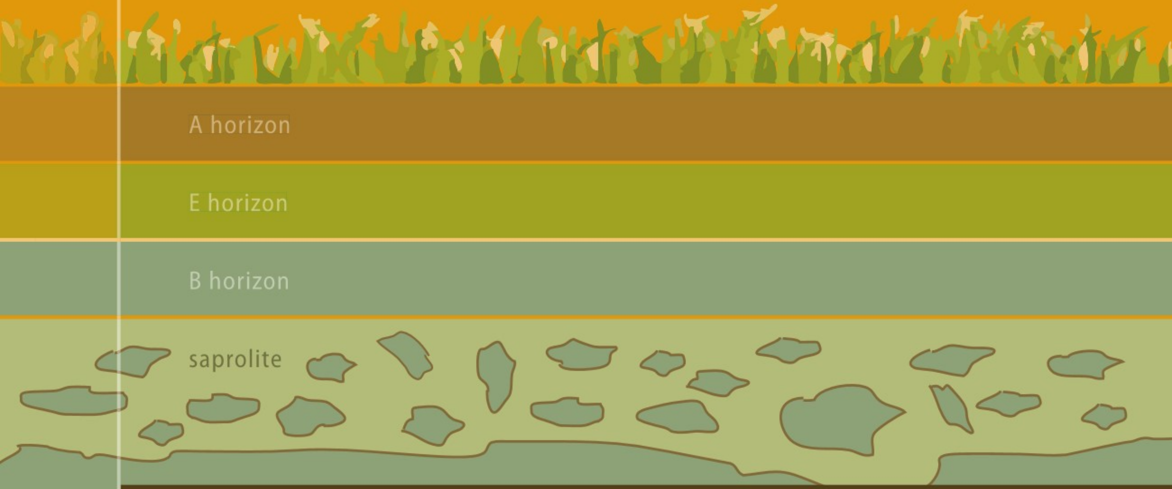
Bruce Velde · Pierre Barré



# Soils, Plants and Clay Minerals

## Mineral and Biologic Interactions

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ISBN 978-3-642-03498-5 e-ISBN 978-3-642-03499-2
DOI 10.1007/978-3-642-03499-2
Springer Heidelberg Dordrecht London New York

Library of Congress Control Number: 2009935566

*Cover design*: deblik, Berlin

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

# Preface

This book represents a rather complicated history of encounters, changes in research interest and some very interesting results. Initially it is the very fruitful interaction of Ecology and Geology. The point of view of ecologists is extremely refreshing for hard science people. Interaction and inter-relationships are the focus of Ecology whereas the traditional sciences, such as Geology, have tried to isolate the natural phenomena so that thye could be studied in a more rigorous manner.

The traditional sciences were of course natural science – based since the world to be observed was at the door step of everyone, mountains, weather patterns, plants and so forth. Chemistry and Physics were defined after Mathematics in order to establish more precise and viable principles of the behavior of the materials that formed the world around mankind. It became quite clear that the observation of the natural world was too complicated to consider all of the possible variables which could affect an observed process or situation. The systems were simplified and taken into the laboratory in order to better master the phenomena observed. Physics concerned itself with non-reacting materials, subjected to essentially mechanical forces. Chemistry was given the task of understanding the interactions and transmutations of matter according to the affinities of atoms and ions. As it turned out the interactions of electrons was the key to the chemical problem. In these endeavors, the systems were simplified to better understand the fundamental principles. However nature remains a multidimensional problem and although great progress has been made using the discoveries of Chemistry and Physics to understand the underlying principles of phenomena in natural systems, much escapes still.

One of the major problems today in the study of the earth's surface: contact between rock, plant and atmosphere, is the understanding of the interactions and influences possible in this zone of intersection of phenomenological forces. For example, most mineralogists concerned with clays, those silicates present and active in the surface zone, feel that the influence of the bio-zone is only negative, one of destruction and dissolution, being part of the general degradation of silicate materials by surface interactions. Plants and bio-agents are generally considered to be classified in the alteration category such as that encountered in the contact of rain water with rocks. However, numerous, little heard authors have insisted for quite some time, over a hundred years, that the interactions can be important and transfer of materials from depth to the surface can condition the soil, interaction zone.

Plants, minerals, bio-agents such as micorrhize and bacteria all interact to form a living community, in the Ecological sense.

The interaction of the sphere of living materials (plants and bio-agents) with the slowly reacting and stable silicate (rock) material under the influence of climate (rain) are the subject of this new approach to science at the surface of the earth.

We would like to thank our many collaborators for their enthusiastic help, from various parts of China, to the Unites States and Canada and parts of Europe. It is clear that Science is a world venture, and a pleasure to be part of.

Closer to us, our colleagues in our laboratory and the technical staff without which we would be more or less helpless, have been a great inspiration during the preparation of this book and the scientific studies that have led up to its expression. No one is alone in this complex modern world. We wish to thank all of those who have contributed to oru efforts.

Paris
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Pierre Barré

# Contents

# Chapter 1
# Introduction: Objectives and Background

## Contents

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_1,

## 1.1 The Need to Understand the Plant – Earth Interface in the Future World of Pollution, Increased Exploitation of Natural Resources and the Quest of a Bio-Friendly Society

In this, the beginning of a new millennium and apparently a new era, more and more questions are asked about the nature of nature. We want bio-friendly processes in farming, in the means of obtaining heat energy and the means of propelling our automobiles. We want this to be done with minimum risk at the same time to ourselves and our children as well as to the biological community which co-inhabits the surface of the world with us. Perhaps this is a too big a problem with many different answers, sometime contradictory, but it is a true challenge to the young people of our world. As it turns out, the world of science is rather poorly equipped to deal with society's new concerns. This is not due to negligence but to a historical process.

First we must put things into perspective. Until very recently and since the philosophical and material triumph of Science in the post-war period of the latter half of the twentieth century, society has come to question some of the *tenants* of this era of material progress. In the Cold War era each of the protagonists, Communist and Democracy (Free Enterprise) were bent on out producing each other in goods and services. The well being of humanity could be measured by its GNP or some other measure of the productivity of a society divided by the number of its inhabitants or participants. Materialism was on both sides of the curtain. A half century of such intense competition entrenched the major themes and objectives of the system. With the fall of the separation of the two organizations, it was seen that the communist countries produced their material wealth often at the expense of the health of the producers. This gave satisfaction to the opponents of this economic system but it turns out that the race to material well – being has taken and is still taking its toll in the western countries also. This is and has been perceived by the populations of the western nations as well as the so-called eastern block. No longer can one equate Science with Progress with Well-being. Change is not necessarily beneficial in itself. Most students today share this view and hence they turn away from the classical fields of Science. It is time to attempt to resolve some of the problems of materialistic society and its over production in a reasonable manner. To do this, many people propose a more biologically friendly approach to sustained systems of development. Few people can argue this today. However there are major problems in such a quest.

First one needs to understand the bio-systems and their ecology (interaction and development) in relation to their environment. Man has altered the surface of the earth to such an extent that it is hardly recognisable compared to its state 4,000 years ago. First the quest for a stable and high energy diet lead to the introduction of grazing and then farming at different levels of intensity in different places on the earth. Gradually the methods of development of the biosphere came to converge into a system of intense agriculture spread over large sections of the inhabitable globe. For several thousand years the agriculture practiced by different communities was bent on conserving the natural resources of the land, which is in a sense sustainable agricultural. Written texts of the ancient Greeks attest this quite clearly. Crop rotation and land use were highly recommended. This traditional farming was practiced in many areas, Europe, the circum-pacific region, Africa and the Asian continent which modified the use of the land to different degrees. However the limits of energy and monetary or resource input kept the objectives much the same: maintenance of soil fertility from one year to the other. With the advent of the mechanisation and above all the use of factory produced chemicals applied massively in the post War period the concept of soil fertility seemed to have become less important. The use of external stimulants was considered to be sufficient to overcome any mechanical or biological problems which would be encountered that would hinder increases production. Such practices have led to the situation which is present today where chemicals used in agriculture seem to be all pervasive and their long term effects as yet only poorly known. Basically many people would like to return to a more "natural" system of food production and use of the earth's surface for the ever increasing needs of humanity.

However, in order to do this it is necessary to understand the basic functioning of the biological – soil systems. Such work has essentially stopped in the last 50 years or so to the benefit of plant development and mechanical – chemical manipulation of the soil. We know how to grow large, productive plants with the aid of fertilizer and phyto-sanitary aids and how to move very large machines that plant, treat and harvest them at an incredibly rapid rate. However, there is little recent information on what is happening in the soil – plant interaction. Modern methods of investigation of the clay minerals for example have not been used to observe the changes brought about by modern farming on the mineral substrate nor the way that organic matter is bound to the clays in the soils nor the reciprocal effects of such relations. What are the major functions of the plant – soil interaction? How can one observe them and control them to benefit a long term and stable interaction? Of course we do not wish to return to the farming methods of our great grandparents nor the significantly lower productivity of these and more distant times. There is a need to feed an ever increasing population. However, this being the case, there are ultimate limits to the use of land from which it can possibly not recover. Soils will be more and more called upon to produce the needs of modern society by the development of bio fuels for example.

Our task here is to outline the structure of the plant – soil interface and to structure the relations which are known. Given this introduction we hope to suggest a number of avenues for research in the future which could possibly aid in the development of our natural resources. In order to do this we propose to use the structure of present knowledge of plant – soil interactions according to the classical methods of investigation. With some new insight it is possible to have a different view of the natural system and perhaps using this basis progress in the understanding of the soil – plant ecosystem.

The framework of interest here is the world of plants and rocks. This is the basis for life on earth. However, one must not forget water, which is the *sina qua non* for life, and also that for the transformation of rocks into soils, i.e. clay minerals.

The two basic ingredients are water and rock, whereupon life can exist. The transformation of hard, un-yielding materials into soft, water conserving materials such as soils, is accomplished by a dissolution – recrystallization or by a dissolution – transformation process in an aqueous medium. Hence in deserts, for lack of water most of the time, little reaction can occur and little life can subsist. In the extreme cold of the arctic, water does not exist most of the time (it is ice) and hence mineral transformations and life do not exist in abundance. The best place for life is where rocks become clays and where the plants can use this substrate to form their life sustaining substrate. This is why temperate climates are called temperate; they foster the abundance of living things. Out objective is to understand the relations between water, rock and plants. Herein lies the secret of the inter-relations of plants and minerals. Each individual actor uses the other to form his life – sustaining needs. Plants and eventually animals are the manipulators of the chemical systems found at the surface of the earth, the bio-zone.

## 1.2 Understanding How and Where the Plants We Know Today Occur and Interact with the Mineral World: The Setting that we Live in Today and its History

The world we live in today seems very old to many people, geologists and planetologists for example. Mountains, forests and other features appear to have been around for quite some time. The major factor of change, recent to say the least, is the transformation of the flora and fauna due to the use of the earth's surface by man. Some recent events, such as global warming appear to be a major threat to the stability of the system also, but put into geological perspectives they appear to be part of the normal course of fluctuating events. One must remember that in the past million years or so, a minor part of the history of the earth since the appearance of oceans and continents which is some thousands of times older, the earth has experienced 20 or more periods of glacial extension and severe climate change affecting vegetation patterns (Potts and Behrensmeyer, 1992, p. 461) and 10 or so in the last million years (Shackelton, 1995). These cycles have greatly affected the disposition of plant and faunal regimes in the continents.

However in the long history of the earth, continents have supported plant life for some 400 million years or so, and these plants were quite different from the majority of those we know now. In fact what we see today at the surface of the earth is relatively recent and some of the major geologic events seem to have played a role in the configuration of the climate and as a result the plants which occur on the earth's surface. We insist here on the plants as a major if not the major conditioning factor of life in that animals can migrate relatively rapidly, given a specific land mass to move about in, to adapt to changes in habitat but plants are more bound to local conditions, or at least some plants adapt to these changes in a more static way. It is important to put the present day configuration of the surface of the earth, mineral and biological, into perspective. The changes wrought by man's activity are enormous, to be sure, but what are they changing? How long have things been as they were before the advent of agriculture and forestry? This is the perspective that one should take before considering the interaction of plants, minerals and the use of these relations by human kind.

### *1.2.1 Configuration of the Surface Environment of the Earth: Mountains and Climate*

The surface of the planet is irregular in that land masses arise out of the oceans at irregular distances. The present day land masses are above all occur in the northern hemisphere, an asymmetry which one should not forget. Also a continent is present at the South Pole but it is covered with ice, unlike the situation at the North Pole where no continent is present but land masses are not far away; North America, Greenland, and the Eurasia. This situation of asymmetry is important to the circulation of ocean water and to a lesser degree the air masses that dominate in climate formation. The sailing contests of "around the world" carefully skirt the Antarctic and are not bothered by detours around bothersome large continents. Their trajectory is essentially north–south. It is a lot shorter in distance and more predictable weatherwise.

Climate on the continents, which is our interest here, is dictated by their situation on the earth (latitude) and their geographic – geomorphological configuration. If continents were not present, Aikin (1991, Fig. 1-5) indicates the general wind and pressure belts which might exist if the earth had no land masses. The inter-tropical convergence zone of low pressure is where the tropics would be found and where rainfall is high as well as are temperatures. To either side (latitude) one finds cellular high pressure zones at 30° latitudes followed by more irregular and smaller high pressure zones near 60° latitude. These air mass movements are both vertical and horizontal due to the rotation of the earth and thermal effects driven by the albedo of the water masses. The salient feature in such an analysis is that there are steep pressure gradients around the equator which are lessened in further latitudes to the north and south. The end result is that one finds a strong rainy zone around the equator and dry climates directly adjacent. As the pressure gradients lessen one finds more clement climates, the temperate ones with more sporadic rainfall. The major movement of air masses is west to east due to the rotation of the earth under the air.

If one considers the oceans only as we see them today, the weather pattern is roughly regular, apparently dictated by air circulations centered on the equator. High rainfall and high temperatures seem to be typical of there areas. Typically in the present day configuration of continents and oceans on the average rainfall drops off to the north and south while temperatures fall less rapidly (Fig. 1.1).

Somewhere in mid-latitude rainfall increases as temperature falls gradually until the polar regions are reached where temperatures are low and rainfall is also. One can follow this by looking at the daily weather map of the world where it is seen to

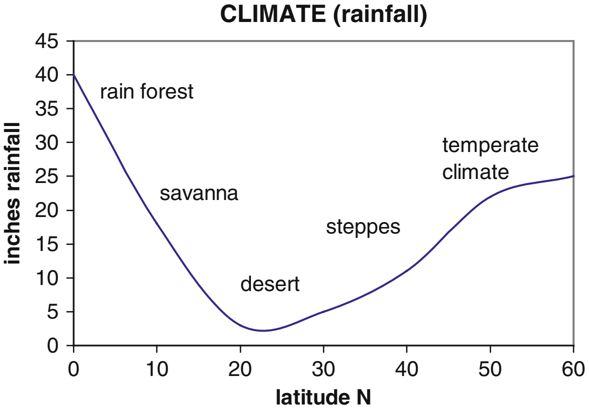


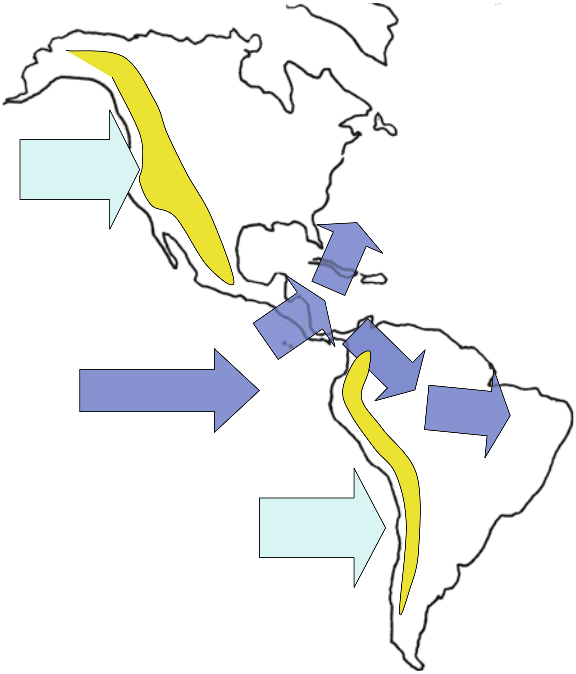
**Fig. 1.1** Relations between rainfall and latitude, generalized from climatic maps (data taken from different maps in the Encyclopaedia Britannica, 1969) The different, general, climate types are indicated on the diagram. On either side of the low rainfall zone, desert, one finds a grassland (steppe and savanna). The decrease in rainfall from tropical forest to desert is much greater than that toward the temperate climates from the desert

rain at or near much of the equator and just to either side one finds no rain. Almost daily rain is centered on the equator in the summer and shifts somewhat to the south in the winter. Deserts adjacent to the tropics have little rain and the temperate, mid latitude climates have variable weather patterns.

However the continents change the simple, ocean dominated, weather pattern to various degrees and in different ways. Basically, the tropical rain belt is nourished by ocean evaporation. These wet air masses come into contact with continents. The Americas are typified by high, north–south mountain chains on their western boundaries with some much lower, and less consequential, massifs on the eastern edge in North America. The high western reliefs, where the weather comes from, act as a barrier to air movement onto the continent and the effect on climate is striking (Fig. 1.2). In North America, especially in the United States, the mountain barrier creates a rain shadow to the east which is gradually decreased by mid continent. This is true in the southern part of South America but lack of significantly high relief in Central America and the north of South America allows the humid equatorial air to move across the land masses to the east into the north of South America where it releases its humidity creating the Amazon forest basin and spilling further south from the equator. Gradually the rainfall diminishes some in that it is not renewed from oceanic evaporative resources.

By contrast Africa, essentially a low relief continent, is strongly affected by the oceanic climate pattern directly with a rain forest at the equator and deserts to the north and south. The equatorial rainfall decreases by the time the air masses reach the eastern edge of the continent where high temperatures are found in the presence of arid climates. Here when the resources of humidity are not renewed enough and the rainfall decreases greatly until there are near desert climatic conditions in the eastern portion of equatorial Africa (Fig. 1.3). The regular weather

**Fig. 1.2** Schematic map showing air movements bringing humid air over continents. For the Americas, the mountain barriers north and south, largely prevent the entry of these air masses onto the land masses, creating a rainfall gradient west to east. Nevertheless these sources of rainfall make their ways north and above all south to create the large, wet areas of forest growth, especially in the Amazon basin region



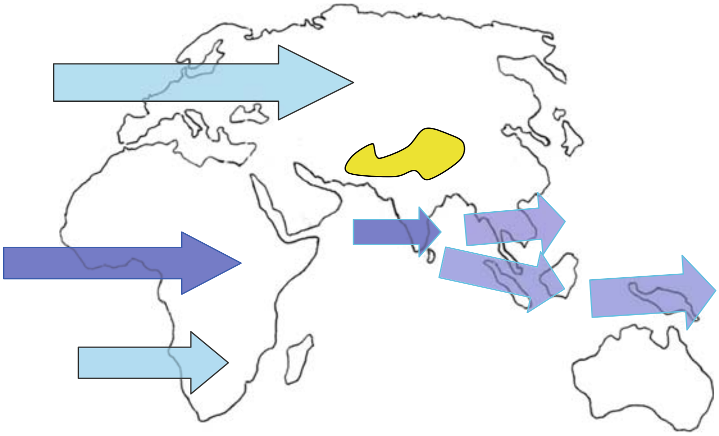


**Fig. 1.3** The normal airflow of air masses over continents with high mountain barriers in their interiors, especially visible in the Himalayan region, is illustrated by the Eurasian land masses. The humidity laden air stream loses its force over Africa towards the eastern edge of the continent, but picks up moisture over the Indian Ocean to create humid climates further to the east over Southeast Asia. The air masses which cross Europe, eventually lose their humidity and leave the increasingly drier regions of the Eurasian continent where the system is aggravated still further by the Himalayan massif which blocks any movement to the north creating the great Gobi desert

pattern of ocean dominated movement picks up again as the air masses gain humidity over the Indian ocean and enter onto the Indian subcontinent. The western edge is subject to high rainfall, especially on the southern part. Here the imprint of global air mass circulations is highly visible (general configuration adapted from Trewartha, 1954).

The south Pacific area is dominated by the equatorial rain climate in that the islands do not make a formidable barrier to the air mass movements and hence the tropics of the equator are wet. Australia, to the south, follows the pattern of desert below tropical rain forests and some change to higher rainfall areas with lower temperatures in its southern areas.

The European area follows the general ocean dominated climate pattern in its western and north, north-eastern areas being only slightly disturbed by the alpine age massifs. However the Eurasian continent is most strongly affected by the highest and most massive of the mountain chains, the Himalaya. Here the equatorial air masses are deviated to the south somewhat, giving high intensity rainfall in Southeast Asia. North of the great mountain chain one finds the greatest deserts present today eventually changing into cold and low rainfall areas below the arctic areas to the north and gradually into steppes and deciduous forest climates to the northeast. This pattern is particularly important to China, where the great desert is followed by the steppes of Manchuria and succeeded eventually by the deciduous forests of Russia on the edge of the Pacific.

Hence it is clear that the configuration of high mountain chains affect the climate to a high degree. These mountain chains, present today, are for the most part geologically recent, that is being formed gradually and cyclically from about 30 million years ago (Lefort, 1996; Duff, 1993; King, 1962). Thus the configuration of the earth, continents and mountain chains which affect the climate patterns due to air mass circulation, has been roughly the same for the last 30 million years. Prior periods showed climates at times significantly warmer than today, as much as 20° at the poles and 5°C at the equator (Duff, 1993, p. 462). One can expect that the climatic configuration created by these 30 million year old events has been more or less constant. However, superposed upon this general topography dominated climatic pattern, the occurrence of glacial periods (occurring over the last million years) have strongly affected the pattern, shifting the boundaries of the climatic zones squeezing them towards the equator in cold periods and away from it depending on the cycle of ice accumulation. These shifts have been strongly felt in most areas except perhaps the very central equatorial zones.

One remarkable fact is that for the most part, excepting northern Southeast Asia, the tropical climatic areas are of low relief and here the bedrocks are old, not having been renewed by orogenesis, and the soils are also very old. This is particularly true of Africa and the Amazon region. By contrast in the Southeast Asia area, especially the island chains, the relief can be locally high and the bedrocks recent, being of volcanic origin. Hence the tropical areas can consist of strongly contrasting geology and topography in the different regions of the globe.

The effects of climate on soils is of course primordial. The climate inductive to prairie – type soils, mollisol in the vocabulary of pedologists, is shown in

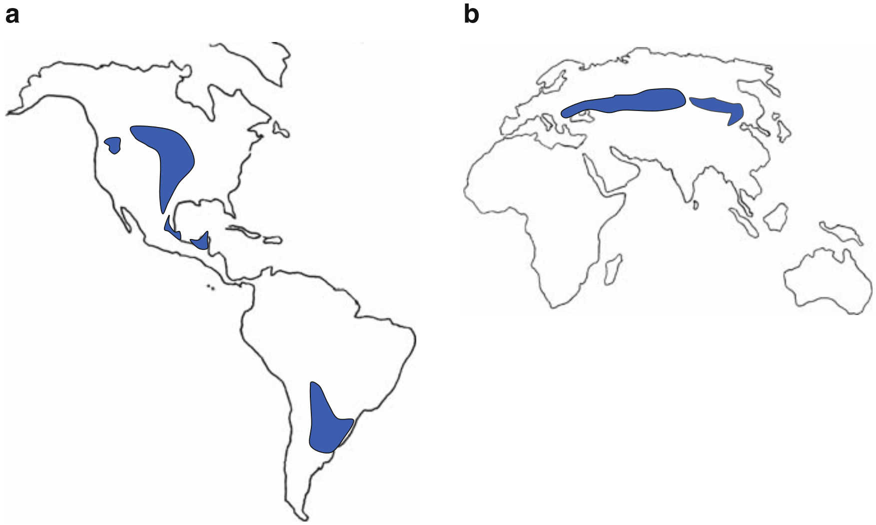


**Fig. 1.4** Consequences of the global air mass movements as it affects the soil types. The grass lands, due to lower rainfall under moderate temperature conditions, create the Mollisol soil facies, rich in organic matter and fertile for crops based upon grassland plants such as wheat, oats and lentils. These distributions follow the climatic boundaries defined by topography and air mass movement, north south in the Americas (**a**) and west east over the Eurasian continents (**b**).

Fig. 1.4. The strong tendency for a north–south trend in the Americas compared to the east–west trend on the Eurasian continent is evident. The mountain chains of the west coast in the Americas re-orient the climate according to this physical barrier whereas the lack of such a barrier allows normal east–west climatic influences to reign on the Eurasian continent.

### *1.2.2 Vegetation and Climate Today and Yesterday*

The largest part of today's plants have originated since the last 20 million years (families) and all genera since 10 Ma (Behrensmeyer, et al. 1992, p. 428), with some strong changes toward grasses for example during more recent periods, the last 13 million years up to 5 Ma. Essentially the dicotyledans are of this more recent era, with the formation of tree species as we know them today and slightly more recently the grasses. Hence the vegetal configuration we know today was created or developed when the mountain chains were formed in the geologically recent past. As vegetal life on land has been abundant for more than 400 million years this suggests that the "recent" geological events have changed things greatly. Particularly the grasses were rather late comers to the vegetal panoply but their impact on the biomass landscape was certainly decisive. The grasses allowed the development of the large grazing animals of the steppes and savannas which became the first motors of human existence in the sense that they were these animals provided the first stages of traction power stronger than that of man himself. These large quadrupeds allowed the development of nomadic hunting cultures and above all agriculture, multiplying the energy available for the needs of mankind. Grasses were of course the basis for a large portion of farmed crops also and still remain primordial for a large part of humanity. The widespread new occurrence of grasses occurred in the last 10 Ma years or so (Adams, 2007), with a peak in ecological diversity near 12 Ma. The spread of steppes propitious to their growth appears to be correlated with the rise of recent mountain chains (Behrensmeyer et al., 1992, p. 430).

Hence these recent changes, recent for the age of the earth but very old for the span of time that human or humanoids have been present which is only a couple of million years, have shaped the earth's living surface as we know it. It seems that the stage was set for the world as we know it in the rather recent geological past. Terrestrial plants were more than common in the Carboniferous period, some 300 Ma years ago. However the ecotones in this distant past were quite different from those known commonly today.

The stage was set, but climatic fluctuations occurred and especially in the last one million years or so. During this period glaciation has created displacements of the vegetal sequences in numerous cycles, up to twenty, (Potts and Behrensmeyer, 1992, p. 461). The cold periods squeezed the temperate climates towards the equator and warming released them making way for greater areas of steppes and then forests which we have known in the period of human occupation during the apprenticeship of agricultural life (see Bell and Walker, 1992, Figs. 4.12 and 4.13 for example). Thus in a given geographical place, the climate and vegetation has changed periodically over the last million years in numerous cycles. However these changes or displacements seem not to have affected the number or types of plant species to any large extent. Nevertheless they are part, and an important one, of present day preoccupations with climate change.

The overall change from megathermal vegetation, broad leaved and evergreen, dominating in the late Cretaceous period gradually changed to one dominated by deciduous trees in the 100–50 Ma period (Stewart and Rothwell, 1993, p. 496) and eventually large sectors of the continents were covered by grasses, depending upon the glacially controlled climate favourable to these plants.

### *1.2.3 Present Day Context of Plant Biomes*

Plants appear to dominate the surface features of soils. In fact soil scientists implicitly indicate that soils exist when plants are present. The upper most horizon of an alteration sequence in soil is one where organic matter due to plant growth is present. This is normal in that the input of vegetal matter is primordial in the development of this surface zone which structures and conditions the alteration sequence beneath (see Sects. 2.3 and 5.1). Different types of plants produce different types of organic matter which attract different forms of microbial life producing the complex chemistry of soil organic matter. The organic matter deposited on the surface, and that exuded by roots or the decayed roots themselves is quickly modified by bacterial and other actions of living matter in the soils zone. The soil zone is defined, in general, where the plants have the greatest influence and where the organic matter being decomposed gives a high organic carbon content and controls many other chemical variables. Elements in soil solutions as ionic species and hydrogen ions (pH) are among the major factors of soil solution chemistry controlled by the plant derived organic matter which affects the minerals in the soils.

The major types of vegetal cover have been identified and essentially defined according to the ratio of trees compared to grasses and other low cover. In a very general way one can divide the great vegetal associations into several types (Morley, 2000, p. 37) with forests dominated by broad leaved evergreens in the tropics, deciduous forests in temperate zones, needle leaved forests in areas of abundant to moderate rainfall and cooler temperatures and, where rainfall is more limiting, one finds areas dominated by grasses, the steppes and eventually shrub lands. The types of forest present are determined by a combination of temperature and range in temperature during the year (Morley, 2000, p. 51). World maps giving the present day geographic distribution of these different types of vegetation are found in numerous texts such as the Encyclopaedia Britannica (1969), Trewartha (1954) or Aiken (1991, Fig. 6-1). In this context, the smaller changes in temperature (from hot to cold) favour tropical broad leaved evergreen rain forests, needle leaved coniferous forests and tundra under abundant to normal rainfall. All of these forests produce acid soils. Braque (1987, p. 53) indicates that the deciduous characteristic of a given plant type can depend upon the climate it has adapted to. Desert and tropical humid climates favour non-deciduous behaviour or trees and shrubs, whereas temperate climate conditions favour deciduous behaviour. Depending upon the average temperature, the major control of soil biological activity, the leaf litter is more or less actively decomposed. In cold, wet climates the humic organic matter becomes a dominant feature in the surface horizons often forming high organic deposits. In hot, wet climates the biological activity greatly reduces the presence of humic matter in the A, soil horizon.

Drier climates and those with contrasted seasons favour grasslands. Intermediate rainfall conditions favor the deciduous forests. Prairie soils are neutral to perhaps basic in pH, rich in humic matter and in general clay rich. The deciduous forest soils are slightly more acid, but tend to have less clay in the surface horizons. Coniferous forests, found in colder and wetter climates, tend to produce acid soil pH. The presence of these general ecotone zones is due to climate, a combination of total rainfall, temperature and variations of both. Neither temperature nor total rainfall are enough to define a climate and the impact it has in creating the vegetation present.

In a very general way the basic regions of the world according to general vegetation type as a function of rainfall and latitude. As mentioned above, the effects of glaciation and glacial retreat determine the importance of the different zones which will shift according to the overall polar temperatures which impact the interpolar space of the earth. At present, in a warming climate, the desert zones expand pushing the frontiers of the grasslands towards the forest cover. However for the moment, based upon studies of flora in the past (late Tertiary and Plio-pleistocene) there seems to be no specific, climate driven, change in the number or types of species present. It is more of a displacement phenomena seen during the many glacial events in the past one million years. Overall today, 31% of the continents are covered in forest and savanna, 24% pasture, i.e. grazed agriculturally, 11% under agricultural practice and planted with only 34% under other conditions, those basically not used by man (Solbrig, 1991).

The biomass production is variable according to the climate affecting the type of vegetation. For example tropical forests produce 20 t/ha, forests in warm temperate climates 17 t/ha, temperate climate forests 13 t/ha, taiga forests 10 t/ha down to 4 in cold climates whereas prairies under temperate conditions (Normandy in France) produce but 9 t/ha, most of in the root zone (Braque, 1987, p. 53).

However climate has a very strong influence on the growth of plants in that they have more or less adapted to a certain general climate. This effect can be illustrated by the data in Fig. 1.5 where the production of corn in the United States in 1919 is shown and climatic variables superimposed on the mapped distribution (Jenny, 1994 and Cox, 1925). These data indicates the natural adaptation and growing efficiency of the corn plant before artificial irrigation methods were used which influenced the growth patterns of this crop.

The soils of the Central United states are based largely upon similar materials, either loess deposits or sedimentary rocks where the clay assemblages resemble one another greatly. Thus the major parameters are temperature and rainfall, which seem to form a zone of preference for corn production. There is an apparent need for between 750 and 1,000 mm of rain fall and a thermal optimum of between 12 and 8°C average temperature. The drop off in corn production to the east is due to the

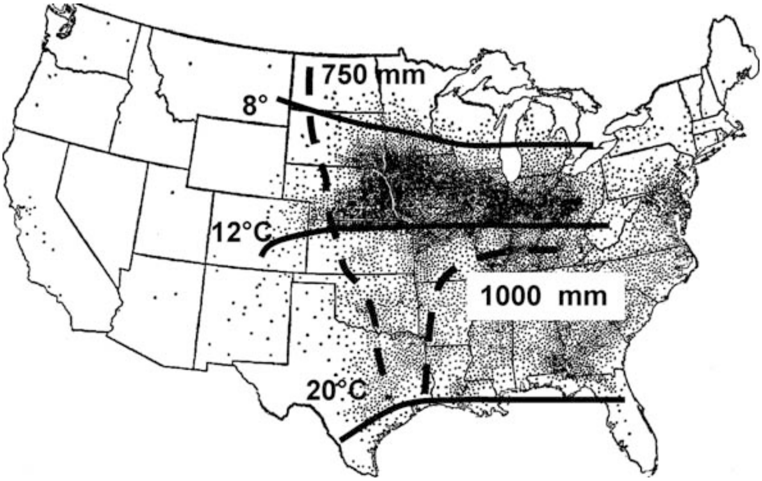


**Fig. 1.5** Composite map based upon a compilation of corn productivity in the United States in 1916 (Cox, 1925) and climatic averages given by Jenny (1994). One sees the optimum conditions for corn productivity, indicated by the amount of culture of this crop, as being conditioned by rainfall (greater than 200 mm per year, and average temperature between 12 and 8°C). This indicates the importance of climate concerning plant growth and prosperity

presence of the Appalachian Mountains which change the climate characteristics and patterns of course.

This example illustrates the inter-relations between climate and plant growth where, as is well known, plants have adapted to certain climates over the course of time. In the case of corn (*zea mais*) the intervention of man in selecting varieties adapted to his needs has not overcome the natural adaptation of the plant before selection. Corn was planted where it grew best in the Central part of the Midwestern United States, familiarly known as the Corn Belt.

### *1.2.4 Local Variations in the Chemical Context (Geology) and Climatic Variables of Plant – Soil Interaction*

The continents are variably inhabited by plants. Twenty eight percent has no vegetation (Braque, 1987, p. 53) and the rest is dominated, as far as biomass is concerned, by forests which produce 80% of the vegetative cover in mass but not in surface area. Thirty one percent of the surface area is in forest and savanna, 24 in pasture 24 in agriculture (Solbrig, 1991, p. 101). These numbers indicate that much of the continent areas are without vegetation, forests dominate in producing biomass but almost half is of use or possible use for agricultural purposes.

This very general pattern of climate and biotome are nuanced locally by two major factors: geology (the composition of the source material for soils) and topography which changes the climate locally. These two factors are of greatest importance in the field, where they often dominate concerning the plants present and the soils that are formed.

#### 1.2.4.1 Geology

Geology as such is a vast subject of investigation, at least to geologists. In the realm of plant – soil interaction geology means chemistry (See Jenny, 1994, Chap. 4). In fact the geology of the surface concerns the rocks that are at the air – rock interface. Sediments, sedimentary rocks, metamorphic rocks and plutonic rocks are the vocabulary of the geologist in this sense. Each type of rock which is given a geological name in fact designates a specific chemical composition, combined with some other criteria of crystal size and relations of texture, species of mineral present and so forth. But what concerns the biosphere is the ratio of chemical elements present, their susceptibility to be destroyed in water interaction and the tendency to create small particles during the process of alteration. Thus chemistry controls such factors as pH, potassium availability, calcium and magnesium availability and phosphorous availability, among other elements. As is well known certain plants have adapted to granitic or acid soils such as broom grass, and calcareous soils which favour the easy growth of grasses and, by extension, common grain crops. Overall, if one looks at the great grain producing areas of the world one looks at the geological map of sediment outcrops (the sedimentary basins) of North America, Western and Eastern Europe and China. Very often these sedimentary basins, where sedimentary rocks outcrop, are a composed of series of flat lying strata, which means nice flat land surfaces amenable to reasonable drainage but little erosion and hence deeper soils (the zones of fine grained material developed by plant – silicate interaction).

However, under the same climate different biomes can be present due ot the geologic substratum. An example is given by Blackford (1993) for Ireland where pine trees were the general forest tree in the period 7500 BC except for the limestone plateau in the north where oak was present. This is but one of many examples of an influence of geological substrate on plant species and growth.

More striking, according to Richards (1976, p. 221) bedrock can change the biome from rain forest in the tropics to scrub land vegetation or even savanna. The influence of the chemistry of the substrate changes the vegetation as much as climate could. However even though the tropical forest climate savanna is primarily grass, the grasses will not be the same as in a contrasted season savanna.

A fact or great importance in this effect is the type or form of mineral present in the rocks of the soil basement.

*Sedimentary rocks* are just that, compacted sediments and hence compacted accumulations of soils which are slightly recrystallized to form minerals similar to those the initial sedimentary material which hardens the material to form a rock. Soils are the major contributors to sedimentation, either in continental (i.e. non-marine) or ocean accumulations. As such they condition the minerals present which will be gradually changed into new minerals as the sediments are buried deeper under others. Depth indicates higher temperatures and hence eventually mineral change. Gharrabi et al. (1998) indicate the conditions necessary to radically change the minerals found in sediments (soil clays) into new, metamorphic minerals. These changes, re-crystallizations, are a function of time and temperature in that the transformation of soil clays into metamorphic minerals is a long process and rather slow in the context of sediment burial in sedimentary basins. It takes as much as 200 Ma at 150°C to produce a decent low grade metamorphic assemblage approaching that of muscovite and chlorite (see Velde and Vasseur, 1992). The transformation of soil minerals into new phases occurs well before the stage of metamorphism however. Virtually all of the minerals in a sediment buried at several kilometres depth for several million years are different in all characteristics from surface minerals. This is essentially determined by the loss of expanding (smectite) minerals from the mixed layer mineral assemblages. However new minerals can form before this point, those normally called metamorphic. Chlorite is one such phase. Velde et al. (1991) indicate the compositional changes which occur in the new mineral formed upon change in temperature due to sediment burial. Again, the deeper the sediment, the higher the temperature affecting the soil clay minerals and the faster the reaction will occur. Initially chlorites form mineral grains of differing composition which become more homogeneous as temperature and time factors increase. Hence if one has a soil based upon a young or little diagenetically transformed sedimentary rock, one can expect that the chlorites found in it will be of rather different compositions. This will give secondary clays with significantly different compositions and properties, such as layer charge. If the material of the rock has been subjected to stronger metamorphic conditions the phyllosilicates will be more homogeneous even though they can have significant variations in compositions due to successive metamorphic events (Saliot and Velde, 1982). Thus one should not be surprised to find that the clays developed from the same initial mineral in a rock have variable compositions, and the point which concerns us the most, different layer charges due to these compositional variations. This means that the same material can form the 2:1 clay minerals with different interlayer behaviours, an observation frequently made which creates variable behaviour of mixed layer minerals and segregation under chemical treatments such as potassium saturation.

*Metamorphic rocks* are sediments where the minerals have been very strongly changed from those of soils. In most sedimentary rocks one finds quartz, the most refractory of minerals which remains largely inert during weathering and soil development. Hence quartz – rich rocks (sandstones) do not make for good plant growth. They are barren to plant sustainers depending upon the amount of clays that were concentrated with the sands. Sediments containing more clays form metamorphic rocks which are most often dominated by micas, and chlorites which are phyllosilicates very similar to soil clays, 2:1 minerals which have a larger grain size than clays. Other minerals can be found depending upon the temperature which the rock has experienced. Higher temperatures tend to destroy chlorite and eventually muscovite mica. However the largest portion of metamorphic rocks contain mica, especially muscovite, the potassic, aluminous phyllosilicte mineral.

Sediments containing carbonates do not change much with metamorphism, maintaining their chemical and mineralogical characteristics.

*Igneous rocks* form a range in compositions from those similar in bulk composition to argillaceous sedimentary rocks (granites) to those completely different from sedimentary materials (basalts). For the most part, igneous rocks do not form ideal sites for plant growth. In temperate latitudes the plant cover tends to be one of small shrubs with dispersed grasses. Extremes of pH accompany the igneous rocks of granite and basalt composition rendering them out of range for normal forest or grass growth.

The differences in vegetation determined by bedrock are largely effaced under conditions of warm tropical climates where the alteration and soil layer are sufficiently transformed so as to form a sort of convergence in their effect on vegetation. Thus under extreme climatic conditions, the climate becomes more important than geological (bedrock) factors, under extreme tundras, deserts and warm tropical conditions.

Loess is a very important component of soils in the northern hemisphere where the effects of glaciation have produced a cover of fine grained wind worn material of varying depths. This is especially apparent on the north American continent where a large part of the agricultural United States is based upon loess based soils. The same is true for Europe. These loess deposits were formed from wind – born sedimentation at the end of the last glacial period, upon glacial retreat. Much of the loessic material forming today in China has most likely the same origins but since the initial deposition of the glacial material is on the arid high plateaus north of the Himalaya chain, it is still susceptible to wind erosion (see Sect. 3.1). The loessic sediment is most often a chlorite – muscovite material, susceptible to rapid alteration at the surface by either water chemical attack or by plant transformations. Other loess material has already been transformed by surface alteration and is part of a very fertile material for plant growth.

### 1.2.4.2 Topography

The local morphology of the land surface can change the effective climate (temperature and rainfall) within a given climate or geographic "region" (see Jenny, 1994, Chap. 5 and Birkeland et al., 2003). Hills and valleys give different vegetal cover, especially in grassland landscapes. Mountains of course produce very strong differences in climate and plant cover.

Figure 1.6 shows some possibilities of these local climatic effects. In Fig. 1.6 the situation in temperate climate prairies where grasses are on the plateaus and woods in the bottom lands can be found in south West England where the acidic granitic soils favored in the period 7700 BC grasses on the uplands and oak – alder woods in the bottom lands. The difference in altitude was 100 m, not enough to change the major climatic factors (Casteldine and Hutton, 1993). Hence one must conclude that local drainage patterns can determine the type of vegetation present.

Sequences of soils developed upon largely the same material but under different topographic conditions (Catena) are an important study in Soil Science. The changes in vegetation are largely controlled by the conditions of water availability in many

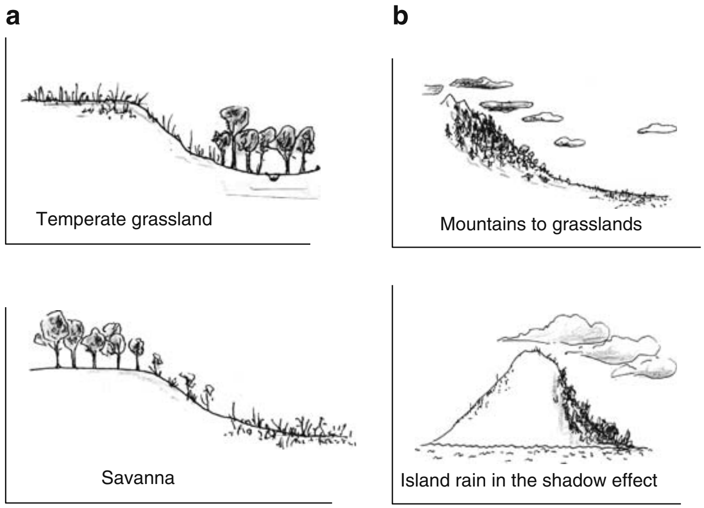


**Fig. 1.6** Schematic representation of the effects of microclimate on biomes. (**a**) In temperate grass lands the valley *bottoms* are places where trees row preferentially. In savanna areas, towards the tropical climates, the trees tend to be on the plateaus. (**b**) In zones of high mountains, especially those of the Americas, the mountain heights have a higher rainfall than the lower plains found in the "rain shadow" to the east. Isolated island in ocean areas frequently are arid to the windward, source of humid air movement, and wet to the leeward, on the protected side of the elevation. Here the lee side is the wet side

instances and temperature when confronted by high mountains. Along with water, soil materials can move also. We will treat this situation in greater length later in Sect. 3.1.

However, even changes in orientation with respect to the sun (north – facing and south – facing) can create differences in vegetation and hence soils. Birkeland (1999, p. 233) shows such an instance for soils in Ohio, a temperate climate. On one side of the river valley one finds mixed oak forests, with a typical forest soil and alteration profile and on the other side of the valley one more typical of grasses. Grasses show higher pH values, more organic matter in the soil horizon and more exchangeable ions, indicating different types of clay minerals present. One side (that dominated by grasses) would be much better for farming than the other (dominated by forest).

The effect of morphology on soils is driven by water resources which affect plant regimes. The effect of altitude is to change the average temperature and hence the plant regime; These changes in vegetation produce different characteristics in the soil properties such as pH, organic matter content, base exchange capacity (exchange ions) which derive from the presence of 2:1 clay minerals and to a lesser extent organic matter. Alterability of the bedrock can be affected also. The topography determines the water regime, and thus the amount of dissolution which will occur as well as the activity of plants. Creek bottoms on the Great Plains of the United States have trees while the uplands have grasses present. The depth of organic matter, clay content and pH are quite different. These factors have been important in the development of the agricultural conquest by man of the land in which he has lived.

In Fig. 1.6 there are two types of landscapes where grasses or prairies are found, the temperate climate grasslands with prairies on the uplands and trees in the bottomlands and savanna grasslands formed in hot contrasted climate zones towards the equator where trees are found on the uplands and grasses in the expansive lower plains.

The importance of major mountain relief is very great in determining vegetation types and soils (see Birkeland et al., 2003). The presence of mountain chains on the west coast of the American continents provides a barrier to normal wind currents with the result that in middle latitudes the moisture laden air masses do not penetrate beyond the mountains, creating drier areas behind them which gradually change into more moisture – rich regimes as one progresses to the east. Thus the Americas have a high mountain wet forest followed by semi-desert and gradual change to prairie and then deciduous forest further east. This succession, desert to prairie (steppe) to deciduous leaved forest is south to north on the European continent. The Himalayas change the direction of the air masses also, with the result that the desert is to their north, followed by prairie in the Manchuria, north eastern China, and then deciduous forests in Russia on the edge of the Asian continent above Korea. Here the succession is on a slight diagonal from southwest to northeast.

Another, well known topographic effect is that of mountain islands in oceans. Here typically the air mass does not bring moisture until it reaches the lee side of the island, the reverse of continental mountain chains. The tropical valley vegetation is found on the slopes facing away from the major air mass movement. The islands of Hawaii are a fine example of this effect.

### *1.2.5 Summary*

These "planetary" factors are in their turn modified by more local topography, plateaus, river canyons, island mountains and so forth which modify the vegetation and the soils which are related to them. The geological materials forming the surface further modify the vegetation which can adapt to different basic constraints of chemistry, mainly acid or basic pH values which strongly affect the plant regimes. Acid bedrocks favour forests while basic pH bedrocks favour grasses given equivalent temperate rainfall resources for example. The vegetation present is not only a factor of climate on a large scale, but on a smaller scale and to a lesser extent. The chemistry of the soil forming material can also change the ecotome, favoring trees with to respect to grasses for example under the same climatic conditions. However at the extremes of climate, tropical or tundra, the major factor is one of rainfall and temperature, which largely affect and modify the effects of bedrock and to a certain extent local topography.

It is important to note that the situation of the climate, topography of the continental surface is relatively recent, 20–30 million years old, and the plants we see today have developed largely since this period. The world we live in is recent, geologically speaking, and has evolved relatively rapidly, compared to the relatively small changes over the long periods of initial plant colonization of the continents.

This is the setting of surface plant – rock interaction where the ultimate chemical changes to form soils (defined as the zone where plants interact with silicate and other matter) dominates.

## 1.3 An Unorthodox but Operational Definition Mineral Types and Functions for Phyllosilicate Clay Minerals

The alteration processes at the surface, either in the water – rock or plant – silicate zone produce fine grained material called clay minerals. Any interpretation of the interaction between plants and their substrate must use clay identification procedures in order to understand the chemical changes and equilibria that occur. As it turns out plants strongly affect the chemistry of the soil in which they evolve and in doing so change the chemistry of the clays present. In order to understand the dynamics of the plant systems one must be able to identify the clay minerals and hence estimate their chemistry.

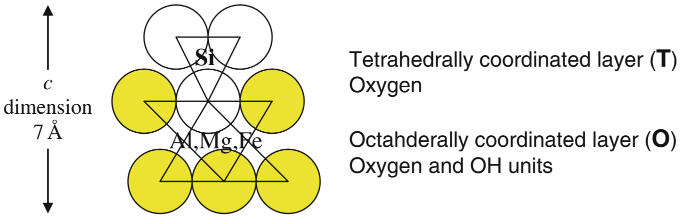
In order to put the reader in a functional framework, it is useful to simplify the nomenclature of clay minerals to give a working understanding of the majority of the materials present at the surface involved in plant – silicate interfaces. Soil clays are a field in themselves. Initially the concept of clay minerals is one based upon physical size. This definition, an anomaly in crystallography, is founded upon the history of scientific development. Much of mineral classification was accomplished in the later part of the 19th century. The basic tool for such an endeavour was the optical microscope. Manipulations of crystals submitted to variations in polarization of light transversing the crystal was used to help identify and classify minerals. Optical petroscopy was the basic tool of investigation. Crystal structures and atomic alignments were deduced from such manipulations. These methods were continued well into the 20th century. As with all things, the method of investigation, the microscope, has a limit of resolution. In this case it is the dimension of 0.002 mm, or 2 $\mu$m. No crystallographic determination was possible below this limit. However, mineralogists could extract and purify materials for chemical identification below this limit of observation. Since it was clear that mineral matter, classsifiable by its chemistry was present at scales below microscopic identification, these minerals, identified using their chemical characteristics, were called clay minerals, essentially, those species not amenable to normal optical identification. Use of X-ray diffraction, practiced in mid 20th century allowed a more correct definition of the crystallographic parameters of this crystalline matter. However clays remained clays, those objects which could not be visually differentiated, having a size below 2 $\mu$m. Thus clay minerals can be crystallographically determined, by X-ray diffraction, but they remain a mixed crystallographic and mineralogical group. In fact any fine grained mineral can be found in the clay fraction, especially quartz and calcite for example. But the largest part of fine grained materials found in nature have a similar crystallographic structure, that of a phyllosilicate. These minerals, found in rocks also where they can be identified optically, are essentially a two dimensional structure where the crystallographic directions $a$ and $b$ are much greater than the $c$ crystallographic direction in the structure.

### 1.3.1 Network Structures

We will initially divide the most frequently found clay minerals, phyllosilicates, into two groups. First we must consider the fundamental structural differences among minerals found in soils which are based upon crystallo – chemical criteria. Clays minerals, whose structure is continuous or almost so in two crystallographic directions and limited in a third., are composed of basic chemical components of which oxygen composes about 50% of the atoms present, and a large portion of the remaining ions are silicon. Hence the name silicate mineral is applied to these crystals. The name is more than simply a name because the basic chemical characteristic of phyllosilicates, as most silicates, is that of the Si-O bond where the atoms are interlinked through sharing of electrons into a strongly co-valent structure. The strongest chemical bonding is between Si and O ions. At times an aluminium ion is substituted for silicon but usually in a minority of silicon sites in the structure. The resultant Si-O polymer of shared atoms is the dominant factor in the structure but it extends in a sheet like array, with less strong bonding between layers of Si-O atoms. The geometry of these arrays of oxygen and silicon atoms is hexagonal where at intervals a silicon atom is missing and a “hole” is present in the sheet. The silicon-oxygen ratio is such that a silicon atom is linked to four oxygens, and hence is called a silicon-oxygen tetrahedron. The dimensions of the atoms in these structures are such that the oxygens dominate in volume and other cations, such as Si, are found in the interstitial points within close packed oxygen atom arrays. The silicon-oxygen array of atoms is always linked, covalently, to one layer of other cation through shared oxygens, a second but lower energy covalent bonding.

This second variation of oxygen – cation linkages in phyllosilicates is one where atoms are bonded with six oxygens instead of four. The co-linked cations surrounded by six oxygens are called octahedrally coordinated ions. In clay mineral structures there is always a silicon-oxygen linkage with shared oxygens linking to the octahedrally coordinated linkage. This type of inter-linkage is called a tetrahedral – octahedral structure, TO (Fig. 1.7).

Thus one can have a tetrahedral and octahedral structure alternating with shared oxygen ions. This is commonly referred to as a 1:1 structure recalling the ratio of silica (tetrahedrally coordinated) to octahedrally coordinated cations. In the octahedrally coordination layer some oxygen ions are linked to hydrogen cations (OH units). The OH units are not co-linked to silicon ions. The presence of hydrogen ions gives a hydrated dimension to the mineral. Upon heating, to temperatures above 400°C or so, these hydroxyl groups leave the structure as water molecules and hence one refers to the clays as hydrated minerals. However there is no water present in the structure as such ($H_2O$ molecules) but water appears when the mineral looses coherence due to heating.



Al = kaolinite
Fe with minor Mg and Al = 7A chlorite
Mg with minor Al = serpentine (non clay mineral)

**Fig. 1.7** Representation of the two cation layer structure of a tetrahedrally coordinated ion layer with an octahedrally coordinated layer of cations. Cations are Si (tetrahedral coordination) and Al, Mg or Fe (octahedrally coordination) with oxygen anions and/or hydroxyl (oxygen with a hydrogen cation) cations (*grey* in the figure). The structure can be designated as a TO structure for tetrahedral – octahedral sequence or a 1:1 structure with two layers of cations. The *c* crystallographic dimension is indicated, perpendicular to the layers of ion is the structure which is the determining measurement for X-ray diffraction identification. In the TO structure the *c* dimension is close to 7 Å

Two variations of site occupation are possible for the octahedrally coordinated site, one where three divalent ions are present, making a cationic charge of six for the unit cell, or one where two trivalent ions are present in the octahedrally coordinated layer sites leaving one site vacant. The first, completely filled, is called tri-octahedral and the second di-octahedral. In soil systems, the most common ionic occupancy in clays is by aluminium and hence most soil clay minerals are dioctahedral in structure. However a non-negligible amount of material can at times be of the tri-octahedral type. The number of sites in the octahedral sites in phyllosilicate clay minerals varies then from 2 to 3. More precisely, the occupancy is between 3 and 2.5 for the so-called tri-octahedral minerals and very close to two ions for the di-octahedral minerals.

As it turns out there is a clay mineral with the TO structure, two layers of coordinated ions, which is called kaolinite. It is almost strictly of an Al-Si composition and hence dioctahedral in site occupation. Very few ions are found to substitute for these two cations. This is unusual for clay minerals which usually show ionic substitutions of one cation for another. The small variation of the kaolinite structure makes its properties quite predictable.

In a more complex, three layer, structure one can find a silicon-oxygen layer interlinked with an aluminium-oxygen, hydroxyl layer which in its turn is linked to another silicon-oxygen layer. This gives a triple cation layered structure, tetrahedral – octahedral – tetrahedral, or TOT. Most often it is referred to as a 2:1 structure recalling the ratio of silica to octahedrally coordinated ions (Fig. 1.8).

