rock types can give rise to andosols such as is the case for a granite in Austria (Delvaux et al. 2004).

6.2.2

Weathering Processes Affecting Vitreous Rocks under Constantly Humid Conditions

Generally the high rainfall interacts rapidly with the highly unstable silicate glass to form an alkali and alkaline earth-depleted mass. Since there are few micro-sites (places where pre-existing minerals transform into new clays, see Chap. 4), there is little tendency to form new clay mineral phases, i.e. those with continuous layer structure edifices. Thus the more glass present, the more alteration will occur. One finds that there is also a loss of silica to the soil solutions which leads to the formation of the silica-poor phases, imogolite and allophane. These are the water/rock interaction minerals

found at the rock-alteration interface (Sifferman 1973, p. 149–151). As one moves upward in a profile, towards the surface one can find gibbsite (Al hydroxide) and some halloysite, depending upon the drainage, age and development of the profile. The presence of halloysite appears to be dependent upon a continuously humid environment. In soils which experience periods of drying, kaolinite is present. In more crystalline eruptive rocks one can find halloysite forming from feldspars in the early stages of alteration (Bates 1962).

In general, under conditions of highest water input one finds that silica and alkali-poor or unstructured phases have formed. As rainfall decreases over the year in adjacent areas, more structured minerals occur, halloysite and kaolinite with eventually smectite or HI phases. Using the comments of Sifferman (1973) one can construct the following weathering schema (Fig. 6.2)

The different variables of ground water flow, presence or not of primary crystals in the volcanic material, seasonality of rainfall and so forth can and do modify the mineral succession relationships in andosol sequences. The zones of contrasted seasonal humidity tend to destabilize the allophane and favor gibbsite-halloysite and eventually kaolinite mineral assemblages.

One can say in general that andosols and amorphous minerals are found as young soils developed from highly glassy materials. Even this is not universal in that kaolinite and smectite mineralogy was found in the surface horizons in soils formed on recent (Krakatoa 1883) ash fall material developed in a rain forest environment (Fauzi and Stoops 2004).

In a very general way, one can outline the relations of chemical activity and mineral destabilization in a simplified diagram such as that of Fig. 6.3. Feldspars and mica are destabilized in favor of kaolinite and eventually gibbsite. Loss of silica and alkalis are the causes of these changes. The higher the rainfall, the stronger tendency to reduce both silica and alkali (plus alkaline earth) elements. Both are essential for 2:1 clay minerals. The balance between allophane or the more mature form of hydrous alumina, gibbsite, is probably one of time.

Fig. 6.2. Relations of clays and humidity in various profiles on glassy materials after Sifferman (1973)

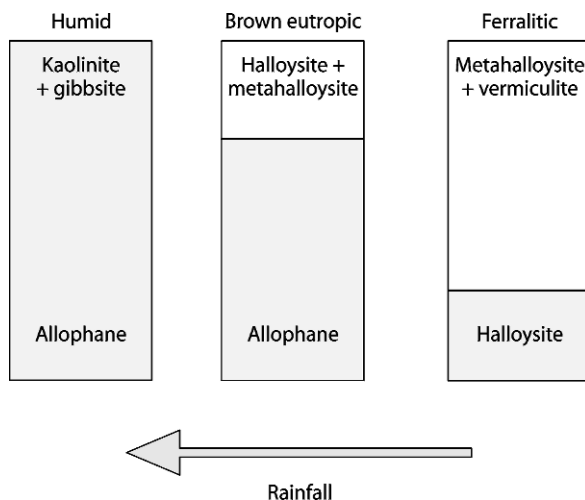
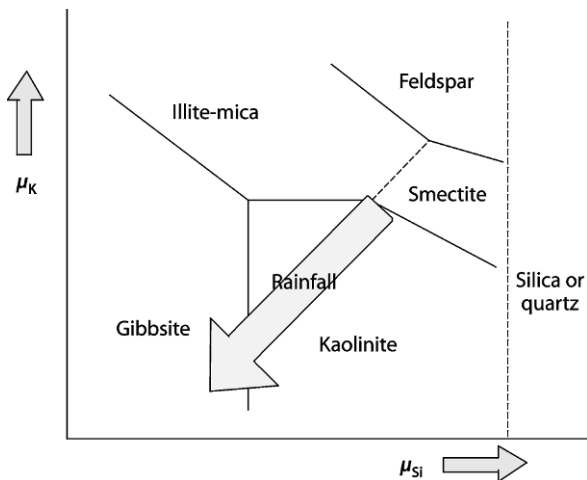