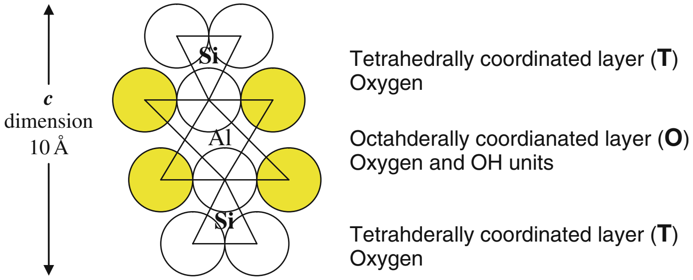


**Fig. 1.8** Representation of a three cation layer structure where two tetrahedrally coordinated cation layers are present (essentially Si cations coordinated with oxygen anions) and one octahedrally coordinated cation layer. Again the octahedrally coordinated cations are related to OH ion units where the oxygen anion is coordianted to with a hydrogen cation. In soil clays the tetrahedrally coordinated ions are predominantly Si and the octahedrally coordinated ions are predominantly Al, but can be Mg ions also. Fe is probably more rare in that the oxidation state of iron would be divalent, more rare in the oxidizing environment of most soils. Trivalent iron ions are relatively rare in phyllosilicate structures. These structures are called TOT (tetrahedral-octahedral-tetrahedral) or 2:1 types because of the three cation layers coordinated to form a completed mineral structure. The *c* crystallographic dimension or the TOT layer is near 10 Å

### 1.3.2 Substitutions and Layer Charge

Substitutions can occur in the cation positions in the Si-O networks in 2:1 (TOT) minerals. One type is an iso-charge exchange with $Mg^{2+}$ for $Fe^{2+}$ ions for instance, typical of the tri-octahedral type of mineral. Also it is possible to have those of different charges, Al for Si for instance where the substitution is in the tetrahedral site. Such non-equivalent substitutions create a charge imbalance, where a trivalent ion ($Al^{3+}$) is put in the place of a quadrivalent ion ($Si^{4+}$). Substitutions which are not charge neutral necessitate the presence of another ion inserted into the 2:1 network structure to satisfy electronic neutrality. These ions can be present in the network structure itself, for example a substitution of $Al^{3+}$ for $Si^{4+}$ with a net negative charge could be compensated by a substitution of $Al^{3+}$ for $Mg^{2+}$ in the octahedral site in the network giving a positive charge locally which compensates for the negative charge at the other site, in the tetrehadral position. As a result the 2:1 layer is charge neutral due to internal compensations of different ionic substitutions.

Another possibility of charge compensation can occur as substitutions on the surfaces of the 2:1 structure between two adjacent units. The ionic substitutions creating charge dislocations (compensation from one site to another) are extremely important in the development of basic clay chemical properties. For example when there is a strong charge substitution not compensated within the network itself, one positive charge for 22 negative charges, the compensating substitution is usually

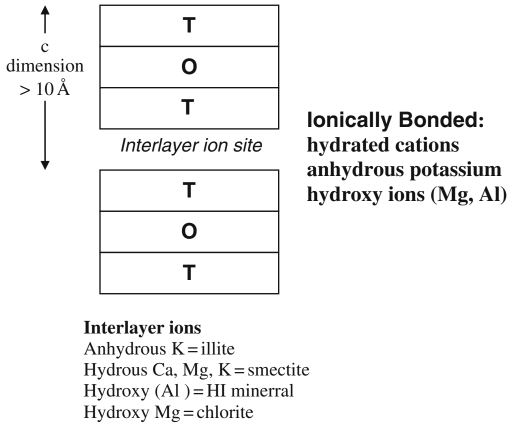


**Fig. 1.9** Assemblage of TOT (2:1) layer unitts which for crystallites of soil clays. Most often one finds that there is a cation occupation between the units which compensates surface charges on the aggregate TOT layers engendered by substitution of cations within the structure of different charges. These residual charges (negative) attract interlayer ions which are situated between the TOT layers (2:1). The cation occupancy, with or without water or hydroxyl anions, determines the interlayer spacing (c dimension) allowing identification by X-ray diffraction methods. These interlayer ions, determining the X-ray diffraction characteristics, give rise to a nomenclature of clay minerals based upon the occupancy of the interlayer ion sites. The *c* crystallograpic dimension or the TOT layer is near 10 Å

made by potassium inserted into the surface oxygen network between the TOT units, forming a mica. The chemical formulation is:
$\mathbf{K}Al_2Si_3\mathbf{Al}O_{10}(OH)_2$ instead of the charge neutral 2:1 structure of $Al_2Si_4O_{10}(OH)_2$
Where K and Al are the substituted ions in the manner of $Si^{4+} = Al^{3+}K^{+}$

The position in of the potassium ion in the structure which is substituting to compensate for the charge imbalance within the 2:1 unit is in between the silicon ion coordinated layers of the structure in what is called the “interlayer” crystallographic site (Fig. 1.9)

### 1.3.3 Interlayer Ion Occupancy

This interlayer site can be occupied by different ions. Usually, the maximum charge compensated in this site is one per a total of 22 negative charges of the oxygen – hydroxyl network. This is a high charge structure and usually designated as a mica. The only ion present in high charge structures at the surface (in soils) is potassium. However, if the average total substitution on the structure is less than one per unit cell (22 oxygens), one develops what is called a low charge structure. Here a variety of compensating ions can be present in the interlayer site. Their species is largely determined by the chemistry of the soil fluids. In many cases, these ions can be exchanged as the fluid composition changes. These are called exchangeable ions. The amount of exchangeable ions present per mass of clay is called the cation exchange capacity or CEC.

Basically three types of cation occupations are present in the interlayer sites:

1. those which are associated with hydroxyl ions, which gives the mineral the name of hydroxyl – interlayered (HI) mineral. The basic interlayer spacing of the 2:1 structure in the *c* crystallographic direction is 14.2 Å.
2. those which are accompanied by water molecules, which gives them the name of hydrated interlayer ions. The basic interlayer spacing in the c crystallographic direction is 15.2 Å. Under conditions of higher temperature than normal or very low humidity the exchange cation layer can contain only one water layer giving a 12.5 Å spacing. This spacing tends to be present more in mono – valent cation substitutions such as Na or K ions.
3. those which are not accompanied by other ions (anhydrous), where the name given is mica or illite, since the only ion of this sort is potassium. The basic interlayer spacing in the *c* crystallographic direction is 10 Å.

The intensity with which the interlayer ions are held is a factor of total charge and charge site, the charge in the tetrahedral site appears to be relatively stronger than that in the octahedral site (Malla and Douglas, 1987). The question of mineral identification lies in the identification of the type of interlayer ion present between the layers of the TOT structure. These interlayer ion sites are the key to determining mineral species and the function of the clays in the soil environment.

## 1.3.4 Identification of Phyllosilicate Clay Types

Our identification of the minerals present and their relative abundance is based upon a curve decomposition method (Lanson, 1997) which allows one to identify and estimate the relative abundance of the different components of a complex diffractogram. Peak position and width depends upon the composition of the mineral present and the relative number of diffracting layers in the crystallites. Smaller diffracting domains widen the peak and shift it to larger peak positions (Moore and Reynolds, 1997). Complex spectra can give large, unidentified peaks using visual examination, whereas the components can be precisely identified using decomposition methods. The use of this very important tool of interpretation fo X-ray diffractograms, the only viable method of clay mineral identification, is given in more detail in the Annex at the end of the book.

In order to interpret the diffractograms one must have some idea of clay mineral structures for those phases found in soils.

### 1.3.4.1 The 1:1 Minerals (TO)

The TO minerals have a basal spacing (crystallographic direction perpendicular to the basic layer structure) of near 7.2 Å. This indicates the presence of one silica layer and, in most soils, the presence of one alumina layer with hydroxyl ions at the surface. This is the kaolinite mineral. The chemical composition is almost constant, to within several percent of the cations present. In some cases, alteration regimes that are very water – rich, a hydrated mineral ($H_2O$ ions present) can occur. Here the spacing is closer to 10 Å, but the mineral is unstable upon heating to about 200°C. Some mixtures of kaolinite and halloysite can be found. Kaolinite is present under regimes of high rainfall but also is part of the normal rock – water interaction reactions which occur in most climates. The water in halloysite is in a way similar to that founding zeolites, loosely held playing little structural role. However the shape of the kaolinite crystals is dramatically changed from a sheet structure to one of a tubular form. This mineral is called halloysite. Thus the soil clays with a TO or 1:1 structure (one tetrahedral unit and one octahedral unit) can be defined as an anhydrous and a hydrous variety.

### 1.3.4.2 The 2:1 Minerals (TOT)

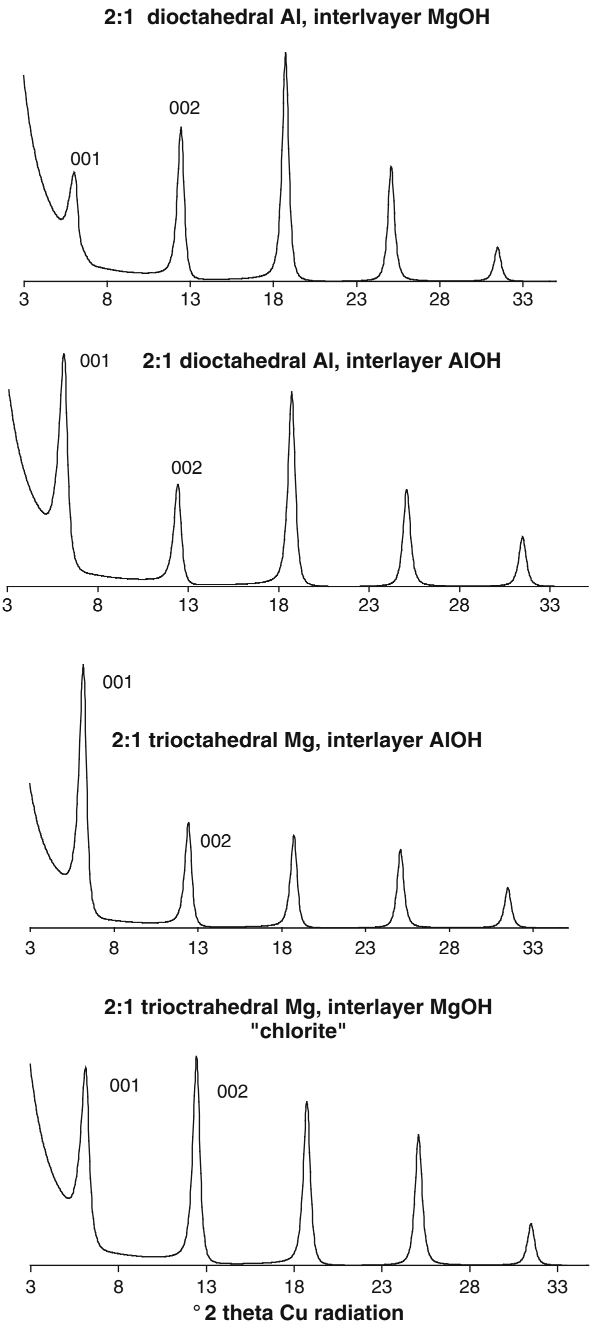
The interlayer ion occupancy of these minerals affects the intensities of the different basic X-ray diffraction reflections of the structure. The most often observed for mineral identification are the reflections dependent on the *c* crystallographic spacing, the *(00l)* spacings (*see* Moore and Reynolds, 1997 for a definitive discussion of the problem). When hydrated or hydroxylated ions are present in the interlayer sites between the 2:1 units or when a less than maximum or ideal number of cations are present, the 001 spacing is by far the most intense of the *(00l)* series (see Meunier, 2007). This is especially frequent for the case for hydroxy interlayer minerals found in soils. This is also the case for hydrated ion structures, i.e. cations linked to water molecules. However, when no OH or water is present and the occupation of the interlayer sites is near maximum, one cation for 12 oxygen plus hydroxyl anions for instance, the intensity of the first order peak 001 is often less than that of other lower order peaks 002, 003. etc. Hence a high intensity first order peak in the range of 15–10 Å indicates either incomplete occupation or the presence of water molecules.

### Smectites

Cations associated with water molecules filling the interlayered sites give rise to the smectite minerals. Normally these ions are easily exchanged for others when introduced to an aqueous solution containing another dominant cation. Smectites are characterised by exchangeable ions. By changing the amount of water present in the surrounding of a smectite, one can change the water content which in turn changes the dimension of the clay mineral. Highly hydrated cations have a two water layer structure (15.2 Å spacing), increasing temperature or decreasing water vapour pressure reduce the amount of water to a one layer structure (12.5 Å) and eventurally an anhydrous state can be reached under conditions not expected under normal earth surface conditions giving a 10 Å spacing. This property of water loss or gain gives rise to the descriptive term of expandable mineral. If another medium is present (organic molecules in liquid or gaseous form) the water is exchanged for the other and hence the expandable nature of smectites is again expressed. molecule changing the interlayer spacing due to the differences in molecular dimension. Smectites are characterised by the ability to expand or contract.

### HI minerals

In the case of a complete occupancy in interlayer sites by MgAlOH complexes, the 001 (14.2 Å) peak can be more or less intense than the 002 peak (7 Å). In the case of stoichiometric structures (fully occupied interlayer sites) the relative intensities of the *00l* peak series are a function of the cations in the interlayer site and in the octahedral layer of the 2:1 mineral. Hydroxy interlayered minerals can be either dioctahedral or trioctahedral in character. All of these minerals can be called chlorites. Further, simple elemental substitution, Fe for Mg, or Al for Mg for example, changes the relative intensities of the different peaks of the (*00l)* series. In Fig. 1.10 the occupation of the octahedral site in the 2:1 structure is either aluminium (a) or magnesium (b) in a di-octahedral configuration or a tri-octahedral configuration (calculations of these spectra were made by Eric Ferrage, Univ Poitiers using the ASN program). The structures contain all Mg or Al ions in both 2:1 and interlayer sites. If we mix the ion types from octahedral sites to interlayer sites the effect is important also. Basically, when Al or Mg are present in the interlayer, site the first order reflection is at 14.2 Å. Hence interlayer ion composition can affect the relative intensities of the X-ray diffraction patterns of the clays as well as can a low occupancy of the interlayer sites.


2:1 dioctahedral Al, interlvayer MgOH

2:1 dioctahedral Al, interlayer AlOH

2:1 trioctahedral Mg, interlayer AlOH

2:1 trioctrahedral Mg, interlayer MgOH
"chlorite"

**Fig. 1.10** (continued)

#### Micas

Minerals with no interlayer water or hydroxyl elements present will be anhydrous, and have an interlayer spacing of 10 Å.

### *1.3.5 Classification of 2:1 Minerals*

Using the above criteria one can construct a classification scheme which focuses on the interlayer ion occupation of the 2:1 (TOT) structure of the mineral. Traditional mineral identification of clays is based upon X-ray diffraction which in fact indicates the interlayer ion population. However mineralogists usually stop when they have identified the interlayer ion site ions with a set of laboratory treatments of the clay assemblages. The different laboratory tests are used to estimate the occupation and stability of the interlayer ion sites is designed to test either the exchange of the interlayer ions with other elements in aqueous solution or the stability of the hydrous state of the interlayer ions, one or two water layers. If the elements in the interlayer ion site are easily exchanged, a treatment with a moderately concentrated solution of $CaCl_2$ or $MgCl_2$ will displace the different ions leaving a structure with a more or less homogeneous hydrated interlayer ion structure in the air dried state. Usually divalent cations are used for this laboratory test, Ca and Mg are the favourites. In this case one has a 15.2 Å structure which gradually de-hydrates, collapse to 10 Å, at temperatures between 300 and 400°C.

Treatment with ethylene glycol or glycerol vapour increases the spacing of the hydrous ion species of clays to 17 Å due to exchange of the organic molecule with water molecules. The micaceous and HI minerals are un-affected by such laboratory treatments. The change in basal spacing upon glycol or glycerol treatment, produces and expansion of the mineral, hence the nomenclature of "expanding mineral" which is roughly synonymous with "smectite" (see pertinent chapters in Dixon and Weed, 1989)

Minerals which remain in the anhydrous state after exchange cation saturation have a spacing of 10 Å are considered to be micaceous in nature and called illite in soil clays. Normally potassium is the interlayer cation. Minerals which retain a 14.2 Å spacing, and do not dehydrate easily nor exchange with divalent cations

**Fig. 1.10** HI minerals. Example of the importance of cation types (atomic mass and resulting electronic density) on the relative intensities of the basal spacing reflections where 001 is the first order, 002 the second, 003 the third and so forth. Peak intensity rations can give an idea of the cation layer compositions. In the case of HI minerals with complete occupation of the interlayer site with hydroxyl coordinated cations (chlorites), the octahedrally coordinated ions can vary significantly. In some cases the TOT, 2:1 structure contains a dioctahedral ion complex (Al ions) and in others a trioctahedral (Mg dominated) complex. Depending upon the interlayer site occupancy and the 2:1 layer site occupancy the ratios of 001–002 intensities change as do those of the other basal spacing bands. For example, with a dioctahedral octahedral layer in the 2:1 structure the presence of Mg or Al in the interlayer site changes the 001/002 intensity ratio completely compared to the 003 peak intensity which is relatively constant. The spectra are obtained by calculations using the *ASN* program developed recently by Lanson and Ferrage in aqueous solution are considered to be HI or hydroxyl ion complex minerals or chlorites. Heating to temperatures above 400°C usually collapses the HI minerals, at least partially, but does not affect the chlorites.

The usual identification procedure using X-ray diffraction methods, done in the Ca, Mg – saturated air dried state gives:

10 Å = illite
15.2 = hydrous cation expandable mineral under room temperature and humidity conditions
14.2 Å = HI hydroxyl mineral

Such a state is reasonably close to the situation in a soil environment.

### *1.3.6 Identification of Smectites and Illites*

In soils one often finds an intimate mixture of 10 and 15.2 Å structures, illite and smectite, apparently in the same crystallite. Examples of the end members frequently present in soils are presented in Fig. 1.11. One can see the typical diffraction maxima of these different types of soil clay minerals. The spectra are decomposed into their components showing individual peaks representing a mineral type and the overall envelope of the spectrum. In Fig. 1.11 we have represented typical high smectite content clay minerals (a) and a highly smectitic mixed layer clay accompanied by an illite. The smectite (minerals of high smectite component can be mixed layered with a 10 Å component, illite, within the same mineral grain structure). These are mixed layer clays. A peak positin near 15.2 Å indicates a nearly pure smectites mineral. Positions nearer to 10 Å indicate a mica component. The major smectite peaks show a peak width at half height of greater than 1° 2 theta, indicating a small grain size and/or an interlayered mineral structure. Small diffracting domain and interlayering tend to broaden the diffraction peak (Moore and Reynolds, 1997). For the illite (lower spectrum in figure) usually two peaks are present. The more narrow 10 Å peak indicates the presence of fully anhydrous interlayer ions, which are called illites (WCI or well crystallized illite). The wider peak at 10.2–10.6 Å in general represents the small grained illite material (PCI or poorly crystallized illite), usually of less than 6 unit layers thickness (see Lanson, 1997 for a more detailed explanation of the X-ray diffraction phenomena).

The smectitic phase X-ray diffraction peaks will be displaced to near 17 Å upon treatment with glycol or glycerol, typical laboratory treatments used to indicate the possibility of swelling, or incorporation of organic molecules in the place of the typical two water layers around the exchange cations, Ca or Mg. The illite peak is not displaced upon treatment with organic molecules and it remains at near 10 Å.

### *1.3.7 Mixed Layer Illite/Smectite Crystals*

In Fig. 1.12 an example of mixed layer illite/smectite clays is presented. In many soils, the mixed layer minerals form twodifferent groups, one smectites rich, S/I,

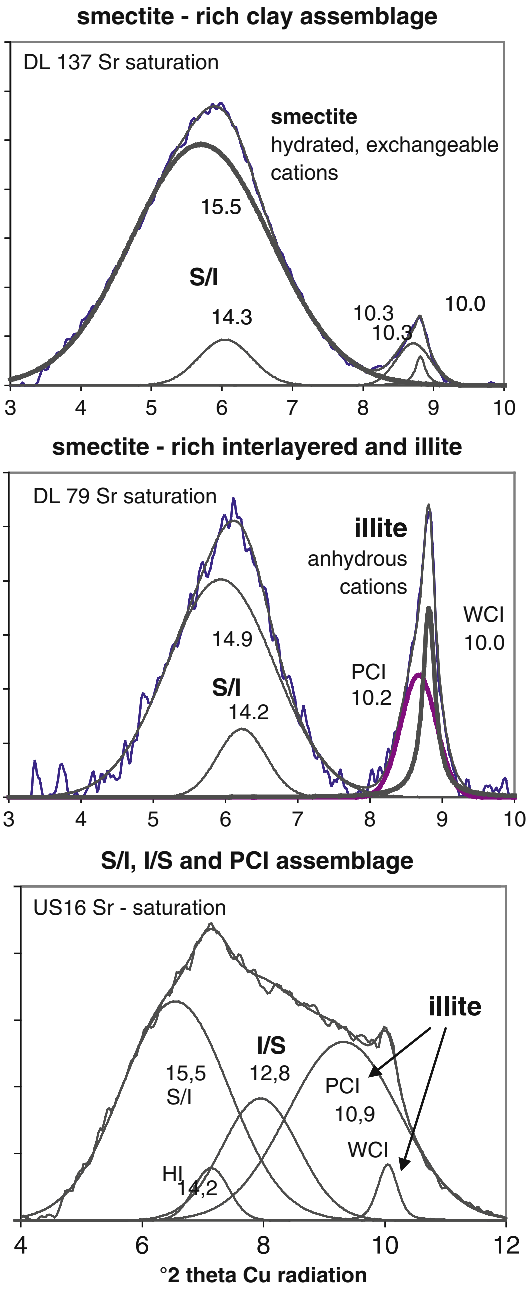


**Fig. 1.11** Examples of two soil clay assemblages from central southern Iowa. Background – subtracted X-ray diffractogram treated using decomposition methods. The *upper* figure (backround subtracted spectrum) shows an assemblage dominated by a 15.5 Å mineral, close to the smectites end member. Curve decomposition shows the presence of a small 10 Å peak indicating a minor illite component and a 14.3 Å peak indicating an HI mineral.. The *lower* spectrum shows a large (in surface area) peak of slightly less than full smectite composition, (14.9 Å instead of 15.2 Å for smectite) indicating a small interlayering of illite with another narrow peak at 10 Å indicting the presence of a significant illite mineral (anhydrous potassium interlayer ions)

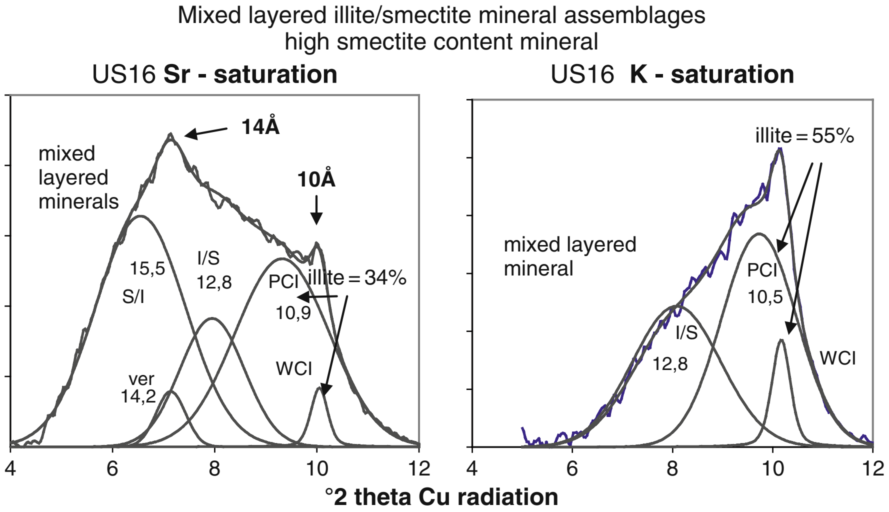


**Fig. 1.12** Example of a complex X-ray diffraction spectrum (background subtracted with component curves indicated for the phases present). The peak envelope shows two maxima, at 14.2 and 10 Å. However the decomposition of the overall curve shows the presence of five components, where the sharp peaks are the effects of only minor components as far as peak surface area is concerned. Two illite-smectite bands are present, one representing a smectite-rich phase (S/I) and the other less smectitic (I/S). The illite component is dominated by the poorly crystallized component (PCI, of small diffracting domain size) and a more minor well crystallized illite (WCI). Potassium saturation shifts the illite-smectite peaks to a more illitic position (nearer 10 Å) and increases the relative surface area of the illite peak. The total illite component changes from 34% of the peak area to 55% upon potassium saturation

with a peak near 15.5 Å and the other illite rich, I/S, with a peak nearer to 10 Å. In the example presented the second illite-smectite mineral has a spacing of 12.8 Å indicating an intermediate composition between illite and smectite. A small HI mineral peak is also present, near 14.2 Å. Normally these minerals are accompanied by illite in soils. In the example of Fig. 1.12 the poorly crystallized illite (PCI) is of greater abundance than the well crystallized illite (WCI). In the overall spectrum one sees peaks (sharp intensities, at 14.2 and 10 Å). However the peak decomposition of the spectrum shows that these intensities are of relatively small surface area, and hence represent only a small portion of the material present. Without using this method of determination, one would miss the importance of most of the material and miss identify it as an assemblage of illite and HI minerals. The S/I, I/S and PCI components are dominant but do not give sharp maxima in the combined spectrum.

Here it is imperative to use curve decomposition methods. Otherwise one would not suspect the presence of two types of illite-smectie mixed layered minerals nor the relative importance of the poorly crystallized, fine grained illite compared to the better crystallized illite component.

## *1.3.8 Identification of Soil HI Minerals ("Vermiculite")*

In Fig. 1.13 one finds what is generally called soil vermiculite or an HI (hydroxyl interlayered) mineral and a small amount of illite, where the major peak is rather narrow, about 0.8° 2 theta, and is found near 14.2 Å. It is not affected by divalent ion cation exchange as are smectites, nor heating to temperatures below 200°C nor to glycol treatment. Very often the soil HI mineral is accompanied by mixed layer minerals, of the type smectite – HI with peak positions between 15.2 and 14.2 Å which show expansion to positions closer to 17 Å upon glycol treatment) or HI – mica mixed layer minerals, with peak positions between 14.2 and 10 Å unaffected by glycol treatment.

Thus we can identify the major types of traditional 2:1 clay minerals using simple laboratory techniques. Three end member types can be identified using X-ray diffraction; illite (10 Å) smectites (15.2 Å) and vermiculite, HI (14.2 Å) after treatment with dilute solutions of divalent exchange cations (Ca or Mg).

Further treatments give more details of the minerals present.

## *1.3.9 Potassium Saturation and Identification of 2:1 Clay Types*

### 1.3.9.1 Smectites

Potassium saturation can often change minerals from apparent HI or hydrous cation minerals to those with an anhydrous interlayer ion population producing an new illite type mineral (April et al., 1986; Fichter et al., 1998; Carnicelli et al., 1997 for example). It has been noted that the relative proportion of illite 001 peak area for clay assemblages increases from saturation with low concentration (0.01 M KCl) to a maximum near 0.5 M solutions (Barré et al., 2007). This treatment changes the basal spacings from 15.2 to 10 Å in X-ray diffraction spectra. The anhydrous layer ions present in the interlayer ion sites of the 2:1 structures do not respond to glycol, glycerol or mild heat treatments (see examples in Velde and Meunier, 2008, Chap. 2 for example). This operation indicates that the type of exchange cation present in the interlayer site can modify the behaviour of the clays to a significant extent. Further the anhydrous ion population of these clays can be extracted by strong cation exchange treatment (1 M SrCl2 for example). In Fig. 1.12 the behaviour of illite-smectite interlayer mineral assemblages is shown under conditions of dilute Sr saturation and under potassium saturation at dilute concentration. Both treatments use dilute chloride solutions (about 0.01 M). In the smectites rich mixed layer mineral the peak position shifts to lower d-spacings, nearer to 10 Å, or the illite position. Two peaks are visible in the first example (a) indicating an inhomogeneous behaviour of the different grains present. In the second example not only do the mixed layer smectites-illite peaks shift but the illite peaks become relatively more important, changing from 34% of peak surface area to 55%. Such a behaviour is frequent in soil clays. Some of the smectites can become illite in appearance upon light treatment with KCl. These are "high charge" components of the smectites

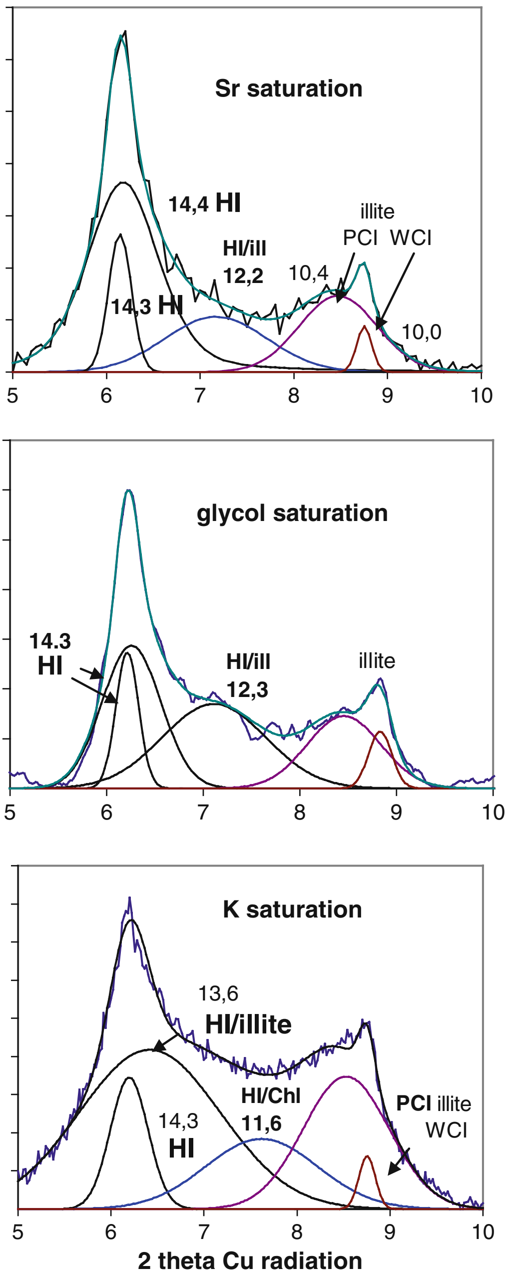


**Fig. 1.13** Example of a soil clay assemblage containing a major component of HI minerals. Smaller components of mixed layer minerals between illite (10 Å) and HI (14.2 Å) minerals are seen (peak positions between 14.2 and 10 Å). Glycol treatment does not change the peak positions significantly indicating that there is no or little smectites present. Potassium saturation decreases the relative intensity of the HI mineral and increases that of the illite peak area indicating that some of the hydroxyl interlayered ions are exchangeable with potassium

minerals which select potassium as an inter layer ion in the anhydrous state. Smectites can be of a high charge variety or low charge type. High charge layers contract to he anhydrous state with potassium saturation and low charge smectites remain in a hydrous state of either two water layers (15.2 Å) or one layer (12.5 Å).

#### 1.3.9.2 HI minerals

HI minerals, those with an initial 14.2 Å spacing after treatment with dilute divalent cation solutions, can respond to glycol treatment in increasing the basal spacing beyond 14.2 Å. These are smectite type minerals where the interlayer hydroxyl cations are loosely bound. They are HI low charge smectites.

Numerous published studies on soils containing HI minerals show a contraction and formation of "illite" upon saturation with potassium (Carnicelli et al., 1997; Ildefonse et al., 1979; Fichter et al., 1998; April et al.,1986; Zanelli et al., 2006, among many others). This capacity to fix potassium in an anhydrous state forming an illite – like mineral is very important for the interpretation of soil clay mineralogy as it is obviously important for the nutrition of plants. If the clay is affected by an exchange ion such as potassium, a portion of the hydroxyl interlayer complex is exchangeable, at least to the potassium ion. This can be called the high charge vermiculite material which in the natural state is hydroxyl interlayered, with a narrow 14.2 Å peak.

The characteristic then of most soil HI minerals is the partial exchange of the hydroxyl interlayer ions which give a 14.2 Å peak with potassium giving an illite peak position (10 Å). Typically the mixed layer HI/illite minerals shift to lower spacings as more illite layers are formed by potassium saturation of some interlayer sites. In the Fig. 1.13 such a behaviour is demonstrated where not all of the HI minerals are potassium saturated, some remaining at their typical 14.2 Å spacing while others either become totally potassium saturated forming the more intense illite peak at 10 Å, and also forming interlayered HI/illlite phases.

The material which remains in the 14.2 Å state will be called the HI or soil chlorite phase. Both normally have a strong 14.2 Å peak compared to the 7 Å peak. Such behaviour is seen in Fig. 1.13 where a soil hydroxyl ion mineral is affected by potassium treatment, with a portion of the material forming illite, and mixed layer minerals while some of the 14.2 Å material remains intact after the saturation.

A special case, and perhaps not all that special, of potassium saturation of interlayer sites in HI minerals occurs in soils derived from loessic materials found in the Po river delta region of Pavia, Italy (data provided by F Terrible, Univ Frederico II Agronomy dept, Napoli). The clay mineralogy of the soils in the Lombardi region near Pavia, shows an apparent illite – chlorite mineralogy. The diffraction peaks are relatively narrow, 0.33–0.15° two theta at peak half height for all minerals, indicating well formed and probably metamorphic minerals having been little subjected to alteration processes at the surface. However, the soils are quite fertile and respond well to potassium fertilization. One wonders how the soil minerals can retain potassium for growth throughout the growing season when there are no apparent exchange sites in minerals such as smectites or mixed layered illite smectites. When the soil clays are subjected to potassium saturation, the peak intensities change, with the first order chlorite peak, at 14 Å, decreasing in intensity and becoming slightly less wide (change from 0.33 to 0.15° 2 theta width at half height). The relative intensity of the 14 Å peak compared to the second order peak at 7 Å changes from 0.66 in the normal state (Mg saturation) to 0.26 in the potassium saturated state

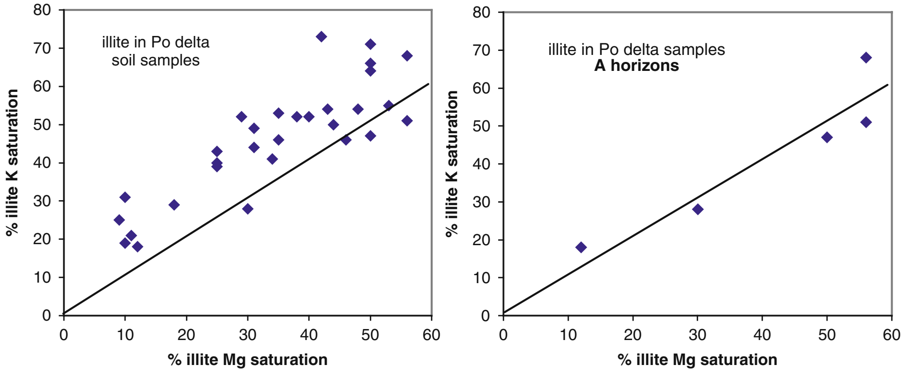


**Fig. 1.14** Plot of peak intensities of illite compared to chlorite (002 peak at 7.2 Å) in Po valley illite – chlorite mineralogy agricultural soils. The saturation of potassium increases the relative intensity of illite in most cases but when one looks at the A horizon soils mineralogy, one sees that the potassium saturation does not significantly change peak intensity indicating that the agricultural practice of potassium fertilization has filled the potential illite interlayer sites which were not exchanged by magnesium saturation

(Fig. 1.14.) This indicates that the mineral initially seen as chlorite approaches the normal peak ratio for a magnesian chlorite (see Fig. 1.10). The illite peak changes from a relative intensity (14, 10 and 7 Å peak intensities) of 28–36%. Thus the illite peak increases in intensity and the chlorite peaks change relative intensity. This indicates that the initial clay assemblage (Mg saturated is in fact one of chlorite – vermiculite plus illite) which is capable of fixing significant amounts of potassium in the interlayer space of the vermiculitic minerals. At first inspection, one would assume that the clay assemblage is near that of a metamorphic rock assemblage, illite plus chlorite. However, the soil clay mineralogy has been altered to produce a potassium fixing mineralogy, one of a highly ordered soil vermiculite with little disorder nor alumina substitutions in the interlayer site (see Meunier, 2007).

In Fig. 1.14 we indicate the average increase in illite peak area for five soil profiles in the Po delta soils mentioned above. Again it is clear that the potassium saturation increases the “illite” component, i.e. the 2:1 minerals with an anhydrous potassium cation interlayer occupation. It is interesting to note that the illite percentages seem almost the same for the different saturation treatments for A (agricultural) horizon samples. This suggests that the fertilizer treatments are more than sufficient to fill the sites in clays susceptible to fix them as anhydrous interlayer ions to form illite.

## *1.3.10 Summary*

Very briefly, one can identify four basic types of soil clay phyllosilicate minerals by X-ray diffraction. The basic state is in the Ca or Mg saturated state and observed at room temperature and humidity conditions.

*TO structure (1;1)*: *Kaolinite* and *halloysite* which are 1:1 minerals. Heating to 110°C or so will contract the halloysite 10 Å peak to 7.2 Å, otherwise a 7.2 Å indicates the presence of kaolinite.

*TOT structure (2:1)*: Three types of phases are possible based upon the 2:1 structure where ionic substitution occurs in interlayer ion site, between the 2:1 layers;

1. 10 Å minerals where anhydrous potassium is present. In this state the mineral is called *illite*.
2. 15.2 Å minerals where the interlayer spacing changes with glycol or glycerol treatment to a spacing near 17 Å. These are *smectites*. Formation of a 10 Å mineral on potassium saturation indicates a *high charge smectite*. Those layers remaining at interlayer spacings above 10 Å are *low charge smectites*.
3. 14.2 Å spacing are *HI minerals*. There are essentially three behaviours and we will give three names to them.

a. One is a stable 14.2 Å spacing after potassium saturation or glycol treatment. This HI mineral can be called a *soil chlorite*. The interlayer ion sites are completely filled with non exchangeable Al-Mg hydroxy complexes.
b. 17 Å spacing upon glycol or glycerol treatment. This is a *soil, low charge HI mineral*
c. 10 Å peak spacing upon potassium saturation. This is a *soil, high charge HI mineral*

One then can use the terms illite, smectite and HI mineral on first inspection of X-ray diffraction diagrams in the Ca-Mg treated state under room atmospheric conditions. The HI minerals can be subdivided into soil chlorites, high or low charge vermiculites upon further treatment.

Although the above is not what one is accustomed to find in text books on clay minerals, the shema outlined for 2:1 mineral types is clearly illustrated by Birkeland (1999, p. 101) following the outline given by Jackson (1964) concerning the alteration or formation of clay minerals in soils from pre-existing phyllosilicates. The nomenclature in these articles is similar to that proposed above and the mineral behaviour is the same. Hence the functional description and mineral nomenclature proposed here is not new, but only unusual.

## 1.4 Recommendations

Therefore we suggest that the normal laboratory determinations and nomenclature commonly used to identify soil clay minerals should be simplified to a large extent. The existence of a diffraction peak position in the moderately treated (Ca, Mg, Sr chloride concentrations of 0.1 M) at between 10 and 15.2 Å indicates the presence of 2:1 smectite minerals. Those with a peak at near 14.2 Å that do not change position upon chemical or moderate heat treatment (below 400°C) are of the hydroxyl interlayer ion type similar to chlorite, a high temperature mineral with a tri-octahedral occupancy in both 2:1 layer units and interlayer sites. Those that do not change peak position from 10 Å upon chemical and heat treatment are illites, of mica like behaviour. Material that is affected by chemical treatments, exchange ions is exchangeable in character. The extent of exchangeability between different ions under different ionic concentrations determines the behaviour of these clays in their soil environment.

A second treatment deals with structures of high intensity charge but that allow cation exchange under certain circumstances. 0.5 M KCl solutions will close the interlayer site with anhydrous potassium ions creating an illite – like mineral behaviour. These minerals can be either of dioctahedral (two ions per unit cell in the octahedral layer, usually aluminum) or trioctahedral (three ions in the octahedral site, usually magnesium) in nature. The increase in illite peak intensity (10 Å) can be at the expense of smectite peak intensity (15.2 Å) under divalent ion saturation or at the expense of the 14.2 Å HI minerals.

Peak positions at near 7.2 Å can indicate the presence of kaolinite. HI minerals (hydroxyl interlayered), have peak positions smaller than those of kaolinite The difference between kaolinite and second order peaks of 14 Å minerals (HI minerals or the high temperature mineral chlorite) is often difficult to ascertain but one can be identify the different minerals by looking at the peak positions at near 3.5 Å where kaolinite is found at near 3.59 Å and HI minerals at smaller spacings, nearer to 3.54 Å.

## 1.5 K Saturation (1 M Solution)

Formation of 10 Å mineral peaks from either HI minerals or smectites layers indicates the presence of high charge vermiculites or high charge smectites.

One problem with clay mineral identification in soils is the difficulty in identifying high temperature phyllosilicates (2:1 minerals) which are inherited from sedimentary rocks or metamorphic rocks. Chlorites are similar to HI chlorites in basal spacings. However, the 001 14 Å peak is less intense than that found at 7.1 Å (the second order 002 peak). Also, in general it is less wider having a peak width at half height of around 0.3° 2 theta while the HI minerals are slightly wider, near or above 0.5° 2 theta on X-ray diffractograms. Mica and the clay illite, with 10 Å are more difficult to differentiate. The relations are given in Table 1.1.

**Table 1.1** Ca or Mg saturation (0.1 M solutions)

| 001 Peak position Å | Mineral name |
|---|---|
| 10 | Illite |
| 14.2 | HI |
| 15.2 | Smectite |
| 7.21 | Kaolinite |

Smectite, illite type and HI minerals can be either dioctahedral or trioctahedral in character (Millot and Camez, 1963). However, it appears that there is often a gradual change from tri to di-octahedral site occupancy in many clays (Righi et al., 1999; Churchman, 1980; Churchman and Bruce, 1988). The general tendency is to increase the alumina content of soil clays at the expense of magnesium – iron types.

### *1.5.1 Summary*

The clay minerals found in soils, are for the most part phyllosilicates, i.e. formed of silica complex structures which have limited dimensions in one direction and much less limited dimensions in two others thus forming a sheet – like structure. Phyllosilicates exist in sedimentary, metamorphic and to a lesser extent igneous rocks also. Hence there is a possible continuum in transformations at the surface between high temperature minerals and those stable in the biosphere soil zone or water – rock interaction zone.

Essentially two types of soil phyllosilicate structures can be considered: the TO or 1:1 tetrahedral – octahedral coordination of oxygen with cations. Silica is dominant in the T sites and alumina in the O, octahedral sites. By far the most common 1:1 mineral in soils is kaolinite. Some occurrence of a hydrous form of this mineral (halloysite) are found. The second and much more frequent mineral type is a TOT, three layer tetrahedral – octahedral – tetrahedral mineral. Identification of different types of these minerals is made by identifying the cations found between the 2:1 layers of the structure. The interlayer site ionic occupancy is determined by two factors: the excess layer charge on the 2:1 layers engendered by substitution of ions of different valence in either tetrahedral or octahedral sites and the chemistry of the soil solutions. Hence these clay minerals respond to their chemical environment. This point is extremely important to the biosphere – mineral interactions.

Thus one has two types of phyllosilicates in soils, 1:1 and 2:1 minerals. The names of the 2:1 minerals are determined by an estimation of interlayer ion occupancy and the possibility to change ionic occupation by cation exchange. Laboratory determinations of soil clays should take these factors into account in order to characterise 2:1 clay minerals as a function of their function in soil systems.

***What needs to be done***

***Operational definition clay minerals***

***Coherent system of clay mineral identification according to function***

***More observations of field examples to validate recommmendations***

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# Chapter 2
# The Soil Profile: The Structure of Plant – Mineral Interaction Space

## Contents

## 2.1 Origins of Alteration Clay Mineral Formation

Overall the transformation of rock into altered material is one that changes the chemical associations of the materials found in rocks. Rocks are formed at temperatures above those of the surface of the earth, by burial and thermal "hot spots" due to movement of molten materials coming from great depths. When these mineral assemblages are exposed to abundant water resources at low temperatures, they become unstable in a thermodynamic and chemical sense. New minerals are formed. If one looks at the overall result of such events, it appears that some elements are taken from the mineral phase while others are left within the solid materials. Li

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_2,

and Schoonmaker (2004) indicate that the composition of average shales, which represent the soils of the earth moved into sedimentary basins, are much the same as average crustal rocks. The upper crust on continents is dominated by aluminous materials (called pelitic rocks) which have relatively abundant alkali an alkaline earth contents. However the shales, sedimentation products due to soil movement, contain much the same Al and Si ratios, but greatly different alkali and alkaline earth contents. The biggest loss is that of Ca and Na from the silicate materials. Strong loss of sodium (some 70%) and Ca (50%) show that chemical segregation is effected by the weathering process. The Ca ends up in carbonate concentrations thanks to biological activity and the sea becomes salty (NaCl) as a residue of the alteration process. The chemical process is of course accompanied by dissolution – recrystallization and other physical processes.

The interaction of water, plants and rock forms small sized silicate and oxide minerals called clay minerals. The most frequent definition, by mineralogists of this fine grained material is a particle with less than 2 μm in its largest dimension. Most alteration minerals, newly formed at the surface, are found in this size category. The definition is arbitrary, being based upon the limits of microscopic resolution which were and still are to a large extent, that of 2 μm. Thus clays are minerals which cannot be identified by optical methods. Traditionally, since the latter half of the 20th century, identification has been done using X-ray diffraction methods.

The origin of alteration mineralogy is due to the inherent instability of rocks in the presence of surface chemical forces and reactions in aqueous solution. This includes those caused strictly by mineral chemistry which we will call water – rock interaction as opposed to those engendered by bio-reactions which control aqueous solution chemistry. In the case of water – rock interaction the agent of change is the slightly acidic rain water in contact with the minerals in rocks. This is a situation of thermodynamic and chemical instability. Rock mineralogy has the imprint of compression and temperatures greater that those found at the surface of the earth. This is due to the nature and origin of rocks. They are hard and durable because they have been formed at higher pressures and temperatures than those of the surface. The mineralogy has responded to these physical conditions by producing phases that correspond to physical constraints other than those of one atmosphere pressure and ambient surface temperatures. Since they have re-adjusted to their physical environment to form hard rock, they will not be stable at the new conditions of the surface. First the temperature is lower than those under which rocks formed and second the ratio of solids to water is quite different, there being more water present under conditions of alteration at the surface than those of rock formation. In fact as sedimented materials are buried and become rocks they tend to lose most of the ambient water that formed the sedimentary material. Those rocks having passed through the high temperature conditions of a molten state of course are still less hydrous. Temperature and the availability of water in relatively large quantities are the hallmark of surface mineral alteration. Basically the rock minerals tend to come to equilibrium with the surrounding water by dissolving in it, either integrally or partially (incongruent dissolution). The materials which do not enter into solution are almost always more hydrous than the initial material. Water – rock interaction is dissolution and hydration. The formation of new minerals at the surface is due to mineral chemical processes and equilibria.

Plants and other living organisms, notably bacteria, can hasten the process of conversion from high temperature, low hydrous state to low temperature hydrous minerals. The processes can be complex but in the end the result is nearly the same as that of simple water – rock interaction. The chemistry of formation of the new surface minerals, usually called clays because of their small grain size, is the same.

## 2.2 Some Fundamental Principles in the Alteration of a Rock are as Follows:

### *2.2.1 Thermal expansion*

First and foremost, rocks are susceptible to effects of differential thermal expansion. Most minerals are anisotropic in their expansion (Clark, 1966) which leads to tension and unresolved stress in a rock where minerals are oriented in various and un-ordered directions. Figure 2.1 indicates such a situation in a multi-mineral rock. Thermal expansion, due to daily heating causes stress vectors which oppose each other across mineral grain boundaries. In cases of parallel contacts, the minerals can have opposing expansion – contraction vectors which create shearing stresses. In cases where a mineral is confronted with another but with opposing expansion

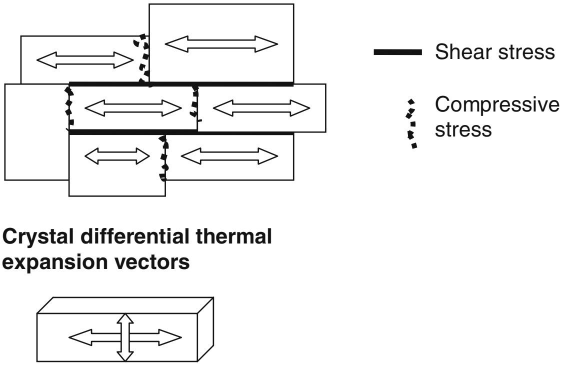

**Fig. 2.1** Diagram representing the importance of differential mineral thermal expansion on rock coherence. Most silicate minerals have strongly anisotropic thermal expansion characteristics which engender opposing forces in a crystal aggregate such as a rock. Double arrows indicate the strongest direction of thermal expansion. Crystal contacts parallel to these expansion – contraction movements create shear stress forces while those at the junction of crystals, pushing on one another, create compressive stress. These forces create tensions and rupture between the different crystals making a type of sand by physical forces alone

fronted into the crystal, the stress would be one of compression or dilatation. Since the differential thermal dilatation coefficients can be on the order of six fold for a given mineral, according to the crystallographic orientation, one can imagine that the stability of a mineral assemblage at the surface of the earth where temperatures can change on the order of tens of hours up to tens of degrees centigrade, would create forces which would overcome those of normal crystallographic cohesion. Such effects lead to breaking of the interface surfaces between minerals or possibly the rupture of a grain itself. A long term experiment carried out at the experimental station at Versailles (Millot, 1964) where broken granite was exposed to atmospheric conditions for 20 years resulted in the formation of much smaller grain size particles even though no new clays or residual minerals were detected. The abundant rain and its quick evacuation leached the dissolved products of mineral degradation into solution with its transportation out of the system, leaving no residue. However the thermal effects on the rock debris were clearly seen in the production of sand and silt sized particles, approaching the mineral grains size of the granite. The fact of breaking a rock into near mineral grain size increases the surface of the minerals and their chemical reactivity. This process should not be overlooked in analysis of chemical reaction at rock – water interfaces. The importance of fracture passages in rocks which are open to water flow and their effect on alteration mechanisms and rates is discussed at length in Velde and Meunier (2008, Chap. 4).

## *2.2.2 Chemical Controls*

Several chemical forces operate at the earth's surface which were not or little apparent under a rock formation regime. The conditions of contact with air, in general a force of oxidation and with rain water, a dissolution and hydration force are the most evident.

### 2.2.2.1 Congruent Dissolution

The first reaction of a rock in contact with water is to attempt to attain a solid – solution equilibrium by dissolution of a part of the solid phase in the aqueous solution. This action is fundamental to understanding alteration processes. The most important aspect of an altered rock is its decrease in density due to the dissolution of material. The more frequent the rainfall, the more material is dissolved and the more the influence of dissolution is apparent. Density can decrease by 20% or so due to increase in porosity (see discussion in Velde and Meunier, 2008, p. 119) or a loss of material. Of course non-silicates such as carbonates dissolve integrally with mineral reaction or formation of new phases such as oceans where the majority of carbonates form anew. The Versailles experiment mentioned in the preceding paragraph demonstrates this principle in that no new phases were observed in the essentially free flow experiment of rain water running over crushed granite. Dissolution in this experimental situation was the major chemical effect in the alteration process.

#### 2.2.2.2 Oxidation

The major chemical principles of surface alteration mineral formation are change in oxidation state of iron and substitution of hydrogen ions for loosely bonded (ionic bonding) cations. The higher the temperature of formation for a mineral, the less stable it is, in general. Some minerals are recalcitrant to alteration, above all those without or few ionically bound cations or without iron. The most striking example is quartz, almost pure $SiO_2$, which is present in most soils even though it should in many cases have been dissolved to meet the activity requirements of silica in solution.

Oxidation is important in that most iron ions in silicates are present in the divalent state. Oxidation is then evident under surface conditions where the normal atmosphere is conducive to oxidation with the resulting change in electronic balance in the mineral which makes most iron – bearing minerals formed at high temperature unstable and induces mineral change. However, when iron becomes trivalent it tends to form an oxide or hydroxyl oxide. In other words it forms its own phase. Thus a large part of new silicate minerals formed through weathering are of relatively low iron content. Iron separates from the silicate minerals, especially when there is enough aluminium to combine with silica to form a clay mineral. This leaves an "iron stain" in the alteration zone (iron oxide), where the more minor amounts of iron take on a strong visual impact, making the altered zone reddish, tan or yellow depending upon the type of iron oxide present. The minerals and their colors are indicated in Table 2.1.

In cases where iron is in great abundance, it can combine in its trivalent state to form a new clay mineral. Thus olivines, pyroxenes and other high temperature minerals are relatively rapidly transformed by weathering into iron bearing clay minerals. Low alumina content of the reacting minerals dictates the formation of a ferric mineral.

#### 2.2.2.3 Incongruent Dissolution: Hydration and Ionic Substitution

The second action is one of ionic substitution of hydrogen from the slightly acidic rain water in equilibrium with atmospheric $CO_2$ for cations in the silicate min-

**Table 2.1** Color of Fe oxides and hydrosulfates (simplified from Scheinost and Schwertmann, 1999)

| Fe oxide | Most frequent color | Composition |
|---|---|---|
| Hematite | Moderate reddish brown | $\alpha$-$Fe_2O_3$ |
| Goethite | Strong yellowish brown | $\alpha$-FeOOH |
| Lepidocrocite | Moderate orange | $\gamma$-FeOOH |
| Ferrihydrite | Brownish orange | $Fe_5HO_8 \cdot 4H_2O$ |
| Akaganeite | Strong brown | ß-FeOOH |
| Feroxyhite | Strong brown | $\delta$-FeOOH |
| Maghemite | Dark yellowish brown | $\gamma$-$Fe_2O_3$ |

erals. The cations Na, Ca and K are extracted from such igneous minerals as feldspars, micas and various minerals of metamorphic origin such as amphiboles. The chemical reaction is as follows

$$H^+ = M^+ \text{ or } 2H^+ = M^{2+}$$

Where $M^+$ is the large ionically bonded cation in the initial silicate mineral.

The residuum is enriched in alumina as well as elements such as iron, titanium or manganese with in general a loss of silica. This residual material is the core of clay minerals and oxide phases found in alteration products. Sodium is largely lost to altering solutions while some Ca and much K is retained in the clays. Very often silica is lost to solution in the initial conversion of high temperature silicates to clay minerals. The elements which remain form clay silicate phases. Magnesium is partially lost in many instances, some being retained in the clay minerals and much being taken into solution. This is due to the fact that Mg is not accepted in large amounts in alumino-silicate clays. When enough magnesium is present in the altering minerals, the new clay minerals will be of relatively low alumina content and high in Mg and often in ferric iron. The general scheme of change in the hydration, ion – exchange process is to form low alkali and alkaline earth phases with either aluminous or magnesio-ferric minerals.

#### 2.2.2.4 Destabilization of Clays and Silica Loss

The last step in the alteration process is the dissolution or destabilization of the newly formed clays themselves to produce, in the long term, oxy-hydroxide phases of iron and alumina. Loss of silica is the key to this change. It is a step wise process where relatively siliceous clays (Si > Al ionic content) are replaced by the intermediate mineral kaolinite (Si = Al) and then the aluminium hydroxide gibbsite (see Pedro, 1966). In this process the presence of kaolinite and gibbsite are considered to be indices of alteration intensity. The assumed sequence of clay mineral alteration is 2:1 mineral (vermiculite, illite, smectites) to kaolinite to gibbsite. These mineral names are elucidated in Sect. 1.4. The important observation is the destabilisation of the clay minerals initially produced by weathering processes which in their turn become unstable chemically and are transformed to a lesser degree than the destruction of high temperature silicate minerals which form clays in the initial water – rock interactions.

Overall one can schematically write the hydrogen ion exchange reaction and that of silica loss as:

Hydrogen ion exchange for cation in high temperature minerals

$$\underset{\text{feldspar}}{3KAlSi_3O_8} + 2H^+ \text{ - > } \underset{\text{muscovite–like clay mica}}{K_{0.9}Al_{2.9}Si_{3.1}O_{10}(OH)_2} + 2\,K + 6SiO_2aq$$

then hydrogen ion exchange in the clays clays

$$\underset{\text{muscovite clay mica}}{2\mathrm{KAl_3Si_3O_{10}(OH)_2} + 2\mathrm{H}^+} = \underset{\text{kaolinite clay}}{3\mathrm{Al_2Si_2O_5(OH)_4}} + 2\,\mathrm{K}^+$$

and eventually hydration of clays after silica loss

$$\underset{\text{kaolinite clay}}{\mathrm{Al_2Si_2O_5(OH)_4}} + \mathrm{H_2O} = \underset{\text{gibbsite}}{2\mathrm{Al(OH)_3}} + 2\mathrm{SiO_2}\,\mathrm{aq}$$

#### 2.2.2.5 Scale of Alteration and Localization of Clay Minerals in Rock – Water Interaction

The silicate minerals in rocks, those that make clays, are affected to differing degrees by the passage of aqueous fluids (rain water) as it moves through gravity flow across a rock. It is evident that the initial contact of this water with silicate minerals in the rock is through fractures and fissures in the rock itself. The larger discontinuities are present due to the relaxation of pressures exerted on the rock during its trajectory from depth to its present day position near the surface of the earth. Tectonic forces tend to deform the rock under pressure and create discontinuities. Also the simple fact of releasing several kilobars of overburden pressure allows differential expansion of the rock creating fractures and fissures. These are the initial passages of water into the un-altered rock. Further, thermal expansion and retraction of the minerals in the rock subjected to diurnal thermal variations creates further ruptures between minerals and within minerals. Thus one finds passage ways of varying size and continuity in the rock itself.

As water enters the rock it will flow at differential rates depending upon the possibility of flow, i.e. width of the passagways. The larger fractures will carry more water, which will be more dilute containing little dissolved material while water moving more slowly through smaller openings will contain more dissolved material due to a more prolonged contact time with the unstable silicate minerals. The result is a hierarchy of flow systems which to a certain extent imitate the effect of rainfall of different intensities on a rock surface. With more rainfall there is more alteration by dissolution but the solutions are more dilute in dissolved components. In the rock itself, alteration intensity by dissolution is greater in large fractures while the smaller fissures and small cracks show less interaction, imitating climates of less rainfall. Clay mineral genesis is favored by slow flowing subsystems where rock – water interaction occurs with solutions carrying a large amount of dissolved materials. Under these conditions, new phases (clays) will form as the solutions become saturated with the elements which make up the clays. Usually these elements are iron, alumina and silica. The end result is that in each alteration system one has a series of chemical sub-systems which produce different minerals depending upon the relation of residence time and the amount of the aqueous fluids present in cracks of different size and the resulting chemical controls of element concentration in solution (Fig. 2.2).

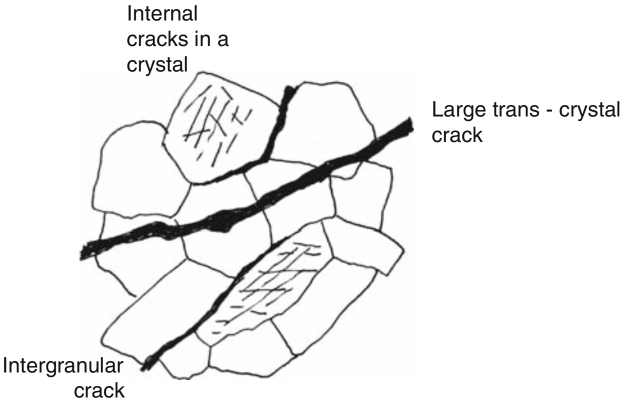

**Fig. 2.2** Different types of cracks and fractures common in rocks due to their thermal and tectonic history. (1) Internal fractures within a crystal (2) inter granular fractures (3) trans-crystal fractures. All lead to the introduction of water into the different passageways in the alteration process of water – rock contact at the surface

The consequences of these factors of scale in the interaction of aqueous solution and silicate minerals is a difference in the chemical controls of the alteration process; In a very general way, the larger the scale of the system, the fewer the number of minerals present in a given site. This is a very well known maxim of phase equilibrium analysis (see Denbigh, 1987, Chap. 5 for example). The greater the number of chemical variables imposed from the exterior of a given system (mineral grain for example) the smaller the number of phases present at equilibrium. In general, the more water flow through a rock or soil system, the more intercommunication of the different parts and the more chemical constraints which will be imposed from outside of a given part of the system.

Concerning alteration mineralogy, if the scale is sufficiently restricted, through the limitation of fluid flow, each high temperature mineral crystal will form a new mineral or set of new minerals depending upon its specific chemistry. As the system is more open to fluid flow with an increasing communication through the formation of dissolution cracks, the diffusing species of elements in the fluids increases (larger and more continuous cracks and fissures) and the number of minerals formed decreases, being subjected to the chemical constraints of other altering minerals in different parts of the soil profile. In a way, the increased number of actors in the alteration process dilutes that importance of each individual one and a more general system is installed. Chemical activity of the different participating elements becomes influenced by adjacent phases and eventually by a large portion of the rock which is altering. The larger the fissure or crack, the fewer the number of minerals present and the less variable their chemistry. In extreme cases where water is plentiful and the rock never comes in equilibrium with the altering aqueous solution the number of phases present is zero, all is dissolved. One can find a more detailed discussion of these effects in Chap. 5 of Velde and Meunier (2008).

One can use the example of a potassium feldspar grain in an altering granite. Initially the altering fluids will be under saturated in potassium compared to feldspar which is the most potassium – rich mineral in the rock. As the feldspar is destabilized, some silica is lost to the solution since it is the most silica – rich mineral, other than the chemically inert mineral quartz. This is shown in Fig. 2.3, which is a chemiographic projection of mineral compositional relations. The overall composition of the feldspar system shifts down from the potassium apex and slightly toward the alumina side of the diagram. The phase assemblage instead of being one of only feldspar (single phase) becomes illite – and feldspar which is a two phase system, shown as Step 1 in the alteration process. The new micaceous phase occurs on the edges of the feldspar. In fact then the earliest new minerals formed are illites, a potassic soil clay mineral. This is the initiation of the alteration process is the initial mineral reaction. The new mineral, illite, takes up less space than the feldspar, creating small voids which inevitably let more fluid into the system.

Following this opening of the mineral grain network to new mineral formation and fluid flow, the feldspar starts to alter internally creating a *primary plasma*. This step (2) is in fact the formation of a mineral assemblage of new low temperature phases. In the case of potassium feldspar, one finds illite, as before and smectites along with fragments of feldspar. The overall composition of the old feldspar volume is now further depleted in potassium and to a small extent in silica and it becomes a three phase system.

More fluid flow induced by further decrease in the volume of solids and the creation of voids leads to a new set of equilibria, the *secondary plasma*, Step 3 in Fig. 2.3 which involves fluids originating from the alteration of other minerals in the rock. In the case of the old feldspar volume, containing three phases, one finds the formation of a new illite, which is less potassic, and kaolinite. Here the number of

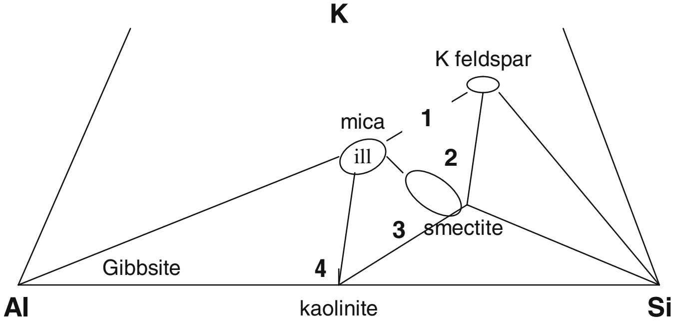

**Fig. 2.3** Diagram representing the chemical relations of minerals common in granite potassium (K) feldspar, mi (muscovite) and quartz. Alteration minerals are illite (near the composition of muscovite) smectite, kaolinite and gibbsite. Initial phase stabilities are between muscite and feldspar (1), which change under water – rock alteration to include smectites (illite – K feldspar – smectites (2) and upon further alteration (more contatct with dilute aqueous solutions) the assemblage illite – smectie – kaolinite forms (4). The alteration process is one of loss of potassium and silica, in going from the assemblage 1–4

alteration minerals decreases as potassium and silica are lost creating a two phase system.

In and along the walls of large fractures which are conduits for rapid water flow to the groundwater table, one finds only kaolinite present. This is the *fissural microsytem*. Only one mineral is present due to the still larger amount of chemical intercommunication. A testimony of such interaction can be seen in the data compiled by Valeton (1972, p. 45) for water compositions in arkosic sediments (those containing quartz and feldspars). The flowing pore water is in chemical equilibria with kaoliite and not with potassium mica nor feldspar according to the equilibrium values given by Garrels and Christ (1965). This is Step 4 in the alteration sequence where the minimum number of phases is seen.

The result of the initial water – rock alteration processes in rocks, which occurs at different scales, is the formation of minerals which have responded to very local chemical potentials creating a large number of heterogeneous assemblages in specific areas or volumes which are not ultimately stable together in a larger system. As alteration of the rock continues, the amount of new clays increases until it dominates the alterite zone above the rock – water alteration interface. The number of clay types decreases. The new mineral assemblages are less dense than the old minerals in the rock due to element moss through the dissolution process. The new mineral assemblages tend to contain fewer phases. Table 2.2.

Some material escapes the system. The spatial distribution of the new phases determined by the old high temperature phases is maintained in the initial grain contact and primary plasma stage of alteration. Due to lower density and the creation of void space within such a system, water can circulate more freely and the chemical potentials imposed by the new clays as well as the incoming unsaturated rainwater become more homogeneous throughout the rock – alteration zone. The clays react to these new chemical constraints forming a more stable, general assemblage with fewer phases present. This process is maintained up into the root soil or plant – soil interaction zone.

In the primary plasma stage of alteration, different old minerals can form the same clay mineral phase, for example smectites, but the new alteration minerals can have different compositions dictated by the old mineral grain chemical composition (see Proust and Velde, 1978). One finds new minerals being formed in old grains reflecting the chemistry of each mineral as it comes into contact with slow moving fluids and their water chemistry. Gradually the chemical potential of a more large system is imposed upon the alteration minerals formed and forming and a new, more

**Table 2.2** Stages of weathering of a potassium feldspar in a granite

| | |
|---|---|
| 1 Fluid flow at mineral interface | illite |
| 2 Fluid saturation within the crystal<br>*primary plasma* | Illite + smectite + feldspar |
| 3 Fluid flow in cracks and fractures<br>*secondary plasma* | smectite + kaolinite |
| 4 High fluid flow in large fractures<br>*Fissural microsystem* | kaolinite |

general chemistry produces different minerals of a more simplified number. This new chemistry is one of lower alkali and alkaline earth ion activity. Loss of K, Na and Ca as dissolved species in solution which is exported from the system decreases the chemical variability of the phases present. In the initial stages of alteration, the activity of these elements is imposed by the altering phases, and is relatively high. As more communication is made with flowing water out of the system, the chemical activity of the more soluble elements decreases, reducing the number of new alteration phases present. Eventually the number of phases in highly altered rocks is two, hydrous iron and aluminium oxides. This is the ultimate stage of water – rock interaction.

This progression can be seen, in a very general way, as alteration clay assemblages become more simplified, essentially losing alkalis and silica. In going from temperate climate multi assemblages of different 2:1 minerals plus kaolinite, increased rainfall in more tropical climates produces more kaolinite and less 2:1 minerals, eventually forming kaolinite alone and eventually gibbsite and hematite, the aluminium and iron oxy – hydroxide assemblages where not only all alkalis are lost to altering solutions but most of the active silica also. Within a single altering rock under temperate climate conditions one can find the various stages of climate controlled soil clay mineralogy, going from alkali – containing clays to kaolinite. Hence the driving force of alteration is the relative amount of water compared to the reacting silicate solids. In fractures with free flowing soil solutions the mineralogy reflects chemical controls of undersaturated solutions and the formation of kaolinite present under conditions of temperate climate. The same conditions are found when rainfall is very intense, under tropical conditions, and the whole soil system responds with a kaolinite mineralogy and under very intense conditions only gibbsite and iron oxides.

Under conditions of temperate climate alteration, the new minerals present are multiple, depending upon the local conditions of water flow and chemical activity. As rainfall increases the clays become more dominated by kaolinite and eventually gibbsite. The temperate climate alteration mineralogy is dominated by 2:1 clay minerals.

A review of mineral alteration products by Velde and Meunier (2008, Chap. 4) indicates that the new minerals formed (i.e. those crystallized into recognizable and stale minerals) are most often 2:1 phases. Table 2.3 indicates the types of minerals formed in the initial stages of mineral alteration, within the original high temperature mineral crystal. The hydroxyl phase gibbsite is indicated whereas the oxy and hydroxyl forms of iron oxide are not in that they are almost always formed in the process of alteration of iron-bearing minerals.

The 2:1 alteration minerals are either high charge (identified as vermiculites), or low charge minerals (identified as smectites). Potassium feldspar is frequently associated with illite, a lower charge and more silica – rich form of muscovite. It is clear from these observations that the major, principal alteration mineral in the initial stages of alteration by water – rock interaction is a 2:1 mineral. These are the most silica – rich of the surface clays. The presence of 2:1 minerals reflects the normal ratio of silica compared to Al or Mg in minerals which favors silica and hence the silcia – rich secondary phases found in alterites and soils.

**Table 2.3** Clay mineral types formed from high temperature silicate minerals

| Mineral | 2:1 | 1:1 | gibbsite |
|---|---|---|---|
| Potassic feldspar | x | x | – |
| Plagioclase | x | x | – |
| Muscovite | x | x | |
| Biotite | x | x | |
| Chlorite | x | | |
| Clinopyroxene | x | – | |
| Orthopyroxene | x | | |
| Olivine | x | | |
| Amphibole | x | | |

An interesting detail, perhaps not all that minor in importance, is the difference in alteration products of potassium feldspars, as detailed above, and the alteration products of muscovite in the same granite. Velde and Meunier (2008, p. 173) indicate that the new minerals formed in muscovites subjected to water – rock alteration processes, is an assemblage of vermiculite (HI mineral) and kaolinite. In general one can consider the presence of Al-OH interlayer ions in a 2:1 structure indicates a high charge, somewhere above 0.6 per unit cell whereas the smectites, described in potassium feldspar alteration indicate a lower charge, somewhere in the vicinity of 0.3 charges. This suggests that the smectite compositional field from low to high charge is represented in these water – rock alteration processes, where the muscovite alters to a high charge mineral and the feldspar, in the initial stages to an illite, potassic high charge mineral, and smectites of lower charge. Loss of potassium from muscovite is compensated by $Al(OH)_2^+$ ions whereas the higher potassium content of the feldspar solutions fixes this element in the 2:1 neo-formed minerals. Thus the new 2:1 minerals formed in granite alteration are high charge forms, forming illite under conditions of high potassium availability due to feldspar alteration, and forming an HI mineral under conditions of lower potassium availability.

### *2.2.3 Biological Degradation of Rocks and Minerals*

Beyond the initial and fundamental interaction of water and rock to form new minerals stable at the earth's surface it is most important to consider the potential action of living organisms. In forest experiments where the land was clear cut (Bormann and Likens, 1994, p. 155), the loss of potassium to stream water was 10 kg/ha in the initial stages or forest re-growth decreasing to half that after four years. The uptake by the growing biomass was initially 2 kg/ha increasing to 31 kg after four years. This indicates that the water – rock interaction process (stream water loss at the starting point of the experiment) is relatively small when compared to the uptake by vigorous plant growth. Hence on can suspect that in the biosphere, living organisms will dominate in the transfer elements and mineral changes which one sees in the transformation of rock to soil. Biological activity is the most important factor in the stability of rock minerals.

Dissolution of silicate minerals has often been attributed to the presence of organic acids (see Barker et al., 1997 for a review). Organic acids are seen in laboratory experiments to hasten the dissolution of different minerals, especially feldspars. These are the actors of the chemical reactions where acidity and chelating effects contribute to the transformation of silicates in to soluble materials (Ullman and Welch, 2002). Silica release rates due to organic acid interaction are 2–5 times higher than those produced by mineral acids. Thus we see that biological controls and interactions can be much more important than those of mineral origin. Often it is assumed that the origin of much organic matter in the form of aggressive acids is due to the degradation of plant material transformed by bacterial action. However there may be a more direct and more efficient interaction guided directly by living organisms towards the transformation of high temperature silicate minerals found in source rocks in soils (Ullman et al., 1997). Raulund-Rasmussen et al. (1998) feel that the interaction between organic molecules and silicates is more a matter of concentration of the acids or other molecules than their specific types. This would suggest that the importance is in the concentration of the molecules and this is controlled locally by plant or other living organisms mor than ambient pore solution concentrations.

The initial stages of rock alteration in the biosphere are affected by the more simple or smaller forms of life such as bacteria, fungi and eventually lichens. Terrestrial life before land plants was most likely algal in nature (Wellman, 2003) where algal mats covered land surfaces forming the initial stages of soils. We have only partial information on the effects and importance of these agents of mineral change at present but it seems that they can be significant in the soil clay mineral formation processes. Intuitively one would think that a rooted plant would need some fine grained and clay type material to prosper though different plants can be seen today to grow, apparently, from rock surfaces where man has tried to present a clean surface of building material. Many pictures of plants growing from a cathedral wall or other "timeless" edifice have been made to show the ephemeral qualities of the efforts of man, the great manipulators of nature.

Bacterial action as an alteration agent is best known at present, in a general way, and lichen or fungal action is less well documented, at least from the stand point of the importance in the formation of clay minerals. In fact all of the forms of life discussed are now know to have and impact on the chemical stability of silicate minerals but in all instances there is little information on the clays or other residual minerals formed in the interaction process. We will consider the information on bacteria, the most simple form of life interacting and that of lichens, a rather complex but fundamental life form in the initial stages of rock – plant interaction in the early stages of alteration.

#### 2.2.3.1 Bacteria

Bacterial interaction for silicates and sulfide minerals seems to have two major impulses: one respiratory action (Blake et al., 1994 or Newmann (2001) for example) where the bacteria are taking energy from minerals by changing the oxidation state of iron. This is called *autotrophic* interaction (Berthelin, 1983). Here the action is primary and immediate. Iron is oxidized or reduced with a consequent change in the mineral present. Normally the silicates which are involved are dissolved and a portion recrystalized (see Banfield and Nealson, 1997 for examples). In some cases even clay minerals, formed at the surface are de-stabilized and dissolved (Kostka et al., 1999 for example). This interaction can be called, here in any event, primary where the energy benefit for the bacteria is immediate. This *primary interaction* can occur on a bare rock which is in contact with bacteria. All that is needed is a bit of water. It is one of the first stages of rock alteration.

A second type of interaction, *heterotrophic* (Berthelin, 1983) appears to be that operated by silicate – dissolving bacteria which to a large extent integrally dissolve the mineral, as far as one has investigated the question at present. The bacteria obtain sustenance from organic molecules in ambient aqueous solutions, often exuded by plant roots and other plant materials (Berthelin, 1983). This effect can be called secondary interaction in that the bacteria are dependent on the organic molecule sustenance for their prosperity which is provided plants, either as root exudates or the decomposition of litter root matter, in order to get vital nutrients from rock minerals in abundance. There is some indication (Banfield and Nealson, 1997; Kawano and Tomita, 2002) that clays or proto-clays can be formed in these processes. The interaction between these bacteria and silicate minerals seems to be encouraged or probably sustained by plant action, specifically root exudation of complex organic compounds used by the bacteria as a source of sustenance. Badr et al. (2006) describe the results of such action in laboratory and hot house experiments which indicate the benefit of this interaction is to the plant and the bacteria. In the case reported, potassium and phosphorous are extracted by several bacterial strains to the benefit of the plants. The relation seems to be symbiotic.

Numerous studies have been carried out to better understand the interaction between plants and silicate dissolution by bacteria. Welch and Ullman (1999) indicate that the ambient temperature affects the bacterial action, but not always in simple ways. A lower temperature (5°C) induces low pH in solutions which increases silica dissolution from feldspars 20 fold while at 35°C the effect is such that the dissolution of the minerals is not distinguishable from abiotic experiments. At 20°C the increase in silica dissolution was 2 fold. Similar results were obtained by Barker et al. (1998) for room temperature experiments. Welch et al. (1999) indicate that the type of organic matter available to bacterial can have a significant effect on dissolution rates, ranging from an increase ranging from 5 to 100 fold or no effect at all. Barker et al. (1997) summarize numerous publications concerning bacterial or organic products of bacterial action relating to silicate mineral dissolution rates which indicate that $CO_2$ and temperature would be controlling factors in general and that biologic enhancement of dissolution can be two to three orders of magnitude that of normal abiotic water – rock interaction.

By contrast, Wu et al. (2008, p. 412) indicate that the overall effects of bacterial interaction on granite in laboratory experiments are only moderate. This could well be due to the fact that bacterial action is mineral selective in a granite where much material, such as quartz, is little reactive to bacterial attack. Conversely, bacterial action would very well be mineral selective, yielding certain elements useful to the ecosystem as a whole. Ullman and Welch (2002) give detailed considerations of the mechanisms of silicate (feldspar in this case) dissolution. Augusto et al. (2000) found that the dissolution rate of plagioclase feldspars in field experiments where forest vegetation prevailed showed little difference with abiotic laboratory dissolution rates. In their observations the dissolution of feldspar was essentially concentrated in the upper 10 cm of the soil profile and strongly pH dependent, which was controlled by the species of tree present.

Thus there is need of proximity of root matter or decomposing plant debris in order for the organic matter to be available to the bacteria and the dissolved ionic species to be available to the plant. Calvaruso et al. (2006) have calculated a chemical budget for this interaction in the case of trees. Augusto et al. (2000) indicate that different species of tree have very different effects on mineral dissolution, assuming that the intermediary between plant and silicate mineral is that of microbial dissolution. Taking the process one step further, seed inoculation experiments with bacteria indicate a strong effect due to plant – bacteria interaction in the dissolution of ambient detrital minerals (Badr et al., 2006; Sheng, 2005 for example).

#### 2.2.3.2 Mycorrhizal Fungi

Cochran and Berner (1996) observed that silicate rock alteration was much higher under higher plants, i.e. more complex than bacteria, mosses and lichens. This is perhaps due to the greater needs of the bigger, more developed plants or due to a more efficient system of mineral extraction. One of the most important factors in root interaction with silicate minerals is through micorrizal contact with the silicate minerals. This has been operating for along period of time, perhaps since plants made their way onto the continents (Johnson and Gehring, 2007) and Taylor et al. (2009) summarize mycorrhizal relations in ecosystems. Basically they are everywhere where there plant roots. Further they have been around since plants became terrestrial inhabitants, more than 400 million years ago. Mycorrhize are fungal extensions of the root – plant structure below ground. They have been around for as long as plants were present on the continents. Their abundance increases the root mass by a factor of about 60 in many cases. Mycorrhize gain their sustenance from plant exudates, based upon photosynthetic energy which they exchange for mineral element extraction from silicates in the soil. Relationships are complex, depending upon plant species, climate and soil chemical characteristics. In general plants with thicker roots have more micorrhizal associations than those with strongly divided systems. Hence trees depend more upon micorrhize than grasses for example. The precise actions between minerals, especially silicates, and the fungi are not yet fully explored but it appears that they have a strong influence upon mineral stability. Not that they destroy higher temperature silicate minerals but that they modify them to the advantage of the plants seeking mineral elements.

Arocena et al. (1999) and Glowa et al. (2004) report the change of phyllosilicate minerals in soils under the influence of fungi which are closely tied to tree root physiological action. It is apparent that the high temperature phyllosilicates in the soils, micas and chlorites, are affected by a subtraction of interlayer ions, potassium and magnesium, to the benefit of the associated root systems. In exchange the fungi receive chlorophyll – produced substances for their metabolism. The modification of the high temperature phyllosilicate minerals is different depending upon the fungal species present, producing a more or less high charge vermiculitic type of mineral as are seen depending upon the type of tree involved. These differences indicate variations in the chemical activity of the fungi and perhaps differences in the general chemical context of the host tree detritus which conditions the soil. Here we see that the phyllosilicates are retained but modified into ion exchangeable clays.

In the laboratory studies of microbial action on silicate stability, generally two types of minerals have been used, phyllosilicates such as muscovite (an aluminous, potassic silicate mineral) and biotite (an iron – magnesium potassic silicate mineral) or feldspars (plagioclase N-Ca, and orthoclase K tectosilicates). Reaction rates have not really been compared directly. However Smits et al. (2005) indicate that the amount of material dissolved or released to the soils through feldspar weathering by tunnelling of fungal hyphae would be quite small, even after 1,650 years, less than 1% of mineral weathering. It is assumed that the faster reacting mineral would be biotite where iron oxidation can occur as well as dissolution and extraction of potassium. Muscovite is generally assumed to be less reactive, holding potassium in the structure, as observed by April and Keller (1990) for forest soil root system related mineral changes. Feldspars appear to dissolve integrally, perhaps forming other clay minerals wich have not been detected. However one does not see why micorrhize dissolve feldspars while being content to just extract K from a phyllosilicate structure. A partial answer is found in the work of Glowa et al. (2003) where detailed chemical analyses were made on mycorrhize themselves and it was found that he major mineral constituents of K, Mg, were found within the organisms whereas Ca appears to be fixed as an oxalate on the peripheral parts of the structures. It is clear that a portion of the mineral elements are part of the metabolism of the mycorrhize themselves. However their extraction powers exceed their needs and are part of the plant – mycorrhize system of interaction. We do not have a good idea of what mechanism would do this in muscovite where charge balance cannot be differentially affected as in biotite where higher ionic change in the structure by oxidation of iron would force out a potassium ion. The extraction mechanism of potassium from feldspar is more obscure. There are questions that remain.

### Fungal Interactions in Partial Modification of Minerals

Fungi are the type symbiotic material. Fungi survive by using energy, chemical, sources supplied by other organisms in “exchange” for transformed materials useful for their host. In soil systems roots are frequently, or perhaps always, associated with mycorrhizal materials which “extend” the chemical realm explored by roots. Arocena et al. (2003) give evidence of fungal penetration from crustose lichens into chlorite interlayer sites indicating that overall dissolution is not the initial bio-reaction with chlorites but one of selective extraction of elements.

Studies by Arocena et al. (1999) and Glowa et al. 2003 give more precise information concerning fungal interaction with chlorites. Both studies involved natural soils under coniferous vegetation. The clay minerals produced by ectomycorrhizosphere interaction associated with roots of Abies lasiocarpa (subalpine fir) produce an expandable clay (Ca saturation and glycol or glycerol saturation) which largely collapses upon potassium saturation. Ca – saturation in the air dried state shows a 14.7 Å spacing, instead of the normal hydrated (two water layer) state of 15.2 Å. The soil materials not associated with the ectomycorhiza did not show significant expandable clay material but a strong chlorite peak. This indicates the formation of a relatively high charge smectite from the chlorites present. It is interesting to note the strong contraction to an anhydrous mica like mineral with potassium saturation.

Glowa et al. (2003) take such a study further in using two different types of ectomycorrhizal fungi in till based soils under spruce (Picea glauca) forest cover. In this study, depending on the dominant fungal material (ECS – A or ECS – B) the chlorite dominated phyllosilicate mineralogy changes to an expandable mineral, to a greater or lesser degree depending on the species present, from an initial chlorite rich soil. Here again potassium saturation largely collapses the interlayer spacing due to the formation of an anhydrous potassium ion layer. Ca saturation in the air dried state leaves a 14.7 Å spacing. The intensity of alteration or transformation seems to be related to the type of ectomycorrhizal fungus present.

From these two studies, albeit based upon coniferous forest soils, it appears that chlorite is not destroyed, at least not to a great extent, but is transformed into a high charge 2:1 mineral which is susceptible to capture large amounts of potassium. The expandable mineral is most likely of high charge as shown by a smaller spacing in the air dried Ca Saturated state, 14.7 instead of 15.2 Å for a bi-hydrate cation structure.

However, Khademi and Arocena (2008) show that the clays palygorskite and sepiolite (non-phyllosilicates, i.e. sheet structure minerals) are completely altered from their initial chain silicate structures to form a kaolinite (TO) mineral under micorrhize action. Thus one sees that plant bio-agents do not appear to destroy sheet silicates (especially 2:1, TOT minerals) but they tend to preserve the basic structure modifying the interlayer ion portion fo the minerals.

To summarize, bacterial have two types of interaction, one primary (autotrophic) and the other a secondary effect (heterotrophic) conditioned by interaction with higher level plant species, via roots. The primary autotrophic interaction, based upon oxidation – reduction of iron, is independent of other life forms. The secondary type of interaction depends on plants for sustenance of the bacteria in that they apparently do not benefit from the destabilization of the silicate minerals. One can deduce that in the primary interactions, bacteria are specialized in interaction with iron – bearing minerals and hence the water – rock interaction processes will dominate in the initial stages of alteration. Bacteria and micorrhize tend to destabilize non-phyllosilicates entirely whereas they allow phyllosilicates to remain largely intact, modifying the interlayer sites in a 2:1 structure to extract elements or eventually store material in these sites. This appears to be especially true of micorrhize actions.

#### 2.2.3.3 Lichens

These plants are a hybrid between chlorophyll species (algae) and fungi. This is a condensation of sorts of the plant root – fungi symbiotic relationships described briefly above. Less data is available for these systems concerning the weathering of silicate minerals than for those of bacteria or fungi. However the information available (to a large part summarized in Chen et al. (2000)) indicates that the same relations hold as those in the microbiotic systems.

Biotite minerals have been observed to be transformed into vermiculite type clay minerals preserving the 2:1 clay framework (Wierzchos and Ascaso, 1996). However ferric clays have been seen to be dissolved as well as plagioclase feldspars which most likely form kaolinite minerals observed at times. However one report (Adamo and Violante, 2000) shows the formation of a mixed layered mica/smectite phase and kaolinite formed on a non-phyllosilicate bearing basaltic rock, mount Vesuvius. In this review paper, the rare reported case of the formation of a 2:1 mineral from a non-phyllosilicate mineral base is very striking. Here the creation of a soil – like clay is apparently the only indication at present of the formation of 2:1 soil clay minerals from non-phyllosilicate minerals. The destabilization of feldspars to kaolinite is most likely a wide spread process, according to this review, but the formation of a 2:1 new soil clay mineral indicates a different relationship in the chain of silicate reactions. If a 2:1 mineral can be formed in the first stages of mineral transformation from non-phyllosilicate minerals, then such a reaction chain could well be responsible for a portion of soil clays. The importance of such a creation is dealt with at greater length in Chap. 4.

Overall, it appears that lichens follow the trends of bacterial and fungal interaction where phyllosilicates are preserved and other silicates are destroyed to form kaolinite for example, such as is the case for plagioclase feldspar. We have less information on mineral formation from other silicate minerals which seem, in a first instance to form amorphous silica rich materials and iron oxides (Chen et al., 2000).

One observation made recently by Balogh-Brunstad et al. (2008) indicates the very important interaction of bio-extractors and plants. It was shown by laboratory experimentation that the installation of the micorrhize system of communication with plant roots decreases the amount of potassium in fluid percolating solutions in a soil. Initially the soil fluids contained potassium and other ions but very rapidly the soil solutions showed strongly reduced K contents. This indicates that the alteration process was dominated by the micorrhize root association allowing little potassium to escape into the pore fluids. The plants (Scots pine in this case) continued to grow with extracted potassium. This study indicates that the symbiosis of the micorrhize – root couple is extremely efficient in obtaining needed nutrients and the destabilisation and formation of new minerals in soils occurs with reduced loss of needed nutrient elements. Thus the measure of soil solution nutrients is not a good indicator of the processes of mineral element transfer between high temperature rock minerals and plants systems.

April and Keller (1990) indicate the complexity of chemical reactions at the bio-mineral interface. They find various products of interaction present at the

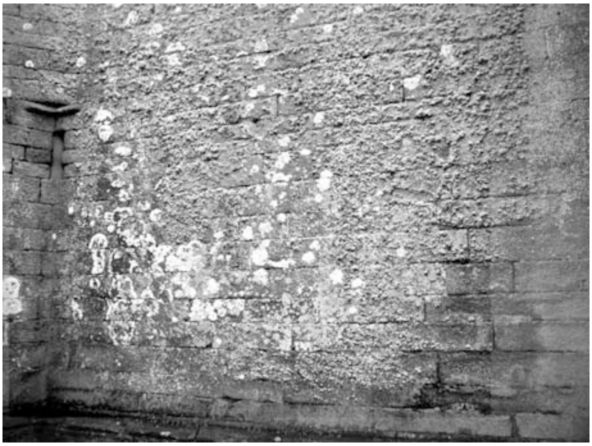

**Fig. 2.4** Indication of the importance of lichen action. The photograph shows a 16th century church wall made of granite covered by the plant community. (Sainte Nonna, Pen March, Finnistere, France) Photo DV

root – clay interface such as amorphous silica, hydroxy – alumina materials and mica with fractured and fragmented portions adjacent to the root surfaces. Fragmentation of the high temperature minerals muscovite and biotite result in fin grained, clay sized, material which is characteristic of soil clays. The transformation of these and other materials is surely complex, but it appears that the phyllosilicates remain for the most part intact while the other silicate minerals are dissolved to form other phases or have the dissolved portions transported out of the soil system in percolating pore waters.

Figure 2.4 indicates the potential impact of the initial stages of bio-rock interaction. Here a venerable church wall (Sainte Nonna, Pen March, 16th century), made of granite has been colonized by lichens of different types (crustose, foliose and fructose) all combining in a concerted effort of bringing down the wall by reducing it to sand and clay.

A more recent event, 20th century in the church yard of Saint Nonna, is shown on a grave stone where crustose lichens have begun their work (Fig. 2.5).

#### 2.2.3.4 Mosses

Carter and Arocena (2000) present data which shows the importance of species in moss – phyllosilicate transformation. Soils under Pleurosium schreberi and Ptilium crista-castrensis mosses were investigated. Both formed on glaciofluvial terrace material. The C horizon soil phyllosilicates were mica, chlorite with minor kaolinite. In both profiles chlorite is lost in the A horizon under the moss. The Ptilium moss leaves an expandable mineral after glycol treatment but in a Ca – saturated air dried state the sample shows a 14.7 Å spacing instead of the

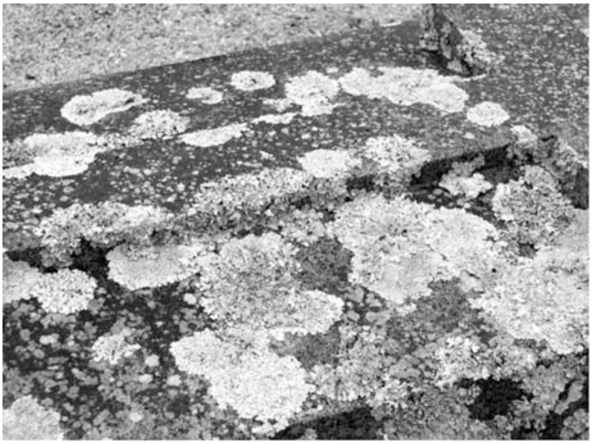

**Fig. 2.5** A more recent event, 20th century in the church yard of Saint Nonna, is shown on a grave stone where crustose lichens have begun their work. (photo DV)

normal 15.2 Å hydrated ion state. Thus one can conclude that the soil clay contains some high charge smectites. Potassium saturation leaves a clay assemblage with a range of spacings from 13.8 to roughly 10 Å spacings with a peak at 12.4 Å. It is clear that the altered chlorite structures have a varied charge and charge site, forming either independent mineral units (ex. the material giving a 12.4 Å peak) or units of random mixed layering of different proportions. Hydration states vary: reflections between 15 and 12.4 Å indicate some bi-hydrated material while peaks at 12.4 Å indicate monohydrated ions and those near 10 Å indicate anhydrous interlayer ions. Here there is clearly a range of charges or charge sites in the mineral structure in the mineral which respond differently to the presence of potassium, some not responding particularly.

The Pleurozium moss clays show a 14.1 Å spacing with Ca saturation under air dried conditions and no change with glycerol treatment. However, potassium saturation leaves the clays with a range of spacings from 12.6 to 10 Å. The 12.6 Å spacing indicated a monohydrate interlayer ion occupancy while the 10A peak indicated an anhydrous inter layer ion state. Again a high charge mineral with differing states of charge or charge site produces potassium interlayer ions. However, in the case of Ptilium moss the mineral is clearly an expandable phase while in the case of the Pleurozium moss the mineral is not expandable after saturation with a divalent cation.

The different behaviours of the clays under these two mosses indicated that each species does not produce exactly the same 2:1 mineral from the chlorite precursor. In one case the new mineral is most likely based upon the 2:1 portion of the chlorite with most of the hydroxyl – interlayer ions extracted and replaced or replaceable by hydrated divalent cations. This is a classic smectite behaviour. In the other case, the mineral does not accept hydrated divalent cations but monohydrate and anhydrous potassium replaces various portions of an initial probable exchangeable hydroxy-interlayer ion layer.

These results indicate the complexity of bio-silicate interactions. However, in general the changes in the bio-horizons are more rapid than those in the "mineral" horizons (saprock and saprolite). The minerals formed are not quite the same either. Climate affects this bio-activity as one could suspect, as shown in a montane series reported by Castaldini et al. (2002). Climate changes the bio-agents (plant biomes) and this changes the chemistry of the soil pore solutions which affects the clay mineral and silicate mineral assemblages present.

### *2.2.4 Summary*

Biological degradation of rocks appears to be much more active, in a reaction rate sense, than that of simple water – rock interaction with silicate material. Various observations have estimated differences of several times to orders of magnitude faster rates for biologically driven reactions compared to water – rock silicate mineral change. However one can assume that such rates are more or less restrained to the biosphere of alteration, where root exudates and plant debris are sufficiently active to encourage microbial interaction or in the case of lichen, such action is restricted to the rock surface. In alteration profiles, the absence or roots at depth should signal the slower rate of reaction transforming high temperature minerals into clays, essentially one of water – rock interaction. Since the root zone is to a large extent restricted to the upper 20 or 30 cm of an alteration profile for most of the root mass (Schenk and Jackson, 2002), one should find that the types of clays in this zone will be dictated by microbial interaction and interstitial solution chemistry which is guided by the type of plants present. Clays in the deeper portions of the profile will be the result of local mineral – water interactions. As we have seen above, microbial action favors the conservation of clay minerals, 2:1 minerals being little altered. However other silicate minerals can be dissolved leaving oxides or kaolinite as an insoluble residue (Khademi and Arocena, 2008).

One point that is important to retain is that the clay minerals found at the surface under weathering conditions are of moderate alkali content to relatively high content. However, the alkali present is almost uniquely potassium, fixed in the clays or calcium as an exchangeable ion. Both are present only in 2:1 minerals, those containing the most silica. Sodium is lost to the altering solutions and ends up in the sea. This is why the term salt, refers to a sodium compound. Magnesium is lost to the sea also. Potassium is largely retained in clays. Plants found along the saline bodies of water, oceans and other evaporitic lakes, are sodium bearing. They are called halophyllic. Halophyllic plants, found near sources of saline water, can adapt to less sodic conditions having a mixture of Na and K ion concentrations in their biomass (Barkaudah and Henderson, 2006). The fact that potassium is retained in clays and not sodium was crucial to the development of plant physiology. It appears that an alkali ion is necessary to plant metabolism, either Na or K which are the most abundant of these elements on the surface of the earth. Hence terrestrial plants use potassium whereas plants living near a saline body of water use sodium.

Terrestrial plants then need potassium, and it is one of the three major fertilizer components, in the NKP triad. This need for alkali ions is extremely important in

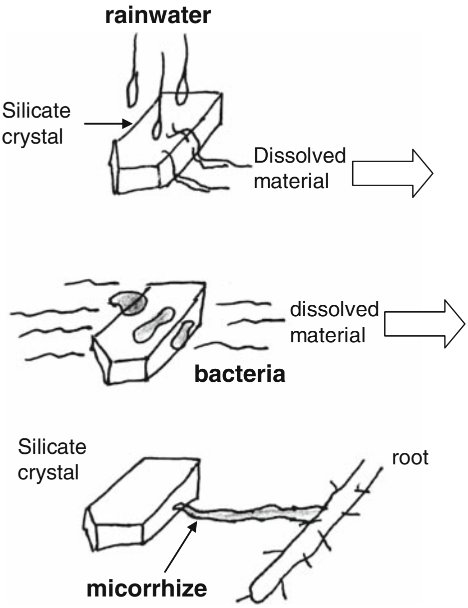

**Fig. 2.6** Indication of the different types of alteration processes in a soil between (1) rain water and silicate mineral with the dissolved material going into the aqueous solution, (2) bacterial action where the dissolved material goes into pore water solutions and (3) micorrhize action where the largest part of the dissolved material is channelled to the plant through the root – micorrhize interface

the chemical impact of plants on surface chemistry and mineralogy as we will see later.

Figure 2.6 shows in a schematic way the different types of interactions that a silicate mineral might encounter in the saprolite to soil horizons of an alteration profile. The water – rock interaction is indicated b the action of rainwater with a crystal of a silicate mineral. Bacteria can colonize the surface of the crystals, and introduce themselves into fractures in the crystals with the effect of dissolution and release of dissolved material, being nourished by root exudates substances and finally micorrhize fungal action linking the plant roots direct to the silicate mineral under dissolution can be seen.

***What needs to be done***

***More complete investigation of the interactions of bacteria and silicate minerals***
***More complete investigation of micorrhize – silicate interactions***
***Development of rates and impact of bio modifiers on soil solutions and silicate chemistry***

## 2.3 The Alteration – Soil Profile: Transformation of Rocks into Clay, Sand and Organic Matter Complexes

The title here is at first rather ambiguous. A number of pedologists prefer to call the upper portion of an alteration sequence the soil, that part which is in fact intimately involved with plant action. In this part of an alteration profile one finds organic matter which indicates the influence of plants through decay of leaf matter and plant roots. However the largest part of most alteration profiles goes much more deeply below the surface where a gradually decreasing amount of new surface minerals is found until a zone of "bed rock" or un-altered material is apparent. In principle one finds a more or less zoned structure of horizontal "horizons" each showing specific characteristics related to alteration processes which transform rock into clay – rich assemblages. These "horizons" are outlined in Fig. 2.7. The soil portion (A horizon) is the contact of inorganic materials, rocks and clay minerals, with the living plant environment. Below this one finds very clay – rich segments which indicate a high rate of rock transformation. Depending on the intensity of alteration and the alterability of the bed rock there is a mixture of clays and rock debris in this zone. However there is no or little trace of the old rock structure, i.e. the relicts of the disposition of the old minerals in the original rock. This is the saprolite zone. The contact zone between clay – rich and un-transformed rock is the saprock zone where one finds the initial stages of rack alteration into clay minerals and mineral debris. This idealized zoned structure is the basis for soil classifications. However often one finds that the rock and saprock zones are very irregularly inter-fingered depending upon pathways for water flow which hasten alteration in a non-horizontal manner. Cracks, fault planes, and other geologically initiated structural irregularities are expressed in this un-even alteration process.

If we consider the different types of alteration processes, physical degradation, plant – rock interaction and water rock alteration, it is evident that the first two will dominate at the surface while the last will be less evident at greater depth in the alteration profile. Intuitively the interaction of rainwater and silicate or rock matter should be most intense in the intial contact zone, the soil – air interface where unsaturated rain water first comes into contact with soild matter. However, the materials present at the surface in the soil zone are already, for the most part in equilibrium with the new, low temperature, hydrating conditions of the earth's surface. Thus

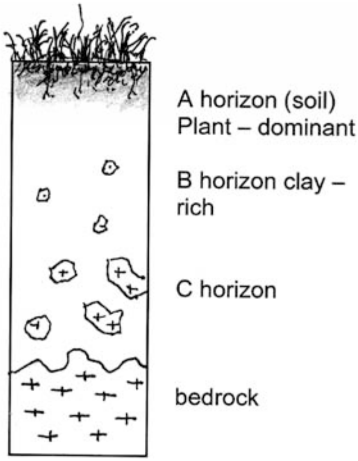

**Fig. 2.7** Simplified schematic representation of an alteration profile where the plant – silicate interface is shown as the A horizon, rich in humic matter and roots, the B horizon of clay accumulation, the C horizon of alteration minerals (clays and oxides) and rock debris, and the bedrock which is initially altered at the interface with the alteration zone

the impact of percolating rainwater will be great at the rock – alteration interface, perhaps more so than in the initial contact zone. Even if the rainwater is saturated and in equilibrium with soil clays, it will be decidedly out of equilibrium with high temperature minerals constituting the hard rocks at the bottom of the alteration profile. Therefore, the rainwater percolated to the rock interface will interact to a large extent and become charged with such elements as alkalis, alkaline earths and silica. Dethier (1986) has indicated that the largest part dissolved material in water making its way to streams and rivers reflects the alteration equilibria found at the rock – water interface. In fact the measure of dissolved material in stream water is a measure of the activity at this interface and not the chemical reactions in the upper portions of the alteration and soil profile. The importance of pathways, residence time, and frequency of rainfall in this interaction zone is detailed in Chap. 5 of Velde and Meunier (2008).

The question can be posed then: Are the chemical and mineral interactions the same through out the soil alteration profiles or are they different? Is the alteration process one continuum imposed by rain water abundance and contact or are there differences in the profile?

## *2.3.1 The Transformation of Bedrock into Soil Clays*

It is striking to note in treatises on geochemistry the change in average composition of rocks in the upper crust of the earth and the result of surface alteration processes which produce soils. The material which results from these chemcial processes is clay rich and when deposited in the oceans becomes shales. This is in fact a concentrate of the average processing of silicate materials. In shales one finds roughly the same concentration of potassium as in the upper crust average (see Li and Schoonmaker, 2004) as well as magnesium but much less Ca (1.50 compared to 3.15%) and far less sodium (0.59 compared to 2.54%). The major elements silica and alumina are roughly unchanged also, with some loss of Si and a gain of Al. Thus the transition from high temperature rock mineralogy to one of clay minerals and residual sand (quartz) is one of conservation of most elements excepting Ca and Na. Sodium makes the sea salty, as we know, and hence is almost totally lost during the process of alteration. Calcium is also lost to a great extend making up the carbonate part of sedimentary rocks through the action of animals which make their shells of it combined with $CO_2$ form the atmosphere. This leaves us with K and Mg being retained in the clays of the soils. How is this effected and why?

One method which can be used to answer this question is to observe the clay – forming processes and their kinetics in the different parts of the profiles. We will start with the water – rock interaction zone of the bedrock and saprock zone.

### 2.3.1.1 Saprock Clay Formation and Transformation Kinetics

The rate of interaction in this zone is governed largely by the inherent thermodynamic instability of the minerals in the bedrock. In principle minerals of higher temperature of formation will be more likely to alter. However the overall effect on weathering kinetics is difficult to assess in natural situations given differences in rainfall and vegetation. The most direct measurement is the total depth of alteration, i.e. the distance to the rock interface. One measurement is the thickness of weathering rids on volcanic boulders or clasts. This situation, a "fresh" rock in an essentially unweathered environment indicates the pure rock – water interaction is a very unsaturated regime concerning the mineral charge of the aqueous fluid Coleman (1986). Rind formation rates, very partial mineral alteration, is measured in millimeters per thousands of years with only 2 mm after 160,000 years alteration in Western United States gravel terraces. This is very little interaction. However, in Costa Rica, the rind alteration zone is measured in centimetres per 240,000 years (Sak et al., 2004). The starting materials are highly out of equilibrium, being basic volcanic rocks, hence on can expect maximum reaction rates for eh physical conditions. It is clear that climate, rainfall, can greatly affect the alteration by water – rock interaction, roughly by a factor of ten in the cases cited.

Another measurement of weathering rate at the rock alterite interface can be the total developed thickness of an alteration profile of granite. Evans and Cameron (1979) indicate that the development of weathering progresses about 1 cm/1,000 years. Here we are in a very inactive climate, the cold region, Baffin Island. The relations of age and depth of solum (alteration zone) are rather linear for this time range. Samples from Rhodesia on granite also (Owens and Watson, 1979), indicate an alteration formation of 11 and 4 mm/1,000 years. The differences between Baffin Island tundra, Rhodesian savanna and tropical Cameroon climates are near one order of magnitude in the differences of their effect of rock alteration as defined by the development of the saprock portion of the alteration profile.

Still another measure of reaction progress in the rock to clay transformation can be made using estimations of clay content for different aged alterites near the rock interface. Data for tephra alteration (Lowe, 1986) in New Zealand indicate similar rates of transformation even though the New Zealand material is much more fine grained and would be expected to be more reactive (Fig. 2.8). The tephra data record to a time span of near one million years and near 80% development. In Fig. 2.8 one sees that the distributions reasonably close to an exponential curve, which is to be expected for first order reactions where the relation $a = a_0 e^{-kt}$ should pertain, $a$ being the amount of reacted material. The function of temperature (t) seems not to be all that important for the temperature ranges considered here in that the Baffin Island data are in accord with those for New Zealand.

Given the above estimations of alteration rate, either in the development of the alteration front, basalt alteration rinds or saprock front progression, or that amount of reaction accomplished in the development of clay from high temperature rock (in the examples cited all of the bedrocks were magmatic in origin) it appears that the times of interaction are relatively long, centimetres depth per 1,000 years alteration in progress of the saprock interface, and near a million years for the development of a totally altered rock. Such lengths of time are on the magnitude of climatic changes induced by glacial epochs which we experience now. These can be considered to be on the order of magnitude of geological events.

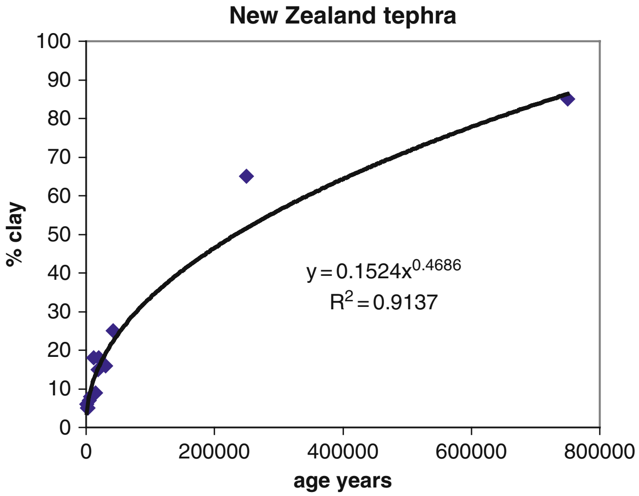

**Fig. 2.8** Indication of he time scale necessary for the transformation of a silicate rock into clay minerals under conditions of water – rock interaction at the surface. The alteration of a volcanic tephra to a very high clay content occurs only after 800,000 years (Lowe, 1986)

#### 2.3.1.2 The A Horizon of Plant – Soil Interaction

The interaction between living matter and mineral matter in the alteration zone is of several orders of magnitude greater than that for simple water – rock interaction. Some mineral transformation reactions can be effected much more rapidly than others. However, we must be very careful here to distinguish between clay – forming reactions, i.e. transformation of a non-phyllosilicate into a phyllosilicate mineral and clay transformation reactions where the nature of the clays is changed and not the existence of the clays themselves. Clay change such as that where interlayer ions are displaced, for example the change from smectite to illite (introduction of anhydrous potassium in a 2:1 structure) or the transformation of chlorite to smectites (extraction of interlayer Mg(OH) ions from the 2:1 structure) are probably not in the same range of energetic values as those where feldspar is transformed to kaolinite with loss of alkalis and silica.

In the laboratory the effects of micro-organisms can be very strong and rapidly accomplished. Barker et al. (1997 and 1998) Ullman and Welch (2002) indicate that the dissolution processes induced by bacteria can enhance reaction rate by two to three orders of magnitude compared to water – mineral reactions in the laboratory. Barker et al. (1997, p. 407) give data showing a typical S curve for reaction progress which is typical of biological reaction rates as described by Odum (1971, p. 186) which including those animal (sheep, Odum, 1971, p. 188) and eventually, according to sociologists of human activity! These types of reaction progress are well known in studies of forest growth and change (Bormann and Likens, 1994). Tree growth and forest recovery follow the same patterns as those of feldspar dissolution by bacteria. However interaction of organic molecules with feldspars in laboratory experiments

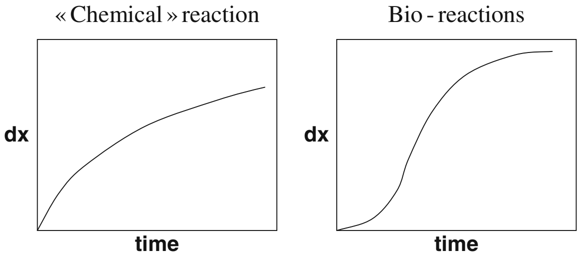

**Fig. 2.9** Schematic diagrams of reaction rates observed for chemical reactions (rock – water interactions for example) and biologically driven reactions. The first is a "C" shaped curve while the bio reactions most often show an "S" shaped curve

(Ullman and Welch, 2002) show exponential curves common in normal first order reaction kinetics (Fig. 2.9).

The reaction rates (measured dissolution) for the bacteria experiments are about 1,000 greater than the organic compounds alone in contact with feldspars. Thus even though the chemical agents are similar, organic acids of various sorts, the bacterial function is much stronger. The S curve reaction progress is apparently a signature for bio-controlled processes in soil environments. An example of bio and mineral reaction rates in the same soil profile context is given in Fig. 2.10. Here the development of the thickness of the A horizon, measured by the organic – rich layer thickness is

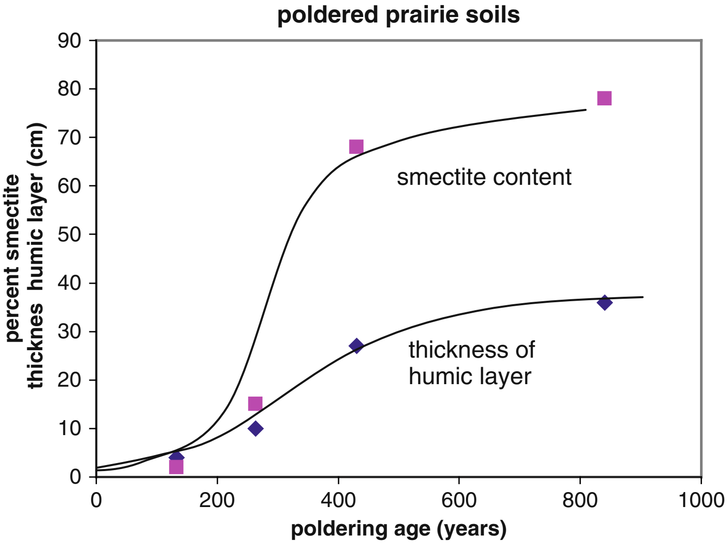

**Fig. 2.10** Illustration of the relations of strictly organic reactions, thickness of the humic layer in developing poldered soils based upon newly sedimented clay – sand sediments, and the development of the smectie mineral, formed from more illitic clay minerals types (illite, smectie – illite mixed layer clays) under the humic zone in the poldered soils; The similarity of the shapes of organic depositon and clay mineral change suggest that the changes in the clays are driven by the biological processes. Both have "S"shaped reaction curves as a function of time. (data from Velde et al., 2003)

compared to the development of smectites from mixed layer minerals. The setting is a series of poldered zones along the Authie Bay near the Baie de Somme in northern France along the Channel coast, where soil profiles were observed as a function of the age of polderization. In each polder the sediment deposition was interrupted and a grazing (natural prairie) system installed. As time progresses (older polder age) the thickness of the humic layer increases indicating organic activity with the installation of the prairie ecotome. Below this humic zone one finds that the clay minerals change, with an increase in the smectites – rich mixed layer mineral at the expense of more illitic (potassic) clays. In that the clays in the humic zone remain potassic in nature, one can suspect that the effect of water – rock interaction is one of potassium loss. However, in that the humic horizon clays maintain potassium content, we deduce that the resources for this maintenance are those of clays below the humic zone exploited by the roots of the prairie plants. More about this later (5.1). In any event it is clear that the two rates of reaction progress are of the same sort, S – shaped in nature. This indicates that not only the organic activity is of this dynamic but it has an effect on the mineral parts of the system. Walker and del Moral (2003, p. 107) give data concerning the dynamics of forest growth after a landslide event. The biomass was measured as well as the potassium in runoff water from the watershed of the slide area. One sees an S shaped curve for the biomass established over a 40 year period and a reciprocal decrease in potassium in runoff water (Fig. 2.11). Here one sees the impact of the growth of plants on the mineral content of the soil and alterite substrate. It is clear that most of the decrease in loss is due to the forest growth as it re-establishes a normal stable state of production.