Fig. 6.3. $\mu_{\text{Si}}-\mu_{\text{K}}$ diagram showing the normal water-rock interaction path of chemical change. Loss of potassium (lowering chemical potential) and decrease in silica (lower chemical potential of Si) change the clay mineralogy from 2:1 minerals, illite-mica and smectites to kaolinite and eventually gibbsite



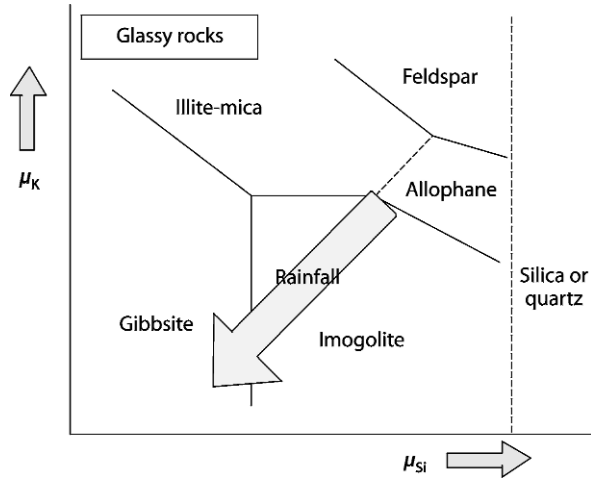
However, in the list of typical minerals in andosols, smectites and kaolinite are not frequently present. These minerals, are replaced by imogolite and allophane. Hence the glassy character of the initial rock materials determine another mineralogy in the initial stages of alteration. Sifferman (1973) reports allophane at the base of alteration profiles in the zone of most recent rock/water interaction and the presence of gibbsite in the upper portions of the profiles. These relations are indicated in Fig. 6.4.

Andic properties (due to the presence of amorphous and poorly crystallized materials) are found in soils forming on glassy materials under climates of lesser rainfall such as described by Takahashi et al. (1993) for xeric soils in California. In these cases allophane or imogolite are present with 1:1 clays and 2:1 clays in the soils. These should probably be considered as early stages of alteration which will eventually become 1:1 and 2:1 soil clay assemblages.

The effect of vegetation on andosols has been reported to be one of enhancement by grasses forming imogolite and allophane and destruction of andosol mineralogy to form more silica-rich podzols under forest growth (Shoji et al. 1993, p. 130) in Hawaiian soils. Meijer and Buurman (2003) give data for soils on an acidic volcanic edifice in Costa Rica where the plant regime varies from fern-grass at altitude, through deciduous forest, tropical forest to grazed land at low altitude. In the chemical data reported one frequently sees an increase in potassium in the uppermost samples of the profiles, the organic horizons (A_h). This is especially true for the fern-grass soil at high altitude and tropical forest profiles. In the tropical forest profiles, one can note the presence of kaolinite, and vermiculite in these horizons whereas lower portions contain the less siliceous mineral assemblage gibbsite, goethite and halloysite. In these Costa Rican soils it is possible that the plants have an effect on the chemistry of the A_h organic horizon.