A similar change in clay mineralogy, S – shaped dynamics, can be seen in the data presented by Mahaney (1986) where the formation of smectites from Quaternary

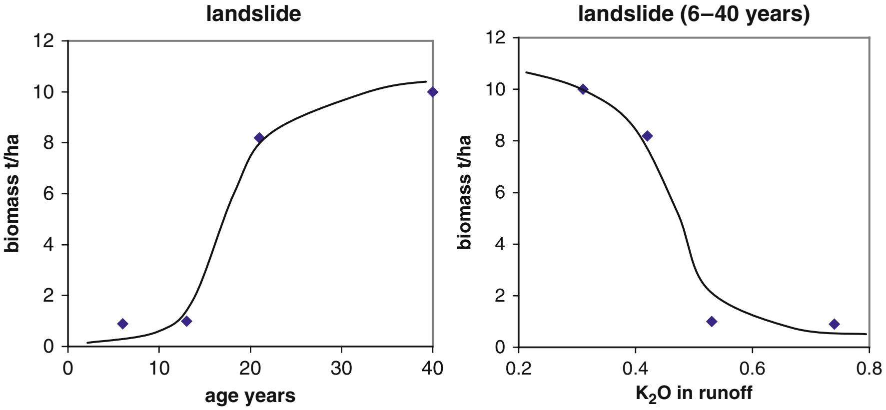

**Fig. 2.11** Control of weathering by plant growth in the case of a landslide in a forested area. Biomass increases according to the "S" curve after the landslide while the potassium present in the runoff (streams) shows a decrease in the opposite sense. This indicates that chemical loss due to the water – rock weathering process is rapidly controlled by plant uptake and sequestration of this element in the biomass (Walker and del Moral, 2003)

soils developed on till in the Wind River mountains of Wyoming show a typical S – shaped change in abundance, formed at the expense of an illite – chlorite mineral assemblage. Here one sees that the smectite is replaced in its turn by soil vermiculite after 3,000 years of smectite increase in the A horizons. In fact one can find traces of this type of reaction dynamics in the generalisations given by Birkeland (1999, p. 225) concerning the development of soil charactistics which attain a "steady state" according to the author. The generalisations of the author are based upon a vast amount of knowledge and observations over a long period of time. Although the data is presented in a very generalized manner, it certainly can be used with confidence. In the development of soil properties the S curve dynamic is quite evident. The author indicates that the time constants for this development vary with the type of soil developed which is essentially one of climatic influence and hence plant – soil interaction. The attainment of steady state according to the author can vary from 1,000 years for organic – rich, wet soils to 1,000,000 years for soils in more arid climates where oxidation is dominant. In looking at the specific parts of a soil profile, A–C horizons, the author indicates that there is a difference in the time necessary to attain the steady state depending upon the horizon, and hence the degree of plant – mineral interaction. The A horizon is the first to come to equilibrium in the example given. The time necessary to attain steady state for the A horizon, that where organic activity is greatest is on the order of hundreds of years whereas the lowest horizon takes near a million years The factor of $10^4$ years for differences in development of the A horizon (bio driven) and the C horizon (water – rock contact) is similar to those found in other studies quoted above.

#### 2.3.1.3 The Effects of Bio-agents

Different bio-agents appear to effect different change in silicate chemistry and dissolution of silicate materials. In some cases there is dissolution and apparent loss of all material to the solutions, in others the minerals are only partly altered maintaining most of the silicate network intact. The relations of the bio-agents to the roots of plants are of great importance. If the minerals from the bedrock are dissolved or modified releasing mineral elements to the soil pore solution this will affect the stability of other clay minerals present. If the bio-agent is directly "connected" to the plant through the roots as are mycorrhizal fungi, the materials dissolved and released will be directly transmitted to the plant without coming into contact with other silicates in the soils and without affecting mineral stabilities. Such a system is suggested by Balogh-Brunstad et al. (2008). In their experiments pore waters in a soil where pine seedlings were introduced we analyzed and observations made on the soil solution compositions as a function of time. The developing plants used more and more mineral nutrients but less and less were present in solutions. The authors attribute this effect to direct up take through mycorrhizal action in conjuncture with the roots of the pine seedlings. Bacteria by contrast would directly affect the silicate minerals and release the dissolved elements into the soil solutions. Hence the relations of bio-agent and plant are important to the overall mineralogy and chemistry of soils.

Feldspar minerals are often cited as being transformed or affected by bio-agent actions in soil zones (see Barker et al., 1997 for a review). Some experiments have been made extracting and culturing bacteria in potassium feldspar and injecting these strains in various crop seeds (Sheng, 2005). The plants of course benefited from such increased biological action close to their roots. It has been observed that some species of bacteria will attack micas for potassium whereas feldspars are much less affected (Liu et al., 2006). Thus, as one would expect, there are different species of bio-agents for different types of work. It appears that bacteria can be influenced by the minerals which they alter, which affect the diversity of the microbial communities (Hutchens et al., 2008) This seems to be another instance of "feed back" or inter influence between the living and mineral worlds.

Escudero et al. (2007) found that lichens in soils can have species – specific effects on plants. This suggests a specialization in bio-agent link ups with plants. From another view point, Augusto et al. (2000) found that different species of trees in a forest had different impacts of feldspar weathering rates. Different plants have different needs and extract the elements necessary for their development at different rates which affects the chemistry and mineralogy of a soil. This can explain, partially, why some soils maintain different minerals in the soil zone whereas others have lost them. Of course there is an interaction between the mineral resources in the source rock of a soil and their use. To a certain extent the type of rock will dictate the plant community which will be present under given climatic conditions. Hence the inter-relations of plant species, bedrock composition and bio-agents in the soils will determine the overall chemical reactions and define the clay mineral stabilities in the A horizon of alteration sequences. In a very general manner, eruptive rocks, either acidic or basic, tend to influence the plant regime to a great extent. Most farmers know that it is not a good idea to plant wheat on granite soils nor on those of basic magmatic rocks. It is better to stick to the sedimentary rock – based soils, where in fact the high temperature minerals have gone through the geochemical transformations to produce sediments, via plant – soil interactions and provide a fertile basis for plant growth of crops used for human sustenance. More on this in Chap. 6.

### *2.3.2 Summary*

The analysis of available data concerning differences in reaction kinetics in the bio horizons (A) and water – rock interaction horizon (saprock – bedrock) suggests two different types of reaction dynamics or kinetics; this means that the processes are quite different, one obeying normal mineral or chemical rate laws and the other with an as yet poorly explained dynamics in three parts. The S curve in initiated by a stage of slow change initially, followed by a strong growth or change dynamic which eventually reaches a stage of slow and more steady change. In fact the S curve is probably in reality a superposition of two reaction rates, one slow which is eventually overtaken by a more long lasting and stronger one.

Taking into account the above analysis, one can designate two active zones in an alteration profile:

1. The A horizon is where plant – silicate interaction is primordial. Reaction rates are relatively rapid, on the order of hundreds of years. The micro-biological elements are largely responsible for these reactions and reaction rates. This being the case, one would expect such systems to be highly affected by temperature changes. When biological activity is possible, i.e. under conditions of adequate rainfall and humidity, the temperature effect drives biological activity which determines the amount of chemical substances available to affect silicate minerals. We will call this horizon or reaction zone the soil portion of an alteration profile.
2. The saprock – bedrock horizon is where water rock interactions are dominant and normal mineral chemical processes dominate. Here the time scale of reaction kinetics is on the order of hundreds of thousands to a million years. The transformation of silicates to clays is long and produces multiphase assemblages in the first instances of reaction.

In general, the thickness of the A, soil, horizon will probably stabilize whereas the depth of the saprock – rock interface will continue to move downward with time (Fig. 2.12).

The bio-agents, bacteria and fungi inter-react with the silicates and plants to alter and transform the minerals present in the alterite zone. Different agents and different plants will change or modify the silicate minerals in the soil zone to different extents depending upon the needs of the plants and the constraints imposed by the bedrock materials.

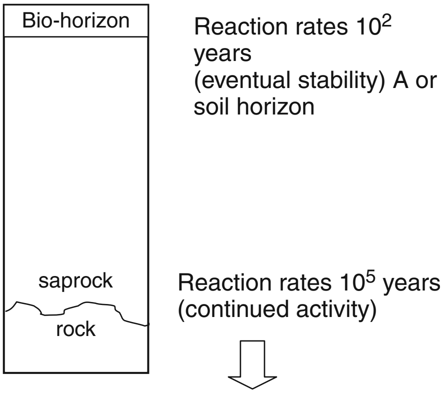

**Fig. 2.12** Indication of the relative changes in mineralogy in an alteration profile. The reaction rates for clays in an organic dominated environment (A horizon) is on the order of hundreds of years, where the interlayer ins in 2:1 structures change composition, and sometimes new minerals form, i.e. kaolinite or chlorite. Reactionrates involving high temperature silicate minerals take much longer periods of time to come to equilibrium with surface chemical conditions. Here the time scale is on the order of $10^5$ years

### 2.3.3 The Alteration Profile

In between the A, soil, horizon of plant – silicate interaction and saprock – rock interface one finds various mixtures of clays (new minerals in equilibrium with their surface environment) and relicts of the old minerals or fragments of rock which have not been altered into more stable mineral assemblages.

It is evident that the zone adjacent to the rock – saprock interface is that of saprock. The name of this alteration zone indicates its transitional nature with the rock below the alteration zone. In fact here the old rock structure persists, i.e. one can imagine the forms of old minerals which have been transformed into new clay mineral assemblages. This is the "conserved structure" zone. Gradually as more and more minerals are altered, the structure becomes less dense due to loss of material by dissolution in the transformation reaction. This change is dealt with in length in Velde and Meunier (2008, Chap. 4). The loss of material due to alteration can represent 30% of the initial rock. Gradually the structure of the old minerals is lost, with a small increase in density, to form what is called the saprolite zone. Here the old rock structure, localisation of the alteration minerals with respect to their parent phases, is lost and the new clays are mixed with other assemblages. This is the saprolite zone, essentially the same mineralogically as that below but one of gradual change where the segregation of the initial mineral assemblages is effaced to form new ones of a general chemical equilibrium. In the saprock zone one speaks of primary plasma, that space occupied by the initial mineral assemblages. In the saprolite zone one speaks of secondary plasma which calls chemical potentials of a more general nature. Often these secondary plasma mineral assemblages reflect an increased loss of mineral constituents, such as alkalis or silica. This change is seen in Fig. 2.2 where we have followed the change in feldspar alteration products to those of the secondary plasma, number 3 in the diagram. The secondary plasma is composed of new minerals, illite, smectites and kaolinite which contain less alkali (potassium) and silica than those of the initial feldspar and the first reaction products, illite in the presence of feldspar (number 1 in the figure) and the primary plasma which contains smectites, illite and the feldspar in the form of fragmented grains (number 2 in the figure). At each step of transformation, some elements are lost, K and Si in this case, which leaves behind a less dense material which is more open to water flow. The replacement minerals are less dense, containing water or OH units, and this also changes the density of the alteration material.

As alteration proceeds the saprock – saprolite zone is extended and the zone of partial alteration is extended. Partial alteration, because the change of old minerals to new one is gradual, leaves islands of old minerals or assemblages (rock fragments) which are often found in these parts of the alteration profile. In fact it is not uncommon to find rock or mineral grain fragments present in the A horizon also. In zones of intense alteration the old mineral grains and rock fragments are quite rare, and one finds at best quartz grains ($SiO_2$) which are very resistant to alteration. The presence of these old mineral grains is very important to the dynamics of plant growth in that deep roots can obtain needed elements in this zone without going to the rock – saprock interface. Figure 2.13 illustrates this disposition of rock and clay mineral material.

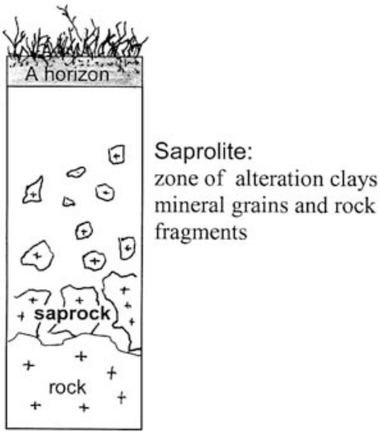

**Fig. 2.13** Illustration of the relations between rock, saprock and saprolite zones of an alteration profile

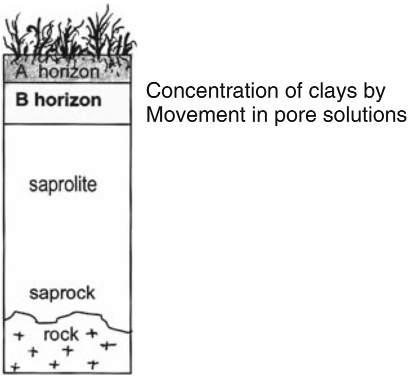

**Fig. 2.14** Situation of the B horizon where clay minerals are concentrated by whysical movement in soil pore solutions

One major feature of many alteration profiles is the concentration of clays in a horizon below the A – organic zone. We will call this zone or horizon the soil, indicating the specific situation of a mixture of organic material and silicates which is the result of organic influences on the silicate and oxide materials. The movement of clays is due to percolation in pore fluids (rainwater) as the surface water moves downward to find its way to the water table. Clay concentration gives a new name to this zone, called the B horizon (Fig. 2.14).

The formation of such clay concentrations is relatively slow. This is especially true for considering the recent (geologically speaking) where glacial epochs have changed the surface geomorphology and plant regimes due to climate change to a great extent.

With a strong chemical attack, due to acid soil conditions engendered by plant activity (usually conifer forest) clays can be further displaced and the remaining material dissolved forming what is called the E horizon. In this zone one finds sand, in the form of the chemically resistant quartz and iron or other metal oxides (Fig. 2.15).

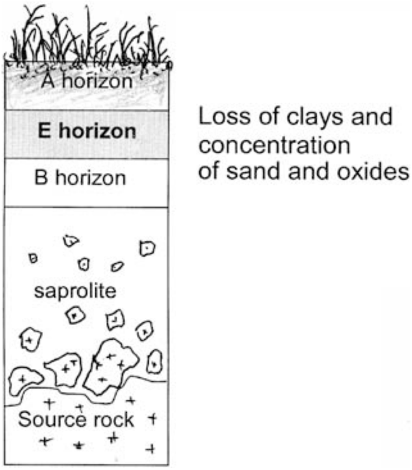

**Fig. 2.15** Illustration of the formation of the E horizon, a zone essentially devoid of clay particles and organic matter. The fine grained material is transported to the B horizon, below, leaving an essentially sandy horizon below the organic, plant silicate contact zone. The E horizon is particular to forest soils or those of high acidity

Soils with a distinct E horizon are most often found in forest biomes except where alteration is very intense, tropical forests for example, where even the refractory quartz is rare. In these simplified examples one can suspect that the structure of soil profile, the different parts designated by the relation of alteration minerals and their place in the profile, can be a function of the climate (alteration intensity) or the type of vegetation present.

Generally then one finds more clays, products of alteration, at the surface of an alteration profile. The consensus is that the clay content reflects alteration intensity, which is greater at the surface of a profile than in the lower parts where pore water in soils and alterites would be more saturated with dissolved elements. However, the analysis found in Velde and Meunier (2008, Chap. 4) indicates that the pathways of major fluid flow are filled with aqueous solutions still un-saturated with respect to 2:1 phyllosilicates. The kaolinite minerals and oxides are formed along the walls of major pore pathways in alterites (saprock and saprolite) indicating that the solutions are highly under-saturated with mineral elements. This suggests that the total reaction of rainwater and silicates in soil – alterites is not accomplished just at the surface of the profiles. The information in Fig. 2.11 where the forest regime as it becomes established strongly controls the total loss of elements to stream water indicates also that the plant regime strongly dominates chemical transfer and reaction in the surface portion of a profile. Yet it has been seen in a multitude of studies that the clay content of the materials in alterite profiles is concentrated in the soil zone (organic interactions). Hence clays can be associated with the A horizon biozone of activity, more so than in the lower parts of the profiles, at least where some of the material present in the alterites is not completely transformed into hydrous silicates or oxy-hydroxides such as large portions of tropical soils.

Jenny (1994, p. 154) correlates data for soil clay content and temperature for soils on different substrates, granites and basic rocks in the Eastern United States Clay content increases from 10 to 60% with annual average temperature increases of 8°C. Such a great change in alteration activity can only be attributed to plant activity which is governed by climate. Here one can conclude that a large portion of the clays in the soil horizon are due to the bio-activity which transforms most of the alterable high temperature minerals into new phases stable in the surface environment.

### *2.3.4 Summary*

The alteration profile is then divisible into different sectors where different chemical parameters are present which determine the physical and mineral properties of the altered materials. The base is the rock from which the alterites and soils are formed. This rock is then transformed by mineral dissolution and crystallization of new, hydrous phases, clays for the most part, as rain water percolates to the bottom of the alteration profile. This is the saprock zone where the initial stages of mineral reaction occur. The reactions are determined by the proximity of available water and its state of under-saturation with respect to the mineral elements in the old, high temperature minerals. The reaction rates for such interaction are very slow. The total dissolution of a rock takes nearly one million years.

By contrast the soil horizon (A) shows much greater rates of reaction. For example, data given in Ruhe (1984) suggest that the rate of transformation of loessic materials across the Midwestern United States into new clays is on the order of 20% in the space of 10,000 years. Thus, if undisturbed, one could expect a complete transformation of the silicate material susceptible to change in the space of less than 50,000 years or a rate greater than $2\ 10^3$ times that of water – rock interaction. The zone intermediate between the A soil horizon can be divided into two horizons, one where the movement of clays by pore water transport forms a clay – rich zone, the B horizon. Below the B horizon where no trace of old rock structure is found, the material is composed of varying proportions of mineral and rock debris along with clays formed by water – rock interaction. Pedologists term this zone the C horizon including the saprock zone of conserved rock structure and the saprolite zone where the rock structure has disappeared. The important point is that throughout the C horizon the reaction rate of mineral conversion is essentially governed by mineral water – rock reaction kinetics. In the soil horizon (A) the reaction rate is much greater due to biological interactions. Plants and microbes work 24 h a day, rain or shine and they maintain an aqueous environment which is the vehicle of chemical reaction for silicate minerals.

### *2.3.5 The Plant – Mineral Continuum, the A Horizon*

The A horizon is what we can call the soil, i.e. the horizon where organic matter is present and silicate minerals are present. This is the zone of plant – mineral interaction. Plants use this portion of the alteration profile to form and extract their necessary elemental mineral needs. Of course water is a part of their interchange as well as portions, i.e. ionic constituents, of minerals. This portion of the plant – mineral interface is very busy, with plant remains, and living matter, bio-agents such as fungi, bacteria and more developed living forms such as earthworms, beetles, moles, termites and so forth. Each is seeking its sustenance in this rich zone of interaction. Each modifies the material it encounters and leaves some different material behind. The most important part of the A horizon, concerning growing plant activity is that concerning roots. Plant roots are the interface between the living, organic world and the mineral world. Concerning plant bio-mass, in forest soils 15–25% of the plant is found in the root mass while up to 95 can be found in the root systems of prairie plants (Gobat et al., 2003, Sect. 4.1). One normally thinks of dead leaves, stems and twigs as representing the organic inheritance of the plant in the A horizon, but this is not the case for prairies whereas it is for forests. Thus a variable portion of the organic matter in the A horizon comes from aerial parts of plants. Roots not only leave behind an organic inheritance but throughout their active lives they produce exudates, organic compounds of varying complexity which are rapidly recuperated by bacteria and micorrhize for sustenance.

Within the surface layers bacteria, fungi and other active bio-agents work on the material or root or aerial plant origin to extract sustenance which is not available due to lack of an ability to capture sunlight and transform it into usable organic compounds. This is the beginning of symbiosis. Given the variable origins of the organic material in soils one would expect it to give rather different intermediate products of degradation depending upon the source material. In Fig. 2.6 we give a very general idea of the cycles of activity. One can consider that the bacteria are a major factor in the transformation of detrital organic material, along with fungi of various sorts and more developed or higher order organisms such as worms, termites and so forth. The most important action is bacterial, at least as that considering the clay – organic interface. The bacteria form two sorts of organic material from the detritus; one is a complex, less oxygen – rich organic material often called humus. The second is a series of smaller molecules, often rich in polysaccharides, which is easily attached to clays. The evolution of the composition of organic matter in bulk is such that with depth the ratio of carbon to nitrogen changes. This is a measure of the maturation of the humic matter. The mineralization of organic matter includes the production of $CO_2$ and nitrogen compounds. The ratio of change (C/N ratio) is a measure of this humification process, where the nitrogen is left behind and the carbon released to the atmosphere through bacterial action. The ratio of C/N is a function of the starting material and maturation processes which are driven by bacterial action and hence temperature. In a sequence of soils under different types of vegetation from the low Alps in France (elevations of 1,100–1,800 m) data from Mariotti (1982, p. 236) one sees the effects mainly of vegetation type, where the most carbon – rich ($C/N = 30$) is from a larch forest and other soil profiles dominated by grasses of different types have lower initial C/N rations (Fig. 2.16). The acidity varies with vegetation type and average temperature, ranging from near 7 under grass to 4.3 under larch. Although the initial C/N values are quite different, the end product of bacterial action is to give a rather constant value at depth, below the active A horizon.

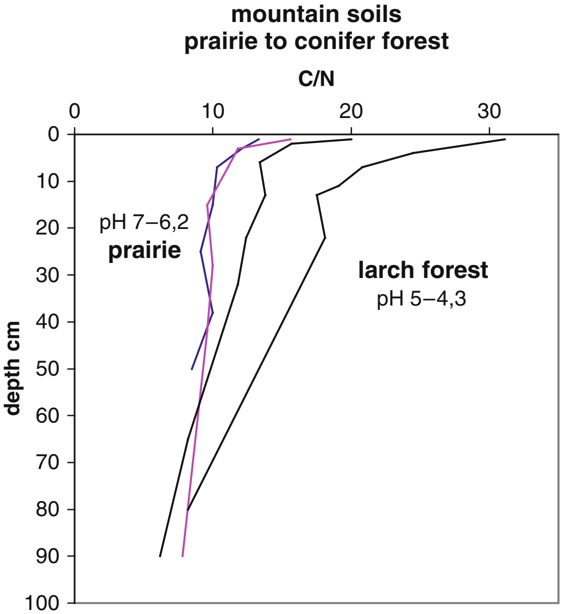

**Fig. 2.16** Relations of soil C/N rations and pH and depth for different biomes in plateau mountain profiles (data from Mariotti, 1982)

This concordance of elemental values with maturation (bacteria action) suggests a driving force in the same direction that enriches the humic matter in nitrogen relative to carbon. Since the C-O bond is easier to break than the different C-C and nitrogen bonds, bacteria tend to use the most efficient and energy saving path to obtain their necessary energy levels.

On the other hand the low molecular weight materials exuded by bacterial do not contain much if any nitrogen. This material is highly reactive in the soil zone. However current debate suggests that the lower molecular weight material could be a major source of clay linkages along with or instead of the humic matter as previously proposed although most past studies indicate a strong relation between humic and clay particles (Cheshire et al., 2000; Cornejo and Hermosin, 1996 for example). Some information suggests that smaller molecule root exudates can affect clay organic interaction greatly (Oades and Waters, 1991). Puget et al. (2000) indicate that young (i.e. less humic) organic matter is responsible for aggregate formation and hence clay – organic interaction. Since these smaller molecules are more carbon – oxygen rich, and hence more easily reduced by bacteria, their longevity should be shorter but is a subject of much conjecture and research effort.

The activity of roots, by the products of exudation is extremely important to the functioning of the A horizon. Root exudates are the fundamental mechanism of transfer of mineral nutrients from mineral to plants. Roots exude complex compounds, such as polysaccharides as well as simple hydrogen ions (see Gobat et al., 2003 for example). Hydrogen for potassium ion exchange would be the most simple means of transfer of mineral to plant. The end result is the acidification of the soil itself. However, many soils are near neutral in pH, especially grasses and prairie soils. Thus although the intense root activity of such plants emits much acid, the overall balance of resident and evolving organic matter and other substances maintains a near neutral soil. However conifer forest soils are most often in the decidedly acid range, ranging from pH of 5 to 4. Soil acidity is than a multifunction phenomenon. In general acid soils are associated with higher dissolved alumina content which is toxic to grasses and other prairie plants. One finds that organic rich soil are often associated with drainage problems or more frequently with cold and wet climates. These soils contain much alumina in solution. The acidity and organic content can be attributed at the same time to climate and the plants which grow in the soils. The lower the average temperature, the slower the development of the soil and hence the evolution of the organic matter present.

#### 2.3.5.1 Development of the A Horizon

Organic Matter

The evolution of the deposed organic matter and internal root material in the A horizon accumulates and evolves to a steady state rather rapidly under conditions of temperate climate. The data from poldered prairie soils (Fig. 2.10) shows a typical "S" shaped curve due to biological action. The thickness of the organic horizon increases until it reaches a more or less stable thickness after about 800 years. Here the initial materials are soil type clays deposited in salt marshes which are grazed as prairies in polder episodes from the year 1,058 until the late 19th century. The deposition and humification process create the humic or organic – rich layer typical of grasslands. According to the schema presented by Birkeland (1999, p. 225) such a development is relatively rapid compared to other types of soils developed under different climate regimes and hence biomes. The time necessary to develop a "steady state" in an alteration profile would be on the order of magnitude of $10^2$–$10^4$ times to reach alteration equilibrium of the silicates compared to the development of the organic A horizon. This is to be expected in that the biological processes concerned are much more reactive than those typical of silicate minerals.

Organic matter production by plants and its residence in soils are not necessarily related. A major factor is the biologic activity which tends to mineralize this material and release it in the form of gases to the atmosphere; $CO_2$, nitrogen compounds and water. Jenny (1994, p. 149) indicates an exponential relation as a function of temperature for the amount of organic matter in soils in the A horizons across the Central United States where the mineral substrate is very similar, loess materials and where primary production of organic matter by the plant regimes is similar. Cooler climates promote the conservation of organic matter in both prairie and deciduous forest soils. He gives an empirical rule that for each decrease in 10°C in average temperature the conserved organic matter increases by 2–3 times. The conservation of organic matter is more critical in the tropics where very little if any humic material is present despite a very high primary production by the plants.

Typically, the most organic – rich soils are found in cold climates, tundra and others, while the most organic poor soils are found in the tropics. Bacterial action, driven by temperature is the dominant factor in the conservation of organic matter in the A horizon of alteration profiles.

The A horizon is the zone where organic matter is decomposed into different organic chemical components but it is also the zone where mineral elements are released to the mineral – organic interface. Notable are phosphorous and potassium. Potassium is only lightly held in the plant material, being rapidly released upon deposition. It is essentially re-cycled from plant accumulation into the soil solutions. Phosphorous is more difficult to follow in its specific interactions but it is clear that it too is re-cycled in the life cycle of the surface. Ammonium or nitrogen compounds are also released in a soluble form into soil solutions by bacterial action in the soil zone, and hence are also re-cycled. However the contribution of bacterial action in the soil zone associated with plant roots is of very great importance to its availability for plant growth.

### Clays

Jenny (1994) gives data showing the relationship between clay content soils (horizons to 100 cm depth) as related to temperature. The relationship is the reverse to that of organic content. The higher the temperature, the more clay present in the alteration profiles formed on basic igneous rocks. In the samples studied, coming from temperate climate areas, the rainfall seems to be less important or directly applicable to a determination of the alteration of rock to clay. The soils studied are from non-glaciated areas and hence the profiles were probably forming actively for hundreds of thousands of years. Nevertheless the relations of temperature seem to be very important for the conservation of organic matter and production of clays, in opposite relationships. However Jenny (1994) reports the relationship between clay content and rainfall for A horizon samples from iso-thermal (average temperatures) situations in loess soils. The clay content is less clearly related to rainfall. Therefore one can say that both temperature and rainfall will be active functions of clay formation in alteration sequences but the temperature factor, fundamental to plant activity, is more dominant than the water – rock interaction factor (Fig. 2.17).

Clay formation is often difficult to follow in that the fine grained material is moved from the site of its initial formation to lower levels in the case of the upper horizons. Depending upon the type of plant regime, the local geomorphology (slope of the area where the profile is formed) soil clays can be moved easily. The clay content of the A horizon is variable depending upon the source material upon which the profile is formed. For example loess tends to have a strong component of clay removal for example due to its strong fine grained sand content. These effects give a high variability of the clay content depending upon local conditions. Typically the clay content is developed at a much slower rate than that of the organic matter, several orders of magnitude in most cases.

However, generally, clay content is lower in the A horizon than the B horizon due to the transport of the fine particles by aqueous solutions. The A horizon, that of plant – mineral exchange, is dominated by plant roots and accumulated organic matter. Clay content is variable but usually lower in the A horizon than that just

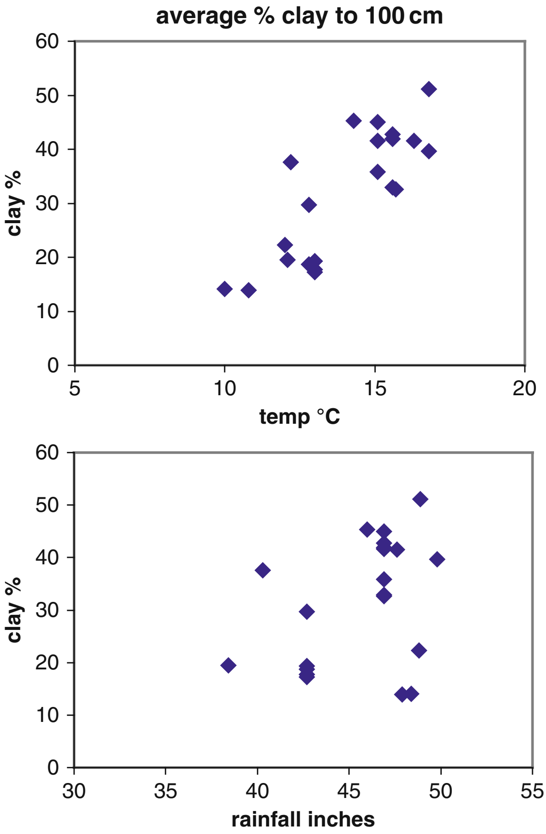

**Fig. 2.17** Data from Jenny (1999) concerning clay content to 100 cm depth in soils from central United states as a function of climate variables. It appears that there is a better correlation between temperature than rainfall suggesting that plant activity, which is temperature driven, is more important than the rainfall or water – rock interaction parameter

below, where root activity is less. The chemistry of this surface zone is dominated by the influx of mineral elements coming from the degradation of plant materials and the acids developed by organic transformations or root exudates, either organic acids or hydrogen ions.

Since rain input tends to move elements either dissolved in solution or in suspension (clay particles) the overall tendency is to lose the chemical elements in solution which control the stability of clays and the availability of plants to recuperate such material. One means of retaining the nutrients present in the soils is to stabilize the clay content.

## 2.4 Soil Classifications: Descriptions and Factors Affecting Alteration Profiles

Our discussion here is centered upon an idealized soil and alteration structure or a surface, A horizon, where plant and biotic activity is dominant. Below this layer, which is generally a true layer, one can find a zone of clay accumulation, the B horizon, where soil solutions have moved newly formed clays downward. Below the B horizon is what is generally called the C horizon where rock and mineral debris are mixed with clays formed from water – rock interactions. This covers the saprock and saprolite zones. The boundaries of the B and C horizon are often irregular and the relations between altered material and the bedrock are most often irregular depending upon the passageways tht give access to altering soil solutions. The assemblage of or at times absence of one or the other zone is used in the soil classification or description system. It must be remembered that the classification system is used as a short hand for an alteration profile description. This saves a lot of time in that soil and alteration profiles are often complex and quite varied from one site to another. It is necessary to identify rapidly the salient features of these natural objects in order to deal efficiently with them.

### *2.4.1 Classification*

The most widely referred to classification system is that of the United States Department of Agriculture Soil Survey Staff (1975). There are others, notably Russian, Chinese and European but in general most often one tries to refer to the categories determined in the USDA system. The concept is based upon essentially a three tier system of soil Order, Suborders and Great Groups. Further details observed in the field can lead to qualifying terms which further modify the nomenclature. In usage in the United States, one often has a type soil defined for an area, with a specific name which embodies the descriptive nomenclature in a single word. The discussion below is based upon the work in Birkland (1999), Jenny (1994), Akin (1991) and Duchaufour (1997).

In the USDA system there are 11 Orders, 48 Subgroups and 230 Great Groups. Usually a description name is based upon a combination of subgroup and Great Group terminology. It is clear that such a complex system of nomenclature reflects the extreme complexity of the objects described. Soil formation and the resulting alteration profiles depends upon many factors. The major factors are

Climate
Vegetation
Bedrock
Duration of the alteration process
Superposition of materials: wind blown, landslide or slump movements, stream carried, etc.

Objects in a five dimensional system are difficult to describe succinctly.

The Orders can be classified in general as being dependent upon:

| | | |
|---|---|---|
| Climate | *Aridisol* | desert climate |
| Vegetation | *Histosol* | organic rich accumulations (bogs, swamps, wet and cold climate vegetation) |
| | *Mollisol* | prairie |
| | *Alfisol* | deciduous forest |
| | *Spodosol* | conifer forest |
| Mineralogy | *Vertisol* | smectite – rich soil (expanding and contraction properties very important) |
| | *Andosol* | amorphous minerals dominant wher the bedrock is highly vitreous (volcanic rocks) |
| Duration of alteration | Entisol | little alteration visible |
| | Inceptisol | rapidly changing soil, hence young |
| | Ultisol | old, evolved soil |
| | Oxisol | strongly oxidized and hence old |

The Suborder classification of each Order describe various general properties of the alteration profiles and the Great Group designations further define certain properties often more detailed such as color, humic content, and so forth. Terms concerning source rock type can be found such as sammitic (sandy), rendzina (calcareous rock) or andic (based upon glassy rocks). Rather rarely one finds specific reference to vegetation type although a certain number are generally assumed to represent plant regimes, usually under temperate climatic conditions as seen in the Order classifications above.

The general conditions of alteration are determined by climate which is rainfall and temperature. The frequency of rainfall can determine very different climates which combined with temperature conditions the type of vegetation growing on the alteration profile. One can find strikingly different climates within short geographical distances by climbing a mountain range. These changes in climate are roughly the same as one finds in going from the lowest part of the area under consideration and the change to tundra or polar climates as outlined in Sect. 1.2. However there are also significant changes in the structure of a soil and alteration profile as a function of time. Birkeland (1999, p. 47) outlines the changes in nomenclature and hence physical – chemical properties of soils as a function of time. One moves down the table below as a function of time:

Entisol
Inceptisol
vegetation – dominated soils types (Millisol, Spodosol, Alfisol)
Ultisol
Oxisol

In general the initial stages show a small but increasing soil (A) horizon as plants establish themselves but in many cases the organic horizon is confounded with the other parts of the profile (C). The formation of an A, B, C structure where soil is distinct from the underlying material indicates a certain maturity (Inceptisol). Overall, the thickness of the A horizon reaches a stable thickness with the B horizon increasing and then the C horizon can dominate is conditions of tropical or Ultisol weathering. Generally speaking the overall alteration profile loses alkali then alkaline earth elements during the formation of clay minerals, especially of the 2:1 type. Movement of the new minerals is the dominant factor in re-distribution of elements in the profiles. As alteration becomes more intense, as a function of time or climate (increased rainfall) there is a loss of silica to produce clays of lower silica content such as kaolinite, and in the extreme oxy-hydroxides are present such as gibbsite, aluminium hydroxide, and iron oxide minerals in different hydration states. The overall tendency is a convergence on the elemental concentration of Al and Fe. These elements hold no interest for plant activity.

This is the classical view of chemical alteration and clay mineral formation during alteration and soil formation.

For each stage of development in the alteration sequence, when there are differences in starting material (substrate), climate and vegetal cover one finds differences in color, humic layer content and grain size distribution in the different parts of a profile. These differences have a terminology used to describe the visible changes (color or texture) or the differences in grain size distribution. Thus the terminology is a mixture of genetic factors, climatic factors and physical appearance. All is necessary to describe and classify the great variation o soils which the product of many variables in natural settings.

### *2.4.2 Results of Soil Forming Processes on the Structure of an Alteration Profile*

The major processes of soil formation, plant – silicate interaction and water – rock interaction have a strong tendency to stratify the profile into zones where one or another of the formation processes is dominant. This gives the alteration profiles their "horizon" aspect. Such displacements and concentrations are due to water movement in the profiles.

#### 2.4.2.1 Downward Movement of Clays and Dissolved Material

The interaction of water and rock or silicate materials is essentially one of dissolution in the first stages of contact where rainwater is very under saturated with possible dissolved elements found in silicate minerals. One of the dominant facts of the initial weathering in saprock and eventually saprolite zones is a loss of density (Velde and Meunier, 2008, Chap. 4) which indicates loss of solids from the rock as they are dissolved in the percolating solutions. This is evident from the observations at the base of the alteration profile but one can expect some of the same action to occur at the surface where the initial contacts are made, in the A horizon.

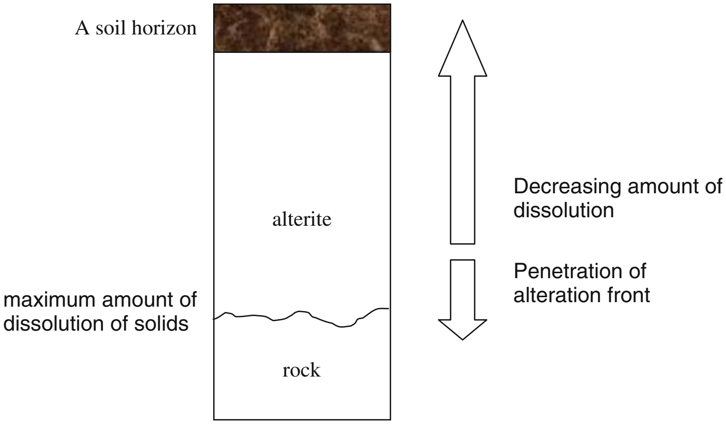

**Fig. 2.18** Representation of an alteration profile indicating the relative amounts of material dissolved from the silicates as a function of position (*vertical*) in the profile. The alterite zone, interface with alterite (clay) rich and un-altered rock is the source of most of the dissolved material due to mineral transformations. The alteration front (saprock zone) descends in the profile as a function of time

Thus the overall amount of material will decrease throughout the alteration profile. However, since the clay minerals developed by the alteration process in the saprock zone should be more stable in the surface environment, the amount of dissolution can be expected to be less than at the rock alterite interface. Therefore one can say that the effect of dissolution will be less important as one goes up in an alteration profile (Fig. 2.18).

However, it is very well known that the new clays are liable to be transported in the pore fluids as they descend in the profile. The deposition of these clays forms the B horizon. Thus although the amount of dissolved materials decreases towards the surface of the alteration profile, a significant amount of solids can be transported downward (Fig. 2.19). Soils developed in the Great valley of California show and increase in clay content below the surface horizon at depths of 50–75 cm as a function of the age of the profile (Foth, 1990, p. 16) shown in Fig. 2.20. This is the developing B horizon. The presence of a developed B horizon enters into the definition and nomenclature of soils.

Under certain chemical regimes in the A horizon induced by the chemistry of the decayed organic matter in the form of litter, a strong chemical dissolution can occur just below this horizon. This is the E horizon developed under acid humic conditions in the A horizon. Essentially every thing is dissolved except the chemically inert quartz grains, leaving a sandy layer in the soil alteration profile. Curiously the clay content of the A horizon is typically greater than that of the E horizon (see Birkeland, 1984, Fig. 10–4) for typical clay content profiles). Since the dissolution of clays is responsible for the E horizon's lack of this material, one wonders why the clays persist in the zone where the acid chemistry is produced, the A horizon. We will treat this subject later in Sect. 5.2. The overall result is the production of another

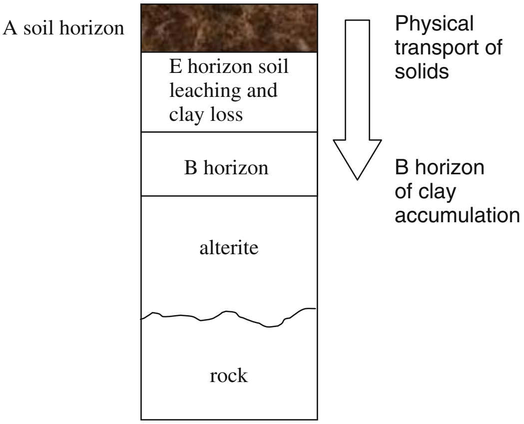

**Fig. 2.19** Schematic diagram of the physical movement of clays from surface A horizons to the new, clay – rich B horizon. Under acid conditions one often finds a clay depleted zone, where sand is predominant; This is the E horizon due to chemical leaching and clay transport

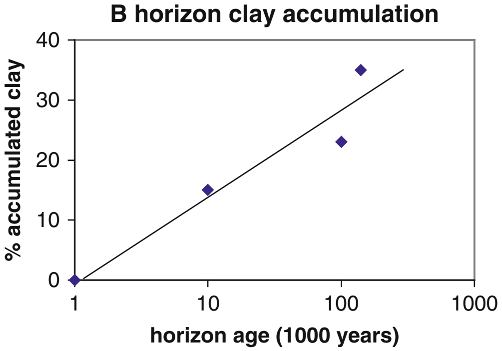

**Fig. 2.20** Illustration of the concentration of clay minerals through the transportation due to pore water circulation in the soil profile. Data from Foth (1990) on clay accumulation in soils of the Great Valley CA USA.at depths near 50 cm

specific soil horizon, the E horizon which is due to chemical dissolution (Fig. 2.15) Again the presence of a sandy layer below the B horizon leads to descriptive terms and classification in soil terminology.

The movement of dissolved material or solids carried by the vector of downward moving solutions in the alteration of rocks gives rise to different zones or horizons which have specific chemical (notably pH) and mineralogical – textural features. The initial movement of clays enriches the B horizons with fine materials while the dissolution of clays and oxides from the E horizon gives rise to a more coarse grained horizon.

Data from Birkeland et al. (2003) indicate that the development of the B horizon is gradual being barely noticeable in Colorado piedmont soils near Denver CO after 10,000 years of formation and quite apparent after 140,000 years of soil – plant activity.

Some variations can be found, according to the type of plants present where a soil is forming. Graham and Wood (1991) indicate that the activity of earthworms can significant enrich the A horzon in clay sized particles compared to those under pine. This is a counteraction to the normal downward movement of the clay fraction.

#### 2.4.2.2 Upward Movement in Alteration Profiles

Carbonates

If water in pore solutions brings clays downward to follow fluid flow, the upward movement of dissolved matter during soil moisture evaporation and capillary movement upward can influence the mineralogy of the profiles to a large extent in arid climates. Two instances are considered here, those of semi-arid steppe or grasslands and more arid evaporitic soils. In the compilation given by Jenny (1994, p. 122) one sees that there is a zone of carbonate accumulation, probably due to capillary transport upon soil drying, that is closely related to rainfall (climate) for loess soil in the Midwestern United States. Under conditions of low rainfall (25 cm/year) carbonates can be found in the soil portion of the profiles, i.e. at 25 cm or so. As annual rainfall increases to 100 cm the depth of carbonate accumulation increases to around 175 cm. The mechanism of carbonate accumulation is not all that well detailed but it can be described in a general way as shown in Fig. 2.21. In general the soil zone, through the activity of plant root exudates and microbial action on plant debris, create a slightly to decidedly acidic environment. The pH at the surface is typically lower than at depth in soil profiles. Jenny (1994, p. 134) demonstrates that the

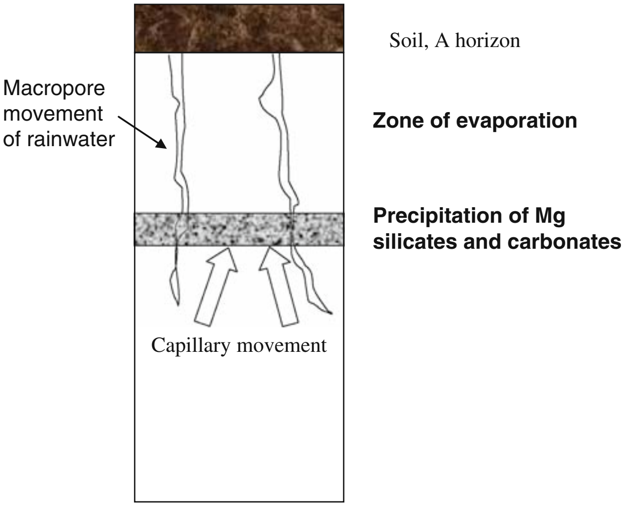

**Fig. 2.21** Schematic representation of the effect of strong evaporation from a soil surface. Macropore movement of rain water moves dissolved material deep in the profile. Subsequent surface evaporation brings capillary water towards the surface but at a certain, variable depth in the profile the capillary water and minor pore water becomes strongly concentrated in dissolved material which precipitates to form new phase in the C horizon, usually of high Mg and Ca concentrations forming carbonates and magnesian silicate clay minerals, sepiolite and more often palygorskite

surface pH of soils on loess in the Midwest region of the United States follows rainfall, pH is highest at lowest rainfall and lowest as rainfall increases. Then one can deduce that the relation of the depth of carbonate concentration is related to rainfall, but more directly to the plant activity which is directly dependent on rainfall. The more plant material, the more acidic the soil, and the thicker the soil (organic zone) will become. Here it is evident that the relations of movement of dissolved mineral material (Ca ions) is largely governed by plant activity.

#### Magnesium Silicates

A more striking case of elemental transport is that found in soils of desert or arid conditions. These soils form magnesium – rich silicates at a horizon well below the surface. These are often called caleche or, when significant carbonate is present, calcrete soils. A summary of their occurrence is made in Velde (1985). In these soils the organic horizon is small and thus not associated with the movement which controls the chemical factors associated with the deposition of the new minerals. The new clays occur below the B horizon of clay transport, and are well within the C horizon (Vanden Heuvel, 1966). The materials which enter into the active system are those of dissolved elements in aqueous solution and the clay minerals in the alterite horizons. Most often the clay sized material in these horizons is smectite and kaolinite – rich. Therefore the clays present contain a significant amount of alumina as well as silica. The presence of a strongly expressed carbonate horizon indicates that there is a strong effect of evaporation, concentrating the dissolved elements in the soil solutions. Along with the carbonates one finds magnesium silicates, which are not stable in the soil, organic, horizon (Millot, 1964). The dominant mineral is palygorskite, the most aluminous of the magnesian silicate minerals. Here on can suspect that there is a dissolution – precipitation process which is necessary to convert the phyllosilicates into the chain silicate palygorskite structure (see Sect. 4.1.6 for further details). The important point here is that the movement of dissolved materials can be stopped, by capillary action of soil solutions which move upward and are concentrated in the upper portion of the humid zone of the soils which is well below the soil zone, in the C horizon (Fig. 2.21). Such a zonation is again produced by movement of dissolved materials in the alteration process.

### 2.4.3 Summary

The development of soils and alteration profiles is one of displacement of material. The salient characteristics of soil – forming and alteration processes is the re-organisation of the materials present at the surface which have or are coming into chemical equilibrium with the chemistry of the atmosphere, i.e. slightly acid, unsaturated rainwater and the products of destruction and mineralization of organic matter. The two agents of change are those of rain water and the by-products of organic activity. Whether or not plants and microbial agents alter directly the silicates present or whether the rain water comes into contact with the unaltered and unstable rock minerals, the transformations are toward hydrated phases, either silicates or hydroxyl-oxides. The action of this alteration is one of homogenization of the mineralogy in zones roughly parallel to the surface of the system, the air – solid interface. Of course irregularities in rock competence (fractures, changes in mineralogy, etc) will create non-parallel alteration zones but overall the changes are in zones which can be described and used to identify the processes and origin of the different materials and the altering agents. The pedologic nomenclature is in fact a method used to describe the chemical forces acting on a given type of material over different periods of time. The natural system has several variables and hence a relatively large number of descriptive terms are necessary to adequately describe a given result of these factors.

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# Chapter 3
# Physical Factors Affecting Soil Profiles: The Three Dimensional Aspect of Plant – Mineral Interaction: Displacements

## Contents

There is an age old maxim: what goes up must come down. It is no less true for mountains and high land masses. As tectonics attempt to shorten the crustal distances making mountains arise, the action of rain, wind and gravitation are designed to put the mountains back in their place. The natural atmospheric forces tend to level the surface of the earth which results in a filling of the oceans, at least at the borders of continents. These actions pass by a destruction of the structure of the rocks making up mountains, either by physical means or mechanical ones so that the smaller pieces can be transported to a situation of lower gravitational potential.

Soils, plant – silicate interaction, are developed upon altered rock material. However, if plants are not present, the altered rock material does not stay in place but is swept to lower level aqueous deposits by streams and rivers into lakes and seas. Thus plants stabilize the material produced by water – rock interaction. Without plants, there is no soil development if one considers that the definition of a soil is the presence of an A horizon. Nevertheless, despite the fixing power of plant regimes and the formation of soils, superficial alteration materials find their way

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_3,

eventually into aqueous driven deposition areas. Given this, it is useful to look at the different aspects of the displacement of alteration materials and their relationship to the forces which move them as well as the ways that plant regimes fix the surface materials. It is very easy to understand that a tree cannot develop well without a certain root – friendly soil zone where some moisture is kept and nutrients can be transferred outside of rainy periods. Most plants develop in soil (silicate alteration products and organic matter). This chapter is designed to help one understand the important points in these relations.

## 3.1 Movement of Clay and Soil Material

The soil surface is the source of much of the material attributed to erosion. One initially thinks of the physical displacement of clays and finer materials by surface run off. However there is a variety of displacements which can be classed as erosive. Landslides, slumping of soils on slopes and clay displacements within the soil profiles all contribute to the movement and re-making of surface soils. All of these processes contribute to a construction of a new material at the surface which plants colonize and re-model to their needs. Each time a landslide occurs, a new soil and alteration sequence is developed on the old surface which has lost its mantle of fine grained material. Also, new profiles and plant regimes are developed on the displaced material where it has settled for different periods of time. The surface of the earth is in continual motion, and plants are motors or brakes on this development.

In fact for a geologist, there is nothing more normal than erosion. Sedimentary rocks are largely the result of the physical transport of fine grained or other material from mountains or upland to deposits in large bodies of water. This is the way the largest part of sedimentary rocks form. Further, it is clear to all geologists that without erosion one would not be able to study the interior of the earth, at least the upper several kilometres. Mountains are created by compressive forces which push rock strata upward to be dismantled at various rates and by different means. This presents the depths of the earth to the inspection of geologists. Volcanoes are a slightly special case, being composed of molten rock which rises rapidly to the surface, but they are affected by the same levelling forces as are tectonically formed mountain chains. Inevitably, these high edifices are all brought to or near the level of the sea. Hence there is nothing more normal, in the long term, than erosion. Further, the transport and accumulation of fine grained material along rivers and sea coasts, clays and silt – sand materials, is the matrix for much of traditional farming. Most of the initial sites of man's agricultural activity have been on secondary deposits of soils transported by either water or wind action. Stream banks, flood plains, marsh areas and loess plains were sought by the first agricultural groups where soils were easily cultivated and water resources plentiful.

In a very general way one can view such displacements, due to the forces of gravity and accentuated or aided by rainfall, in the context of a hill side (Fig. 3.1). The high ground is usually relatively densely covered by vegetation, while the slope is less so. Along the slope one finds displacement of material, and hence erosion. At

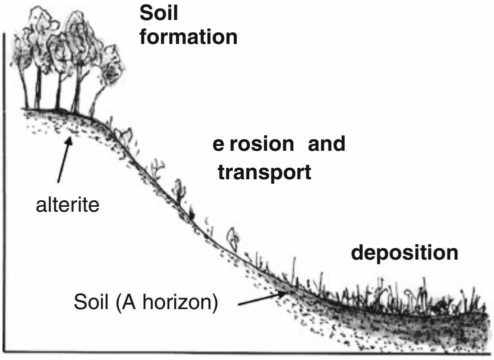

**Fig. 3.1** Diagram indicating the different zones of surface alteration and accumulation on a typical semi – arid savanna type landscape. The alterite is formed on the stable uplands where plants are well situated to prevent displacement of surface, soil, material. Erosion, i.e. physical displacement of material, occurs on the slopes and accumulation of soil material occurs on the *bottom* land areas. The material present at the base of the slopes is a composite of old alterite and newly accumulated soil material coming from areas of higher altitude

the foot of the slope one finds a zone of deposition. There is in general a contrast in the type of vegetation which occurs in the different parts of the profile. The uplands show a developed zone of alterite and soil, The slope has a small extension of these zones while the foot of the slope shows a zone of accumulation of the fine grained material which is missing from the slope. The soil development is usually different, being thickest at the foot of the slope. Differences in plant regime and displacement of material lead to these differences. The end result is a strong inhomogeneity in the development of soils and plant regimes.

This being the case it is useful to understand the relations between the movement of materials at the surface and plant actions which affect them.

## *3.1.1 Movement of Clay Particles Within the Soil Zone: Internal Loss of Material*

### 3.1.1.1 Translocation of Clays From A to B Horizons (Local Vertical Transfer)

The movement of clays developed in the A horizon by movement in pore water solutions has been outlined in Sect. 2.3. The physical movement of clays is effected by water movement where the small clay particles are held in suspension by Brownian motion through thermal agitation. For various reasons, the velocity of water movement lessens, often due to a greater density of the materials in lower parts of the alteration profile below the soil horizon. There are fewer pores and crack passage ways in deeper parts of alteration zones. The soil horizon is characterized by a relatively great amount of pore space through biologic action. Earthworms, moles and plant roots create open spaces in the altered silicate material which allow water to pass through and be replaced by air in drier periods which is necessary for healthy plant growth for non-aquatic species. These spaces are the preferential passages for pore water and the vectors of clay transport. As one moves downward in the alteration profile these spaces are less frequent, pore water movement slows and clays are deposited. These materials form what pedologists call cutanes, zones of oriented clay particles which fill pore space (Fig. 3.2). The accumulation of clays forms the B horizon, where clay accumulation is the primary and diagnostic characteristic. Loessic deposits fine grained deposits due to wind transport (see 3.1.3) show a typical accumulation of clays below the A horizon forming the new, clay rich B horizon as a function of time (Ruhe, 1984). The time factor for this accumulation is not negligible, tens of thousands of years. This time factor is in between the soil clay (bio-influenced) and water rock interaction time frames (Sect. 1.2). The case of clay

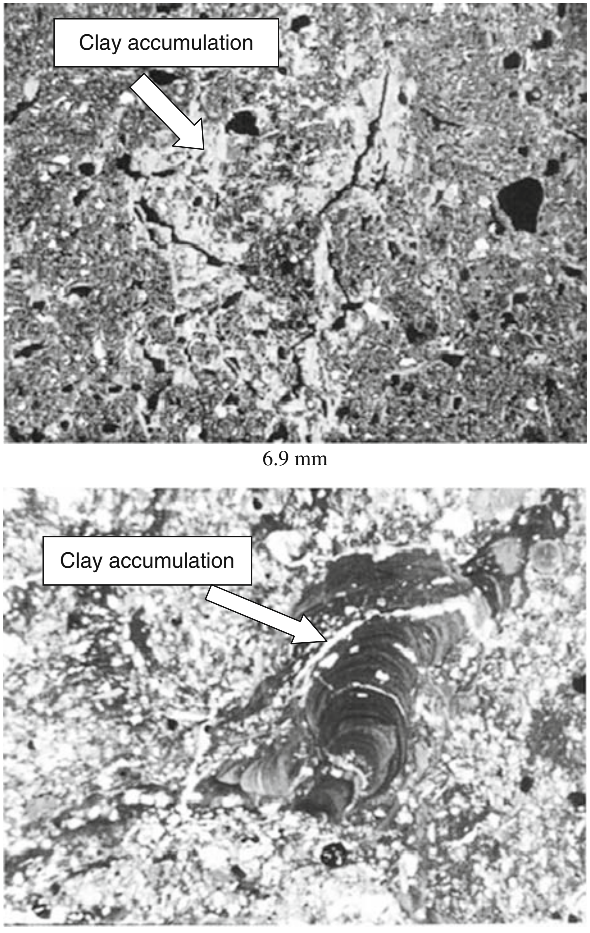

**Fig. 3.2** Micro photographs of soils where clays have been transported within the alteration profile and deposited at a lower level. The accumulation of clays is called a cutane. This material follows pore passageways in the soil structure

migration in loess is probably one of the most rapid in that the basic altered material is fine grained where much of the material is quartz sand and not susceptible to chemical or physical change, hence many small passageways are immediately available for clay transport around these grains.

#### 3.1.1.2 Translocation of Clays Within Profiles Along a Sequence of Soils: Down the Profile and Down Slope Transport of Clays Within Soils: Lateral Displacement

Movement within soil – alteration profiles is extremely important under specific circumstances. The local movement of clays down from the A organic horizon to that just below, the B horizon, is a very well recognized phenomenon. However the lateral movement of these materials within the alteration zone is less well recognized and reported. Down hill movement of clays in the subsurface can be an important factor in the redistribution and accumulation of matter in alteration zone. This concept enters into the ideas of soil Catenas (see Birkeland, 1984, p. 235). Lateral movement of clays by gravity and fluid movement within the alterite can concentrate clays in toe slope areas while the slopes themselves are more clay – poor and the uplands above the slope much more normal concerning the vertical movement of clays into the B horizon. It is clear that there is often lateral movement of the clays in the materials on the slope. The concentration of clays at the bottom of slopes gives rise to many different characteristics which affect the vegetation through differences in water retention, and texture. Basically, grasses can do much better in a clay – rich environment, more so than trees especially in arid or semi – arid climates. This is one reason why one finds trees on the uplands, shrubs on the slopes and grasses on the bottom lands in semi – arid areas. Frequently the slopes have thin soils and shrub vegetation. The accumulation of clay as a function of position in the soil catena in Mediterranean climates can be seen in the data given by Paquet (1977). Different effects occur in such landscapes, not the least of which is a change in clay mineralogy as a function of position in the topographic sequence. In general, illite and kaolinite are found in the uplands areas, kaolinite and oxides on the slopes and smectites dominate in the lower part of the topography. The change in clay mineralogy is most likely not a function of transportation but one of plant – soil interaction favoring different types of clays according to the vegetation present (see Chap. 5). One result of clay transportation within the soils in a lateral sense is that the clay content accumulated down slope tends to decrease drainage and hence to change the parameters which influence the type of vegetation present.

In more arid areas, the decrease in drainage favors the implantation of grasses while more drained soils, upland favors trees and slopes shrubs due to the unstable situation of the materials at the surface. In more temperate climates, one finds more trees in the bottoms (stream valleys) and grasses on the uplands. The vegetation sequence is reversed.

One very important, and very simple observation that can be made is that in almost any stream, small to large, during a period of constant rainfall heavy or light up to soil saturation, one finds clay sized particles in the water. Stream water tends to be brown or yellow during periods of constant rainfall, colored by clay particles. This is the case even in areas of pastures or grasslands where there is little slope to the landscape and where the vegetal cover is maximal and surface runoff is minimal. The reason one finds these clays in the streams is that they are transmitted through the soil profiles themselves into the water table and then into the streams. It appears then that a significant amount of clay material is evacuated from soils within the structure of the alteration profile itself. This clay material is essentially suspended in the aqueous medium by Brownian motion due to its small grain size and will hence be transported long distances before deposition. Often such material ends up in oceanic, salt water bodies where the electrolyte (NaCl) promotes flocculation and deposition along the shore lines or on Continental platforms.

An example of such transport of clays within the profile is given in Fig. 3.3 (data kindly supplied by B Zhang, Univ Nanjing, China). The example is found at the Red Soil Station of the Nanjing Academy of Science Soils Institute. The slope is less than 5 m from hill top, the upland forest site, to an accumulation on the edge of a rice paddy which is an old stream bed. Diagrams of clay content show an accumulation in the forest site at near 50 cm, typical of B horizon accumulation while in the slope site, there is no accumulation and in the toe slope position one finds a stronger accumulation near 1 m depth.

It is important then to consider that a non – insignificant portion of clay transportation is made within the soil and alterite profiles where the fin grained material is taken in subsurface transport into streams and thus into areas of deposition.

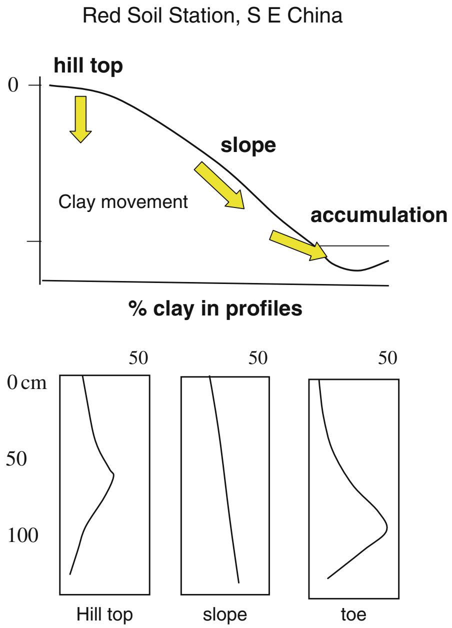

**Fig. 3.3** Illustration of a situation of low topographical change where clays are seen to accumulate in the upland profile on the hill top under forest conditions, clay movement within the alteration profiles is indicated by a loss of the B horizon of accumulation on the slopes and a strong accumulation at the base of the slope. Data courtesy of B Zhang, Univ of Nanjiang Department of Agriculture and Director of the Chinese Academy of Sciences Red Soil Station in Southeastern China

### *3.1.2 Erosion of Fine Grained Materials From the Surface and Transportation by Water*

A very large amount of work has been done on soil erosion, to say the least (see Toy et al., 2002 for example). This has been a subject of intense research for several decades and a known problem, especially in agricultural areas, for some time although classic texts on agricultural practice in the first half of last century did not seem to be preoccupied with the problem (Cox, 1925 for example). Severe climate change, relatively short term, in the 1930s brought about an awareness of the strong consequences of certain managerial practices on grasslands in the United States. A bit more recently, Xu (2005) has demonstrated the relation between forest cover (density) and rainfall on erosion of soils on the Chinese loess plateau. Even though this area is highly modified by human activity, the effect of plants, forests in this case, is primordial in the displacement and retention of soil materials due to erosion processes. Thus not only human intervention as agriculture but also more natural vegetation such as forests can have an important effect on the loss of surface material by erosion. Probably the greatest part of present day surface erosion is due to interaction of rainfall on cultivated land. However, under conditions of natural vegetation probably little surface erosion would occur in densely forested areas and humid grasslands. But in more arid areas of grasslands, shrub lands and sparse forests significantly higher amounts of erosion will occur. This was expressed by Langhein and Schumm (1958) in their observations on the non-linear relations between sediment yield (displacement of soils) and rainfall. The drier climate areas, those of sparse vegetation, the higher the sediment loads in streams compared to those areas with a greater vegetative cover.

It is difficult to say where the masses of sediments have come from which constitute the geological depositions in basins and the formation of sedimentary rocks found in materials of more recent geologic history, the Tertiary or Quaternary periods for example. Whatever the source, erosion of fine grained material certainly did occur, probably at a slower rate than in areas of intense farming today but it did take place in any event. There is no particular evidence that less deposition of sediments occurred at higher latitudes than those in more desertic parts of the globe. However climate has changed frequently and the further one goes into the geologic record the less information is available on this aspect of erosional history.

Given that the clay and silt fractions are the most generally affected by surface runoff, one would expect that they would be rapidly taken from their sources before being deposited. The smaller the particles are, the longer they stay in suspension in water and the further they will be transported. Typically near shore deposition in ocean basins is of fine grained, clay – rich material which eventually forms what are called shales by sedimentologists and geologists. The more the surface is covered by plants, especially grasses, the less surface erosion will occur. If the vegetation becomes sparce, leaving bare spaces open to rain fall influence, the greater will be the tendency to have surface run off and translocation of fine grained material. Numerous scientific journals are dedicated to this problem.

As mentioned above, surface transport is the most often studied and important aspects of erosion concerning agricultural effects. The action of raindrops falling on bare soil, which is especially important to studies concerning agricultural practices, is the initiation of the loss of soil fertility. The impact of a rain drop is such that it dislocates fine material making the way for further dislocation. As the matrix of a soil loses its fine materials, clays and silts, the larger grains are destabilized from their positions and become vulnerable to water movement (Fig. 3.4).

Once included in a moving rivulet of rain water, the clay and silt increase the density of the fluid and give more force to dislodge other material as it flows down slope. Of course erosion processes need a gradient to move material and the greater the difference in altitude, the greater the effect of the erosion. The phenomenon of surface erosion is one of increasing intensity as the system begins to increase in magnitude of the slope, rilling (surface movement) along plowed lines, becomes gullying (deeper erosion into the soils structure, often just to the bedrock) and eventually this leads to failure such as slumps and land slides.

Rain water surface erosion is greatest when the soils have no vegetative cover. In a natural state, i.e. without the intervention of agricultural man, arid areas of sparce vegetation are the most susceptible to erosion of this sort. However the normal agricultural practices leave the soil without vegetal cover for at least a part of the year in many climates and hence vulnerable to erosion. Even without such effects, plowed surfaces, the vegetal cover can be primordial in stabilizing soil material, as in the relations of forest cover and erosion on Chinese loess plains reported by Xu (2005). Basically, the more surface area covered by plants (leaves) the less erosion per surface area. This is simply due to the change in velocity of the rain drops as they encounter vegetal matter, diminishing the impact on soil grains.

Methods of countering or minimalizing soil erosion of agricultural surfaces are numerous, usually concerning questions of reducing pathways down slope (contour plowing) and stabilizing down slope movement by creating small retainers or vegetal zones along the contours (see Toy et al., 2002, Chap. 7). The most sure strategy overall is to maximize vegetal cover during periods of highest rainfall.

The distance of movement of materials originating from rainwater surface erosion is proportional to the size of the grains present. The clays tend to be carried the furthest while gravels will end up at the bottom of the local slope for the most part. Some of the material which finds its way into the rivers or streams will be moved

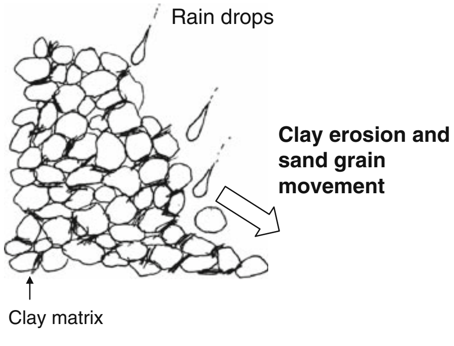

**Fig. 3.4** Illustration of the effect of rain, in the form of raindrops, on a clay – sand soil without vegetal cover. The rain loosens the sand grains by displacing the clay particles, which enter into the run off water moving the material into a water transport mode

yet farther due to the increases force of the flowing water, i.e. velocity and cross section of the flowing water. Also, the higher the slope gradient, the more material will be moved and the further it will be moved from its source. Therefore one can expect more surface erosion by water in areas of low vegetal cover.

### *3.1.3 Surface Erosion by Wind Action and Consequent Loess Deposition*

Wind action is similar to that of rainwater but it operates on much finer material. The capacity of displacement is a function of the viscosity of the moving fluids and water is then much more effective than air. However, wind erosion can be very important under certain climatic conditions. In the Continental United States one can divide the country roughly in half, east – west, the western plains being susceptible to wind erosion and soil loss while the eastern half is subject to water erosional loss (Toy et al., 2002, p. 9). Most of the arid areas north and south of the tropical rain belts are subject to wind erosion such as one finds in Australia, Africa, and China which are classic examples. These are the hot deserts (Obruchev, 1945). These are the areas of present day dust transport followed by satellite photography (see Prospero et al., 2002). In order for dust to be put into the atmosphere there must be a scarcity of plants at the present day surface and a relative abundance of fine grained material. Barren mountain tops do not produce much dust. However, the large and flat sedimentary deposits in arid areas formed by intermittent flooding and sediment transport are ideal producers of dust. Eventual sedimentation of this wind born material creates what is called loess. Displacement can be over relatively short distances, hundreds or over thousands of kilometres depending upon the energy of the events that put the fine grained material into the air. The pre-requisite for airborn transport is a lack of plant cover at the surface.

A general schema explaining the phenomenon is given in Fig. 3.5. Two pre-requisits are necessary, (1) a source of fine sediment which is eroded to given a water born deposition and (2) a low plant growth regime where wind erosion can occur because the surface deposits of clays are not anchored in a soil.

Several areas of today's land masses have strong imprints of past loess deposits. Most often one thinks of China where the process is very important, and even today 2 mm of dust is deposited annually in Xian, the ancient capital in western China. This is the equivalent of the A horizon of soils being renewed every 100 years. As far as one can tell the origin of the fine grained material is from sediments deposited in the great central desert areas. For the most part this loess is largely composed of illite and chlorite, typical low grade metamorphic materials (observations by the author for samples from west central China). These are the hot deserts (Obruchev, 1945).

A second type of loess is that of a cold origin where continental glacial outwash plains, periodically dried but free of vegetal cover, provided sources of fine grained material in abundance. These wind born materials accumulated over the last 2.4 million years or so (Catt, 1988). Similar material to that of the hot desert loess

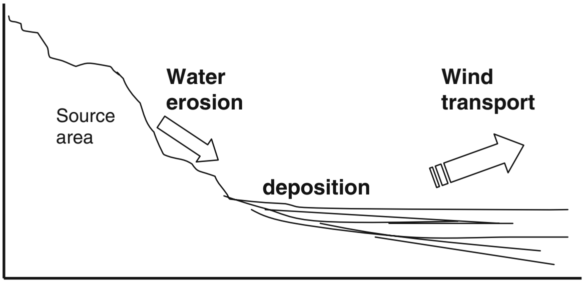

**Fig. 3.5** Schematic representation of the origin of loess. Water erosion moves fine grained material onto depositional areas, usually very flat and of a significant surface area, where the sedimented material is moved again, this time by wind effects moving across the flat, dry sediments. The principle factor of less displacement is the depositon on a flat surface where plants cannot establishes foothold either because of climatic conditions, dryness, or because the arrival of material is too rapid and each season produces a new sediment before plants can anchor the fine grained material

of China is found in sediments of the Po river delta and glacial sediment found on the shelf of North Eastern United States (Velde and Church, 1999). These are sediments originating from the most recent glacial epochs where outwash of fine grained material coming from sedimentary and metamorphic rocks was eroded by wind and deposited further from the glacial front. The same minerals, illite and chlorite, are often dominant in till and other glacial deposits in Northern Europe (Gillot et al., 1999, Teveldal et al., 1990).

However the clays in loess deposits in the United States and Europe (Burras et al., 1996; Ransom et al., 1988; Kuzila and Lewis, 1993; Jamagne, 1973, for example) originating from continental glaciation (cold) phenomena indicate that such minerals can in fact be rare in the loess itself. The clays in European loess and those loess and tills of the continental United States are illite/smectite assemblages which are common in soils. Given that the loss of chlorite and the formation of illite/smectite mixed layer minerals can be rapid, on the order of tens of years under mild climates in salt marshes to thousands of years under climates of northern latitudes (see p. 309 in Velde and Meunier, 2008), one can suspect that the soil clay mineralogy can change rapidly under the influence of plants as they fix and transform the clays in the A horizon. The loess deposits in the humid areas of northern Europe and Continental United States could well have been modified before transport as fine grained wind born material or during the periods of deposition. In fact the tills found in Illinois, near the loess deposits (Willman et al., 1963) can contain little chlorite and large amounts of smectites mixed layered minerals. This suggests that these tills, materials moved by the glaciers themselves and deposited in zones which become resources for wind transported materials, were in fact based upon soil materials scraped from the landscapes to the north. When this material is eroded on flood plains in front of the tills and subsequently moved by the action of wind, it already has the imprint of soil processes. However other tills, from nearby areas can show illite – chlorite mineralogies which are altered in soil development sequences (Drooste et al., 1966).

In Europe and the Central Plains area of the United States, the loess accumulation, wind born material, is not great, less than a meter over flat areas and tens of meters along rivers and streams where secondary deposition is important. However in China the loess mantle can be very important, tens to hundreds of meters. Whatever the thickness, the impact on plant life is very great. Loess provides a ready source of potassium, through the alteration of illite or muscovite, and magnesium and iron through the loss of interlayer ions in chlorites. Thus loess deposition can be important to the type and vigour of plants installed upon it but more importantly, it provided an ideal substrate for agricultural experimentation in the Neolithic period.

If the observations confirm the following, one can surmise that the "cold" loess of the glacial periods was of a complex nature, much having passed through a soil stage or having experienced a soil forming process after deposition and cover by other material. This is particularly the case for the North American loess. In Europe some loess is of the illite – chlorite mineralogy, in the Po valley accumulations. However this loess was deposited on the Alps where plant action was reduced due to the altitude and the reigning cold climate. However the loess found in France and Germany shows evolved illite/smectie mineralogies with little illite – chlorite mineralogy. This suggests that a soil forming process has affected the material. In the arid areas, the loess comes more from the direct disintegration of low grade metamorphic rocks which are deposited in such abundance that the plant regimes in the rather arid climate which prevailed did not change the mineralogy greatly. This is still the case.

The "hot" loess developed from desert alteration of rocks is more illite – chlorite rich, and has thus experienced little plant driven soil – silicate interaction before its wind born deposition. In principle the desert type of loessic materials should be more liable to change and alter under plant interaction giving a high rate of potassium and magnesium, iron flux to the soil solutions.

Loess deposition is probably one of the more underestimated modes of displacement concerning the continental surfaces. It is very difficult to discern the moderate amounts of deposition when it falls on a growing and active plant community. Loess is fine grained and a large portion of the materials can be composed of clays similar to those found in soils, specifically 2:1 minerals. Also if the sedimented minerals are unstable, being of high temperature origin, they can be converted into surface or soil clay minerals in a short period of time. If the deposition rate is relatively low and plant activity high, much of the soil clays could be of loessic origin but would go un-noticed in routine analysis of clays.

### 3.1.4 Summary

The renewal or displacement of clay materials within a soil profile either vertically or laterally can be a strong factor in soil and alteration profile development. It is probable that much of the clay concentrations in valley bottoms or zones at the base of long slopes can be due to lateral transport. This enrichment of clays will change the structure of the soil which can favorize a specific type of plant regime, grasses for example. Increased clay content tends to keep the soils more humid, through somewhat poor drainage, and thus change the hydric regime. Development of the clay poor E horizon under forest growth indicates that grass plants will not be favored by clay transport out of their soil environment. Thus the dynamics of particle movement within the soils can influence the type of plants which will be present.

Movement of fine grained material through wind transport deposits the clay sized fraction evenly on the surface, on hills or in valleys, but it will also have an influence of the plant regimes. Most likely the addition of clay materials will increase the fertility of the surface materials replacing 1:1 clays (kaolinite) by 2:1 clays which are more prevalent in loess materials.

The formation of fine clay mineral materials by alteration or plant action is not static. Once the materials have formed their displacement can be an important factor in further plant – soil interactions.

## *3.1.5 Transportation and Displacement by Mass Mechanical Failure: Landslides and Slumps*

### 3.1.5.1 Rock and Soil Slides

Massive transport of soil and alteration materials, as well as bedrocks, is the second aspect of displacements of material at the surface. Rugged mountainsor hilly terrains are more likely to be eroded by massive movement events than water transport of clays in flowing solutions. Mountain streams are notoriously clear, indicating that they transport little clay sized material. However landslides, rock slides and earth slides are common alongside of these clear streams.

In a very general view one can consider the mass movement of materials in two ways. One is due to high relief, or slope, where the material becomes unstable by having the base of the slope undercut, with the result of a large slide movement forming a C shaped displacement zone (Fig. 3.6). This is the sliding mass with rotational failure schema of Gray and Sotir (1996). The instability created by a discontinuity at the base of land mass determines the change in resistance of the slope material at a given, punctual site, which allows gravitational forces to cause a large scale displacement based upon the mass of the material on the slope.

This action, rotational, is treated in most texts on landslides and the physics of rock mechanics (Cornforth, 2005, Chap. 1; Duncan and Wright, 2005, p. 57). Much interest for this type of phenomenon has been given to denuded slopes (man made events caused by the removal of plants) which become highly unstable. In this type of displacement the surface (soil zone) and subsurface material (alterite and bedrock) is affected in the same manner. The physics of the process slope and mass, determiners the depth of material affected. Here the major factor is the disturbance of the shape of the lowest part of the slope. The undercut factor decides the movement of the material to the largest extent.

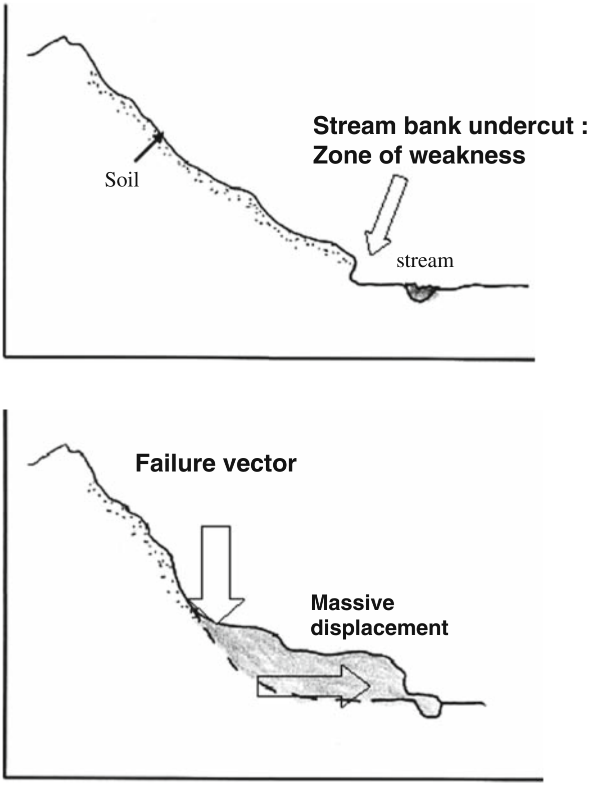

**Fig. 3.6** Scenario of massive slope failure due to a destabilisation of the slope material by an undercut at the base of the slope. The failure movement is directed by a vertical movement, which moves to the surface below the slide area on the lower slope. This is a rotational movement, or "C" shaped failure profile

A second cause of movement on a slope is the development or augmented contrast in the physical properties of different layers of material. The contrast in physical properties between two layers of material produces potential instability at the interface between the two layers. For example, if a bedded sediment is uplifted on a mountain side, the contrast of physical competence between the different layers can cause planes of weakness in the material at the interface of the layers and encourage dislocation along these planes. The effect is much more likely to be prominent when the materials on a hill side or mountain slope are bedded roughly parallel to the surface. In such an example the failure in competence is guided by a contrast in the materials of the bedrock.

In both types of slope failure described above one will find a re-organization of rock materials and some soil or alterites materials. However the large part of the material deposited down slope is that of un-altered rock. Thus the large part of the displaced material is much the same, chemically, as that of the mountain or hill side.

### 3.1.5.2 Soil Slides

Another type of failure is formed along planes of weakness in which the difference in physical properties is engendered by surface alteration and soil forming processes which contrasts the properties of the soil, alterite and bedrock. This is the sliding mass with planar failure schema of Gray and Sotir (1996) called infinite slope and plane slip surface failure (Duncan and Wright, 2005, p. 57). On a hill slope, one often finds the development of a soil layer, often under grass. Here the alteration process works to produce a less dense material than that of the bedrock. If the alterites is of an important thickness, there can be another interface of contrast between the soil and the alterite. Such an instance is indicated by Morgan (2005, p. 35) where surface soil has a significantly greater shear strength (4–9 kPa) compared to the underlying alterite with 2–3 kPa shear strength resistance. The fact of the topography of a slope indicates that the bedrock is rather competent otherwise there would be no hill. Alteration creates a surface layer of very different physical properties: one of lower density, one which can change its mass when rainfalls and enters the porous soil and one where plants put down roots into their substratum.

However the fact of its development, changing the density and porosity of the surface material into a more or less homogeneous layer of ever increasing thickness creates with time, a more and more unstable situation. The interface between rock and alterite is highly unstable. The increased mass at the very surface of this layer by plants and rain filled soil periodically heightens the contrast between the two layers as rainfall events occur. Hence it is almost inevitable that the soil layer will fail and become unstable, sliding to a lower region of potential energy. Such a situation is outlined in Fig. 3.7. The "soil slide" is a very common feature of mountain landscapes.

It might seem paradoxical that plants would tend to create a situation of instability where they will be displaced and destroyed by their own development, yet it is a common case in land movement on slopes. Here the soil developed and the alterite zones are thickened downward creating a new landscape and habitat for plant life, one built on altered material for the most part and amenable to rapid colonization by other or the same species.

In the cases of slump and landslide one finds a mixture of altered materials and those of the bedrock. In such situations the alteration processes again take over, water – rock interaction and plant modification of alterite. However in the case of surface soil failures (soil slump or slide) there is a mixture of materials which strongly represents a situation of the C portion of an altering rock sequence where new clays are present with old parts of the disaggregated and altered rock present but with the new mineralogy of soils, the plant – silicate interaction zone. Here the plants can take hold rapidly in that they have a favourable base for root growth and the access to nutrients furnished by the clays (2:1) present.

If what goes up comes down, it occurs with or without the help of plant – rock interaction. The different forms of slope failure take place depending upon the importance of the slope, and the relative competences of the materials present or the geometric development of the slope itself.

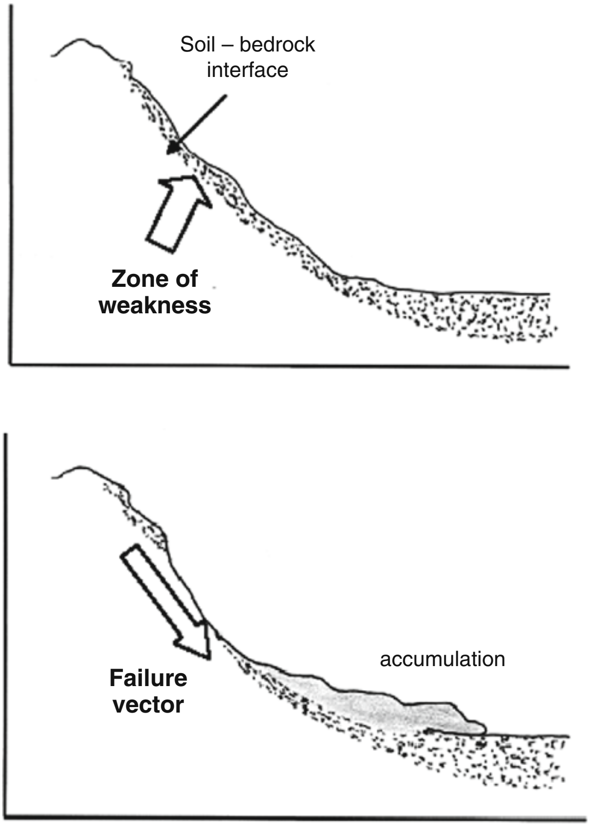

**Fig. 3.7** Massive failure due to a parallel vector to the slope. The major cause is the contrast of alterite and soil structure compared to the bedrock or more consolidated substrate material. The origin of he weakness in the development of an alterite of low competence and the more stable root zone created b plants and their roots

Hence one has two basic types of failure, one rotational, with deeper movements initiated at the surface down slope and the other planar where the instability occurs at a mor superficial level.

## 3.2 Retention of Soils and Clay Material by Plants

### *3.2.1 Surface Displacement and Plants*

The principle function of plants is the preservation of an environment that is amenable to their survival and growth. They need a source of water, lasting beyond the periods of rainfall and abundance. They need certain mineral nutrients, such as potassium, calcium and phosphorous for example which are found in the mineral environment that they grow and prosper from. Most plants need air around their roots a significant portion of the time, in the soil, in order to maintain a balance of chemical processes of degradation of their own dead material and an extraction of other elements through biological action. Some plants of course have adapted to anoxic environments but since the largest part of the surface of the continents is drained, the normal procedure is to keep this situation functioning. Soil, a mixture of clay minerals, debris of other minerals and organic matter is the habitat of the plant substrate. It is to the advantage of plants to develop and preserve the alterite zone of the surface where these interactions can occur, the A soil horizon. Hence the roots in the soil not only are the vehicles of chemical exchange but they can also provide a sustaining structure to preserve this environment. Roots must anchor the soil and try to foster it. However different plants have different root types and they do a varied job of anchoring the soil to the bedrock from which it is developed and develops. Such differences are a part of the history of the plants (genetic inheritance) and adaptation to different climatic and bedrock – alterite situations. As we know plants on a calcareous plateau are not the same as those on a granite massif. The types of plants, their adaptation to the local chemistry and the local soil substratum are reflected in their shape, root structure and plant chemistry. As climate changes, the substrate has perhaps less effect on the physical and chemical characteristics of the alterites zones and the thickness of the soil substratum. Plants must adapt and have over the several million years of their existences. Thus the relations of plant species, soil type and climate are all variables in the statement of how plants behave. Further plants of a single species can adapt to their environment, slopes, hydrodynamics and so forth. This also gives a specificity to each situation in which one finds a plant in its environment.

Given the rather large variety of variables in soil – plant relations (species, climate, slope, soil chemical substrate) one must be aware that any generalization is likely to have as many exceptions as cases confirming principles. However, we would like to trace several principles here to act as a guideline for further thought.

The largest body of information on the effects of roots in the stabilization process of soils involves trees. This is normal in that the disciplines which are most interested in retention of surface materials and the stability of the plants present on a long term basis are those of forestry. Forests grow, now, for the most part on hills and slopes not to mention mountains. These are areas where agriculture is difficult. In the past much agricultural land was present on slopes and hill sides (up to the late 19th and early 20th century). As tractors replaced animal traction, the hill side cultures were gradually abandoned with the exception of vineyards. Thus the areas of land slides and massive failure were those where trees were left to grow. By contrast surface erosion, the displacement of clays and sand to gravel sized material in moving water, is the domain of agriculture where flat land is more often laid bare to the effects of rain without the protection of plant cover. The lack of vegetation leads to the displacement of fine grained material.

How do plants intervene in the stabilisation of surface materials? In the first place it is in their interest to do so. Plants need a substrate of fine-grained material which is loosely bound leaving passageways for air to infiltrate into their substrate. Soils are characterised by a relatively high state of oxidation. Roots need water to sustain the plant but they need air to fulfil their functions as exchangers of oxygen and nitrogen. As roots grow they create passage ways in the soil which are open to air movement when the root dies to be replaced elsewhere by another. The clay – organic substrate of soils gives rise to the formation of what are called soil aggregates which are tightly bound assemblages of clay particles and organic matter containing pores of small size. In these pores one finds capillary water which can be extracted by plant roots. Also the clays fix mineral element necessary for plant growth. Erosion and massive movement of materials takes away their substrate and the means of gathering mineral and water resources. If erosion occurs, this soil substrate will disappear and the vegetation will be in dire straits.

Obviously plants have a mechanism to preserve the transfer substrate necessary to their well being. Roots play not only the function of gathering water and mineral resources but also they play a role in fixing the soil substrate in place to avoid erosion and mass movement of surface materials.

Several observations can help us to understand the role of roots. Gyssels et al. (2005) indicate that the erosion rate, measured by material taken off of the land surface by streams and rivers, report that the erosion rate is decreased exponentially with increase in vegetation cover. The corollary is that the decrease in erosion is exponentially related to root mass. This suggests that plants will do best in keeping soil present below them where they are the most abundant. Thus erosion by water run off will be lowest in strongly vegetated areas, temperate forest or grasslands or tropical forest and humid savannas. The relation is non-linear as indicated above, and related to annual precipitation (Langbein and Schumm, 1958). The overall relations from low rainfall to high rainfall show a non-linear relation, reported by Xu (2005) for soils based on loess in China. Figure 3.8 indicates these relations in a general way.

In stages of low rainfall, the sparse plant cover is sufficient to maintain the soil in place.

There seems to be a sort of threshold, around 450 mm/year total rainfall where plants cannot maintain the soil in place with great efficiency. The range of 400–500 mm/year rainfall is one of high erosion intensity. When enough water resources are available to promote strong growth of forest cover one sees a strong decrease in erosivity. One must however be very careful in applying average rainfall to such information in that in some areas and climates rainfall can be abundant for short periods of time and therefore much of this resource is lost by rapid runoff while in other climates the regular rainfall in of much more benefit to plant growth.

De Baetz et al. (2007) indicate that not only root density but also the rooting characteristics of specific plants can affect the run off erosion to a large extent in Mediterranean climates. Hence not only is root density important but different plants can be more or less efficient in holding soils in place. For example Devkota et al. (2006) indicate that given similar slope and soil physical properties different grasses are more or less efficient in their role of stabilizing recent landslide areas. Hence there is an obvious diversity in the effect of roots on holding soils depending upon the plant concerned.

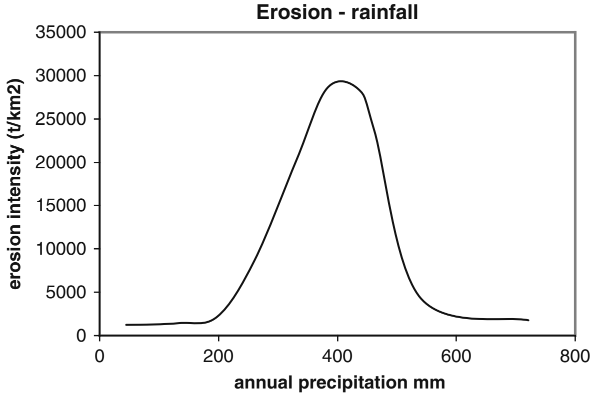

**Fig. 3.8** Relations of erosion and rainfall, shown in a very diagrammatic manner. This relationship is illustrated by Xu (2005) for soils based on loess in China where the substate is similar and the major variables are climatically controlled. In the graph it is evident that under conditions of low rainfall erosion is less important, a maximum is reached in areas of semi arid conditions, where vegetation is sparce, and erosion greatly reduced under conditions of higher rainfall and greater vegetal cover

### 3.2.2 The Physical Role of Roots in Stabilizing Alteration Materials

The means of holding soil, clay rich materials, in place is determined by the roots of the plants which are of course anchored in the soils and hence the clay – organic matrix. This is a role not often considered by specialists in the study of plant physiology and stability. There are exceptions of course as seen in the very interesting paper by Greenway (1987). First, all plants do not have the same root structure or distribution with depth in the soil zone and beyond. Also it is important to consider that a certain amount of root mass goes below the A horizon and the B horizon for that matter and enters into the C or alterite horizon. Roots are considered to be present mainly as a relay of soil nutrients for the plant, mineral and above water resources which are combined with carbon in the atmosphere and via sun energy transformed into complex organic molecules. This function is normally considered as the major importance of roots. Second, roots anchor the plant to its substrate and assure its place at the surface and they assure its survival. In early stages of alteration development roots can fix themselves in rock cracks and crevices. However most of the root mass for most plants is found at the surface, between 20 and 50 cm depth in an alterite and soil material. In temperate grass vegetations 60–80% of the root mass is in the upper 25 cm of the profiles. In tropical forests the depth is greater, near 50 cm as is the case for desert and shrub land vegetation (Schenk and Jackson, 2002). The depth of root structures is dependent on several factors, one being physical stability, slopes and the density of the plants, and the other is probably based upon the necessity to reach mineral resources in less altered parts of the profile such as is the case in tropical forests. Many texts show the adaptability of roots to develop in according to the resources that they are afforded by the materials upon which they grow. Roots go, basically, where they can find resources for the growth of a plant.

However the results of root growth due to plant colonization can be variable given the same climatic conditions. Gabet and Dunne (2002) give data which indicate that the type of vegetation can give very different soil holding properties. The information is given for the semi arid climate in Southern California where different vegetations of grass dominated or shrub dominated areas were observed. A series of strong rain events, an El Nino winter, provoked significant landslide activity. The relations between the number of slide events per surface area and the amount of material removed by the slides are rather striking. Figure 3.9 shows the relations of the number of landslides per surface area (km$^2$) and the volume of the material moved.

There are more landslide events in the grass cover areas, but the sage or shrub cover areas deliver more sediment overall with fewer but larger events of material displacement. This indicates that the grass yields more easily (number of events) but the amount of material moved is less than that of the sage brush vegetation cover. The reason lies, most likely, in the fact that the sage plant regime has a deeper rooting which holds for a longer time but when it finally gives way, more material is displaced. Indicative values for maximum rooting depth are taken from Shenk and Jackson (2002) used in conjunction with the data from Gabet and Dunne (2002). Hence the slump failure of grass leaves more of the land surface bare, and without vegetal cover on hill sides in this semi arid climate. The sage shrub regime has a

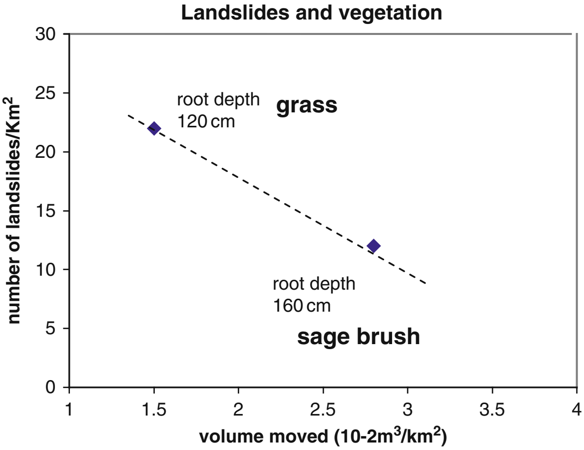

**Fig. 3.9** Relationship of total mass movement and number of movement events as a function of vegetation type (data from Gabet and Dunne, 2002). Sage brush and grasses were present on California hillsides during El Nino rain events which destabilized the slopes. Grasses show more frequent failure events, related to surface area while sage brush shows fewer event but a total of more material moved. This is most likely due to the rooting depth of the different plants, where grasses are shallow rooted and allow failure more often but of a superficial nature while the sage brush is more deeply rooted and when failure occurs, it is more massive

more conservative effect for the plant cover but the erosion, or mass displacement of material, is greater overall.

The placement of roots is important also, especially in the case of shrubs and trees with woody roots. If the roots penetrate to the rock or saprock zone, they are better anchored and more resistant against landslide movement (Abe and Ziemer, 2001). Hence the depth of alteration, soil and alterite materials, will play a role in the stability of surface materials on slopes and the capacity of different plants to stabilize these materials. In general one can expect that the tree root system will be more effective is stabilizing slope alteration material in that the rooting depth is significantly greater than that of grasses and of different depths depending on the species (Schenk and Jackson, 2002). However, other factors apparently come into play to form grass slopes on mountain hill sides and forests on mountain tops. One obvious factor is the above ground dimensions of the two different plant types. The forest, tree, has a large mass above ground which is solicited to move down slope by the ever present force of gravity. Wind has an effect also in that its energy is strongly transferred and absorbed by trees. Grasses have a much smaller proportion of their living mass above ground and hence have an advantage against the above ground forces of gravity and wind.

#### 3.2.2.1 Root Structures

The distribution of roots for a given plant species is not uniform with depth. The greatest amount of root mass in near the surface with a decreasing amount present as depth is greater. This is the case for several reasons, not the least of which is that the greatest amount of nutrients, mineral and aqueous, are present at the surface soil materials. However, in times of need, water must be reached at depth and roots reach for it there. Also, if the nutrients are in low abundance at the surface, roots will move downward to fine more un-altered, and mineral nutrient rich material at depth. Figure 3.10 indicates the distribution of roots as a function of depth in the case of trees or shrubs, those plants with woody roots compared to climates at different latitudes (Schenk and Jackson, 2002).

Abe and Ziemer (2001) indicate that the high distribution of roots in the upper horizons, of 40 cm or so, is roughly 70–90% of the total root mass. The extension of these roots is largely lateral with a high amount of branching. The spatial distribution is essentially parallel to the ground. In the lower parts the roots change orientation and become more vertically oriented, with diagonal branching. In the deepest rooting zone the roots are essentially oriented vertically. This structure is very important concerning the mechanical resistance of roots to solicitations by land movement or forces exerted upon the above ground plant by wind or water action. The forces exerted on plants via their interaction with wind are essentially lateral with the result that tension is the major force exerted on the roots on one side of the plant root mass while compression is exerted on the other. The same forces are exerted continually on plants growing on hillsides. Extension and compression are the main constraints imposed on the surface roots. Root tensile strength

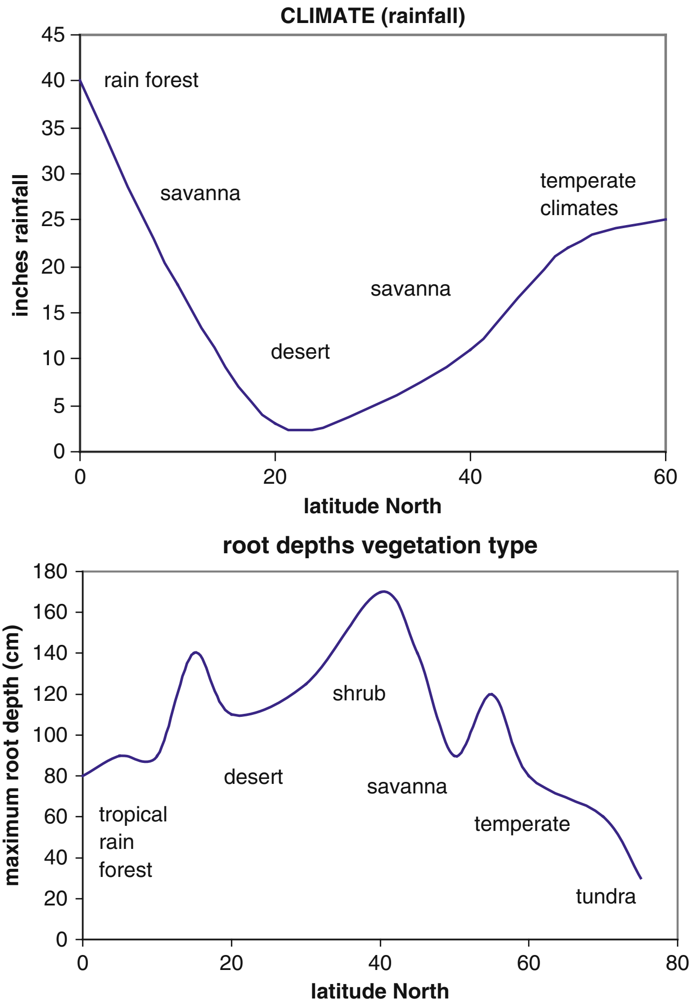

**Fig. 3.10** Relations between climate as a function of latitude where rainfall can be compared to the average rooting depth of plants present (data from the Encyclopedia Britannica, 1969 and Shenk and Jackson, 2002). As rainfall is less abundant, rooting depths increase across the major climatic vegetation zones

is the essential measurement considered under such circumstances. If one observes the root system of a tree felled by a strong windstorm, the surface, horizontal roots are rarely broken but the more vertically ones are frequently broken or snapped. The surface roots are pulled out but the deeper, more vertical roots are most often broken from their rock or alterite masses.

As depth increases, the forces remain similar for solicitations transmitted by the above ground portion of the plant. These result in the pullout forces measured by a traction vertical force as indicating a factor of plant stability and resistance to erosion (see Pollen, 2007 for example). However at depths below the large root mass, one finds a change in mechanical characteristics of the soil – alterite stratification and a plane of weakness is often observed due to a contrast in physical properties. In these zones one is more likely to find lateral movement dominating more than vertical movement engendered by the above ground part of the plant. These lateral forces solicit the shear strength of the roots.

If one considers the internal structure of a root, it is clear that it is not made to resist shear (i.e. transversal) forces. The more or less linear nature of roots is easily seen in their structure. The fibrous nature is due to oriented growth material roughly along the long axis of a root. The internal structure is engineered to conduct fluids from the plant to the root ends as well as from the root to the plant. Roots are essentially pipelines with a resistant wall structure. The cellular material is structured parallel to the axis of root growth and extension**.** This being the case, the orientation of the cells and the reinforcement of the root is along its length. Thus the strength of a root is in the direction of its length and hence traction compression forces are best revisited along the axis of a root. The lateral direction, across the axis of the root is less well defended against solicitations. Hence shearing, trans-root forces so to speak, are not as well accommodated in deep roots. A very general schema of root distributions and solicitations for a tree is shown in Fig. 3.11. Greenway (1987) indicates that the angles of 40–70° from the horizontal give the best resistance to rupture for most roots.

Roots are well adapted to avoid a tree from falling, (compression – traction forces) or being uprooted, but not to avoid the lateral displacement of the A horizon

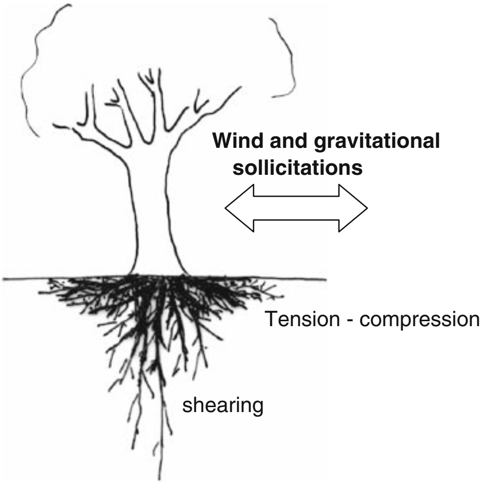

**Fig. 3.11** Illustration of the major mechanical effects of roots of woody plants as they are disposed geometrically. Roots have a maximum resistance to tension and compression in the direction of their length which is used to advantage when the roots are parallel to the surface and solicitations are of a horizontal nature. However these movements parallel to the surface, down slope on a hill side, are poorly compensated by vertical roots whose resistance to shearing, cross tensions to the axis of the root, is not as great as that of longitudinal resistance

soil mass (shearing forces) along a slope. However, many plants and especially trees adapt to the needs of slope stability by reinforcing their strength by re-orienting their growth according to the forces present. In Fig. 3.12 the orientation of roots is shown to be adapted to slopes (Fig. 3.12a) with definite thickening on the down slope side and a more special case in Fig. 3.12b where roots have reinforced the tree resistance along the edge of a sunken road, following the bank downwards, almost vertically,

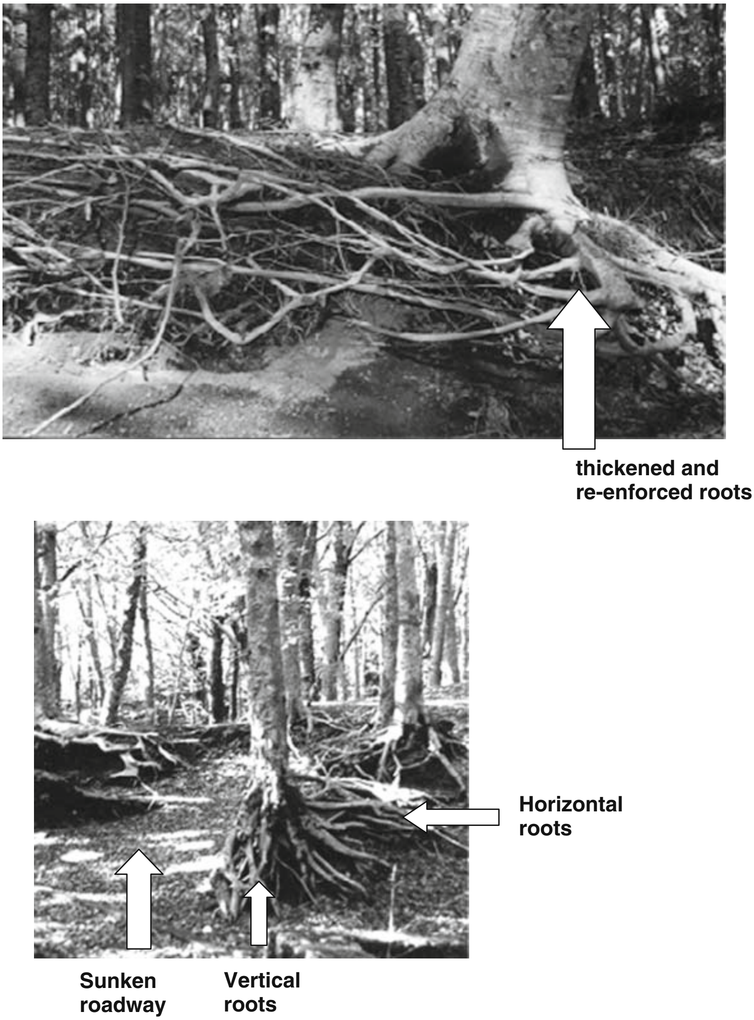

**Fig. 3.12** Illustration of root adaptation to the local geographic situation. In the *upper picture* the roots on the down slope side are greatly thickened to reinforce the stability pf the tree whereas in the *lower* photograph the roots become vertical along the trace of an old sunken path where they sustain the trees and retain the soil against erosion. On the flat terrain side of the tree the roots are deployed in a traditional horizontal pattern. These illustrations demonstrate the high degree of adaptability of roots which use their strong points to fix and sustain the aerial plant mass (photos BV)

to strengthen the stability of the tree and also undoubtedly to retain the soil from being washed away, which in the end happened in this friable Andosol terrain near Sorrento, Italy. Woody roots are often seen to be adapting to the structure (geometry) of their surface environment.

Grasses have a much more un-oriented nature to root growth and are hence resistant in all directions where they occur. To a certain extent this is due to the rizhome system where grasses can reproduce by growth of new shoots from roots. This necessitates a strong root mass near the soil surface and lessens the root structure at depth, although not entirely. In general, grass roots tend to be concentrated near the surface (A horizon), and then do not provide protection from shearing along the competence contrast zone between the surface layers and the substrate of alterite profiles. This is in contrast to woody plants which tend to have more vertical root structures which often attain the bedrock as anchors. However in arid climates grasses will explore to greater depths for water and nutrients changing the structure of the root masses. One can say that most generalizations on root structures will be valid only in a comparative way due the high adaptability of plants to climate and geomorphological (topographic) effects.

One can ask: How does this work? The major factors of resistance to movement provided by roots are measured by the tensile strength of the root which is related to the shear overall strength (Tosi, 2007). Hence the measurements of root tensile strength are pertinent to both compression – tension forces at the surface or in the A horizon as well as the deeper stability at depth in the C horizon where shear forces will be more important. Tensile strength is an inverse function of root diameter (Tosi, 2007) and hence to resistance to rupture (Pollen, 2007; Waldron and Dakessian, 1981; Docker and Hubble, 2008; Greenway, 1987 for instance). Then in general small roots are more efficient at resisting forces that promote movement. Root density varies of course between plants. The difference between tree and grass root densities is about a factor of 50 in the first 30 cm of soil depth. Amato et al. (2005) show that the resistance to slope failure is related to root density. In brief: the more small roots the more resistance to rupture of a root mass in the soil. Grasses seem better adapted to this situation.

Another factor is the relation between the root and its bond to the surrounding soil. Waldron and Dakessian (1981) indicate that the bond strength is an important factor. As a soil becomes more hydrated the root – soil bond is decreased and the system becomes more subject to failure. Here pull out or roots from their surroundings can be suspected to play a large role in stability. Thus the observation that most slope failures is not only due to the increased load on the system due to the increased water content but also to the decreasing in bond strength between soil and root.

To summarize, the high density of smaller roots at the surface in the A horizon of an alteration profile forms a massive, resistant layer which promotes the stability and resistance to movement of soil materials. Plants protect their immediate environment. These effects are not only important for landslide or mass movement but also for erosion by runoff during periods of intense rainfall (De Baetz et al., 2007). However the progressive alteration of the substratum in a profile is a very important factor.

Morgan (2005, p. 35) Shows the relations of soil and substratum shear strength. The upper layer (A horizon) in a semi-arid zone is relatively resistant to shear forces and hence landslide events. However the altered zone below is much less stable having a shear strength about half that of the A horizon. In the zone below the plant roots, increased weathering (water – rock interaction) increases the clay content and hence decreases the internal angle of friction, which is a measure of the resistance to shear. Basically, the larger the grains, the more difficult it is to move them one over the other. The more clay, the easier it is to produce a sliding movement and eventual failure. Clays are small particles with a strong crystal asymmetry, essentially plate like in morphology, which lends itself to orientation and eventual deformation. Clays have a sort of plastic property, appreciated by potters, and this property lends itself to soil mechanical failure. Roots fix the clays and reinforce the plastic matrix. However below the root zone, the fundamental properties of the clays begin to dominate. It is along the interface between the root – reinforced A and A–B horizons and the underlying C horizon that the failure of a surface cover is likely to occur. The mechanical resistance contrast between the two is very great and creates instability.

To a certain extent then the structure of roots, or their disposition in space, determines the resistance of the surface layer of plant – soil interaction to the forces of erosion. Grasses have a dense occupation of the surface and thus provide good resistance to rain dislocation of surface particles. The woody roots (trees and shrubs) give better resistance to lateral forces which indicates better resistance to landslide and massive surface displacements. Roering et al. (2003) conclude that the type of root structure and spacing of plants with specific structures must be taken into account in explaining the failure of surface material on slopes.

One can schematize the development of soil profiles and alteration mantles as they will affect the stability of the newly produced alterite layers (Fig. 3.13) when the root zones begin to lose contact with the bedrock in the weakened alterite zone. The example is one of essentially grasses which eventually have less deep root structures, more so than trees or shrubs.