Typically, gibbsite is abundant at the rock/water interaction interface. Also one finds kaolinite or the hydrated form halloysite. Towards the plant/clay mineral interface one can find smectite in some abundance. It appears that the alteration intensity of silica loss is greatest at the base of the profile. This would seem to paradoxical in that the

Fig. 6.4. $\mu_{\text{Si}}-\mu_{\text{K}}$ relations for imogolite and allophane weathering assemblages formed from glassy eruptive rocks. Loss of potassium and silica (shown as lower Si and K chemical potentials) forms allophane and imogolite in the fields where smectites and kaolinite would normally be present



water which reaches the rock interface should be the most highly charged in dissolved ions and hence at least a little silica. Conversely the rainwater falling on the soil surface should be the least saturated. However, if one considers that significant silica can reach the surface by plant action (phytoliths) one can imagine a source of silica beyond that of rainwater/kaolinite interaction (Derry et al. 2005; Farmer et al. 2005). This can be stretched to the existence of podzols in tropical forest areas (Lucas 2001, p. 138). Clearly the types of plants present can have a strong impact on soil clay mineralogy.

6.2.3

Mineralogy and Hydration State of Andosols

Clay Mineral Origin in Andosols and Andic Soils

In the brief description above, it appears that andosols, soils based upon the alteration of glassy silicate materials, will first produce unstructured materials which cannot be called minerals because they lack a determined composition and mineral structure (crystallographically identifiable). Allophane is one material and the hydroxyl-iron complexes are the other. Further there is a strong association between organic matter and these elements, Al and Fe. These materials are typical of the initial stages of rock/water alteration in andosols which are themselves due to high water input and constant humidification. Alkalies, alkaline earth elements and silica are evacuated by percolating solutions. Another important phase is imogolite, a much more stoichiometric phase of nearly equal portions of Al and Si. The diffuse organization of this material makes it essentially non-detectable by XRD methods, infrared is the major method of identification (see Farmer et al. 1983). In this phase one finds Si in roughly equal proportions with Al.

Under different conditions, either as replacement of crystalline phases such as feldspar or in zones nearer the surface of the alteration profiles, one can find halloysite ("hydrated" kaolinite) and gibbsite. It is not clear from the data in the literature if the presence of these minerals is due to a kinetic process, taking thousands of years, or

specific chemical conditions. One can imagine that gibbsite will replace allophane, which is largely of the same composition. However, the presence of halloysite indicates the conversion of imogolite, which has a similar Si/Al ratio. Thus both gibbsite and halloysite may be successors of allophane and imogolite, or perhaps form under slightly different chemical conditions that the first two phases. The minerals which give the physical and chemical characteristics of andosols (high water content, low density, high capacity to fix phosphorous) and perhaps not the stable end product of silicate equilibria.

One can outline the following classification based upon phases present:

- imogolite, allophane – *early andosol*
- gibbsite, halloysite (imogolite) – *mature andosol*
- kaolinite, smectite (imogolite) – *andic soil*

In any event, the phases typical of andosols are probably not stable under long term equilibria.

Hydration State of Clays under Humid Conditions: Seasonal Effects

The striking feature of clay minerals from tropical areas is their hydration state. Typically one finds allophane, a very highly hydrated alumina mineral. It is found basically at the rock/water alteration interface. However, when rainfall is unequally distributed over the seasons (contrasted seasonal climates) even though the rainfall is in total high, one can see that the highly hydrous minerals are replaced by less hydrated ones. Lowe (1986) has commented upon this effect, where he notes that contrasted season assemblages are less hydrous in tephra soils in New Zealand. Observations from many authors indicate that allophane is replaced by gibbsite in the upper portions of profiles those which are less permanently hydrated. Goethite is another highly hydrated mineral which is replaced by hematite in laterite deposits when the effects of contrasted seasons are felt in the upper portions of the alteration profiles. Halloysite, hydrated kaolinite, becomes kaolinite in the upper portions of soil profiles. Thus one finds that the existence of high and continuous hydration states in soils is reflected in hydrous minerals while under conditions of more contrasted humidity, the hydration state is reduced and hydroxyl clay minerals are found. We then have a direct reflection of chemical constraints on the clay minerals in profiles formed under conditions of high rainfall. The permanence of hydration promotes the amorphous or poorly crystalline minerals whereas contrasted seasons gives rise to more structured and less hydrous phases.

6.3

Weathering Trends as a Function of Time

6.3.1

Weathering Trends as a Function of Time under Tropical Conditions

General Trend

Mohr and Van Baren (1959, p. 302) present a general scheme concerning the alteration of surface materials under tropical conditions as a function of time. If alteration is

based upon the exchange of hydrogen ions for other ions in silicates, the end product will be iron-aluminum deposits. Their arguments are based upon observations for volcanic deposits but should be valid for others in a general way. The evolution series is divided into juvenile, virile, senile, and laterite stages. The authors insist on the relation between plant activity and the stages of evolution or weathering. The vegetal cover diminishes over the senile stage to be almost absent during the formation of laterites. This is reflected in the overall color of the soils, being brown during the active stage and more red in color with decline in organic matter in the soils.

Thus one can take the tropical weathering scheme as a model for all other situations with adequate water. Alteration will inevitably produce a sterile oxide-dominated soils without silicates or phyllosilicates. However such a process takes about a million years or so, so that one must have stable climatic conditions and little change in topography, conditions which have not been fulfilled in the northern hemisphere until about the last 4 000 years or so.

The presence of high amounts of kaolinite, iron oxides and gibbsite will indicate past conditions of intense weathering under conditions of plentiful rainfall, continuing for long periods of time.

Climate, Vegetation and Host Rock

Ségalen (1995) indicates the special distribution of soil types or alteration facies for tropical climates. His classification shows gradations of soils by color and hence oxidation state and iron content along with silica content as it affects clay mineral stability (smectites). Basically, and schematically, one finds yellow soil types with iron oxides and kaolin present in tropical forest zones, where the iron oxide is hydrated (goethite). On the edges of the forests under contrasted season climates one finds grasslands with red soils but where silica content is higher and smectites are present along with kaolinite. These relations are above all valid for soils formed on pelitic or aluminous rocks such as granites and sedimentary or meta-sedimentary rocks.

The Indian subcontinent is an exception having large surfaces covered with basalts, an iron-rich and alumina-poor rock. Even though the climate is equatorial and humid, though far from enough so as to form a rain forest, the soils are vertic, i.e. containing very much smectite. In this instance there is a tendency to maintain a siliceous mineral because the next alteration step is difficult to attain, the formation of kaolinite. However in some cases the stage of iron oxide laterite is attained.

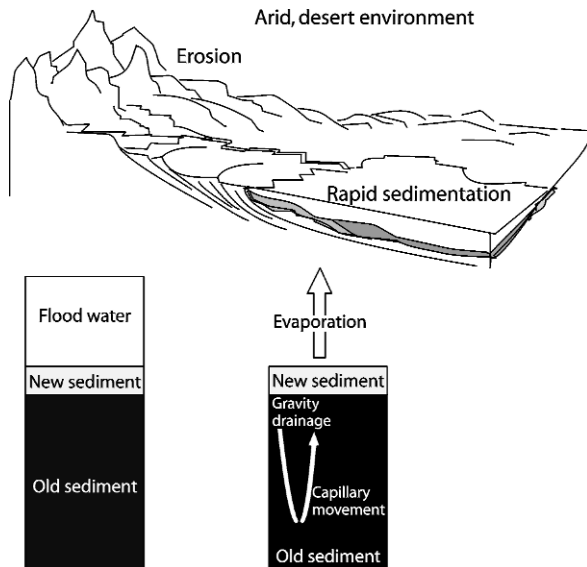
6.3.2

Weathering Trends in Semi-Arid and Arid Climates

Desert Alteration Profiles: The Effect of Evaporation

Desert soils are typified by high, episodic erosion rates and high sedimentation rates. The violent and highly episodic rainfall events cause this state. Figure 6.5 indicates a general relationship of this situation. The alteration profile, dominated by newly deposited materials, is one of episodic high water influx and subsequent evaporation of the waters found in the shallow profiles. Since the erosion zone on slopes is of high activity and usually occurs under conditions of sparse vegetation, few soil clay miner-

Fig. 6.5. Desert erosion and deposition. Diagram indicating the trajectories of water and sediment in a desert environment



als are found here. The major process is thermal expansion-contraction which breaks the rock into its individual mineral components and breaks the minerals themselves. The zones of deposition can support more stable plant/silicate contact, though this is variable and depends upon the rates of deposition.