Initial stages of soil formation occur as roots fill most of the soil space and firmly anchor them into the bedrock by penetration or close contact. Little or no slide erosion occurs in these stages of soil evolution. Also the loss of soil clays is minimal. In most mountain streams, where plants are taking hold on bare terrain, there is little clay in the water. In the next stages, the soil thickens but there is a development of alterite, i.e. where the direct presence of roots and organic matter is less important. Here there are still large portions of mineral grains and rock debris which contribute to the cohesion of the material against the forces of gravity and displacement. In the last stage, the soil and root zone is largely independent of the advancing alteration front developed on the bedrock. In these situations the properties of the soil zone, stabilized by the roots of the plant cover, are much different from those of the underlying alterite which is much less coherent and liable to failure. The interface can become a zone of instability under conditions of high rainfall (increased weight of the soil zone) and differential fluid flow at the base of the soil zone. Such

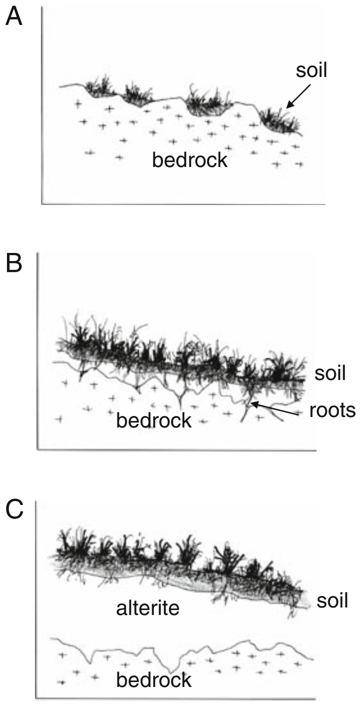

**Fig. 3.13** Development of an alteration profile where the plants are closely anchored to the underlying rock mass n the initial stages (**a**) but as alteration proceeds the roots are less anchored to the rock, but still are to a large extent (**b**) and in the third instance when a thick alterite zone is present the roots rarely reach the rock substrate (**c**)

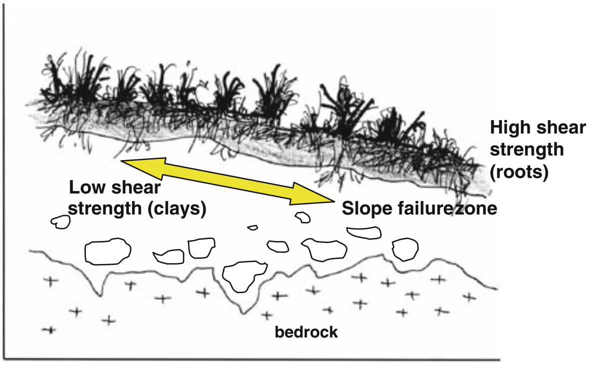

**Fig. 3.14** Representation of the situation where the root mass of the plant regime is shallow as is the case for grasses, forming a strong and resistant surface layer which is de-coupled from the bedrock by the development of the alterite zone. It is at this contrast point, rigid root mass zone and low density alterite zone that the slope failure is initiated for shallow rooted plants

a situation is more important on a slope, of course. Unless there are strong anchoring deep roots present, the surface zone is highly likely to be decoupled from the alterite (Fig. 3.14).

The presence of roots is hence of great importance for the stabilization of the developing soil zone formed by plants and water – rock alteration. However, if the alterite beneath the soil zone has significantly different properties from the soil (root and silicate grain size) failure can occur and the work of the plant biomass has to be re-initiated. In a sense the strong development of plants, especially those that have rather shallow root systems, can be a danger for their immediate survival on hill slopes.

Coming back the classification of failure as being or a rotational or planar type (Gray and Sotir, 1996), in the case of plant occupancy of the surface, one could expect a planar failure in the case of grass cover and a rotational failure in the case of tree cover. In the case of grasses, the structure of the surface is highly occupied by a dense and rigidifying mass of roots near the surface. Here the zone of instability is nearly planar and near the surface. In the case of shrubs and trees the root structure is less dense and presents a greater depth for some roots. The zone of root intensity is more dispersed. In this case the resistance to movement is more evenly distributed in a way and will lead to resistance at the surface and to a certain depth. In this case the failure zone will have a more curved aspect, rotational. The mass of material displaced will come from greater depth than in the case of grass cover. Hence we see the reasons for the differences in the amount and frequency of landslide displacement shown in Fig. 3.9. The tendency for grasses to create a rigid and resistant zone a the surface (A horizon) leaves them un-coupled from their substrate which is more plastic and liable to failure, given the importance of the discontinuity of physical properties between the root mat and the underlying clay – rich alterite zone (Fig. 3.14). The case of woody plants with a more vertically oriented root mass gives a more gradual change in resistance properties between the A horizon and the alterite substrate. Here when failure occurs it is more deep seated, and gives a "C" shaped structure of rotational failure. However a more deep seated root mass leaves the surface layer in contact with rain fall more vulnerable to surface soil erosion.

In order to overcome the inconveniences or each type of root structure resistance it would be advised to intersperse woody plants (trees) with grasses so that the surface rainfall erosion will be reduced and the deeper rooted trees will protect against planar, surface sliding effects. Mono-species on a hill side is not a good thing. This is another way of calling for bio-diversity, but in a very simplified manner.

## 3.3 Fixing and Accumulating Clays in the Surface Horizons

### 3.3.1 *Plants as Accumulators of Soil Materials*

#### 3.3.1.1 Salt Marsh Grasses

The role of plants in maintaining soil material in place is quite well know and well studied. The role of plants in accumulating soil materials is perhaps less well known. If one looks at the structure of salt marshes, one can see that the limit between reworked muds, deposited and eroded by tides, and the stable, plant anchored marsh is rather well defined. The interface is well marked by grasses and sedges which are rooted in the muds forming an approximate ten centimetre escarpment. The advance of this vegetal material into the realm of the sea is encouraged by the accumulation

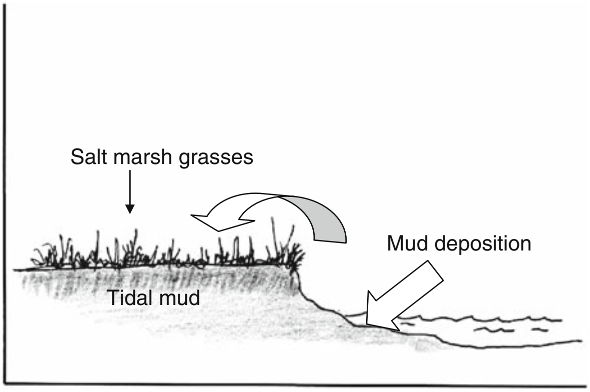

**Fig. 3.15** Diagram of deposition of coastal clay – rich sediments in tidal mud flat zones. The establishment of plants on the shore fixes sediments which accumulate with high tide movements. The plants allow the sediment mass to increase and grow seaward as the plants fix more and more of the sediment. Deposition seaward of the plants is subject to tidal erosion and displacement

of sediments, deposited during high tides, into the grass marsh areas. Figure 3.15 indicates these actions. The continual movement of suspended materials is stopped by the grasses which create a barrier to erosion and which capture the sediments deposited on the grasses at high tide and stabilize them making a plateau of material which advances into the tidal zone as clay sediments are deposited on the grasses which establish root zones further into the mud flats with time.

Such actions can occur only when deposited materials exceed those taken into the sea, i.e. when sedimentation exceeds erosion along the coast of sea – land contact. If plants are not present, the mud banks move and are moved continually by tidal movement. However, if plants anchor the suspended and deposited materials, the land front can advance into the sea. Such actions are probably responsible for much of the shallow water deposition of muds in the past which form organic – rich sedimentary units which in turn develop hydrocarbons through the maturation of the organic material deposited in the clay – rich sediments of the marshes. Since organic materials are responsible for the black color of sediments, to the largest extent, the black shales known for their organic content can probably be associated in many cases with the plant – sediment interface common in salt marshes.

### 3.3.1.2 Grasses and Loessic Materials

If the accumulation of sediment in salt marsh grass due to entrapment of clay material in water born vectors is clearly established, and visible in many instances, the capture and accumulation of wind born material in grassed areas is less well established. However, the dense foliage and high root mass density at the surface typical of grass vegetation is ideal for trapping fine – grained materials. The problem is that wind born clays are usually not abundant, on a yearly massic basis, and tend to be difficult to detect within an abundant vegetal structure. However, one often finds that grasses have clay rich root zones, especially near the surface. In a garden, when one trims the grass along a cement or stone walk way, there is a very important amount of clay material associated with the roots growing over the stone or cement substrate. This trapping effect can probably be extrapolated to an accumulation of wind born material at the surface of grass vegetation. In forests, the vegetal cover is less dense, and a larger portion of the wind born material will be transported downward in the soils, to be evacuated in the ground water or deposited in the B horizon, often below the clay deficient E horizon.

#### 3.3.1.3 River Sediments

The accumulation of clays and clay – rich sediments in valley bottoms is not an accident in that when it occurs, the valley is normally covered in grasses and/or trees. These elements tend to slow the movement of flowing water and promote deposition and enhancement of the soil materials. The frequent inundation and deposition typical of such geomorphologic settings is conducive to growth of grasses which can regenerate their root structures and move “upward” to follow sedimentation, as is the case in salt marsh environments. One must remember that the fine grained sediment which is entrapped by grasses is rich in organic mater (nitrogen – bearing in many instances) and potassium – rich clays developed in soils. In fact the entrapment process is a system of re-cycling of the surface resources in soils that have been lost through erosion of different sorts. What is lost in one place is often re-used and becomes an important resource in another. The clay (soil) rich valley bottoms have always been prized land from the time of the Neolithic farmer to the present. Displacement of soil resources is frequently not lost to the bio-geological cycle.

Figure 3.16 indicates the relative emplacements of the different types of clay and soil movement in a landscape. This is valid for temperate climates where rainfall is more or less regular throughout the year. Slump and landslide occurs on the strong slopes, movement of clays on or in the soils occurs on the less inclined slopes, and deposition of clays occurs through the action of flowing water which leaves a deposit when the flow exceeds the capacity of the stream bed to convey the water present. The effect of flooding, extension of the water flow path, leads to a slowing of the velocity of the water and a lowering of its capacity to carry matter in suspension. The slowly moving water cannot maintain the material in suspension and it is duly deposited on the surface of the stream banks and flood plain. These lead to terrace deposits and stratified layers of sediment accumulated over reasonably long periods of time. In the example given, one can deduce that the material once deposited can be re-mobilized as soil profiles are developed and clays move down slope within the soil profile or on its surface. Significant erosion of clay material from vegetated soils in temperate climates is rare. The erosion that one sees these days is largely due to the effect of denudation of soils materials by agricultural practices in temperate climates.

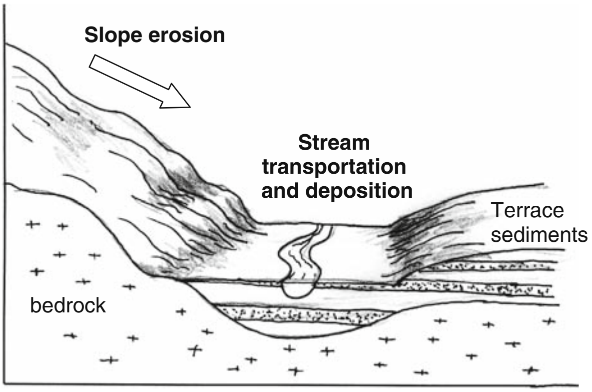

**Fig. 3.16** Diagram of the general situation of surface movement and accumulation of soil materials with erosion. Slopes lead to displacement of fine grained material, stream beds and flood plains lead to the accumulation of this material. The movement of materials by streams and rivers is of course in general towards the sea but a temporary zone of accumulation often occurs along the stream beds in the forma of terrace sediments which can eventually be eroded and transported seaward

Toy et al. (2002, p. 9) indicate that significant erosion (tolerable according to the authors) occurs by water on cultivated lands east of the Mississippi River in the United States, while significant erosion west of this approximate boundary is by wind action. The boundary is essentially that of old forest growth to the east and prairie growth to the west. This leads one to believe that the old structure and soil conditioning effected by plants is capable of out living the intensive mechanical and chemical conditioning of modern agriculture, to a certain extent.

## *3.3.2 Plants and Clays in Profiles: Stabilization and Regeneration*

### 3.3.2.1 Control of the Physical Environment by Plant Cover

Several studies have been conducted on the effects of denudation of a terrain and recovery of plant cover (see especially Bormann and Likens, 1994 among others). The recovery process which in effect controls the physical impact of rainfall, gravitation al forces and wind effects is essential to the well being of plant regimes. Walker and del Moral (2003, p. 106) give data which indicates the type of change effected by plant re-growth after landslide in the Himalayan mountains (Fig. 3.12). It is evident that the growth of plants follows the S curve dynamics and the loss of soil material by erosion and loss of potassium from the remaining soils diminishes according to the strong slope dynamics of the S curve. In this instance the alterite material is largely devoid of soil (the plant – silicate interaction zone) and hence plants must re-conquer and change the alteration substrate in order to come to a state of sustenance for forest ecosystems. Bormann and Likens (1994) show similar data for forest recovery after clear cutting in a New Hampshire forest area. Rapid changes occur after the clear cutting which start from a soil based system, i.e. a layer of clay – organic conditioned materials developed by a plant regime. All that is necessary is that plants re-conquer the soil materials and develop to protect them from erosion. Here loss of potassium in stream water is reduced 50% after just 4 years of plant growth. Biomass storage of $K_2O$ increases 14 fold over the time span. A portion of the potassium comes from organic litter in the soil, but also a significant portion comes from the mineral resources in the soil necessary to increase the biomass rapidly. This material is used by the plants instead of being lost by dissolution and stream transport.

The dynamics of plant regime recovery are of great importance in that not only landslide or clear cutting of forests can occur but also forest fires can burn over different types of forest, leaving them open to a re-establishment of a protective shield over the soil. Bormann and Likens establish a three part dynamic system where the initial stages of recovery are those of recovery and re-organization, the initial low slope of the S curve. Once the system gets established, root growth and extraction of mineral resources among other things, the dynamics of growth increase sharply forming the aggradation part of the growth curve. This is the steep slope of change. The maximum of the curve represents the transition stage where maximum possible change has been reached and a tendency to establish a steady state of slow change takes over. The steady state, one of very gradual change, shows a lower amount of biomass production than that attained previously and changes in other chemical properties of the ecosystem are decreased somewhat. Bormann and Likens are careful not to propose a true steady state for the ecosystem, as constant conditions do not really exist for long periods in nature, but the rate of change is minimal during the mature state of an ecosystem.

One of the principal overall observations based on such studies are that plant regimes re-install themselves on perturbed sites minimizing loss of minerals and mineral resources. The plant system attempts to use extracted resources to a maximum in re-cycling them through the decay of plant litter. Hence the surface soil zone tends to be one of small change with time while the water – rock interface continues to change at roughly the same rate with time. Plants establish a more or less closed chemical system at the surface and attempt to maintain the soil zone intact physically through the stabilization due to root growth and colonization. Chemical loss is minimized although some material is lost through mineral dissolution and release of matter from plant and mineral decay as rain water percolates through the system to the inevitable evacuation by stream flow. Also, on slopes, the inevitable development of the soil zone and the alterites produces an inherent unstable situation where the underlying rock has strongly different properties from the solum leading to physical instability.

Plant regimes also minimize the effects of degradation of their soil substrate. Leaves disperse the energy of rain drops which can erode soil (clay) particles. Roots reinforce the inherent coherence of soil materials at the surface thus preventing slump displacements and eventually landslides. Plants cover the surface and retain the water that arrives via rains. They maintain water in place in the soils which enables them to survive during periods of dryness. These are all truisms known to each of us but the impact is often overlooked. In fact plants attempt to control the physical forces which would otherwise degrade the soil substrate that they need to thrive. One must look at this aspect, control of external forces, in order to understand the structure of the bio – geo communities.

Egli et al. (2004) present data for a series of soil profiles along a mountain valley where slopes vary from 35 to 60%. The vegetation is forest of different dominating species depending upon the altitude (ranging from 100 to 200 m). In all but one profile the AE or E horizon (in the upper 20 cm of the profile) show a clay content superior to that of the parts of the profile immediately below. Despite the strong slopes, the plants (trees and under growth) were able to maintain more clay than that below this surface layer. Thus the importance of plants on soil clay stability cannot be overlooked.

#### 3.3.2.2 Grasses

Plants found in prairies and savannas tend to have a dense root system at the surface. A part of the reason is that *graminae* can reproduce from root growth extension, which they colonize a surface area even though they are cut systematically in lawns and prairies. The dense root mat is a strong characteristic of these plant regimes. Casual inspection of the root mass, frequently called turf, is its high clay content. In fact the root mass captures and holds clays which enter the system from air transport of lateral displacement, erosive processes. Wider spaced and more coarse roots present in trees do not fix as much clay at the surface. In this manner grasses are better conservers of soil clays. Perhaps this is due to the lack of general leaf cover that they provide. In forests the strong erosive effect of falling rain drops is mitigated by leaf cover and as such rain fall is much less erosive than it is in prairie landscapes. Hence it seems that there is a compensation for soil loss depending on the morphology of the plants in a given biome.

#### 3.3.2.3 Clay Content and Possible Re-generation of Clays

Clay minerals, the <2 μm fraction of soils and alterites, are generally found in greater abundance in the upper parts of an alteration profile. Barshad (1959) indicates that grass vegetation is more effective in clay formation than tree or forests. This suggests that in fact that the clay content of the A horizons of grass soils are more clay rich than those commonly found in forests. Generally one attributes the difference in clay content to the accentuated movement of clays by percolation and dissolution in the A horizons of forest soils, assumed to be to high acidity. However this is not always the case, even in sandy soils, one can find an enhanced clay concentration in the upper most layers of forest soils (Teveldal et al., 1990) and Birkeland (1984) suggests that such might be a common case, using his Fig. 10-4. Thus the loss of clays within the soil profile is not necessarily inevitable, but highly probable especially in forest soils. However, an intriguing data set is given by Tice et al. (1996). In an experiment with forest growth, a conifer forest landscape was planted in pine in one area and oak in another in mountain California. After 40 years of forest growth, an analysis of the soil – alteration profile indicates that the pine forest has, as would be expected, less clay in the A, surface, horizon. However, the oak forest shows a higher percent of clay (Fig. 3.17). Thus the pine forest shows clay loss, but the oak forest shows an increase in clay in the surface A horizon. One can pose the question of whether or not the clay content at the surface was not a product of oak tree – soil silicate interaction. Very similar results were obtained by Graham and Wood (1991) for soils in southern California (Mediterranean climate). Deciduous tree cover showed an increase in clay content at the surface whereas chaparral and pine cover showed a lower clay content at the surface. However these authors indicated that the increase in clay content under oak compared to pine was due to a transportation to the surface of clays by earthworms. Thus in these cases the clay content can be a factor of biological activity outside of the plant – soil interaction itself.

In general, as indicated by Barshad (1959), grasses tend to have a higher clay content of the A horizon in their alteration profiles than that for other plant types.

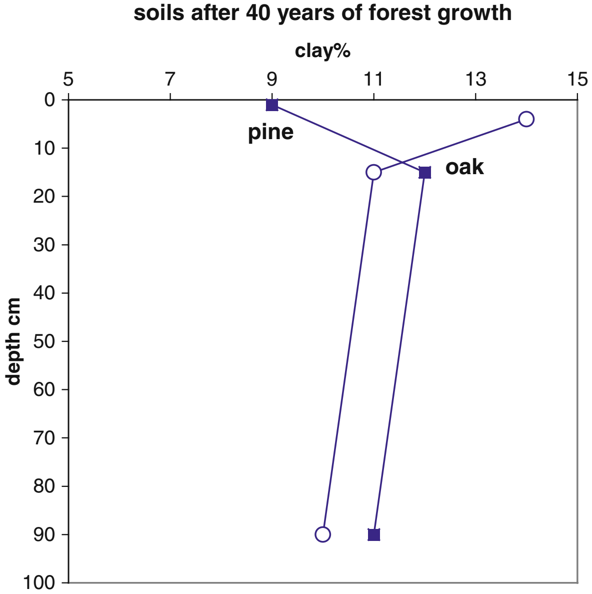

**Fig. 3.17** Instance of an increase in soil clay content engendered by change of plant regime (Tice et al., 1996). Soils under pine trees planted in a former pine grove are compared to oak tress planted a the same time, after 40 years of growth. The clay content of the oak forest soils is significantly greater than that of the opine plantations. This effect could be due th the formation of new clays (subject treated in Sect. 5.5) or the effect of earthworms or other fauna brining clays to the surface due to a change in nutritional advantage by the oak tree litter

Forests tend to loose clays by either fluid suspension and movement downward in an alteration profile or perhaps by chemical destruction and leaching. The root structure of grasses is more dense than that of trees, in the surface horizon, and hence one can propose that grasses tend to fix clays more than do trees. This indicates that the type of plant will engender a lower or higher clay content at the surface. Then the movement of clays can be retarded by plant type or perhaps augmented by the plants themselves due to the density of the root structures. The possibility of soil clay creation, i.e. crystallization is an intriguing prospect and will be further pursued in Sect. 5.5.

It is probably fair to say that without plants there would be almost no clay accumulation at the surface of continental masses. The retention of clays is the key to the system. Plants get several nutrients from clay masses: mineral nutrients and water which is absorbed or held in soil aggregates in micropore sites. The root masses are a barrier to water and erosion. Different climates have fashioned different plants, by adaptation, and each situation is one of constant change. Plant succession sequences change the populations and proportions of different types; fire, heavy rains and floods change the proportions of soil – rich material available and new plants form on sites where the environment has been ruptured or changed. As with most situations in nature there is a reciprocity in each situation, one element gets something from another and eventually a sort of steady state is attained for a certain time. One must always remember that the nature of nature is to efface the continents and reduce them to mud at the bottom of the ocean. In doing so, the structures of the continental surfaces changes and plants adapt to these changes. Plants attempt to maintain an optimum for their survival, any other reaction is suicide. However some things cannot be overcome and changes occur. Happily geological forces occur which renew old structures that have been levelled. Mountain chains are erected and resulting local climates change also. Conifers can be found in temperate climates due to the high altitudes of mountains. As erosion occurs the high altitudes are lessened and the climatic situations conducive to high altitude tundra growth are lost. However, wait awhile (several millions of years) and another mountain chain will be formed. Glaciation changes (in the last several millions of years) the climatic zones favoring different types of vegetation. Conifers grow in areas where deciduous trees were formerly present, grasses invade the edges of former tropical zones and so forth. In fact the surface of the earth is in a constant state of change and plants adapt to these forces. Along with these adaptations one finds mutation and change within the different groups or types of plants. Thus the state of plant and soil clays is in a constant state of flux with few constants from the scale of tens to hundreds of years to millions of years. Perturbations solicit adaptation and this changes the chemistry of the soil and alterite zones. New plant successions can have other new needs and promote a new chemistry that will affect the clays. We will look into this in the following chapters.

***What needs to be done***

***Establish the physical characteristics of roots***

***Resistance to rupture***

***Effect of directional growth***

***Relations of root properties (density, resistance to rupture, etc) to deformation modes***

***Relations of rooting to resistance to rainfall erosion***

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# Chapter 4
# Clay Minerals in Soils: The Interface Between Plants and the Mineral World

## Contents

## 4.1 The Silicate Clay Mineral Types Present in Soils

The presence of different clay minerals in soils, the plant – silicate interaction zone, is most often due to an incorporation of clays formed in the water – rock zone into the bio-zone and the initial transformation of rocks by living organisms such as lichens, and bacteria. Thus there is some inheritance from underlying mineral reactions and those engendered by the successive stages of bio-activity.

The first stages of surface interaction which form clays, appear to be under the influence of bio-agents, such as lichens and mosses. Eventually higher order plants can establish themselves in the substrate of humic and clay minerals formed. Without plants and bio activity, the products of physical breakdown of rocks and those products of water – rock interaction which are of low enough intensity to produce clays are likely to have been washed away by rainwater. One must be reminded

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_4, © Springer-Verlag Berlin Heidelberg 2010

that all chemical reactions forming new minerals from rocks involve water. Deserts and ice packs are poor reaction vessels.

Among the silicate clay minerals one normally finds the aluminium hydroxide phase gibbsite but the iron hydroxides and hydroxyl phases are rarely mentioned.

### *4.1.1 Kaolinite and Halloysite, 1:1 Minerals*

1:1 clay minerals are composed, for their silicate part, by a two layer structure where one layer is occupied exclusively by silicon cations and the other in large majority by aluminium ions. The aluminium is in octahedral coordination with oxygen atoms, shared with Si cations, and hydroxyl cations. This mineral is highly hydrated (hydrogen content) and therefore less thermally stable than the 2:1 minerals. The ratio of Si to Al is very near one. The kaolinite structure is not subject to cation substitutions for the most part and its composition is thus near Al, Si, O and H. The absence of alkali ions suggests that its conditions of formation and stability have low alkali ion activites. The presence of Si in equal quantities compared to Al indicates that the activity of silica in solution is still reasonably important. Kaolinite and halloysite can be considered to represent an intermediate step in water – rock interaction and alteration of silicate materials to oxides and oxy-hydroxides.

However, kaolinite is often found in the initial stages of rock- water interaction. It is formed locally, in a given mineral type due to very local (scale of the crystal) chemical potentials (see Velde and Meunier, 2008, Chap. 4). Usually, the kaolinite formed in the early stages of rock alteration is a minor part of the newly formed clays. Kaolinite persists up the alteration profile under very many climates and biomes. Its presence as a majority of the clays in alteration clay mineral assemblages indicates strong weathering, or strong chemical action which reduces the silica content in the clay assemblage.

Halloysite (see Joussein et al., 2005 for a review of halloysite occurrence and crystallochemistry) is a hydrated form of kaolinite, in that a layer of water molecules is “interlayered” between the 1:1 structural layers. Further, halloysite can contain some iron is substitution for aluminium ions, up to 7 molecular percent substitution The interlayer spacing is 10Å. However, the presence of water makes a curved surface of the sheet forming a tubular morphology. The interlayer water is not stable, being expelled rather easily upon heating. There is a certain affinity of halloysite for potassium, intercalated with the water between the 1:1 layers. This explains the somewhat anomalous high cation exchange capacities when these minerals are present where there are apparently few or no smectite minerals present in soils.

Halloysite seems to be present in soils when the alteration zone is frequently saturated with water. Some tendency to lose the water forming kaolinite is seen in upper parts of soils where wetting and drying occur compared to deeper zones below the water table or in more permanently wet conditions. It seems that halloysite is an initial stage in the formation of kaolininte under conditions of strong weathering, i.e. surface soil and alterite zones.

## *4.1.2 The 2:1 Clay Minerals in Soils*

### 4.1.2.1 The End Members

The « backbone » of soil clay mineralogy in areas of fertile soils are the 2:1 minerals. These minerals can fix potassium and other base cations (Ca; Mg), major nutrient and probably also ammonium, another major nutrient. They are the only materials in soils to have a significant amount of cation fixation capacity which can retard the inevitable loss of these elements to the sea. Weathering is an inexorable loss of alkalis and alkaline earth elements. Local conditions of chemical potential or chemical activity of different ions in solution can determine the mineralogical expression of these minerals. In fact the 2:1 minerals are similar in nature and crystallographic expression, but the chemistry of the interlayer site determines the chemical and physical response of these minerals to plant solicitation and the treatments in the laboratory used to identify the different characteristics of the 2:1 mineral base in soils.

The most reasonable method of designation of these minerals is their initial nature in the soils themselves. This means a first investigation without chemical treatment of the soil material. Basically one would like to understand the interaction of the clays with plants, their chemical action, either by release of ions or fixation of ions. Hence the “un-treated” state can give insight into the function and chemical action of the clays in their environment. After such an initial investigation has been completed and recorded, some chemical treatments can elucidate the reactions of the clays under different conditions of chemical solicitation engendered either by plants and the bio-sphere of the natural water – rock interactions. These steps can be used to describe a function- reaction situation which will be used to designate the behaviour in terms of a mineralogical classification. Of course the use of such a classification does not obey the rigours of official mineralogy as currently practiced, but it can be useful to understand the function and interaction of these clays with their plant – dominated environments.

Our classification of 2:1 soil clay minerals, as outlined briefly in Sect. 1.3, is based upon the occupation of the interlayer ion sites between the 2:1 units and the stability of the ions found in these sites in natural specimens. Three basic types of interlayer ion occupation can be defined:

1. Anhydrous potassium ions forming a stable, non-variable cell size. These minerals are classically called illite. The basic cell dimension perpendicular to the 2:1 layers is 10 Å.
2. Hydrous cations of various types forming either one or most often, two water layer complexes which can be changed by changes if temperature or relative humidity.These minerals are classically called smectites. The double water layer hydration state is 15.2 Å and the mono – hydrate gives a spacing of 12.5 Å. Relatively easy removal of interlayer ions and replacement by other ions indicates a 2:1 structure with a low charge.

3. Hydroxy coordinated interlayer ions, usually Al but also probably Mg form a structure with a 14.2 Å spacing. These minerals are usually called HI or soil vermiculite when the interlayer ion is dominated by Al ions in an incomplete layer (see Meunier, 2005), and chlorite when the Al interlayer complex is more complete and in some cases magnesian. If the hydroxy layer ions are displaced by potassium these minerals are high charge smectites.

These three poles of interlayer ion occupation form the basis for the soil clay minerals with a 2:1 phyllosilicate structure. The interlayer site occupation can be either inherited from higher temperature phyllosilicates, such as mica or metamorphic chlorite, or possibly be formed under conditions of soil formation as suggested by the laboratory studies of Bauer et al. (2006). The behaviour of the minerals in fixing different cations in soils is dependent upon the chemistry of the soil solutions and the affinity of the different ions to enter into the interlayer ion sites. The attraction of different ions is most likely a function of the total charge on the 2:1 structure (charge imbalance usually below a positive charge of 22 for a unit cell). The excess negative charge, non-compensation of the cations present, is compared to the structural anionic charge generated by the ten oxygen and two OH ion units in the structure. The tendency to hold a cation or attract a specific ion into the interlayer ion site can probably be attributed to the amount of charge and/or the site where the charge imbalance originates, i.e. in the surface silica dominated layers or in the central octahedrally coordinated sites. Competition between Ca and K ions for sites in synthetic smectites shows a variability depending upon the site and intensity of the charge generating the electronic imbalance in the structure (Velde, 1985).

Given the nature of the likely precursors of the soil 2:1 mineral structures, it is highly likely that the material present is not homogeneous. If the high temperature bedrock contains phyllosilicates, as does a very large portion of continental rock, the individual grains will be of different chemical compositions to a varying degree. Thus, initial chlorites of diagenetic or metamorphic origin can reflect the orogenic history of the rock maintaining crystals of different composition formed under different physical conditions. The differences in composition will most likely give rise to slight differences in charge and charge site in the crystal from one grain to another. Thus individual layers or crystallites will behave slightly differently under the same chemical solicitations. In this way a type of mineral behaviour, say potassium incorporation, will be of slightly differing intensities giving a range of responses to ambient chemistry and when investigated by X-ray diffraction (the only viable method of routine clay mineral analysis). Instead of having a single crystallographic response one will see a slight range of responses which widens the diffraction maximum. One must consider that the clay "phases" in soils are in fact a group of crystallites which have similar but not identical physio-chemcial properties. This leads to what is called mixed layering in 2:1 clay minerals, common in soil environments. This being the case, inspection of many X-ray diffractograms allows one to be rather optimistic concerning the formation of groups of mineral grains having the same or very similar characteristics. One can in fact use the term minerals, in the sense of a type of identifiable behaviour for a given range of chemical composition.

#### 4.1.2.2 Mineral Identification and Mixed Layering: Case Studies

Accepting these premises, one can proceed to establish a working definition of soil clays with a 2:1 structure as proposed above. Of the three types of structures one can propose that the smectites have a relatively low deficit in layer charge, around 0.3 charges per unit cell (22 negative charges). This allows cations to move in and out of the interlayer site depending upon local chemical gradients of bi-valent cations in solution. These cations are hydrated. The selectivity between bivalent ions and monovlent ions is strongly in favour of the bivalent ions. Thus in smectites Ca is favored over K ion occupation of the interlayer ion site. Treatment of the clays with concentrated potassic solutions still leaves portions of the material in a hydrated cation state even though the ion is monovalent potassium.

In high charge 2:1 structures either Al or K is selectively fixed under natural conditions. The high pH and relatively high Al content of pore solutions favors the formation of Al (OH) cations and their fixation to form HI minerals. However a strong presence of potassium will favour its incorporation as an anhydrous cation forming what is called illite. Laboratory experiments by the authors indicate that although much cation occupation can be changed by using concentrated solutions of potassium for example, the Al hydroxyl (or Mg) interlayer sites will not be completely exchanged. In the case of the HI minerals it is probable that the fixed material is well structured and polycationic which gives the mineral a more stable chemical character. The same is true for potassium minerals, so called illites. These minerals can in part be transformed into apparent smectites when submitted to strong bivalent cationic solicitation. The potassium is replaced by hydrous bivalent cations. However, not all of the material becomes smectitic in behaviour and some remains in the anhydrous potassium state.

The situation of some layers having a given chemical response to cation selection and others another response gives rise to what is called mixed layering. In this state some of the 2:1 units in a crystallite have a given cation interlayer occupancy while others have another. Since most crystallites appear to have a basic two component behaviour, series of mixed layer minerals can be identified between the three poles of behaviour; illiite, smectites and HI minerals. Thus illite – HI minerals can be found in soils, illite – smectites also, and HI – smectites as well. Figure 4.1 indicates these relations. The zones around the poles can possibly give rise to some three component behaviour, as suggested in the figure but at present it is not know how much, if any, there is to be found commonly in soil clays.

The main interest in these minerals is their capacity to fix with varying degrees of chemical attraction potassium or eventually ammonium. These are mono-valent ions, or ionic groups of similar diameter which find a place in the 2:1 minerals and can sooner or later be extracted by bio-activity. The fixed, anhydrous potassium and eventual ammonium is a vital reservoir for plant nutrition.

One characteristic of 2:1 soil clay minerals is that they most often occur as a mixture of layer types; high charge, low charge or Al, MgOH, K, Ca, Mg $H_2O$ interlayer occupancies. This is not the case for clay minerals formed in the water – rock interaction zone where non-phyllosilicates are altered to new phyllosilicate clay minerals. The process of formation of the clays, 2:1 structures, is surely

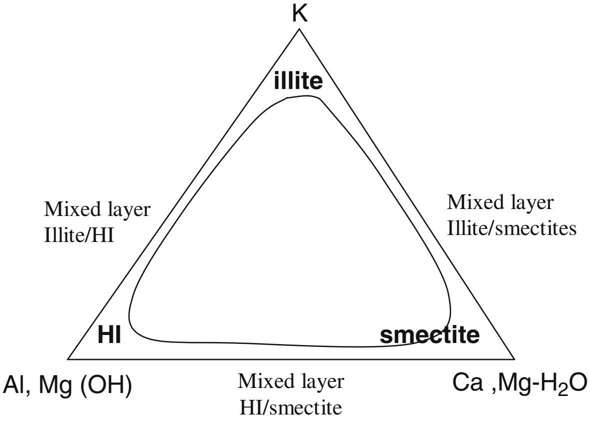

**Fig. 4.1** Representation of major sol clay types as a function of interlayer ion type. K (potassium) = illite: Al, Mg(OH) = HI hydroxy interlayer ion minerals: Ca;Mg-$H_2O$ = smectites minerals with hydrated exchange ions, dominantly divalent. Mixed layer type minerals are formed between the HI-K (hydroxyl-interlayer/illite), K-Ca, Mg-$H_2O$ (illite/smectites) or Ca,Mg-$H_2O$-HI (smectite/hydroxy interlayer) mineral types

complicated but certainly not that of normal water – rock interaction. We will look briefly at the major groups of mixed layer minerals, those phases with characteristics between the poles of the diagram shown in Fig. 4.1.

Illite – Smectite

In general, the water – rock interactions in the initial stages of weathering do not produce mixed layer clay minerals (see Velde and Meunier 2008, Chap. 4). The structures formed during the initial destruction of high temperature minerals form more or less mono phase clay minerals, either smectites or kaolinite or illite, in various proportions in a given alteration site. As the minerals are brought to the surface, their characteristics change. Old, high temperature phyllosilicates such as muscovite, chlorite or biotite are likewise transformed in the soil zone (see Righi et al., 1997)

Several examples are given to indicate the changes which can be expected using moderate chemical treatment of these soil clays. The first example is the effect on several illite/smectite minerals. Initially the clays are saturated with a weak solution (0.01 M $SrCl_2$). Potassium saturation was made with a strong solution of KCl, 0.5 molar. In the sample proposed in Fig. 4.2, two samples of high smectite content mixed layer illite-smectites are shown, one with a significant amount of illite present and the other almost without an illite component in the clay assemblage. Potassium saturation affects the mixed layer clays in similar manners, shifting the major peaks to slightly lower *d* spacings or higher two theta values (less than the double water layer hydration state indicated b a peak at 15.2 Å) indicating the increase in potassium in interlayer sites either as a mono – hydrated ion (giving a one layer water structure and a 12.5 Å component) or by creating an anhydrous illite – like potassium inter layer population with a 10 Å peak. One suspects that the one water

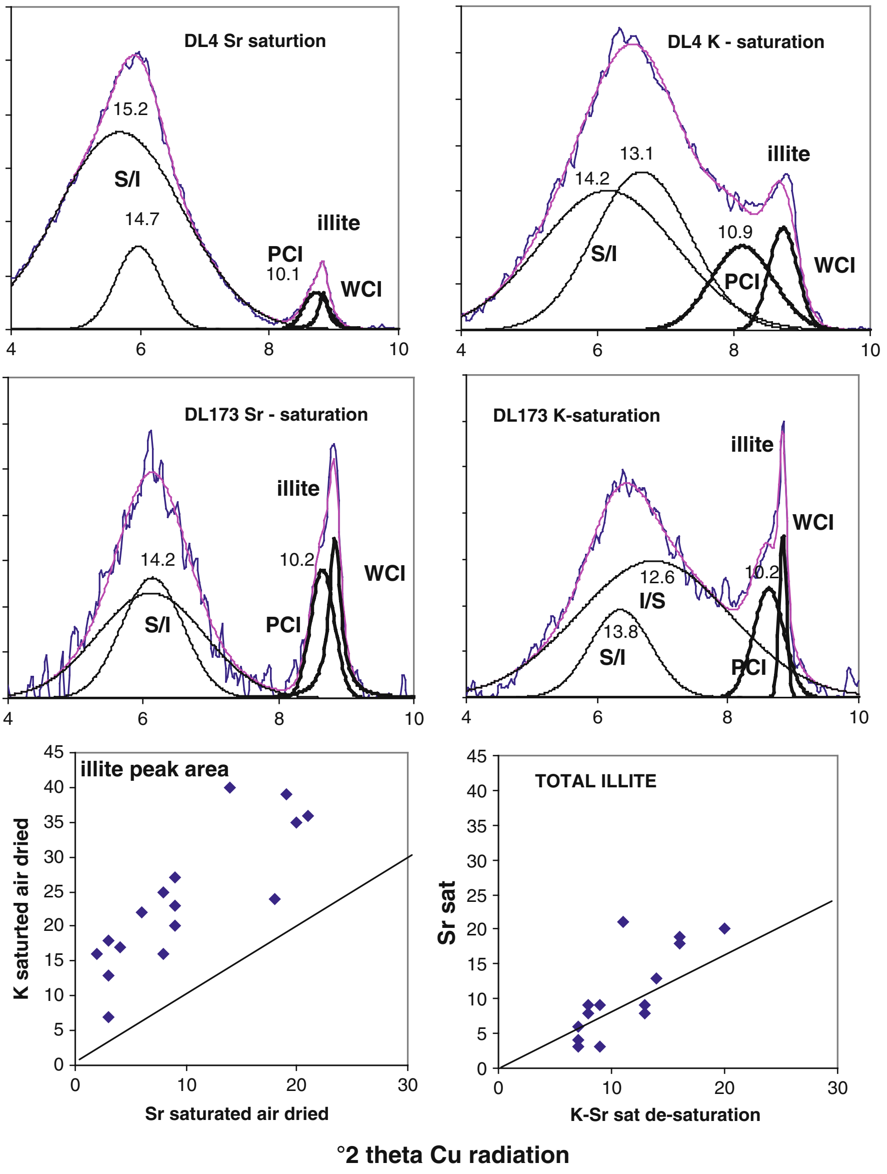

**Fig. 4.2** Iowa prairie soils in K (O.5 M KCl) saturated state and comparison of the low concentration Sr-saturated illte peak areas with K saturated areas with the Sr – desaturated KCl clays (K-Sr de-saturation) Potassium saturation increases the illite peak ares relative to the Sr – saturated samples whereas the de-saturation of potassium brings the clays back to an initial weakly Sr – saturated illite peak area. This indicates that the potassium saturation producing illite peaks is reversible. One would expect that such a process would occur in soils which are treated with potassium fertilizer in the Winter to be de-saturated by plant growth needs during the Spring and Summer. Background – subtracted X-ray diffractogram treated using decomposition methods

layer potassium structure is rare in that the major peaks remain in the range of an interlayered two water layer structure (towards 15.2 Å).

The most important effect in the first example (DL4) is the formation of a stronger illite component, especially the 10 Å well ordered illite of rather narrow peak width (WCI). This effect is important in that it indicates that portions of the mixed layer, illite – smectites material, has large zones of high charge layers which all become anhydrous upon potassium saturation. This effect is visible in cases where illite is initially absent (DL 4), or almost so, and where it is strongly present (DL 173). In the first example the poorly crystallized illite peak (PCI) is stronger also. We see in both examples shifts in the mixed layer mineral (S/I where smectites is the major component) and the formation of a more illite – rich mineral (I/S) with a peak at 12.6 Å. Thus potassium saturation produces illite, anhydrous potassium interlayered mineral and illite layers in the mixed layer structures.

Potassium saturation in strong concentrations of KCl was made on 16 samples from a geographic area of several kilometres squared in central Iowa. The results show that there is a systematic change in relative peak area for the total illite peaks (PCI and WCI, poorly and well crystallized material). A systematic increase of about 10% of the peak areas is seen for a range of initial illite content, 2–20% (Fig. 4.2). It is apparent from these data that high charge smectites are present in all of the samples. When the same samples are de – saturated using a 0.5 M SrCl2 solution, the initial illite content is found, indicating that the formation of these anhydrous potassium layers in the high charge smectites is exchangeable if a strong exchanger is used. This action is known in agricultural soil testing where "non-exchangeable potassium" is identified and extracted when a strong exchange solution is used, such as ammonium acetate or others. Lower concentration solutions of divalent ions do not affect the anhydrous potassium layers it appears.

Another data set, taken from samples presented by Velde (2001), for samples from various top soils across the central prairie United States (Fig. 4.3) shows very similar clay reactions but to weak potassium concentration saturation (0.01 M KCl). Shift in illite – smectites peak positions toward the 10A illite position and increase in the surface areas of the illite peaks. These are all old prairie soils under cultivation. It is clear that illite layers in a strongly random mixed layer structure can form as well as groups of illite layers in a crystallite which form the "new" illite minerals. In fact the changes are nothing but cation selection by layers with different charges and affinities for cations in solution. The reversibility of the change in cation abundance to a smectites (divalent cation with two water layers present in the interlayer site) shows that the clays react to their local chemistry, changing their X-ray diffraction characteristics but not their basic nature.

→

**Fig. 4.3** Illustration of the effect of potassium on mixed layer illite/smectites mineral assemblages of diffeent proportions of illite layers in the different phases. Highly smectitic clays show little effect while those with more illite layer present in the initial state (Sr-saturation) show a greater increase in illite (10 Å) peak area. Not only is there more of the illite mineral present ut also the mixed layer peaks shift to a position nearer to 10 Å indicating more illite layers in the structure

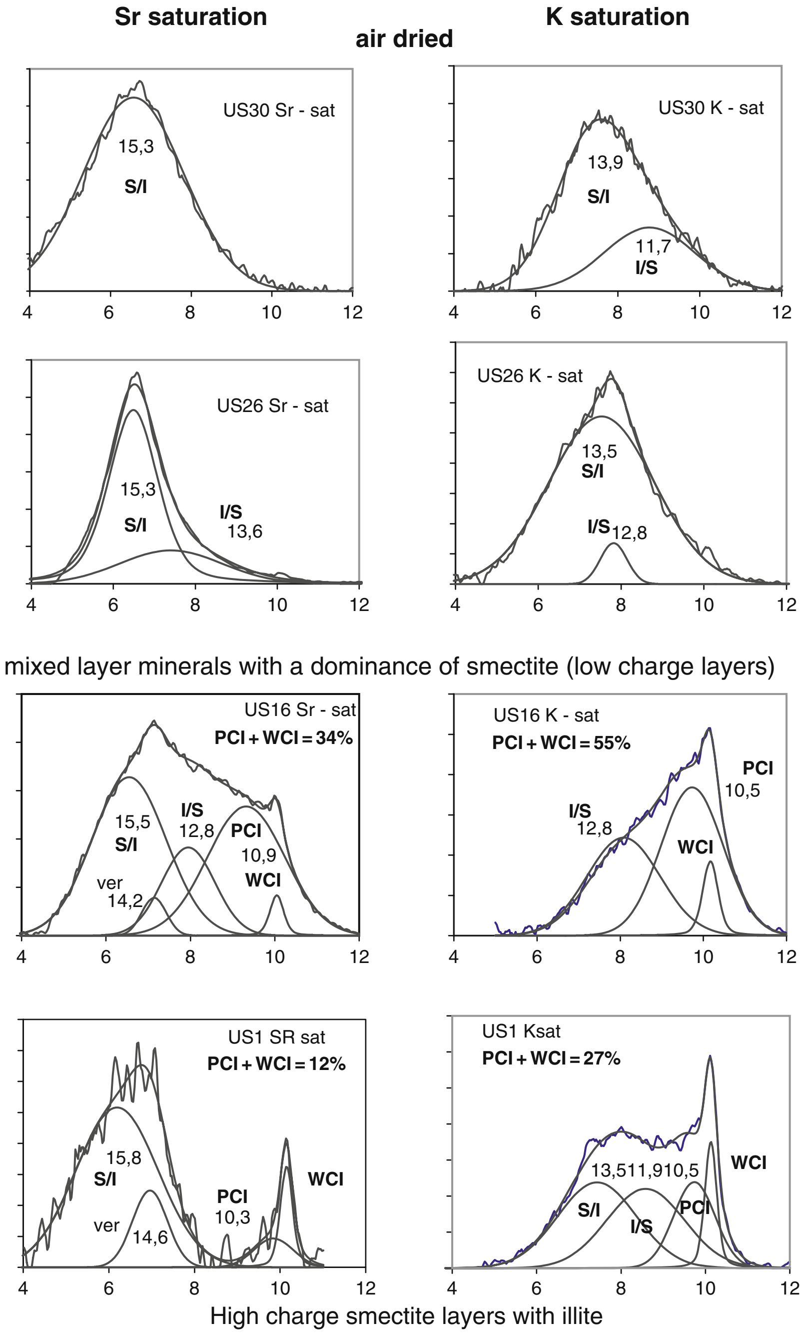

**Fig. 4.3** (continued)

The reverse, potassium de-saturation reaction, can be effected by plants, of course. Here the extraction of potassium produces a smectitic layer. In Fig. 4.4 which presents data given by Velde and Peck (2002) for clays from the experimental farm at the University of Illinois (again old prairie soils). The extraction of potassium reduces the peak surface area of the well crystallized illite peak, (WCI), increases the surface area of the poorly crystallized illite peak (PCI) and does not significantly shift the illite content of the illite – smectites (S/I) phase evidenced by the same peak position. This occurs over a time period of 40 years where only corn was grown without fertilizer addition to the soil. In a second step, over 40 years again under the same conditions, the poorly crystallized illite (PCI) loses illite layers to form a mineral at 11.2 Å, more smectites – rich. The mixed layer mineral loses illite content seen in a shift in the peak position to higher values. The increased change in clay mineralogy is due to the introduction of new hybrid corn varieties which significantly increase the grain production and hence the amount of potassium extracted per year. Hence in this experiment it appears that the illite is the first mineral to lose potassium, and this is followed by the illite layers in the illite – smectite structures. Similar results are reported by Barré et al. (2007) for laboratory experiments using rye grass growing from a clay substrate of illite and mixed layered minerals. Here the demonstration includes potassium saturation and plant extraction from a complex clay assemblage.

### HI Vermiculites, Chlorites, Smectites and Illites

HI minerals are identified by the presence of a 14.2 Å 001 peak position. This spacing indicates the presence of an organized hydroxyl ion interlayer mineral. High temperature minerals are called chlorite. These minerals have both the divalent ions Mg, Fe present in the hydroxyl complexes and Al ion complexes. Soil clay minerals can have Al ion complexes, most commonly admitted, but also most likely a significant amount of divalent ion complexes and this most often Mg ions (Righi et al., 1993). Potassium can displace some of the hydroxyl complex ions to form illite, the anhydrous interlayer ion mineral. In some layers $H_2O$ can be displaced by organic molecules as in smectites. However, much of the material remains in the hydroxyl form and this is called HI, hydroxyl interlayered mineral or soil chlorite. Thus the behaviour of HI minerals under chemical treatment can form different interlayer ion occupancies and apparent different soil clay mineral types. If laboratory treatment can change the apparent mineral type by substitution of different interlayer ions soil pore solutions can certainly effect the same changes if they are sufficiently concentrated in the appropriate cations.

Often, a given soil sample will have material of these different types present at the same time. In Fig. 4.5 the Sr – saturated (0.01 M $SrCl_2$) sample shows a strong, but slightly complex 14.2 Å peak with minor amounts of mixed layer minerals (12.3 Å peak) and illite minerals dominated by the PCI type (peak at 10.4 Å). One can see little if any smectite behaviour in an initially largely HI mineral assemblage upon glycol treatment. However with low intensity potassium treatment (0.01 M KCl) illite (PCI) is much more apparent in peak surface area. A significant amount of

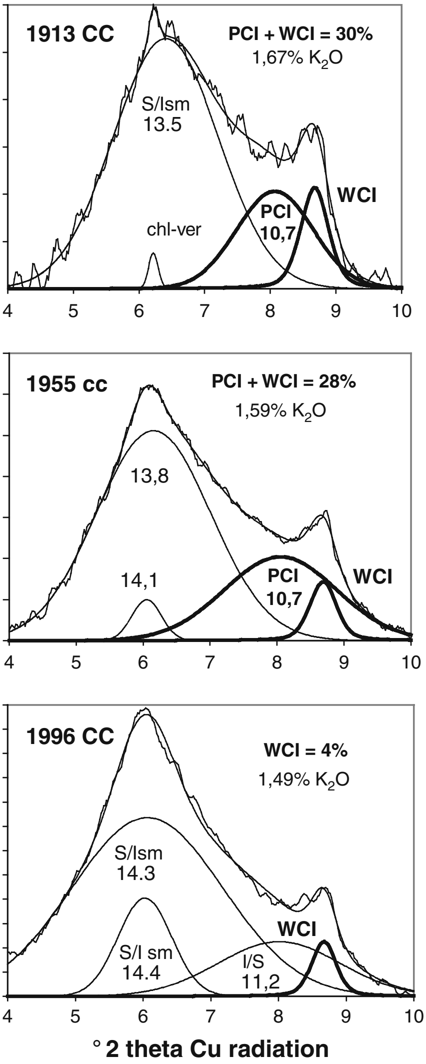

**Fig. 4.4** Effect of potassium extraction on illite/smectites mineral assemblages in an experiment of unfertilized continuous corn growth for 80 years in an experimental plot at the University of Illinois (Velde and Peck, 2006). The extraction of potassium is shown by the decrease in illite content (WCI and PCI; well crystallized and poorly crystallized forms of the 10 Å phase). Background – subtracted X-ray diffractogram treated using decomposition methods

mixed layer mineral (shift in peaks to the illite position, 14.1 and 11.5 Å) shows that there is an important portion of high charge material present where the hydroxyl ions can be displaced in favour of anhydrous potassium ions. Hence here we have an HI mineral with an important portion of exchangeable hydroxyllated cations present, showing a high charge smectites (vermiculite) behaviour. Much material has both HI and vermiculite layers present in the same structure forming mixed layered minerals.

A similar behaviour but one showing apparently only high charge layers and HI layers can be seen in different samples from the Po delta plains near Pavia (data

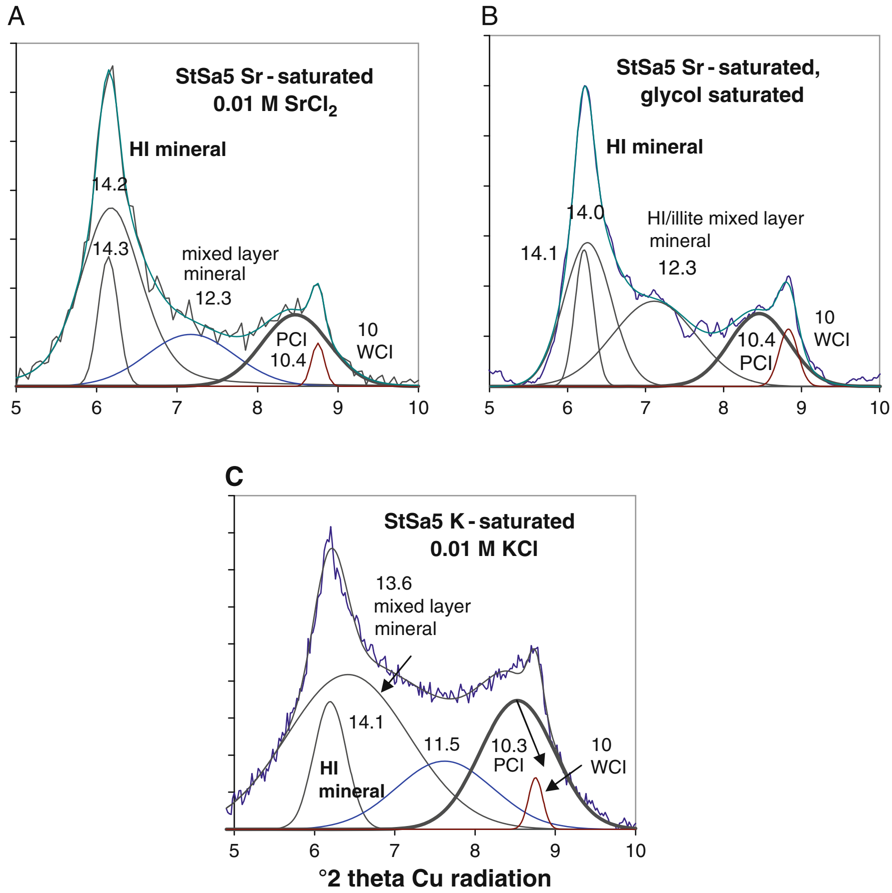

**Fig. 4.5** Effect of potassium saturation on a HI – illite mineral assemblage (Saint Savignien, Charents, France). The HI mineral, peak position at 14.2 Å is not displaced by glycol treatment, but a significant portion of the HI layers are filled with potassium upon saturation in weak concentration of KCl solution. The poorly crystallized HI mineral shifts upon potassium saturation from 14.1 to 13.6 Å, becoming slightly more illite – rich, whereas the PCI (poorly crystallized illite) peak area increases significantly. This suggest a significant exchange of hydroxyl interlayer cations with potassium in many of the HI mineral crystallites. Background – subtracted X-ray diffractogram treated using decomposition methods

supplied by F Terribile, Univ Frederico II, Naples). Figure 4.6 shows Mg treated samples (0.5 M $MgCl_2$) and those treated with strong KCl solutions (0.5 M KCl).

The Mg samples show strong sharp 14 and 10 Å peaks indicating the presence of chlorite and illite. There is no indication of a smectites mineral (peak towards 15.2 Å) in the samples. Potassium saturation only slightly widens the 14 Å peak but strongly increases the intensity of the 10 Å illite peak. The potassium saturation also changes the relative intensity of the first order and second order chlorite-vermiculite peak (14.2 and 7.1 Å), showing a weaker intensity 14 Å peak which indicates a

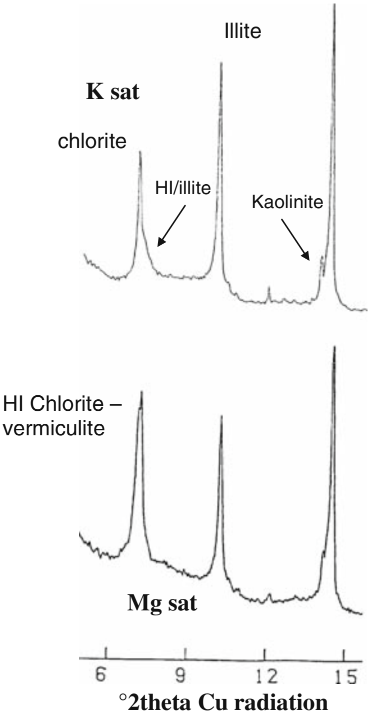

**Fig. 4.6** Effect of potassium or magnesium saturation on an apparently simple illite – chlorite clay mineral assemblage from the Italian Po valley sediments. Peak widths are narrow, indicating a high degree of order in the interlayer ion position and a relatively large number of coherently layers in the crystallite structures. The relative intensities of illite change between Mg and K saturation, and the relative intensities of the 14 and 7 Å peaks of the chlorite minerals indicate the presence of a well organized HI component which is replaced by potassium. Lower intensity of the 14 Å indicates an increase in Mg content of the exchanged minerals

change in interlayer ion composition of the 14 Å minerals, most likely due to a loss of aluminium ions being replaced by potassium. An identical behaviour was noted by Ross et al. (1985) for HI clays in soils which had experienced manure fertilizer treatments for 6 years.