Mineralogy of the Desert Soils: Sepiolite and Palygorskite

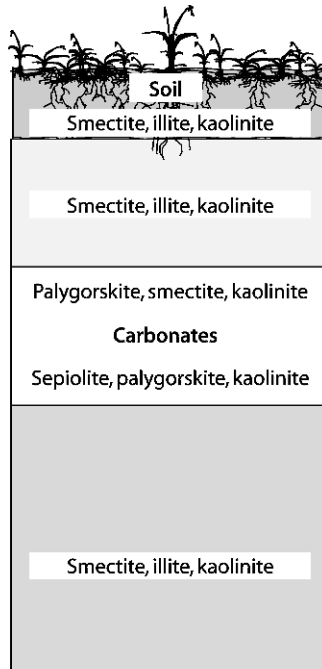
It has been observed for some time that desert or arid soil soils can at times produce a special mineralogy below the soil zone, i.e. the plant soil interaction zone. In these profiles, below the B horizon, one finds an accumulation of carbonate material and at times the presence of magnesium silicates, sepiolite and palygorskite (Singer and Galan 1984). Sepiolite is a magnesium silicate, trioctahedral in nature with a needle-like morphology. Palygorskite is a dioctahedral magnesium, aluminum silicate with the same morphology (see Velde 1985, p. 229 for a summary of the chemistry and chemiographic relations of these minerals,). Palygorskite is the more common of the two minerals in soil parageneses. These minerals are found occasionally in soils but their presence can be due to aerial input, at times over great distances (Bain and Tait 1977). The trajectories of Saharan, palygorskite-laden dust are varied and at times astonishing, ending up in Scotland, Florida and deep sea Atlantic sediments for example. In general sepiolite and palygorskite are not stable in the plant/silicate horizon, be it ever so thin. The formation of palygorskite is restricted to reasonably well drained alteration profile, being replaced by smectite in hydromorphic zones (Paquet 1977). These magnesium silicates are formed under specific hydrologic conditions.

We will use the careful description of Van den Heuvel (1966) as a model to explain the genesis of sepiolite and palygorskite in alteration profiles. In the surface A horizon (plant silicate interaction) and in the B horizons where soil minerals are displaced

downward, one finds 2:1 and kaolinite minerals. In the C horizon, developed in recent sediments, one finds strongly expressed deposits of secondary carbonate material. Here one finds palygorskite. Further down the profile palygorskite and sepiolite are found together. Below the carbonate zone only palygorskite is found along with the 2:1 and kaolinite mineral assemblage. The presence of secondary carbonate is the sign of solution saturation and precipitation of calcium reacting with solutions initially in equilibrium with air. Evaporation increases the concentrations of dissolved species until they precipitate as carbonate. The silicates palygorskite and sepiolite are then most likely reaction products of interaction between Recent sediment clay minerals and saturated aqueous solutions. If we consider that Mg is more soluble than Al and Si, the percolating aqueous soil solutions are most likely to be charged with this element as well as Ca. Little Mg is taken into the carbonate phase and it then is in overabundance relative to the equilibrium values with other silicates. The solutions must be alkaline in that sepiolite is stable between the pH values of 8 and 10 (Siffert 1962). The carbonate zone (the term caliche is used in the Western United States) is then one of palygorskite-sepiolite formation. These relations are outlined in Fig. 6.6.

In fact the limit of capillary movement upward during the normal dry periods is where the concentrated solutions (Ca, Mg, Si, OH) interact with the aluminous minerals kaolinite, smectite and illite. Illite is the mineral most affected by reaction and then kaolinite. Smectite appears to remain present in all zones of the profile. Here the dissolution of minerals at the surface (soil zone) are re-precipitated within the profile.

Fig. 6.6. Indication of the minerals present in a desert soil profile where solution concentration provokes the formation of palygorskite and sepiolite frequently in the presence of carbonates



Desert formation of sepiolite-palygorskite
in soil sequences

Only alkali elements are lost as illite becomes unstable under conditions of high Si and Mg activity.