It is quite apparent that HI minerals, identified as such in the untreated conditions, can have a variety of behaviours under different chemical treatments. These chemical treatments can occur under conditions of plant activity giving different types of minerals due in fact to different chemical compositions of pore solutions in the soils due to the influence of plants as will be seen in Sect. 4.2.

#### 4.1.2.3 Origin of Mixed Layer 2:1 Clays in Soils

Laird and Nater (1993) have indicated that the illite-smectite mixed layer minerals can be found preferentially in the fine fraction of prairie clays which is shown in Fig. 4.7.

This is a rather well known fact, but interesting to recall here. The grain size is smaller when the expanding minerals are present in the illite – smectite paragenesis. This must indicate some genetic paths in the formation of this material. In general one thinks of crystallization procedures when one invokes small grain size materials. However, we believe that most of the clay material in soils (in the

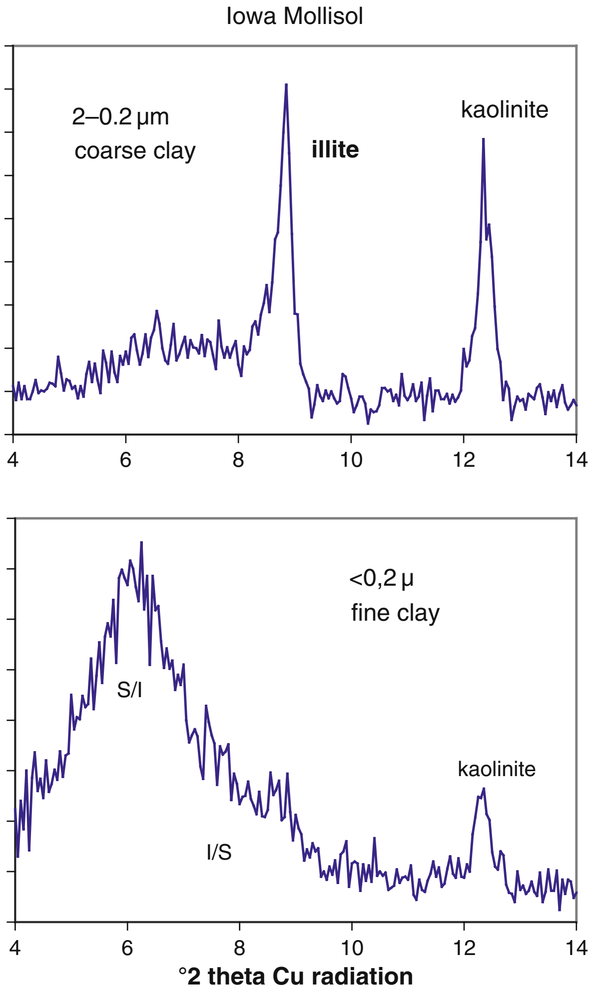

**Fig. 4.7** Indicaion of a change in clay mineralogy with particle size. The example is an Iowa Mollisol where the coarse clay has a dominantly illite – kaolinite mineralogy while the fine clay fraction shows a dominant smectite – illite mineralogy

plant – silicate interaction zone) has been formed to a large extent before it is present in this zone. The transformation of various high temperature phyllosilicates into soil clays of smaller dimensions and of mixed layer character can be seen in the descriptions of Righi et al. (1999), Gillot et al. (2000), Olsson and Melkerud (1989), Moberg (1990) among numerous studies. The characteristic of these transformations is the formation of smaller and smaller particles, but the chemical properties of the basic 2:1 mineral are retained to a large extent. Thus the 2:1 clay minerals in soils appear to be the product more of transformations, larger grains to smaller grains, than dissolution and crystallization reactions. However Gillot et al. (2000)

demonstrate that the individual crystals of high temperature phyllosilicates can change their composition within the 2:1 layers, in fact observations indicate becoming dioctahedral when initially trioctahedral (Righi et al., 1993).

Using TEM morphological observations Gillot et al. (2000) on soil minerals in eluvial E horizons of Spodosols in Finland have shown that nearly all clay particles exhibit dissolution features, which are seen both on edges and basal faces of the high temperature crystals. Moreover, the development of dissolution features results in a mosaic pattern: large particles are divided into smaller platelets by a continuous network of fine fissures and finally aggregates with diffuse boundaries and fluffy or cloudy pattern are formed. Large particles slightly affected by dissolution display an electron-diffraction pattern typical of ordered or semi-ordered stacking structures whereas electron-diffraction patterns from aggregates display ring patterns similar to turbostratic disorder.

Thus it appears that the weathering of high temperature phyllosilicates, micas and chlorites, produces mosaic like structures, partially dissolved where the 2:1 layers can have a modified compositon. The overall trend of phyllosilicate mineral weathering is to form dioctahedral lower charge 2:1 minerals from micas. Change in layer charge indicates change in chemical composition of the 2:1 unit layers.

An illustration, by X-ray diffraction observations, is given in Fig. 4.8 where an initial detrital, high temperature phyllosilicate assemblage of clay sized material, glacial flour deposited on the Atlantic shelf and re-deposited by storm action, is deposited in a Delaware Bay salt marsh where *spartina* grasses cover the sediments and fix new material. The development of soil clay minerals from high temperature chlorite – mica mineral assemblages in this instance is from the top downward in that the constant influx of high temperature mineral sediments is incorporated into the soil from above. The initial fine grained mineral assemblage is illite (mica) and chlorite concerning the phyllosilicate phases. In the figure the top most sample is the least altered with transformation of the phyllosilicates increasing downward. The initial alteration reaction is to form S/I, a smectite – rich mixed layer mineral. The relative proportion of the illite (peak area) decreases, whereas chlorite appears to remain relatively un-changed. The relatively less important in peak surface area of illite and the presence of a S/I mixed layer mineral are the major features of the diagram. One can propose an illite to mixed layer mineral transformation accompanied by perhaps a portion of chlorite. The second stage (going from root zone to lower root zone) indicates a strong loss of chlorite and the formation of an illitic I/S mineral. Poorly crystallized illite (PCI) is lost in the process of forming an illitic mixed layer mineral. The S/I mineral peak broadens and increases in relative surface area. Both mixed layer clays have distinctly wide diffraction peaks indicating fine grained and poorly organized structures. The interaction of the chlorite structure with the other minerals is not certain but it appears that the presence of a tri-octahedral interlayered mineral is largely lost. From the deposition rate in the salt marshes one can estimate that the reactions or transformations observed here occur over a period on the order of less than 15 years.

Here soil clays developing from a fine grained mixture of high temperature material are present in a short period of time. This indicates the action of bio-agents. One

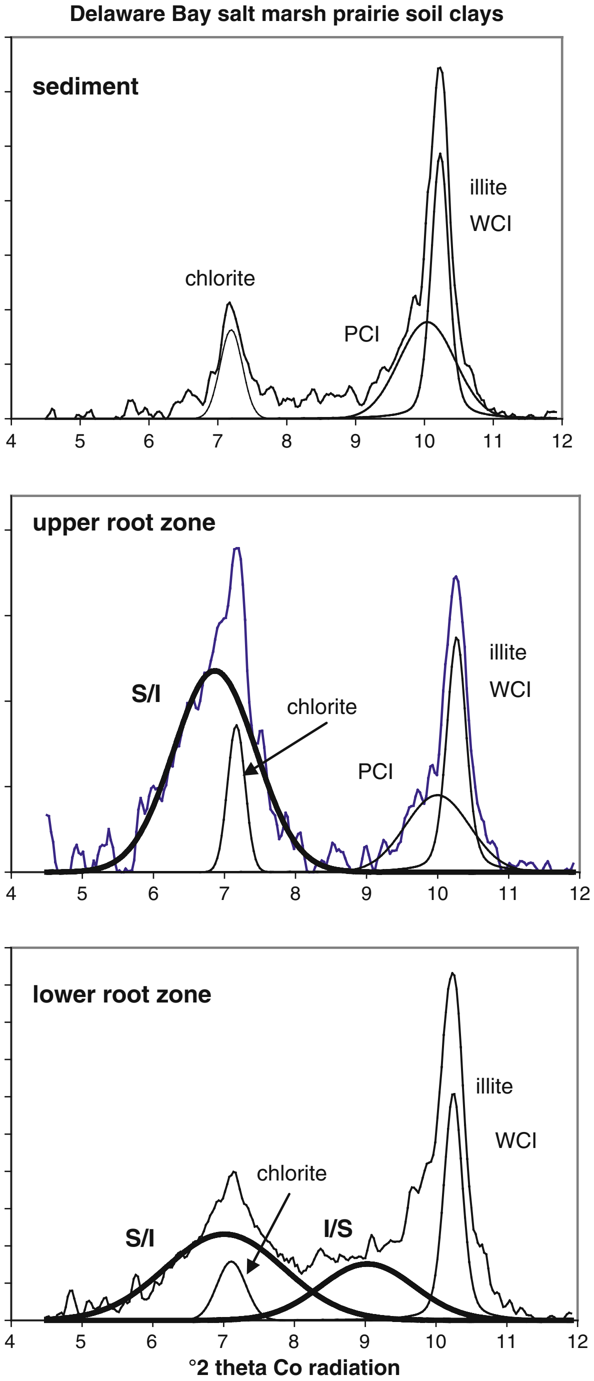

**Fig. 4.8** Indication of mineral change in a sequence of soils developed in a Delaware Bay (USA) salt marsh (Velde and Church, 1999). The sequence shows alteration of an initial illite – chlorite

would not expect the existence of a dissolution – recrystallization process over such short time spans (See Sect. 2.2). The appearance of less well organized crystallites of a mixed layered nature indicates that the process or transformation is not totally homogeneous and that the different layers in the structures will probably have slightly different properties, such as charge and charge site which produce two types of mixed layer minerals, S/I and I/S.

#### 4.1.2.4 Chlorite Alteration

Millot and Camez (1963) attributed most of the vermiculite or HI mineralogy to the alteration of chlorite in soils from mountain terrains of eastern France. According to these authors and many others since, chlorite can be a major source of clay minerals in soils.

Chlorite minerals altered by biological action (micorrihze) can be transformed into pure smectites in their laboratory behavior (Arocena et al., 1999). This is an apparent case of stripping the interlayer hydroxyl ion layer from the 2:1 substrate. Since it is assumed that most of the ionic substitution in chlorites which compensates charges in the tetrahedral site occurs in the interlayer site (Deer et al., 1962) one can expect that the a chlorite stripped of its interlayer ions will have a significant charge from one 2:1 layer to another. Several studies have indicated that the charge on the 2:1 layer changes and the ionic composition of the octahedral layer also. The alteration minerals change from a trioctahedral character to a dioctahedral one which means a loss of Mg, Fe and a gain of Al. These ionic displacements seem to occur in silicates at low temperature. Bauer et al. (2006) have shown that such changes can occur over short periods of time, however at temperatures of 80°C and under strong chemical conditions (several molar KOH solutions).

When the chlorite 2:1 layer has been significantly modified by such elemental displacements, the altered chlorite becomes indistinguishable from altered dioctahedral micas an forms part to the mixed layer "illite/smectite" mineral assemblage common to evolved soils. Thus altered chlorites (trioctahderal high temperature minerals) become to a large extent indistinguishable from mica alteration products.

From the above observations one can conclude that the reactions forming 2:1 clay assemblages is a complex process, using several materials to produce inhomogeneous phases. The different behaviors of the structures after treatment in the laboratory indicate the ability of the layers to react to chemical agents. These laboratory behaviors can probably be found to a lesser extent in the soil clay situations as they minerals are subjected to different pore solution chemistries, developed by plant action and rain water dilution.

◄

**Fig. 4.8** (continued) mineralogy deposited at the surface of the salt marsh sediments which progresses downward I the profile. This is the reverse of normal rock weathering alteration profiles. The initial chlorite component is altered as is the illite to produce two illite – smectites minerals typical of soil clays. The new minerals are the result of interlayer ion extraction of both the chlorite and the illite Background – subtracted X-ray diffractogram treated using decomposition methods

### *4.1.3 Complex Mixed Layer Minerals (KS):* Smectite, Kaolinite and Kaolinite/Smectite Mixed Layer Minerals

The overall tendency in alteration sequences is to lose alkali then silica compared 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. 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 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. Often, kaolinite is identified with strong chemical alteration but it can be produced in the initial stages of water – rock alteration.

However, an increasing number of reports of a "mixed" interlayer mineral, kaolinite/smectite, indicate that there is a possibility that a transition between 2:1 and 1:1 minerals can be found in alteration sequences. Among the situations where one finds kaolinite/smectite mixed layered mùinerals is in alteration sequences of eruptive rocks, where silicate glass is probably a factor of alteration (Wilson and Cradwick, 1972; Schultz et al., 1971). This seems to be independent of climate conditions.

### *4.1.4 Oxides and Hydroxides*

#### 4.1.4.1 Al-Oxy-Hydroxides

In soils and weathered rocks, aluminum may form different hydroxides, the most abundant being gibbsite (α-alumina trihydrate: $Al(OH)_3$) while its polymorphs bayerite and nordstrandite are much more rare. *Boehmite* (alpha-AlOOH) is common in bauxite deposits but less common in soils.The aluminium oxides and hydroxides have a non-distinctive grayish-white color, which is easily masked in soils except when large concentrations occur. These minerals form platelets in which the *(001)* faces are considerably more developed than the *(hk0)* ones. This is due to the fact that the Al-OH-Al bonds in the a-b plane (layer) are much stronger than the hydrogen ones between layers in the c direction. Consequently, the gibbsite morphology looks like that of clay minerals. For this reason, it was called "hydrargillite". Aluminum hydroxides may accumulate in the most weathered rock levels in tropical countries forming bauxite deposits. As do Fe-hydroxides, gibbsite may form also in the earliest steps of the weathering process. Thus, this phase is competing with clay minerals for aluminum ions. We will not consider these minerals in detail in this work. For detailed descriptions see the review papers of Schwertmann and Taylor (1989) and Hsu (1989) for Fe and Al oxy-hydroxides respectively.

#### 4.1.4.2 Gibbsite (Aluminum Hydroxide)

The hydroxyl aluminium mineral gibbsite is generally 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 aluminium exportation. Gibbste is 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 more arid climatic zones essentially. Gibbsite is however rare in soil clay assemblages, the plant – clay interaction zone, 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 often sufficiently high that it will poison many plant species (Wolt, 1994). High concentrations of alumina cannot be tolerated by many plants. However, if the plants send roots to sufficient depths, they can probably extract silica that is the product of mineral dissolution in the deeper saprolite or saprock zone and bring it into their biotic sphere deposited in the aerial parts of plants as phytoliths. This silica, in an amorphous and highly reactive form, will be combined with gibbsite to form kaolinite and probably also smectites (becoming HI mineral in most cases) in the soil zone.

It must be remembered that the water which reaches the water – rock alteration zone at the base of alteration profiles is often present due to a rapid drainage along major fracture or pore systems. It is not charged with ions from dissolution of minerals nor through the equilibration of clays with the aqueous solution. Thus the presence of gibbsite in the early stages of weathering, in the saprock zone, 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 rock types, alumina poor, will not lead to the formation of gibbsite in the early stages of alteration.

#### 4.1.4.3 Transition Metal Oxy – Hydroxides

Fe-Oxy-Hydroxides

Different species of Fe-oxides and hydroxides are formed in weathering or soils reflecting the moisture, pH, Eh and microbial activity conditions. The $Fe^{3+}$ cation is framed in different oxide or hydroxide crystal structures. These iron minerals

**Table 4.1** Color of Fe oxides (simplified from Scheinost and Schwertmann, 1999)

| Fe oxide | Most frequent color | |
|---|---|---|
| Hematite | Moderate reddish brown | $\alpha$-$Fe_2O_3$ |
| Goethite | Strong yellowish brown | $\alpha$-FeOOH |
| Lepidocrocite | Moderate orange | $\gamma$-FeOOH |
| Ferrihydrite | Brownish orange | $Fe_5HO_8 \cdot 4H_2O$ |
| Akaganeite | Strong brown | ß-FeOOH |
| Feroxyhite | Strong brown | $\delta$-FeOOH |
| Maghermite | Dark yellowish brown | $\gamma$-$Fe_2O_3$ |

The most common coloring agents in soils are goethite and hematite. The ratio of hematite (red) to goethite (yellow brown) seems to be controlled by the pH of the soil (Schwertmann and Taylor, 1989).

become a dominating phases in the final stages of weathering because of their low in aqueous solutions. They form thick indurated horizons in the inter-tropical zone (laterite). However, they are present in all the weathering process including the initial steps where they are associated with different types of clay minerals. They have a great importance in the distribution of iron since after oxidation, $Fe^{3+}$ ions expelled from the silicate structures spontaneously form oxides or hydroxides. Scheinost and Schwertmann (1999) show that the colour of oxides, hydroxides and hydroxy sulfates is determinative for that of soils (Table 4.1).

Mn-Oxy-Hydroxides

Manganese oxide minerals have a black color. They show even a greater tendency than iron oxides to occur in concretions. Manganese-rich micromorphological zones in peds that are black, often also contain large amounts of iron oxides. The main mineral species are *pyrolusite* ($MnO_2$), *birnessite* $(Na,Ca,K,Mg,Mn^{2+})Mn_6{}^{4+}O_{14}{}^{*}H_2O$, *lithiophorite* $(LiAl_2Mn^{2+}Mn_2{}^{4+}O_9{}^{*}3H_2O)$, and *hollandite* ($BaMn_8O_{16}$).

### 4.1.4.4 Laterites

A special case of alteration under tropical conditions is the formation of laterites. These are depositions of strongly bonded iron oxides and aluminum hydroxy oxides forming a crust. These alterations are found in the present savanna areas bounding the tropical rain forests of Africa and South America. The difference in the mineralogical expression of the two alteration types is probably due to climate; in the savannas the seasons are contrasted, with high rainfall during one season and a contrasting dry season. Tropical forest have constant rainfall all year round. The vegetation is of course different also, rain forests are tree dominated (broad leaved evergreens) 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 concentrated aluminum in the form of gibbsite or boehmite, hydrous and anhydrous alumina, and especially iron in the form of hydroxyl – oxides. 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 potential as a resource of iorn and their qualities as construction materials. The striking feature of these phenomena is a zone of accumulation of oxides and hydroxides below the soil zone. This accumulation zone is one due to intense leaching and transport of fine grained material (Aleva, 1994) and its deposition below the surface. Laterites are complex, showing the formation of concretions and nodules which indicate local, intense migration of ions to form specific mineral concentrations (Boulangé, 1984, pp. 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, pp. 4–6). These soils sequences were formed under conditions of intense rainfall for a part of the year and a more dry regime for the 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 occur over long periods of time. One can assume that laterites are the products of alteration which must have persisted over at least tens of thousands to millions of years (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 over long periods of time contrary to those in the northern hemisphere,which are strongly affected by recent glacial cycles. In most places where they are found today the oxide crusts appear to be unstable and can be seen to be breaking up. Hence one can assume that the laterites are a fossile of sorts, corresponding to climatic conditions no longer active.

The saprock zone (recent water – rock interaction) usually contains kaolinite and smectite along with iron oxides (goethite). Gibbsite and goethite – hematite become important in the bauxitic and duricrust zones. Quartz appears in most horizons indicating its chemical inertia.

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 intital 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.

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/year) to moderate (850–1,400 mm/year) to high rainfall (1,200–2,200 mm/year). Under high rainfall one can find vermiculites type minerals at the rock – alterite interface whereas above this zaone 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.

#### 4.1.4.5 Red Soils

One can consider red soils to be the product of contrasted season alterations. Here strong dissolution occurs during the rainy season and strong evaporative movement and dehydration of hydroxyl-oxides 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.

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.

### *4.1.5 Poorly Crystallized Silicates Imogolite and Allophone (Allophone Si – Rich, Imogolite Si = Al)*

These minerals, found in alteration sequences, are often precursor phases to others. They are formed through the rapid precipitation of Si-Al, forming a rather nebulous phase, allophane, with various Si/Al ratios and Si-Al imogolite with Al=Si. Both are formed during the alteration of vitreous rocks or under conditions of alteration under high pH control (Farmer and Lumsdon, 2001; Farmer, 1999).

Allophane and imogolite are called minerals. But only imogolite has ionic coordinations ordered over short distances which can be identified by infrared or perhaps Raman spectral methods. There is a regularity only in small atomic molecular domains so that X-ray diffraction does not show coherent domains. Allophone by contrast appears to have much more variable chemical relations and only on the molecular scale so that there is no characteristic or much less so as would be seen by infrared means of identification. Allophane is pratically undeterminable using X-ray diffraction. On the contrary imogolite presents some broad diffraction peaks. Both minerals are currently detected in soils using a combination of infrared spectroscopy, thermal and chemical analyses. Even if still debated, the short range "crystalline" structures of these minerals have been approximated (Cradwick et al., 1992; Wada, 1989). Allophane contains a hydrated network of Si-Al-O atoms. Both

$H_2O$ and OH units are present. The stoichometry is slightly variable but usually is between 1:1 to 1:2 Al/Si atoms. Imogolite a hydrated network of SiAlO atoms with a rather well organized tubular structure which is not detectable by XRD methods. The ratio of Si to Al is near 1.

The key to the presence of both imogolite and allophane is a continous humid condition of alteration environments. Under conditions of contrasted climate they are no longer present and are probably transformed into gibbsite for allophone and kaolinite or 2:1 minerals for imogolite. They represent hence humid alteration conditions, and the presence of highly reactive substances, for the most part. The allophone 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.

#### 4.1.5.1 Rainfall and Vitreous Rocks

Imogolite and allophane are typical of soils formed on glassy rocks in various types of climates (andisols). The nearly constant moisture content of andisols maintains the stability of these minerals. Under drying conditions these minerals become unstable and rapidly transform into halloysite. They form complex associations with organic matter in the humic horizons of these soils. The preferential complexation of Al by humic compounds may inhibit the formation of allophane. Imogolite has been identified in spodosols where its formation is related to the degradation of the Al-organic matter complexes.

Andosols represent a combination of two specific variables which combine to produce very characteristic 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 cation exchange capacity (CEC) often related to the amount of amorphous or extractable alumina (Shoji et al., 1993, p. 2; Garcia-Rodeja et al., 2004). Although fresh or immature Andosols usually select Ca over K, it has been noted in several instances that slightly more mature Andosols (containing 1:1 minerals) can strongly select potassium (Ndayiragije and Delvaux, 2004). In general, Andosols are fertile. This fertility is most likely due to a continued high weathering rate of glassy materials which furnishes plant nutrients (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 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 the review Catena 2004 Vol. 56). However continuous humid conditions are very important for their formation.

Several principal factors then are necessary to produce these special soils, high rainfall, 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, 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 is a glassy 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. Andosols 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, pp. 113–123) are:

*Allophane*, *Imogolite*, *Gibbsite* the hydroxyl form of aluminum, *Opaline silica*.

*Halloysite*, the hydrated form of kaolinite.

#### 4.1.5.2 Weathering Process

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 Sect. 2.1), 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. 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 allophone. These are the water – rock interaction minerals found at the rock – alteration interface (Sifferman, 1973, pp. 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).

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 allophone and favour 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 eruption, 1883) ash fall material developed in a rainforest environment (Fauzi and Stoops, 2004).

#### 4.1.5.3 Clay Mineral Origin in Andosols

In the brief description above, it appears that Andosols, soils based upon the alteration of glassy silicate materials, will first produce un-structured 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 earths 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 organisation 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 along 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 allophone, 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 allophone 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 Andoslos (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, allophone 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.

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 Podsols under forest growth (Shoji, 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 decidous 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 Ah horizons. 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 (HI) 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 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 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 podsols in tropical forest areas (Lucas, 2001, p. 138). Clearly plants can have a strong impact on soil clay mineralogy.

### 4.1.6 Some Minerals Formed and Found at the Surface but Not in Soils

Not all minerals formed at the surface are associated with soils, i.e. the zone of plant activity. Two are notable, as follows:

#### 4.1.6.1 Palygorskite

Palygorskite and sepiolite are minerals which can be formed in alteration profiles due to the effects of evaporation. These magnesian minerals formed in desert soils where capillary action precipitates saturated solution material to form magnesian silicates. They are not stable at the surface, in the soil zone (Paquet, 1970; Badraouri et al., 1992). Khademi and Arocena (2008) demonstrate one possible reason for this instability. Bacteria are efficient in extracting Mg from thse non-silicate minerals leaving kaolinite in their place. Hence they are most likely to disappear in many soil formation processes, in the biosphere. These minerals are relegated to areas of very low water activity near the surface where rain water 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, Chap. 7). Hence these minerals are in fact present in the C horizon of alteration profiles but not in soils, and usually in sedimentary deposits where soil is little developed at the surface (see Sect. 2.4.2). An interesting case of palygorskite formation is documented by Hillier and Phandande (2008) where the mineral is formed in arid climate agriculture in cases of flood irrigation. It is found in below surface horizons due to salt accumulation. Surprisingly the formation of this mineral can occur over periods of 40–50 years or less.

#### 4.1.6.2 Zeolites

Zeolites are tecto silicates classified in roughly the same mineralogical and structural family as feldspars. The contain alkali ions and have a high silica content. Such minerals would not be expected to form in soils nor in regimes or water – rock interaction. However, in regimes of intense evaporation of surface waters, zeolites are known to form. Spiers et al. (1984) describe such a situation in surface environments. Zeolites as well as palygorskite can be found in the evaporate crusts of saline lakes, features which are not related to lateration profiles. Jacob and Allen (1990) observed that in fact alkali zeolites were unstable in the A horizons of arid soils in Texas. But as with palygorskite, when soil pore waters are drawn to the surface under conditions of intense evaporation, one can find under certain circumstances the formation of zeolites as deposites in saline sediments. These are minerals which contain the elements which have been taken from alteration zones under conditions of water – rock interaction. However, if the water carrying these elements does not reach a large body of water (the ocean) then one can at times find a re-deposition of the dissolved elements in the alteration sequence. In the case of zeolites, the zone of deposition through evaporation of pore waters is in the A and B horizon unlike the palygorskite occurrences which are found in the B or C horizons.

The zeolites are high in silica and alkali content, especially potassium, forming clinoptolite, the potassic low temperature zeolite phase. They are accompanied by amorphous silica. The alumina needed to form the zeolites appears to come from smectites in the soil profile. The zeolites are accompanied by an increased clay content of illite, also a potassium mineral. Such occurrences are rare, of course in that they go counter to all of the normal alteration chemical principles, but it is logical that waters draining alteration sequences, enriched in alkalis and silica would produce such minerals if they were found in an evaporative environment.

It is unlikely that any plants will be found in such evaporitic environments, or only as sporadic islands of vegetal activity. Hence it is not appropriate to classify zeolites as soil clay minerals as is the case for palygorskite.

This overview of clays and clay minerals present in soils and alteration zones indicates a vide variety of minerals, with different structures and chemical compositions. One can classify them into the silicates where silica is linked to aluminum ions through bridging oxygens. These minerals are the the 2:1 phases (HI, illite and smectites), 1:1 phases (kaolinite and halloysite) which are crystallized and can be identified by X-ray diffraction. Minerals of similar composition but lacking long range organization can be present and usually dominant when present. Oxides and hyroxy-oxides can be important and at times dominant. Such are the results of interactions of rainwater with rocks and the modulation of this material by plants.

## 4.2 The Critical Clays, the 2:1 Clay Minerals in the A Horizon: Examples in Soil Profiles Showing the Effects of Plants and Their Bio-agents

In looking at the literature on clays and clay types found in natural settings, it is apparent that certain features of plant regime can affect the type of clay mineral present in the soil zone. Given the same climate conditions, differences in topography or plant succession can effect transformations in the clays. The best examples, or most clearly observed, are those where human intervention has varied the vegetal cover of essentially the same soils based upon the same materials under the same climatic conditions.

### *4.2.1 Trees of Different Types: Conifer and Deciduous*

Tice et al. (1996) report changes is soil clays over a 41 year period where oak and pine forest were compared. Observations were made on soils developed from granitic material under a Mediterranean climate. The initial and surrounding vegetation was shrub and sparse grass. Plantation of pine and oak was made and the soil clays observed after a 41 year growth period. The soil – alterite profile clay mineralogy shows a strong soil vermiculite (HI) component which becomes illitic upon potassium saturation in the alterite zones. This is the case for both both oak and pine forest soils. However in the A horizon, the pine clay mineralogy is the same as that at depth but the oak forest shows a large loss of vermiculite and the formation of illite. Archived samples show the vermiculite mineralogy in all samples. Hence the oak forest has provided enough potassium to change the soil vermiculite into an illite by forming an anhydrous potassium interlayer mineral. Here the 2:1 structures of the minerals are most likely very little affected by the plant regime. The only change has occurred by a strong enough presence of potassium furnished by oak leaf litter to saturate the high charge sites in the HI material.

The plant regime controls the chemistry of the soil solutions sufficiently to change the interlayer ion site populations.

### *4.2.2 Trees and Prairies: Contrasts Brought About by Plant Regime*

#### 4.2.2.1 Fluvio – Glacial Sediment Clays

Clays in soils in Denmark, (Madsen and Norberg, 1995) based upon fluvio – glacial materials were determined for different plant regimes. The regimes have been present for 60–75 years. The different plants were spruce (*Picea abies*), soils under a large oak tree, under heather – crowberry and another under grass vegetation. Clays in the lower, B horizons of the sandy soils showed similar clay suits essentially smectite minerals and a lesser amount of kaolinite. The clays are dominantly 2:1 types with exchangeable ions present in the interlayer positions.

1. Under spruce trees the clays develop a strong HI or soil vermiculite character in the surface soil horizon. The interlayer sites are filled, most probably, with an incomplete Al hydroxyl layer. However a large portion of the clays remain as smectites.
2. Under heath cover the clays develop a HI – vermiculite mineral suite and a strong illite phase is present.
3. Grass produces a similar mineralogy to that of the heath, with illite and HI vermiculite.
4. The oak tree changed the clay suites the least, but a definite shift to an illite phase is visible.

The initial clays, those deeper in the profile which were probably present at the surface in the early stages of the experiment, were affected by the plant regime producing phases that indicate high charge layers of 2:1 minerals, expressed either as illite (anhydrous potassium interlayer) or HI – vermiculite with Al-OH interlayer ions. One can suppose that the initial clays have a lower charge, and most likely they have less access to hydroxyl-Al and K ions. In the cases of grass -heather, a significantly greater availability of potassium produced the illite mineralogy.

Augusto et al. (2001) have identified the effects of Al incorporation into high charge 2:1 mineral layers (vermiculites) as induced by different types of tree regimes, conifer and deciduous at two forest soil sites. Test vermiculites were imbedded in soils under different tree forests. The results, after a three year experiment, indicate that the type of tree present can effect fixation of hydroxyl-cations and that the soil type is also important. Thus the plants and the overall alterite chemistry combine to determine the activity of different ions in the soil solutions. None of the tree types appears to have induced an illitic (potassium) mineral in the vermiculite test minerals. However, not only Al but also Mg hydroxyl ions were detected as being fixed in the clay interlayer sites. The experimental design was such that the effect of plant regime was tested at different depths (0–40 cm) in the soil – alterite materials. There is a significant difference in reaction effects, decreasing with depth, in all cases. The greatest clay change is effected in the upper 5 cm of the profiles, essentially in the leaf litter zone. This is direct evidence that the chemistry of soil solutions affecting clay mineralogy is driven by plants and that the results are seen in a short period of time, in this case 3 years.

#### 4.2.2.2 High Mountain Wet Prairies

Unpublished data gathered by Velde, illustrate some of the effects of plant control of clay minerals in young soils in these cases based upon granite (Bighorn mountains, Sheridan Wyoming) and rhyolite (Hebegen Lake, western Montana). Three series of samples were taken from zones near the natural prairie – forest interface in high mountain prairies. Soils below isolated trees or forming small groups of 2–5 individuals surrounded by prairie or soils from natural prairie were sampled in triplicate. Sampling was within 20 m one from the other at each of the sites. The soils were relatively young with a maximum of 30 cm depth to bedrock. No significant layered or horizon structure was observed, i.e. A, B and C horizons. Strong organic content was found throughout the soil zone. In general, the prairie soils showed strong illite content and much less interlayered illite-smectite material. Soils under both aspen (deciduous) and spruce (conifier) trees showed significantly more S/I and I/S minerals in the XRD diagrams (Figs. 4.9 and 6.10).

The spectra are very similar for the three types of forest cover. Illite is the dominant soil clay mineral present. Hence in the initial stages of weathering, the potassic 2:1 mineral dominates. In all spectra one finds a small HI – soil vermiculite peak indicating the presence of a hydroxyl interlayer ion in some of the clays. The major difference from one biome to the other is in the mixed layer mineral content. The illite/smectite mineral is most present in the spruce forest soils and least present in the prairies soils. These observations suggest that the prairie regime favors the formation of a high charge 2:1 mineral where an abundance of potassium, from the decomposition of the granite, is fixed as an anhydrous layer in the minerals.

If we assume that the conifer and aspen trees are replacing prairie vegetation in these boundary zones, it is apparent that the first soil clay mineral formed in abundance from the underlying rocks by interaction with prairie plants is illite. Since both the granite and rhyolite contain much fine – grained muscovite, this is not surprising. A small but definitely HI mineral peak is present. One should note that there is a significant amount of PCI present (poorly crystallized illite, PCI), indicating the possible presence of soil illite. Illite remains a major component of the soils under conifer and deciduous trees but very much interlayered illite – smectite is present as well as a persistent HI mineral. It appears that in these cases the initial stages of tree colonization engender the formation of smectitic minerals.

These observations are similar to those made on the four vegetation types in Danish soils where spruce develops more smectitic (low charge 2:1 structures) and HI – vermiculite soil clays (Madsen and Norberg, 1995).

#### 4.2.2.3 Sequoia and Grass

A comparison of clay minerals developed under *Sequoia gigantea* trees and surrounding grass (prairie) (BV unpublished) gives similar information to the above observations of mountain prairie and forest clay suites but in a more limited time frame. In France the sequoia, a tree from northern California, was introduced and

**Fig. 4.9.** (continued) unexpected to see illite (10 Å mica – like mineral) present. However it appears that the tree soils are more active in extracting the potassium of the clays in the top soil forming smectitic minerals

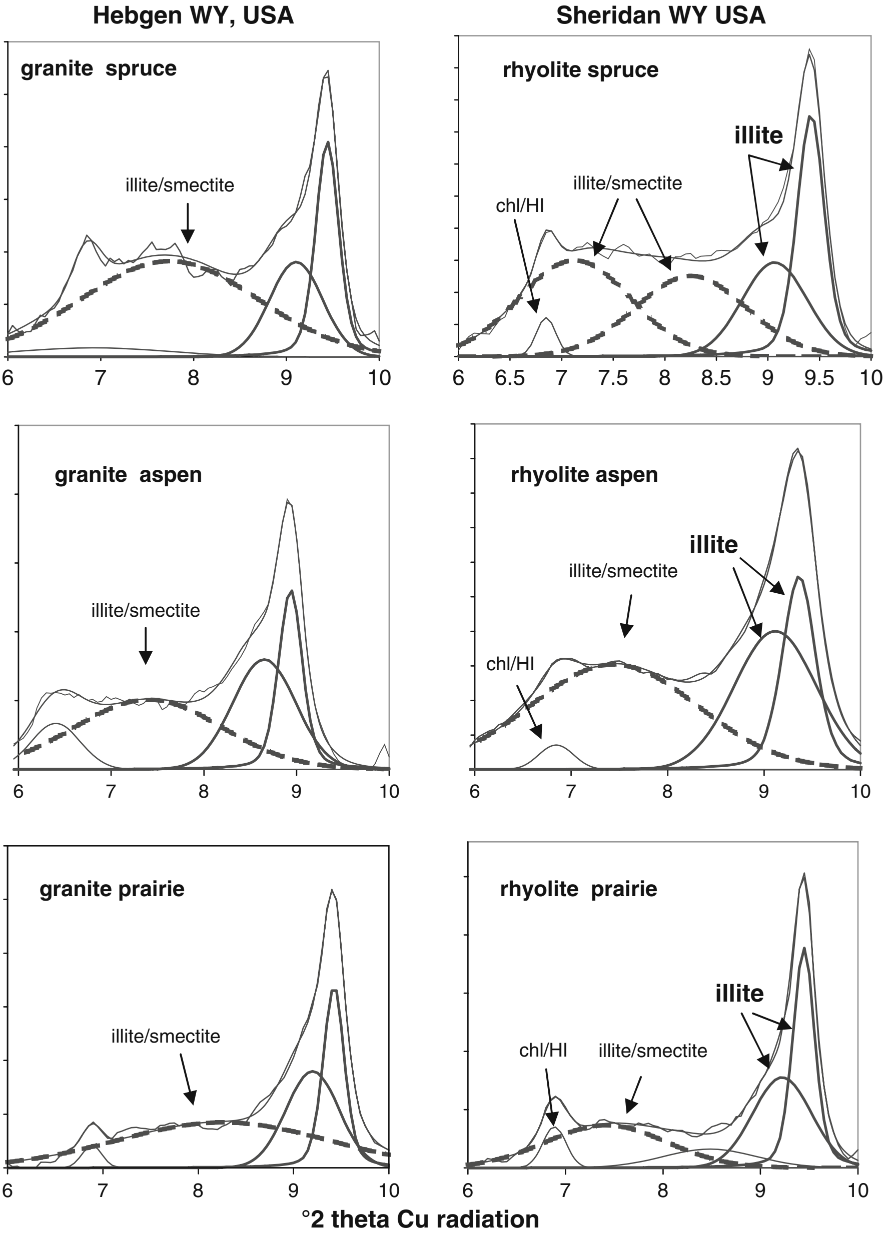

**Fig. 4.9.** Example of the effect of different biomes on clays during alteration of granitic rocks in the Rocky Mountains (WY) USA. Background – subtracted X-ray diffractogram treated using decomposition methods. The samples came from soils beneath trees or on prairie within tens of meters of one another. Spruce tree soils show a strong illite/smectites component, aspen (deciduous trees) show a similar mineralogy while the prairie shows a much stronger illite component. All soils have a small HI mineral content. Since the granites and rhyolite contain muscovite, it is not

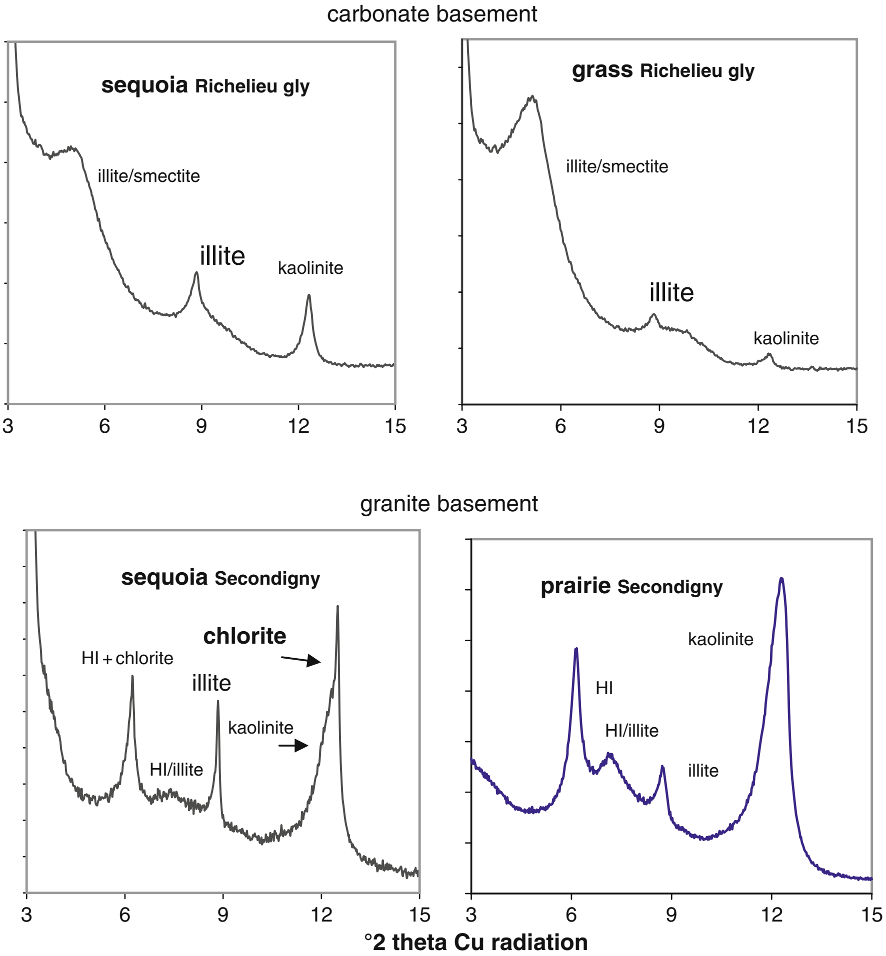

**Fig. 4.10** Example of the soil clays developed under sequoia trees after 150 years growth compared to those of surrounding prairie (Richelieu, Vienne and Segondigny, Deux Sevres France). The clay mineralogy is similar in the carbonate basement soils with an decided increase in illite under sequoia whereas the granite basement soils produce Hydroxy interlayered minerals either HI (aluminous or magnesian) under prairie or chlorite (magnesian) under sequoia. This sequence indicates the importance of rock chemistry in forming new soil clays as well as the influence of the types of plants growing in them

used to form a part of the romantic style landscaping on great domains in the 1850s. The trees planted in the parks around older castles grew and developed surrounded by trimmed grass or natural prairie. The previous land use of the terrain in the parked areas is not known. However we do know that the plant regime was determined and maintained from given dates. Thus in such instances we have a means of comparing the effects of two given plant types on the soils under them.

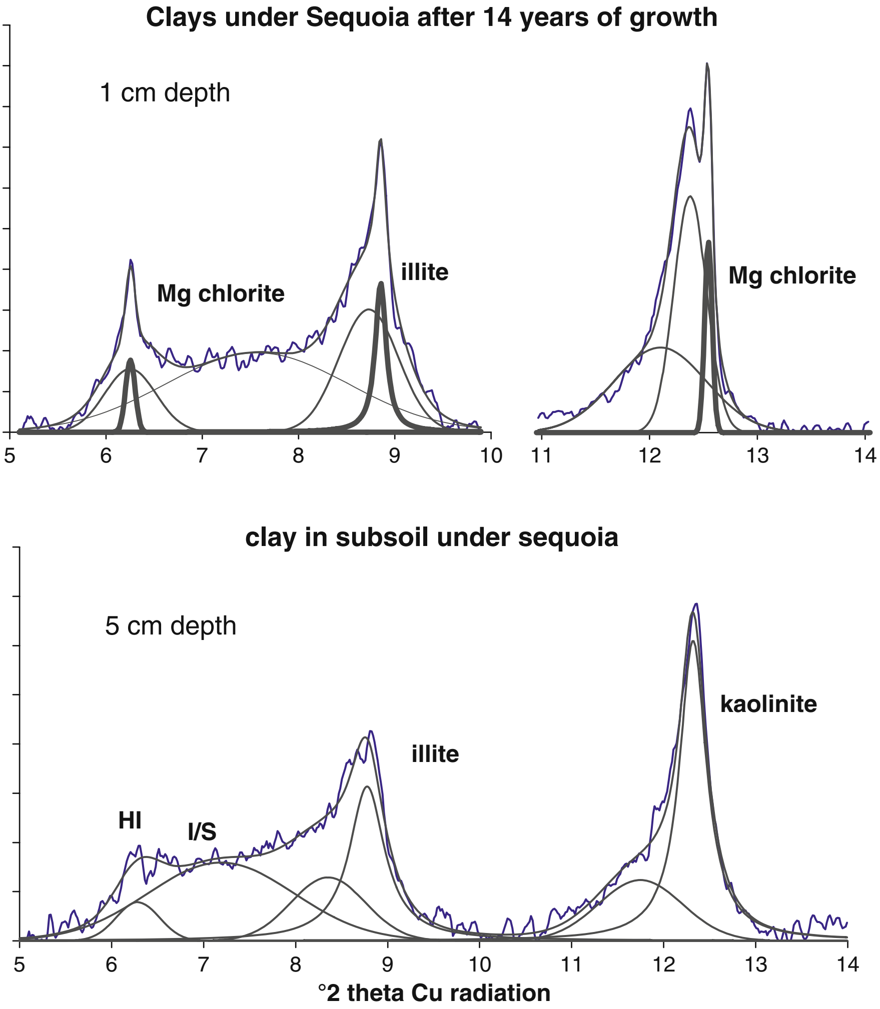

**Fig. 4.11** (**a**) Soil clays under sequoia after 14 years of growth. Background – subtracted X-ray diffractogram treated using decomposition methods. The upper diagram indicates the presence of a magnesian chlorite, formed by insertion of a Mg hydroxyl interlayered layer in a smectites. The 5 cm deep sample below the top soil shows the initial clay mineralogy found at depth and around the tree in the grassed area (La Percerie, Vienne, France). This rather rapid change in interlayer ion occupancy type changes the apparent clay mineralogy, where the chlorite is chemically inert compared to the smectites minerals it replaces; However potassium saturation extracted the interlayer Mg hydroxyl material, indicating that the interlayering was not polymerized and hence rather unstable. (**b**) Photograph of the 14 year old sequoia. (photo DV)

Comparison of the soil clays under the two plants shows differences in fine clay potassium content, usually higher under sequoia, and the clay mineralogy where illite tends to be more distinguishable. Six pairs of sequoia – grass soil samples

**Fig. 4.11** (continued)

gave an average $K_2O$ content of 3.21weight percent for sequoia clays and 2.78 for those under grass. This is not enormous but still 15% more potassium under sequoia is potentially important. The samples were collected on essentially two types of subsoils, one on carbonate and the other on granite, gneiss and loessic materials. The carbonate soils, more basic pH being controlled by carbonate fragments in the top soil, showed mostly smectite/illite mineralogy while the granite – loessic soils, more acidic, showed strong HI mineralogy. All soils contained kaolinite in the clay assemblage. Thus initially it is apparent that the type of subsoil, or alteration substrate, is important in defining the clays present. The 2:1 clay minerals indicate a hydroxyl component in the interlayer sites which is lacking in the carbonate substrate soils. In all soil types the sequoia showed a tendency to have more potassium minerals and an equivalent or a higher potassium content that that found for the grass soils. X-ray diffractograms are shown in Fig. 4.10 which indicate the differences between plant regime clays on different substrates. Two minerals differentiate the two plant regime clay assemblages: illite present in all cases but more abundant in the sequoia soils, and chlorite present in three of the more acidic soils under sequoia but not present in the corresponding prairie soils. The chlorite is identified by the sharp peak at 14.2 and 7.1 Å. In the sequoia Secondigny sample the 7.1 Å peak is distinguishable but less so for the 14 Å peak where HI minerals are strongly present and mask the chlorite peak. Such a chlorite was also identified under sequoia for a tree planted for just 14 years compared to the surrounding grass (Fig. 4.11) where the both the 7 and 14.2 Å peaks can be clearly seen. Here there is also an increase in a sharp illite peak indicating an increase in the potassium component of the clays as well as the presence of the chlorite peaks. Thus the increase in the potassic (illite) and (chlorite) components of the clay assemblages can occur over short periods of time (14 years). However, as the image in Fig. 4.11b indicates, the size of the tree in question is such that one could expect significant control of the soil surface chemistry.

When identified the intensity of the 7Å (002) peak of the chlorite was more intense than that of the 14.2 Å peak (001). This indicates that this new soil clay mineral contains magnesium in a hydroxyl interlayer site (see Sect. 1.3). This comparative study indicates that the soil substrate (chemistry) can influence the phases produced under two different plant regimes in a parallel manner, a similar conclusion to that of Augusto et al. (2001) concerning the effects of soils under different types of trees at two different sites as they affect a high charge 2:1 vermiculite mineral.

Plant regimes can nevertheless control to a certain extent the type of interlayer ion present in the interlayer ion site of 2:1 minerals (illites and chlorites) by controlling soil pore fluid chemistry. However, the effects are modified by the general chemistry of the soil substrate, the bedrocks. For the moment we do not know the dynamics of such processes or the reversibility of ion exchange in interlayer sites. The presence of anhydrous potassium indicates a relatively fixed site where normal ionic concentrations in soil solutions will not significantly modify the interlayer ion population. The time necessary to build up a strong hydroxyl layer is less well understood. In the sequoia experiment, the chlorite formed after 14 years was unstable in 1 M KCl solution, whereas the chlorite formed over 150 years was not affected by the treatment. Hence the chemical stability of the hydroxyl phases is perhaps a function of greater periods of time than the formation of anhydrous potassium layers.

In certain instances the forest – prairie plant regime can concord to produce the same type of clays at the surface. In Fig. 4.12 oak forest and prairie soils (maintained for nearly 100 years) show a change in clay composition (clay type and hence soil chemistry) developed on a sandy soil on a site near Paris France. The deeper samples (45 cm) show a strong HI mineral content, whereas the oak forest and prairie both show a dominance of illite (potassic 2:1 clay mineral) in the surface (soil) A horizons. In these examples it appears that both oak forest and grassland replace a significant portion of the interlayer HI hyroxy ions with potassium, which is held in the anhydrous state giving a 10 Å spacing. In this case there is a convergence of clay mineral types by the action of the plant regime at the surface in the organic A horizon (Fig. 4.12).

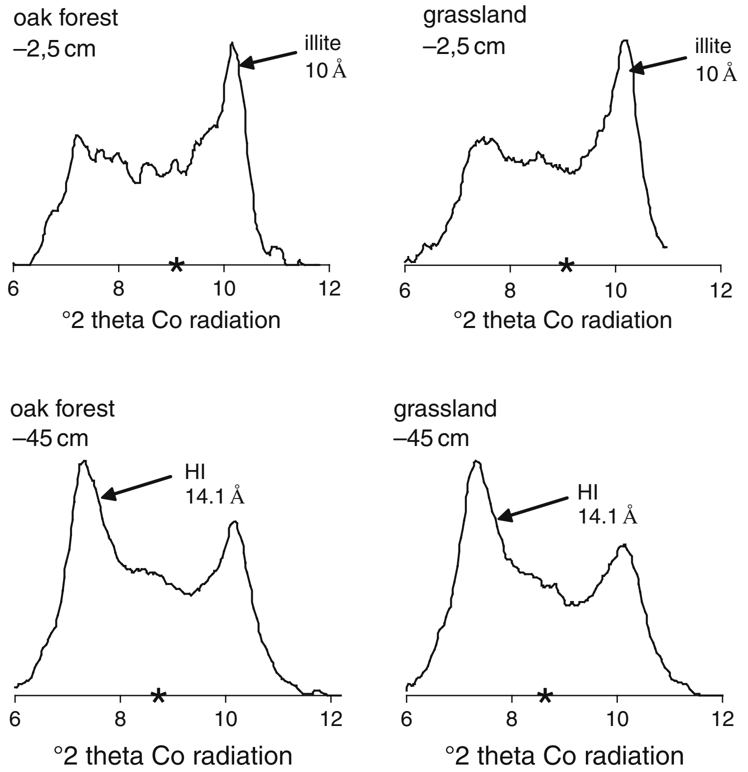

**Fig. 4.12** Grassland and oak clay mineralogies at two different depths on sandy soil (ENS facility at Folljuif, Yvelines, France). Spectra are an average of four sampled sites

### 4.2.2.4 *Shrubs and Prairie:* Red and Black Soil Sequences

In a number of semi-arid steppe climates, it has been noted that basalts and basic rocks produce alternating red and black soils, most often depending upon topography (Bühmann and Grubb, 1991; Herbillon et al., 1981;Vingiani et al., 2004). Typically the black soils are found in small basins or shelves along a topographic sequence in rolling hill country. On the slopes one finds red soils. The red soils are composed dominantly of kaolinite and iron oxides and the black soils are more smectite – rich. However, close inspection indicates that the soil clays contain smectite/kaolinite mixed layer minerals. The mixed layer minerals in the red soils have a larger kaolinite component and the black are more smectites – rich. The proportions vary from one site to another. Typically, the soil clay composition becomes more potassic at the surface and the clays have a small illite component whereas it is almost absent in the deeper C horizons. On the slopes iron oxide and kaolinite rich mixed layer minerals dominate. Further the black soils, as one would expect, have a higher organic material component.

In general, the clay content of the black soils in the depressions is greater than that of the red soils on the slopes. Hence one finds more clay and more organic matter in black soils. It is well known that grasses thrive more in wet, clay rich soils, especially in semi-arid climates. On the slopes one finds scrub and sparse grass. The studies showing clay mineralogy were conducted on grazing or farmed land so that these vegetation types have been effaced for the largest part. Nevertheless one can propose that the depressions were grass – rich and the slopes with less vegetation. The difference in biome led to a difference in clay mineralogy, where reducing conditions fixed the iron in a divalent state in the smectites (Vingiani et al., 2004). The chemistry of the bedrock, basalt, leads to the strong effect of iron on the clay mineralogy. The plants determine the local chemical constraints, reducing environment in the black soils and higher potassium content at the surface producing some illite. This favors the presence of iron-rich smectite at the surface horizon. In soils with kaolinite/smectite mixed layer minerals developed on normal pelitic (aluminous) materials, one finds a lower smectite content in the surface horizons in the clay mineral structures (Churchman et al., 1994).

Here it is clear that plants and bedrock, guided by topography can lead to special clay assemblages under the influence of the chemistry engendered by the biome. In this case, the limit between 2:1 minerals and 1:1 minerals, the major change in silica content of the phyllosilicate clay minerals.

From the above studies one can conclude that the type of biome can influence greatly the type of 2:1 clay interlayer ion population, from hydroxyl interlayer ions (HI-vermiculite) to illite (anhydrous potassium) to smectite (hydrated exchangeable cations). Similar soil substrates, bedrocks or sediments, give similar results. However if the substrate (source rock) is strongly different, the clay suite will be different. Nevertheless the tendency of sequoia trees to form potassic clays seems to be trans-source rock in nature, even though the clay assemblage is significantly different under different chemical (bedrock) influences. The lesson here is that one should remember that the type of clays in a soil can be a function of the plants as well as the source rock. The source rock imposes a basic chemistry, acidity and relative abundance of different cations, whereas the plants impose a chemical flux which conditions the clays present. We do not have sufficient data at present which can indicate the extent to which plants can influence the charge on the 2:1 minerals which will in turn determine the type of cation fixed in the interlayer sites.