The typical desert water regime is one of extreme low activity for the largest portion of the year with intermittent high input (desert rainstorms). The heavy rains cause flooding and rapid saturation of the soils. Under high evaporation regimes the water tends to leave the system from the top with the result that the aqueous solution left behind becomes highly concentrated in dissolved salts. An extreme case is the formation of salt pans in flat, dry lake beds. In these cases the salts themselves are formed at the surface because little downward movement of the solutions can be effected. In better drained situations, the water can move downward by flow in macropores but the capillary movement still bring up much solution of high concentration of certain elements. When some downward movement occurs, the highly soluble chloride salts can be evacuated to a distant water table. The more insoluble silicates remain, sepiolite and palygorskite. It should be noted that the first magnesian mineral to form, palygorskite, is the most aluminous indicating that the initial reaction solutions are richer in alumina than those below where sepiolite (low alumina content) occurs.

An interesting case of palygorskite formation has been noted by Pharandre et al. (2000). In Indian soils, based upon basalt alteration of the Deccan plateau, intensive flood irrigation has produced palygorskite in smectitic soils. Farmers who use sprinkler irrigation, more expensive, do not have the problem of palygorskite formation in their agricultural soils. The palygorskite changes the physical properties of the soils making them less workable and it reduces the cation exchange properties. If we make the parallel of desert hydrology and that of flood irrigation, the same flux of water occurs and the same evaporative forces concentrate dissolved salts in the capillary water. It seems that the phyllosilicate to chain silicate (smectite to palygorskite) reaction occurs in the two instances. However in the Indian soils the smectite is iron-rich forming on basalt, whereas the palygorskite in alkaline desert soils is magnesian. In order for the reaction to occur in the Indian soils, it is unnecessary for the iron in the smectite, dominantly Fe^{3+} must be reduced to Fe^{2+} . This is possible in the flood irrigation situation where much organic matter is available at the surface which will aid in reducing Fe^{3+} to Fe^{2+} . In cases of sprinkler irrigation, the water does not stay within the soil, and instead of surface evaporation, most flows to the water table. There is little time for evaporation and iron reduction in such a situation and hence no palygorskite is formed.

Sepiolite-palygorskite bearing soil materials can be assumed to be due to high surface evaporation and concentration of OH, Si and Mg in the capillary solutions. These minerals represent a rather special set of physical and chemical conditions, High and rapid rainfall and low drainage but without standing water at the surface during the evaporation cycle.

6.3.3

Summary

Soils under climatic extremes, high rainfall or very low rainfall, show two inverse processes. Under conditions of high input of unsaturated water, most minerals are found to transform to low silica or non-silica forms. In these cases the alkali and alkaline

earth elements are lost and eventually silica also. Solutions are evacuated, and in any event they are of low concentration for the elements taken out.

Soils under desert conditions, where the small amount of water which arrives is strongly concentrated in time, show the effect of evaporation of surface waters upwards in the soil. The effect is seen below the soil zone where the evaporation/water table interface is present and water evaporates forming strong concentration of dissolved elements, the pre-evaporation zone of rising water. Here new minerals form which combine the dissolved elements into new phases. As the major dissolved elements are alkaline in nature, the pH is high in these evaporitic concentrates, and the minerals sepiolite and the more aluminous magnesian silicate palygorskite crystallize along with carbonates. These minerals are not stable in soil profiles under temperate climate conditions, probably due to their requirement of high pH conditions which are not favored by the decay of organic matter in the A horizon. Here the movement of water is upward, the elements become more and more concentrated and new minerals form by crystallization from solution.

Thus the tropical mineral regime is one of elemental loss while the desert, evaporitic soil regime is one of elemental concentration. The two are quite opposite but then the hydrologic regime is inversed also.

Suggested Reading

- Fitzpatrick E (1983) *Soils*. Longman, London, 353 pp
Jenny H (1994) *Factors of soil formation*. Dover, New York, 281 pp
Millot G (1964) *Géologie des argiles*. Masson and Cie, Paris, 499 pp (English translation 1970: *Geology of clays*. Springer-Verlag, New York, 429 pp)