### *4.2.3 Climate, Plants and Soil Clays*

An example of the effect of climate, essentially determined by rainfall and its seasonal variations is given by Sifferman (1973) for soil clays developed in Cameroon. One finds tropical rain forest climate and biomes and a shift, to the north, towards the savanna climate and biomes. The author follows these variations as they affect the clays in soils. Soils developed on both acidic and basic eruptive rock substrates were investigated. The major climatic variation considered was annual rainfall, under similar temperature regimes. Such climatic control inevitably varies the vegetal regime, going from tropical forest to savanna in a contrasted seasonal regime. The rainfall varies from 12 to 1.7 m per year. In the high rainfall regime (mount Cameroon) one finds, on these glassy eruptive rocks, a strong development of amorphous materials strongly associated with organic matter in the surface soil horizons. The silicate and other mineral phases are dominated by the amorphous allophone and the crystalline, low silica minerals gibbsite and halloysite (hydrous kaolinite). A small amount of smectite is present, a 2:1 more silica rich mineral. As rainfall decreases and becomes more contrasted into two seasonal regimes, dry and wet, the clay mineralogy changes becoming less rich in allophane and containing different forms of kaolinite. Gibbsite (aluminium hydroxide) decreases in proportion and is replaced by vermiculite, the aluminium hydroxyl interlayered form of smectite. The proportion of 2:1 minerals increases, initially representing only about 5% of the mineral phases. The amount of organic matter also decreases. The final stage observed is the transformation of vermiculite to an aluminous chlorite, i.e. a 2:1 mineral with non-exchangeable aluminium hyroxy units present.

The author attributes the increase in interlayer aluminium to the presence of organic matter, very abundant in the smectite forming regime and much less abundant in the chlorite forming regime (p. 156). It is possible that the type of organic matter could have a role in the availability of the aluminium. Different plant regimes tend to produce different types of organic matter as it decomposes in the soil. Andosol soils are known to fix aluminium on organic mater forming a very stable humic- mineral complex. In the grassland soils of Mount Cameroon this association has not been noted. One should then consider that the presence of free alumina in soil solutions can be controlled to a certain extent by the type of organic matter present, highly complexing or less so. The end result is that the high rainfall clays contain much less Si than those of the savanna soils formed in drier climates. A higher proportion of 2:1 clays are present in this regime also, towards 20% of the soil minerals.

In this sequence the climate differences engender a difference in plant regime, and probably a change in the chemical control of dissolved elements in the soil solutions depending on the complexing power of the organic material issued from the biologic degradation of the plant detritus. A schematic diagram of the climate – clay relations is given in Fig. 4.13.

In this climate – biome sequence, formed on the same rock substrate, the high rainfall tropical forest soils contain very much amorphous or poorly crystallized material, as well as gibbsite. As rainfall decreases the amorphous materials are replaced by 1:1 clay minerals, initially kaolinite and then mainly halloysite. The relative amounts of 2:1 minerals remain roughly constant, increasing some in relative amount with initially smectite, then soil vermiculite (HI mineral) and finally one has noted the presence of chlorite, probably a magnesian interlayer 2:1 aluminous mineral. As one sees more 1:1 clays there is less organic matter present indicating the strong link between organic matter and amorphous silicate and oxides in Andosol soils which globally become 1:1 clays. It is interesting to note that the relative amounts of 2:1 clays remains roughly constant, being present in the upper parts of the soil – alteration sequence.

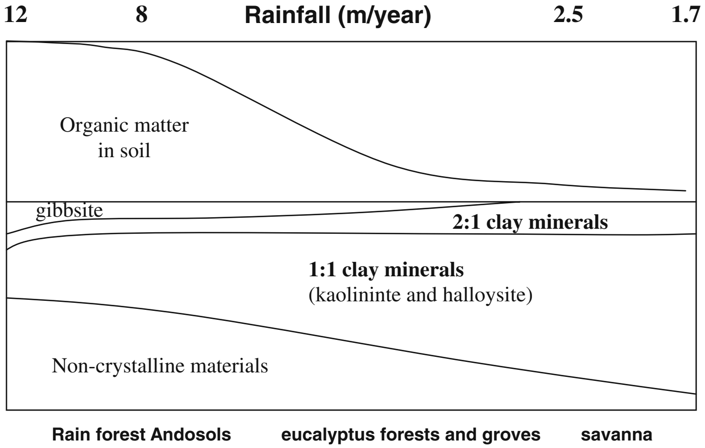

**Fig. 4.13** Representation of the effects of rainfall on vegetation and clay mineralogy in the African rain forest – savanna zone Andosols developed on volcanic materials of Cameroon (after Sifferman, 1973). Organic matter follows rainfall in this sequence, as does the importance of non-crystalline materials. High rainfall produces gibbsite while lower rainfall produces more kaolinite and a certain amount of 2:1 clays

Climate, as it controls the vegetative materials and affects the through put of water in the system, then should be considered in assessing the types of clays present in a given soil. Plant regimes can vary the clays present under similar climate conditions but the second variable is certainly that of climate.

***What needs to be done***

***Studies of rate of change of clay minerals when plant regime is changed. Studies of effect of different plant species on clays***

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# Chapter 5
# The Chemistry and Mineralogy of Plant and Soil Interactions: Plant as Manipulators of Their Environment

## Contents

## 5.1 Soil Properties Pertinent to the Prosperity of Plants

### 5.1.1 Terrestrial Plants and Peri-Maritime Plants: Alkali Content

Terrestrial plants are tied to the earth. They are relatively immobile, at least for each generation, and they must adapt. The earth forms a base for growth in what is called soil. However this material, necessary for plant development, is

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_5,

composed of a variety of components. Much of the interaction of plants and the surface of the earth is in the surface tens of centimetres where most of their roots are developed.

If one looks at the composition of plants from peri-maritime and adjacent arid areas in Syria (Barkoudah and Henderson, 2006) it is clear that there is a reciprocal relation between sodium and potassium. This stems from the relative availability of the two alkali elements, apparently interchangeable in plant metabolism chemistry. The sea is salty, a simple truism but not all that innocent. Seawater concentrates elements that are not incorporated into solids during the weathering cycle and sedimentation cycle. Elements that find their way to the sea as dissolved ions are basically Ca, Mg, and Na. These are not retained in alteration products of the water – rock interaction process. Sea animal activity efficiently decreases the concentration of Ca, which combines with Mg to make carbonate material, decreasing the overall content of these elements in sea water. Potassium is present in only low abundance mainly because it is held in clays. Sodium is not held in clays. Hence terrestrial plants are potassium – based, not sodium based. The plot of Na and K in Fig. 5.1 indicates the gradual changes in plant chemistry as the relative proportions of sodium and potassium are available in the plant environment. The data represent plant ash compositions for four *salosa* shrub species, which indicates a small range of K-Na variation for each. This indicates that the different *salosa* types adapted to more and more potassic environments but also that each plant type can adapt to a certain extent to its chemical environment. However, by and large, most terrestrial plants are potassic, and sodium is of very low abundance in plant ash. Thus the needs of potassium are of great importance for plants and the soil clay resources of this element are key to plant – soil interaction. This demonstration indicates that plants are highly adaptable to their chemical environment. Not only do they adapt, but they manage to constrain some chemical parameters so that they can prosper given certain necessities such a mineral element components.

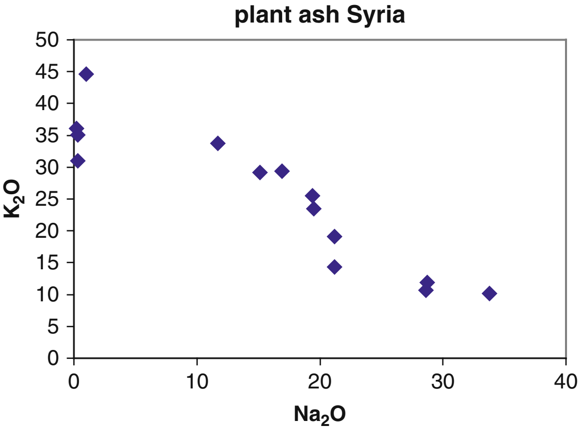


**Fig. 5.1** Data for plant ash of different salosa plants in Syria (Barkoudah and Henderson, 2006). The reciprocal relations of sodium and potassium indicate that plants need alkalis for their metabolism and that depending upon the local chemical resource they can adapt to the use of one or the other

### *5.1.2 Elements Needed by Plants*

There are basically two sources for the elements which make up plants. The atmosphere supplies carbon and nitrogen. The soil and alterite supply water and mineral elements. Sun energy is captured and transformed into the complex chemistry of plants. This is one of the most efficient methods of energy transfer that we know of. Thus the materials necessary for plant growth are found in two distinct environments air and earth. One normally thinks of rock and mineral destruction by transformation as the major source of mineral elements for plants. These elements are brought into the aerial plant by the root system. However, much of the mineral matter used in plants is in fact re-cycled. Leaf and other litter on the surface of the soil is gradually incorporated into the soil through bacterial action. During this process, and by simple rain water washing, much of the mineral elemental material is released into the soil solutions. The relatively dense root system in the soil zone captures a large part of this material which is re-incorporated into the plant. This occurs on a short time scale, yearly input and decomposition, or longer scale through plant death and decay.

Figure 5.2 indicates these cycles. The soil is the major source of water and nitrogen and a large quantity of the mineral elements such as K, Ca, P, Mg and Si. The

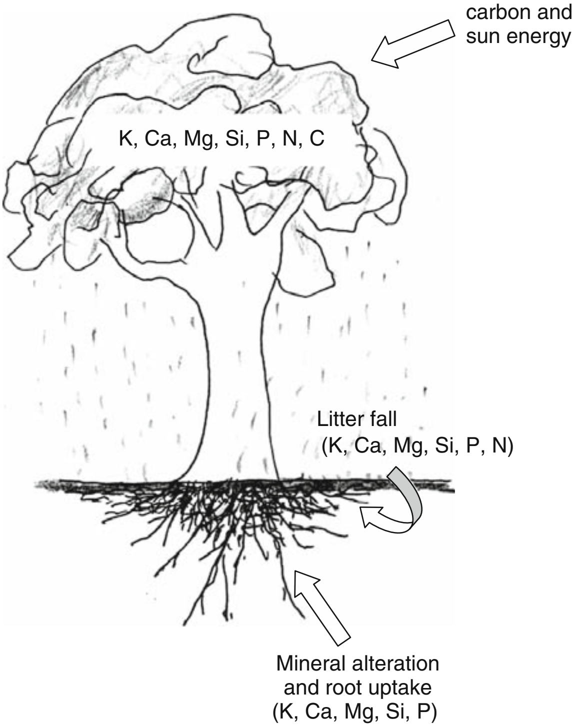


**Fig. 5.2** Illustration of the mineral element cycling in the biosphere. Water – rock alteration transfers some elements into the pore solutions where plants can absorb them. Also bio-engendered alteration of minerals releases mineral elements that can be incorporated into the biomass. Litter fall and root decay release these elements which can be re-cycled into the biomass. The movement of mineral elements from the rock sources into the biomass and their re-cycling is a fundamental concept in exchanges at the earth's surface

action of rain water, dilution the soil solutions and carrying away some of the various elements represents a loss of nutrients to the system. Some of this material is recuperated by root action at depths below the soil interaction zone. Plants basically try to keep an equilibrium between deep resources and re-cycled resources. Data from numerous studies can be used to point out this chemical structure. Potassium is often a striking example as it can be concentrated in the soil horizon accumulation through root action. It is most evident when the source rock is potassium – poor, however in certain cases, as in the example given in Fig. 5.3 for a young mountain prairie soil (Righi et al., 1999) one can see the change in $K_2O$ content and $SiO_2$ as a function of time in the A (plant) horizon compared to the B horizon. The plant zone maintains the potassium content whereas the lower zone more clearly affected by water – rock interaction shows loss of these elements.

Beyond the mineral elements, of course carbon and nitrogen are concentrated in the soil zone through accumulation of plant activity and re-cycling. There are other interactions necessary in order to keep a balance between the needs of plants in the different environments where they are found. Some of the vital elements, those readily soluble, must be kept out of the immediate soil chemistry cycle. These are among the ingenious uses of minerals to the advantage of the plants in the biosphere.

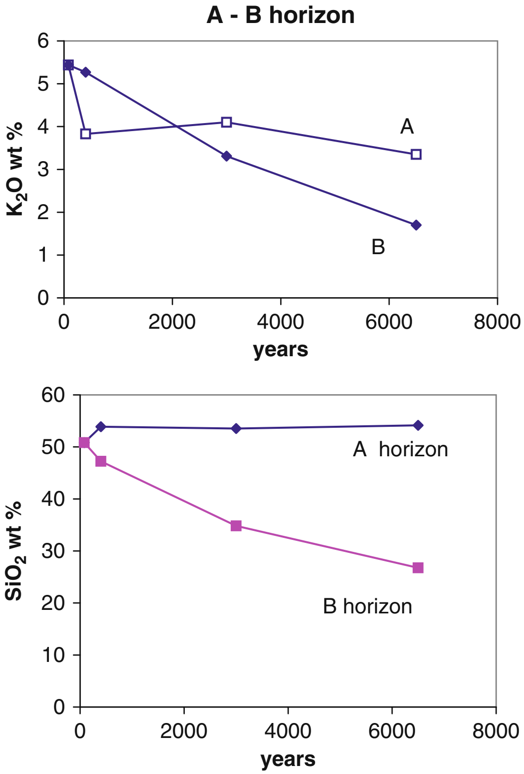


**Fig. 5.3** Demonstration of element loss in the organic A horizon compared to the deeper C horizon where water – rock alteration reactions prevail as a function of time. Both potassium and silica are conserved in the A horizon whereas they are progressively lost in the deeper C horizon. Data from Righi et al. (1999)

Some of the major problems for a plant are assuring the availability of the elements necessary for growth. The transfer and retention mechanisms must be assured in order to have a ready supply throughout the growing season. For this plants use the capacities of clay minerals and organic matter.

## *5.1.3 Clay Minerals*

### 5.1.3.1 CEC Cation Exchange

Exchange cations are in fact those elements necessary for plant growth such as K, Ca, Mg and perhaps ammonium. Their capture and release are primordial for plant growth.

Clay minerals have a large surface area compared to their volume due to their sheet structure which has a small development in one direction compared to the others. The ratio of 1:20 is common. This fact gives a clay particle a large surface area compared to a sphere for example. In some minerals the mineral surface is largely un-charged, i.e. the structure has all atoms with electronic compensation. The kaolinites are such minerals where the large surface of the sheets is without charge whereas the crystal edges are charged due to incomplete bonding of oxygen and Si, Al cations. Other minerals with cationic substitutions within the structure (see Sect. 1.3) leave residual charges on the crystal surfaces. These charges attract cations from aqueous solutions. Thus the surfaces of clays are "covered" with cations in proportion to the charges on the minerals surfaces. Kaolinite, (a 1:1, TO structure) has no residual surface charge due to internal substitutions for example, and has only charges on the crystal edges where un-terminated bonding leaves cations or anions with residual charges. Kaolinite has an attraction of 5–10 milli equivalents of a cation charge per 100 g of clay due to un-terminated bonds on crystal edges. In such cases the amount of charge and cations fixed to the surface varies as a function of the crystal size, the smaller crystals having more edge sites per mass. The more coarse sizes (10–20 μm) have an exchange charge of 2 milli equivalents of cation per 100 g of clay while the fraction 1–0.5 μm have a charge of 10 milli equivalents. (Grim, 1954, p. 137). These are the lower limits of cation exchange for clays.

TOT or 2:1 minerals with a low charge due to internal cation substitution of ions with different charges in a given coordination site (tetrahedral or octahedral in the TOT structure). The charge deficit can be 0.4–0.6 per unit cell $O_{10}(OH)_2$ which necessitates compensating cations to migrate between the layers of the structure (TOT or 2:1 layers) where they maintain electrostatic neutrality within the overall clay silicate structure. These ions are easily exchanged with other ions in solution following the laws of mass action (elemental concentration in the solutions). Smectites are such minerals with low layer charges that have cation attractions (exchange capacities) of near 135 milli equivalents. The amount of charged ions attracted is of course due to the amount of substitutional charge but also to the site of the charge (see Velde, 1985, p. 123).

The measurement of exchange ion capacity, ions easily attracted to the surface of or in interlayer sites in a mineral, is its cation exchange capacity or CEC. Measurements of exchangeable ions are usually made using solutions of 0.5–1 molar cationic strength. Commonly one uses ammonium ions ($NH_4^+$) to displace cations on natural clays and measures the ammonium present in order to estimate the number of ions and hence charge attracted to the clay particles.

Clays then have charge sites of two sorts, compensated between the crystal structural layers and on the edges, but the cations in solution have different electrostatic and chemical properties. The cation properties are multiple, one being a function of ion size and charge which is in fact concentration of charge per unit surface to the ionic spherical influence of the cations. If two ions are of similar cationic diameters and different charges the selectivity for fixation on a charged surface is in favour of the higher charged ion. Ca and K ions are a good example. The double charged Ca cation is much more strongly selected by clay surfaces than potassium. Not only do relative charges on cations affect selectivity of different species but residual charges on clay structures that attract ions can effect cation selection. The charge intensity and the site of the charge (tetrahedral or octahedral site) play a role in cation electivity. Figure 5.4 gives an idea of such selectivity. This indicates that the clay mineral itself can determine the relative propositions of different cations selected as exchange ions.

The selectivity of one cation over another can also be affected by temperature and ionic concentration which is due to the differences in dissociation constants

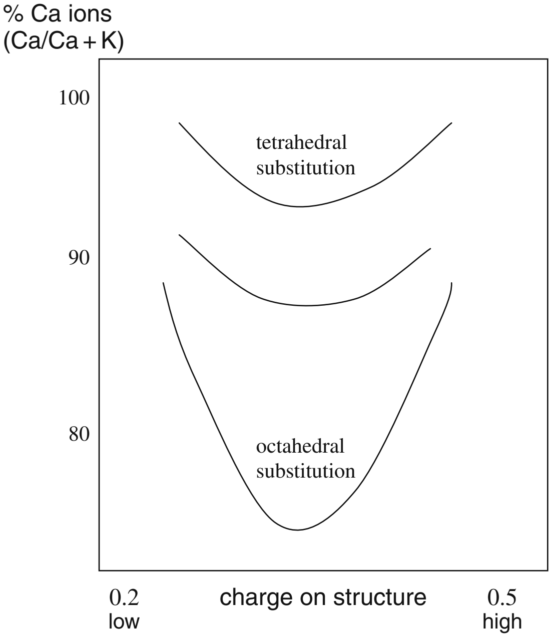


**Fig. 5.4** Illustration of the importance of charge on the 2:1 structure in the caion selectivity between K and Ca cations (mono- and di-valent) and the site of the charge imbalance (data from Velde, 1985). The amount of charge changes the selectivity as does the site of the charge in a non linear manner. It is clear that the cation selectivity for mono- and di-valent cations is a complex system

of the different salt forms which release the cations in solution as individual ions. (see Velde and Meunier 2008 for a more detailed discussion). The major factor in clay induced CEC (cation exchange capacity) for a soil is the mineralogy or crystal structure and internal ionic substitutions of the crystallite.

In general, in most soils the CEC (exchange ions) is dominated by the divalent ion Ca and, to a lesser extent, Mg ions. These ions are divalent, and thus have a higher surface charge density than mono valent ions such as potassium. Usually potassium represents only about 10–15% of exchanged ions in soil samples. Thus the selectivity has done its work leaving the divalent ions as dominant cations present and readily available to plants.

There are two principles which are very important to remember when considering cation exchange and the availability of exchange ions. In fact the exchange principle, one ion being replaced by another, is just part of the equation of ionic availability. A major effect is due to dilution of the system. If a clay – organic complex contains a given number of ions on exchange sites under a given set of conditions, the total number of ions can be changed according to the concentration of ions in the aqueous solution which equilibrates with the ion exchanger. As aqueous solutions become more dilute in exchangeable ions, the amount of these ions fixed on clays and organic matter diminishes. Thus in climates of high rainfall input, one would expect that the exchange cation content would be small. In soils where periodic rainfall produces flooding and evaporation (arid climates) the exchange cation population should be high. This principle is outlined in Fig. 5.5.

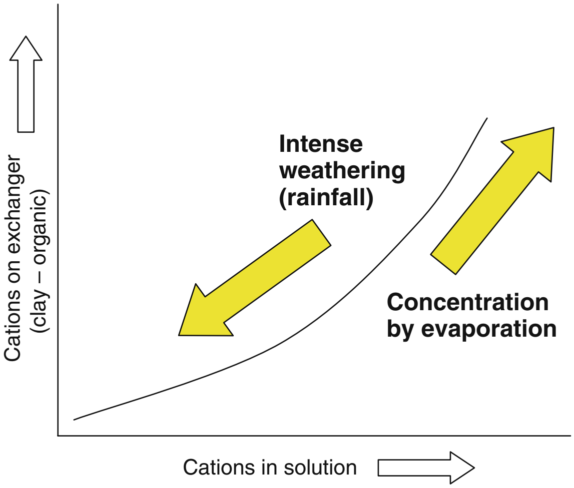


**Fig. 5.5** Relations between the amount of water relative to the soil materials and the cations found on the exchangers in the soil The more it rains, the more dilute the solutions and the more cations will be desorbed into the dilute pore water solutions. If the soil solutions are concentrated by water loss due to evaporation, the amount of ions exchanged onto the soil materials will increase. Hence the amount of exchanged cations on soil materials is determined relatively, by the dilution of the pore solutions. If a soil is charged with cations due to an influx at the surface, this amount of absorbed cations can be reduced by rainfall cycles

A second principle, also very important, is that hydrogen ions ($H^+$) behave in fact as cations in aqueous solutions. That means that a $K^+$ ion adsorbed on a clay can be displaced into solution when it becomes acidic and one has the relation $H^+ = K^+$. Acid soils show a high hydrogen ion content, reducing the number of what are called the base exchangeable cations. The normal cations are usually associated with OH units. As plants need mineral elements for growth, acidic soils or those under high rainfall tend to diminish these resources by displacement or dilution.

#### 5.1.3.2 Fixing Potassium in 2:1 Clays

Exchange on high charge minerals can induce apparent irreversible exchange, fixing the ions within the structure. The case that occurs in soils is when potassium is in sufficient quantity to form a layer of cations which is anhydrous, i.e. the cations are not surrounded by water molecules which renders the ions for all intents and purposes immobile or inaccessible to normal cation exchange in solutions of relatively dilute concentration, i.e. less than 0.2 M. However, experiments by the author (BV) on soils from central Iowa USA indicate that much of the apparently fixed, anhydrous potassium, can in fact be extracted suing strong (1 m $SrCl_2$) exchange solutions (Fig. 5.6). In the figure the amount of anhydrous potassium mineral (illite) is estimated from X-ray diffractograms using peak decomposition methods (see Lanson, 1997). In the figure the proportion of illite present in the Sr saturated state at low concentration levels (0.01 M $SrCl_2$), normal smectites with two water layer hydrated cation layers, is compared to that for the same samples in the K – saturated state, where there is a tendency to form an anhydrous layer of potassium cations. In Fig. 5.6 the same samples after the potassium treatment have been de-saturated using strong (1 M) $SrCl_2$ solutions. The peak positions are nearly coincident with an equivalence of illite content between the initial state and the K-sat to de-saturation state. Hence in these clays the collapsed (anhydrous ion after K treatment) illite layers can be exchanged with strong cationic treatment. When the solutions are less concentrated in strontium (0.01 M) the potassium remains fixed in the layers. Barré et al. (2007) have shown that the capacity to fix potassium in mixed layer illite/smectite clays can be a function of the solution concentration of potassium ions. Hence the concept of exchange ions and CEC (cation exchange capacity) is to a certain extent ambiguous when considering potassium as the exchange ion. The higher the ionic concentration, the more ions enter into the structure. Other ions do not seem to show such a behavior in that they do not tend to form anhydrous cation layers in the 2:1 structures and increasing the cation concentration in solution does not change their presence greatly.

#### 5.1.3.3 Potassium and Ammonium

It is of course well known that potassium is an important part of plant physiology and that nitrogen (and its soil form ammonium) is important also. As it turns out, the potassium ion and the ammonium complex ($NH_4{}^+$) have roughly the same “ionic” dimensions. In soil chemistry practice, the potassium ion is displaced by strong

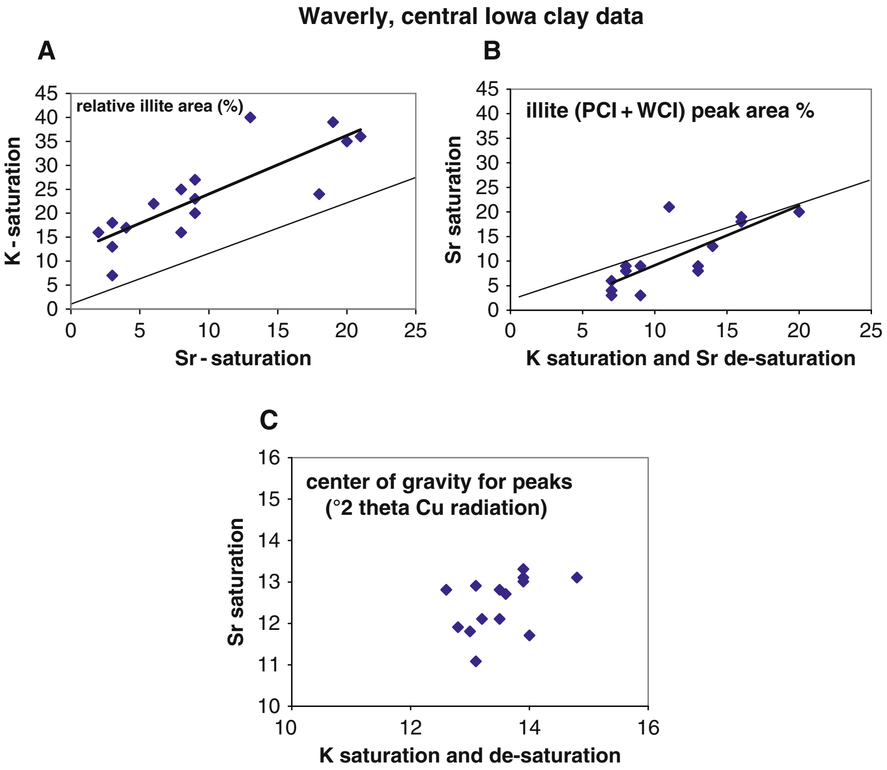


**Fig. 5.6** Reversible effect of potassium saturation and de-saturation. Saturation of several Iowa soil clays shows an increase in the illite content (fully saturated interlayer sites where the potassium is anhydrous) shown in Figure (**a**). In comparing (**a**) to (**b**) one sees a subsequent return to the initial state by de-saturation with strong $SrCl_2$ solutions. In this case the formation of a "new" phase, illite, from smectiet layers in the clay aggregates is simply one of cation exchange, where the illite, is stable under conditions of low concentration of exchangeable ions in solution but can be restored to its "initial" smectite state under conditions of strong activity of Sr in solution. However some of the smectite layers in the mixed layer minerals (illite-smectie) fix potassium in a more irreversible manner, indicated by the overall weighted peak position (center of gravity, cg) measurement (**c**). This indicates that much of the potassium in the apparent illite minerals in these soils clay can in fact be of an exchangeable nature, whereas the illite layers formed by potassium saturation in the mixed layer minerals can be less exchangeable mineral forms

solution concentrations of ammonium. This is a standard practice used to measure the amount of "exchangeable potassium" and other cations in the soil materials. However in soils, it seems that there is not an easy inter-relation between the two ions. In mixed layer minerals and illites from prairie soils, ammonium seems not to be selected in preference to potassium (experiments of the authors). However soils which have been treated with continued potassium fertilizing agents show a propensity to capture ammonium under laboratory conditions (Liu et al., 2008). There is little indication of the presence of anhydrous ammonium interlayers in illites in soils even though they can be produced in the laboratory and are found in metamorphic rocks. Thus even though ammonium could be found in the clay structures it seems that it is not present under normal plant growing conditions. This situation could be due to the strong mineralizing power of bacteria in soils. When fertilizing agents are used in agricultural practices, the sequence of treatments and the concentrations of each ion in the soil solutions should be considered so that one or the other is left for plant use.

Numerous studies have been made on soil materials and soil clays in order to establish the relative fixation capacities of K and $NH_4^+$ in clays. It is known that fully ammonium clays of the mica type can be produced in the laboratory (Sucha et al., 1998) and they are found in natural high temperature rocks (Juster et al., 1987). Therefore the pure ammonium phase can be found in nature as well as in the laboratory. However, what is the selectivity between ammonium ions and potassium in natural soil systems? Laboratory experiments (Evangelou and Lumbanraja, 2002) using high charge vermiculite (smectites) indicate that the presence of potassium enhances ammonium fixation compared to Ca. This suggests that there is a relation between potassium anhydrous layer formation and ammonium capture. Such an effect has been seen in studies of field experiments using long term (20 years) fertilizer treatments on rice paddy soils (Liu et al., 2008). In fact potassium saturation and ammonium saturation of the same clays indicates that ammonium forms more 10A mica like layers than potassium as seen in Fig. 5.7 based upon data from Liu et al. (2008).

The soils investigated in the studies cited have a strong HI (vermiculite) content similar to the material examined in the laboratory studies noted above. More information is necessary in order to assess the $K^+$-$NH_4^+$ relations in the smectites/illite mineral series.

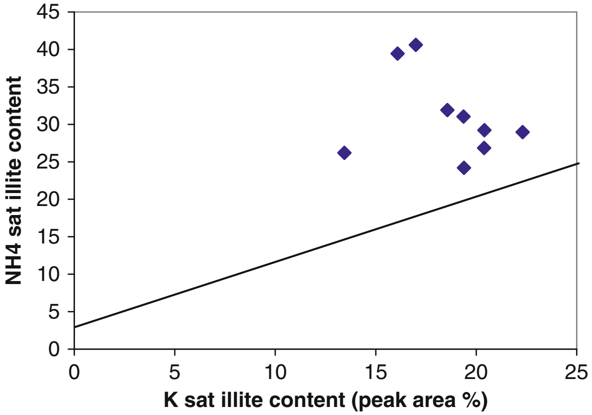


**Fig. 5.7** Relations of illite peak surface area under conditions of potassium and ammonium saturation (illite %) for some Chinese red soils (loess bases) which had received potassium fertilizer treatments for 20 years. The long term of potassium treatments enhances the fixation of ammonium producing an ammonium illite mineral (anhydrous ammonium interlayer ions)

#### 5.1.3.4 Plant Extraction of Potassium

The possible formation of anhydrous potassic 2:1 layer structures is in fact rather common in different types of soil clay assemblages. Samples from several sites throughout the United States Great Plains (Velde, 2001b) area show significant formation of illitic layers upon contact with relatively dilute KCl solutions (0.01 M). These clay assemblages in the soils are essentially smectite/illite interstratified minerals plus kaolinite. Also samples from cultivated soils in the Po river delta area near Pavia Italy (data communicated by F Terribile, Univ Frederico II, Naples) show significant illite formation upon K-saturation. The clays are basically two mineral assemblages, a 14.2 Å HI (HI chlorite – high charge vermiculite) plus illite in these agricultural soils. The spectra of Ca – saturated clays show a slightly more intense 7 Å than 14 Å peak indicating magnesium occupation in the interlayer site. The HI chlorite minerals are not affected by Ca exchange ions, retaining the OH interlayer ion structure instead of a double water layer associated with smectites as hydrated Ca cation interlayers. However they are affected by the presence of potassium, which apparently expels some Al and possibly Mg ions to form illite (anhydrous potassium layers) as seen by an increasing intensity of the 10 Å peak. Further the ratio of 14 to 7 Å peak of the HI mineral changes to a lower relative intensity for the 7 Å peak indicating a higher magnesium interlayer occupation for the 14 Å clays that remain. This is seen in Fig. 5.8. Therefore, the initial assemblage contains HI – chlorite (some Mg chlorite and some aluminous HI minerals) which is affected by potassium saturation to form a more magnesian chlorite and more illite.

The potassium saturated samples, compared to Mg saturation, generally show an increase in illite with the presence of plentiful potassium, indicating that in most samples there is exchangeable Al and Mg-OH present, but mostly the Al-OH is extracted by strong cation exchange. However, when looking at the A horizon samples only (Fig. 5.9) there is little difference if any between the two treatments. This indicates that the farming practices provide more than enough potassium to the soils to sustain the extraction needs of the plants grown in them. The results of K – saturation in deeper soils indicates that they have less available potassium than the surface agricultural zones.

Of course plants can effect the de-sorption or extraction of potassium from clays also. This has been demonstrated by Barré et al. (2007) where laboratory experiments using rye grass grown for several weeks effectively stripped out near 40% of the potassium from the clay assemblage they were grown in. From this study it appears that all of the common 2:1 clay types, smectite – rich interstratified mineral (S/I) illitic interstratified mineral (I/S) illite and soil HI phases can be affected by addition or extraction processes.

The quantities of potassium fixed and released as anhydrous interlayer ions is far greater than the potassium available as exchangeable ions by CEC mechanisms in soils. Hence the resources of potassium in clays are not in the exchange sites classically measured as base exchange ions (exchangeable basic cations, i.e. Mg, K, Ca) but those fixed under conditions of higher potassium concentration in solution. The

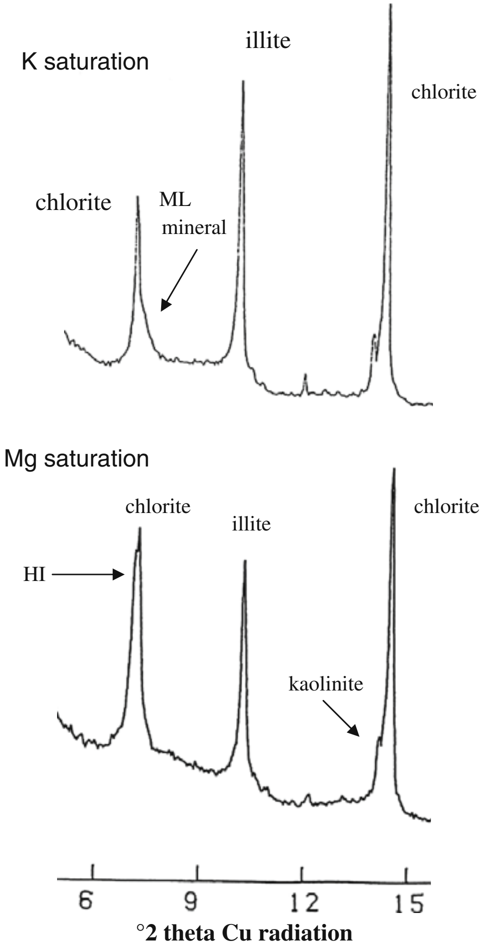


**Fig. 5.8** X-ray diffractograms for some soil clays of Po valley sediments under agricultural exploitation. The differences between potassium saturated and magnesium saturated samples indicates that the increase in the relative intensity of the illite peak compared to the chlorite 7 Å diffraction peak shows an increase in minerals with an anhydrous potassium layer. However the lower intensity of the 14 Å compared to the 7 Å peak of the chlorite shows that the loss of chlorite is from an aluminous interlayered mineral (HI) which has exchangeable aluminum hydroxyl ions present, replaced by potassium ions. Here the apparent chlorite mineral, with a narrow and sharp peak at 14.2 Å has an HI component which responds to potassium treatment

example of grass and sequoia on clay types given in Sect. 4.2 indicates that the amount of fixed potassium (illite) can be greatly influenced by the plants present which determine the activity of this element in the pore solutions which eventually saturate the clays. In this way the clays function as a reservoir for potassium, filling when un-needed material is present in solution and emptying when there is a need manifested by the plants.

Potassium is not the only ion useful for plant growth, Ca and Mg are also among those found in plants and their availability through de-sorption from clays is certainly important. And of course phosphorous is of great importance. However, we do not at present know all that much about the cycle of phosphorous fixation and release on the organic material and on clay mineral materials.

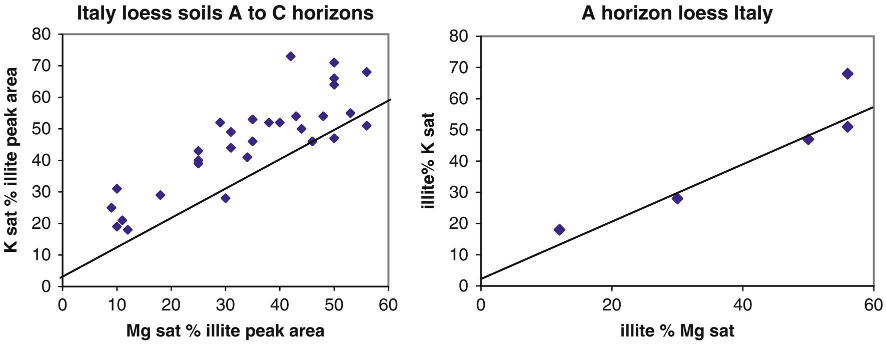


**Fig. 5.9** Measurements of the clay peak relative intensities of the Po delta soils shows that the potassium saturated clays have, on average, a higher peak area than the chlorites but when one looks at A horizon clays, the difference disappears, due to the use of potassium fertilizer which saturates the HI minerals with an anhydrous potassium layer to form an illite – like mineral

### *5.1.4 Cation Exchange in Soils*

Each of the two chemically active major components of soils, organic matter and clay minerals, have a capacity to fix in a temporary manner cations. Cation exchange is just that but the total exchange of cations is a function of the amount of ions in the exchanging solution: the more dilute a solution the fewer ions will be fixed on the exchangers. If we know the exchange capacities of each major component, how do these exchange values fit into observed CEC (cation exchange capacities) and ions exchanged in soils? Sposito (1989, p. 171) indicates values for soil type which reflect at the same time organic matter content and clay type:

| | |
|---|---|
| Ultisol (very mature oxide, hydroxide minerals) | 0.06 moles of charge/kg |
| Alfisol (forest type, HI minerals) | 0.12 |
| Mollisol (prairie type, smectite/illites) | 0.22 |
| Vertisol (smectite – rich) | 0.37 |
| Histosol (essentially organic matter) | 1.4 |

Looking in more detail at data for soils with moderate amounts of organic matter and clays one can observe in several studies that the CEC of soils is within the range of clay mineral cation exchange capacities for the amount clays present in the soil. Figure 5.10 shows the relations of several studies for CEC, soil carbon and clay content. The values of clay CEC are indicated for values between the low values for kaolinite and illite, at 5–10 milli-equivalents charge for 100 g of clay to 130 milli equivalents for smectites (black lines in Fig. 5.10). CEC values are usually between several milli equivalents per 100 g and about 30 milli-equivalents. This is not a large range of values to be sure. For the most part the exchange capacity observed in soils does not exceed the theoretical maximum capacity for pure clay samples as is the case for the four soil series shown in the figure. Thus it is clear that the chemically and exchangeably active part of the organic matter does not overshadow the clays as cation exchangers. This is not the opinion of Sposito (1989) who advocates a more important role for organic matter (humic components) as cation exchangers. He uses values of 2–4 times the CEC of clays attributed to humic materials in order to calculate the CEC potential of a soil. However the values of exchange capacity vary apparently according to different specific field examples. Black (1968, p. 224) indicates a value of 6 milli equivalents per percent carbon in a sandy soil which is four times that of smectites clays. CEC for soils with several percent organic carbon rarely show such high cation exchange capacities. In the figure of examples cited here, the CEC is not related to the amount of organic present, ranging from 10 milli equivalents for 1% organic C to less than less than 0.5 milli equivalents, if one does not take into account the exchange capacity of the clays present. The problem of the role of organic matter as a cation exchanger undoubtedly resides in the assessment of the type of organic matter present. Overall, there appears to be a tendency in the series shown to decrease CEC as clay content increases. the active fraction in the soils. The estimation of organic matter is solely based upon organic carbon content. This does not take into account the type of organic matter; immature, evolved or mature. If the organic matter is immature, not much of the material will have active bonding capacities. If the organic mater is highly evolved, towards a carbon-rich type, the number of active sites will be limited. Thus the type of organic matter present will determine the role it will have in cation exchange.

Concerning clay minerals, if kaolinite is dominant, the CEC contribution will be low, as is the case in the Hainan soils in Fig. 5.10 where the clays are mostly kaolinite. However there are other mineral materials which have varying and at times very high cation exchange capacities such as vermiculites. The soils from the east Coast of the USA shown in the figure indicate variable cation exchange capacity but higher at lower clay amount, suggesting that the vermiculite has an effect as an exchanger in these soils. The samples from Sweden (Andrist Rangel, 2008) from soils with some vermiculite but significant amounts of illite-smectite mixed layer minerals and illite show which higher cation exchange capacities for lower clay contents following rather closely the theoretical exchange values for smectites (lower line in the figure).

Other materials in soils, can contribute to the cation exchange capacity but in a rather erratic manner. These are the amorphous silicate materials (imogolite and allophone) and oxides (iron) and hydroxy-hydroxides (iron and gibbsite). Such minerals or materials found in soils are highly active on their surface sites but can combine with organic matter or other elements such as phosphorous (see Dixon and Weed, 1989). Silica – alumina amorphous matter is well known in Andosols, those based upon glassy eruptive rocks. These soils are usually extremely fertile, largely due to the fixation of cations and the presence of large amounts of organic matter.

From the above, it appears that the prediction of CEC based upon the constitution of a soil is difficult to foresee. Knowledge of a number of variables is necessary in order to estimate the chemical surface activity of a soil. One major piece of information necessary is the type of exchanger present, be it organic matter in different stages of evolution or clays of different structural and hence exchange types. As we will see further on, the effect of plants on their environment largely determines the parameters of cation exchange, in forming or controlling the type of clays present or in the formation of organic components which are of course entirely due to the vegetal regime present, in natural settings.

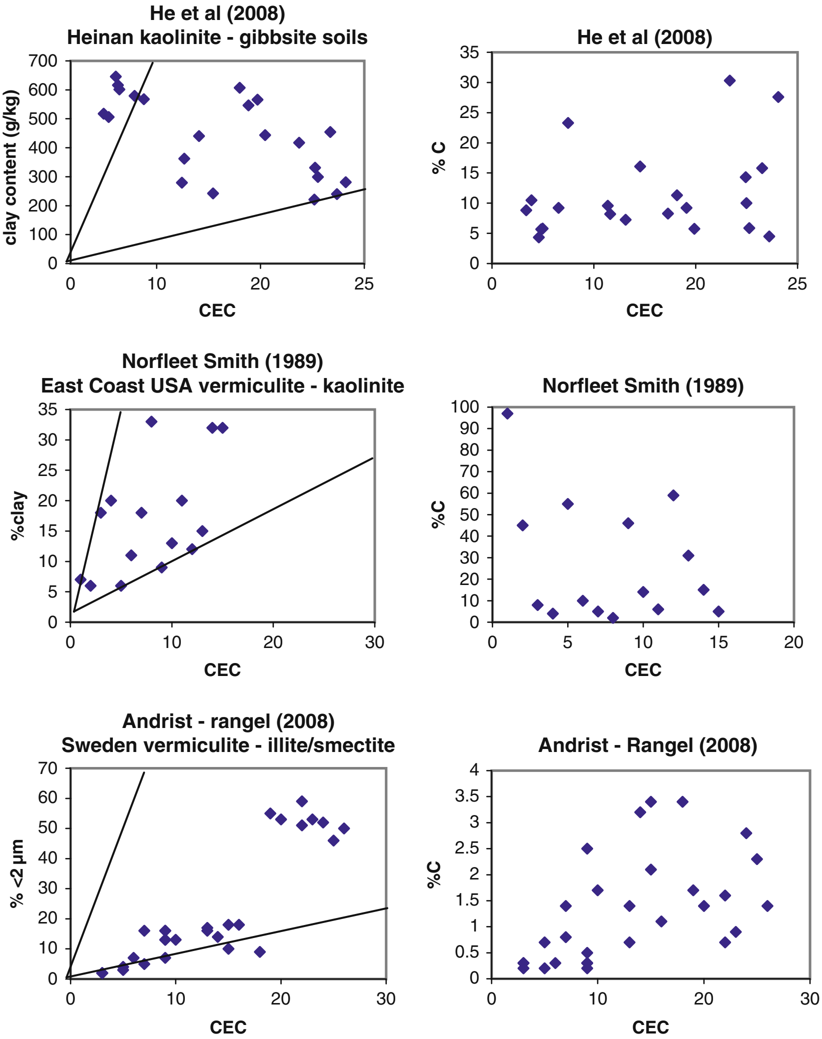
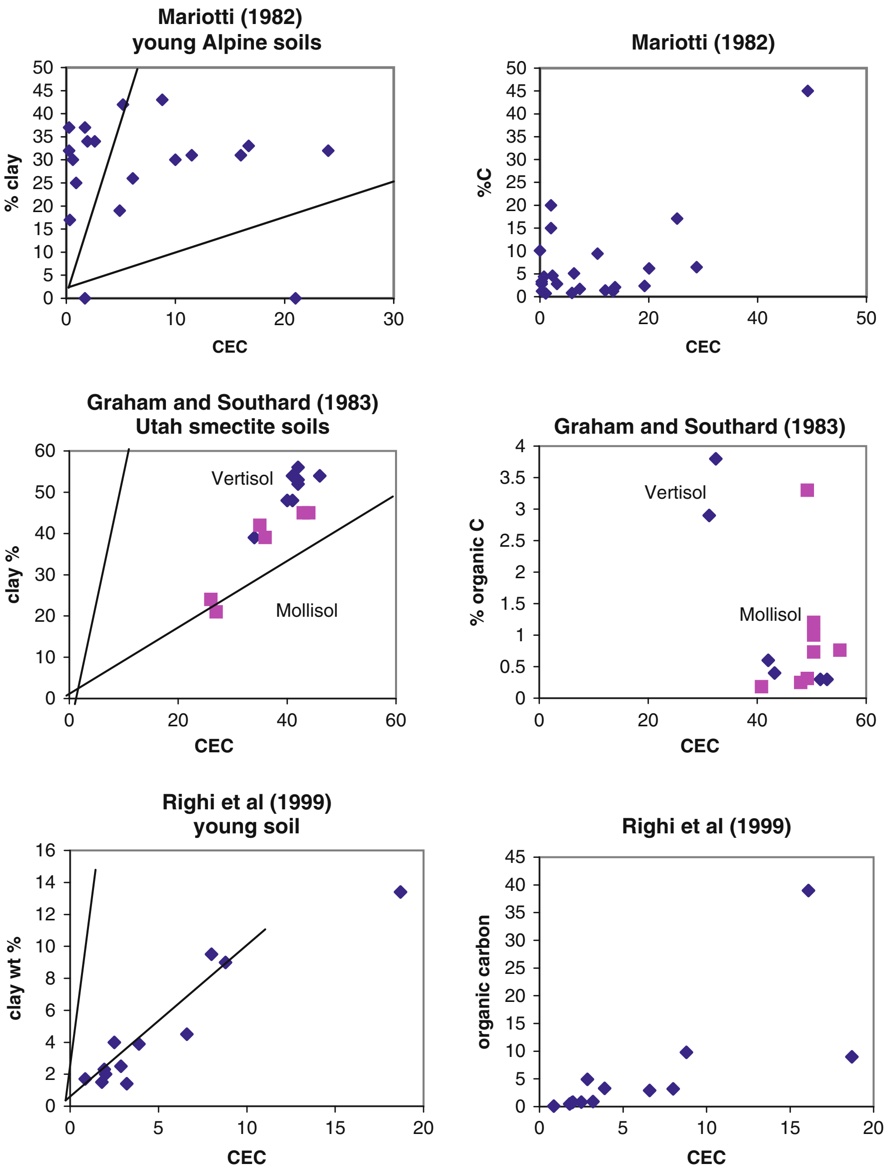


**Fig. 5.10** Assemblage of clay content, organic carbon content and cation exchange capacity (CEC) for several soils (Mariotti, 1982**;** Andrist-Rangel, 2008; Righi et al., 1999; Norfleet and Smith, 1989; Graham and Southard, 1983; He et al., 2008). The relations are relatively clear concerning clay content and CEC, where the lines in the figures represent the estimated maximum CEC for smectites and minimum CEC for kaolinite. Most of the CEC values fall between these limits. However there is little or no correlation between organic content and CEC. One can assume that in soils with modest amounts of organic material present in a relatively evolved state (humic) the dominant cation exchanger is the clay material



Mariotti (1982) young Alpine soils

Mariotti (1982)

Graham and Southard (1983) Utah smectite soils

Graham and Southard (1983)

Righi et al (1999) young soil

Righi et al (1999)

Fig. 5.10 (continued)

Cation exchange is a complex system dependent upon several factors at the same time. In the first place, it is extremely rare to find that exchange follows ionic activity in solution or more less so ionic concentration.

### *5.1.5 Role of Clay Minerals in Critical Nutrient Exchange: Potassium and Ammonium*

As we have outlined above, clays are present and respond to the needs of plants in the A horizon where the interaction between plants and soil mineral materials is the greatest. Clay minerals are, initially, the response of interaction mechanisms between rain water and silicate rock material as it is brought in contact with the surface environment. These reactions continue as long as there is rock and rain water which comes into contact with the surface materials. A prolonged contact is necessary for such an effect to be useful in the formation of clay minerals. If water is moved through the system at too great a rate, it will be below saturation with the silica and alumina of the silicate phases and will not produce a new mineral. Thus bare rock appears to be little altered in that there are few new minerals formed. Plants slow down the water flow, by root action and accumulation of mineral debris at the surface which allows the rein water solutions to equilibrate with the silicate minerals and eventually to produce new minerals by an over-saturation with dissolved elements, notably alumina.

The alteration front in alteration profiles continues to proceed downward into the rock surface once the mechanism of plant water retention becomes important. As time goes on, the thickness or the alteration material, largely clay minerals, becomes more important. On old cratons where little vertical movement of the rock basement has occurred over several millions of years, one finds alterite zones of several to tens of meters thickness. Without plants the alterite materials would be washed away into streams and oceans leaving a largely little altered rock surface. However, the protective cover of plants which allows the formation of soils is such that the alterite zone of fine grained material, clays, is stabilized. The relatively soft and little resistant clay mantle is where roots can penetrate with ease, where water is fixed and released easily and hence a zone where plants can develop a strong root system with ease. The plants need, or at least benefit from, the alterite cover that they stabilize. Clays provide a medium where chemical exchange is enhanced and where the development of root systems necessary for this exchange and the mechanical stability of the plants can occur. As it turns out several mineral elements from the underlying rocks are necessary for plants to survive well. Of course different types of plants can do without with less of different elements as they have adapted to different chemical environments.

There are essentially two types of mineral elements which are used by plants, those with alkali or alkaline earth chemical characteristics which are ionically charged and those more co-valent in character. In the first category are the elements such as Ca, K, and Mg. and the second elements such as Si and P. The ionically charged elements are strongly associated with clays. Cations are attracted to the surfaces of clays or the interlayer sites where they are fixed in different states of ionic bonding intensity. The weakly bonded ions are fixed onto the clay surfaces or interlayer sites and can be exchanged for other ions easily depending upon the ionic concentrations of elements in solution, or their lack. If a clay has a certain number of cations attracted to its charged surfaces they can be exchanged according to the laws of mass action. The higher the concentration of another element in solutions in contact with the clay, the more of the element fixed on the clay will be released to the solution. The ion concentration tends to attain an equilibrium of concentrations according to the affinities of the elements for the charged clay surface. The lower the concentration of elements in the solution, the more of those fixed on the clays will be taken into the solution. This is the effect of dilution or leaching by rainwater which contains little mineral matter. Leaching is assumed to be the major factor in alteration processes. In the end this has to be true in that rain keeps flowing over and into soils bringing more mineral matter into solution. However, plants need a certain number of these elements for their development and growth. They cannot afford to have them all swept from the surface layers of the earth. Thus there is a subtle interchange of elements from different parts of the altering surface towards the plant horizon of interaction. If plants wish to retain some elements they need to be available throughout the growing season and extractable by biologic processes.

Clay minerals are then the vehicle of mineral element exchange for a certain portion of those elements necessary for plant growth and prosperity. The exchangeable elements as outlined above are made available to plants in the surface layers of the alteration zone. The relatively abundant elements such as magnesium and above all calcium, are fixed on surfaces of clays as exchangeable ions. However certain elements are in fact present in more tightly bound states in the interlayer sites. These are potassium and ammonium ions. Although ammonium is not a mineral element, it is exchanged from the atmosphere to bio active organs in the soils, usually driven by bacterial action. The ammonium ion, $NH_4^+$, is easily absorbed into plant root systems and a valuable source of nitrogen for plants. As it turns out, the ammonium ionic unit is roughly the diameter of a potassium ion and often can be found in clays or on clays as is potassium. It is known that ammonium can form anhydrous layers in 2:1 minerals producing a sort of ammonium mica (Sucha et al., 1998). Smectites accommodate ammonium also as an interlayer exchange ion (Sucha and Sirahova, 1991). Potassium has been studied more as a mineral component than has ammonium. Although ammonium is commonly assumed to be present as an exchange ion it is not commonly assumed to be present as an anhydrous interlayer ion in a mica – like mineral. However there is no reason that ammonium not be present in a 2:1 structure as an anhydrous interlayer ion.

#### 5.1.5.1 Non Exchangeable or Extractable Cation Occupancies

We will use potassium as an example according to the concepts of soil chemistry. Huang (2005) gives a resume of the types of potassium chemical relations in soils, and hence on soil clay minerals. Usually one has exchangeable potassium, assessed using strong exchange ion solutions, ammonium acetate is frequently used, to displace the potassium form the clays. Fixed potassium, or non-exchangeable potassium is that which resists the exchange treatment. It is most often assumed to be present in interlayer sites as an anhydrous state. Estimations of fixed or non exchangeable potassium are often made by treating the clays with strong HCl solutions to dissolve the fine fraction minerals and extract potassium with hydrogen cations or a less destructive method using tetraborate solutions can be used (Moody and Bell, 2006). Coarser minerals such as micas or feldspars remain intact after these treatments and the potassium found in solids is then considered to be structural potassium, in fact material of high temperature origin. The question which is very important is: how much of the fixed potassium or even structural potassium is available to plants? The same question can be asked for ammonium, often a proxy for potassium in clays but virtually absent from silicate minerals. It is unlikely that ammonium will be present in detrital or high temperature micas or other phyllosilicates but it can be found as "non-extractable" ion material in soil clays. Thus the origins of potassium and ammonium ions in soil materials are different, potassium being a mineral element while ammonium has its source in atmospheric nitrogen. However both can be found and exchanged between clays and plants.

The non exchangeable or non-extractable potassium is in fact a type of ionic fixation that is not that of the high temperature minerals but not that of the superficial or poorly held ionic species on clays.

#### 5.1.5.2 Nutrient Cycling

In general it is clear that potassium and ammonium are important for plant growth. Extraction of potassium from soils seems to be related with plant activity. Tripler et al. (2006) report that the stream water content of potassium and ammonium are seasonally related. During growing seasons of forest cover, the stream water concentration of these elements is greatly diminished, by a factor of two or more. Moments of leaf fall, and return of potassium to the soil in the autumn, outside the growing season, greatly increase the potassium content of stream water. Calcium and magnesium stream water content are much less sensitive to growing season driven forces. Thus it is clear that there is a strong relation between potassium retention and use, as well as ammonium, in natural forest systems among others. In more detailed experimental observations, Scherer and Ahrens (1996) show that the ammonium fixed on clays in soils in a non-exchangeable state can be extracted by plant action localized near the roots. This action, exchange of hydrogen cations for ammonium, is plant species related as well as dependent upon the mineral present, in this case either illite (anhydrous potassium interlayer ions) and vermiculite (hydroxyl ion and other cation interlayer populations). Thus the conditions and mechanisms of potassium and ammonium fixation on and in clays seems to depend upon several variables according to the solicitation of the plants present which are extracting these nutrients.

If plants extract these elements at variable rates how do they get fixed in or on the clays? Initially one can observe the effects of amendments which are renowned for their efficiency – animal manures. Ross et al. (1985) show that the use of such fertilizing agents increases the illite content drastically after 6 years of use. In the experiments vermiculite (HI) minerals are largely converted to an illitic form with both potassium and ammonium present.

The initial starting point is the CEC, or easily exchanged cation population, essentially on organic matter and on expandable clays. This material does not select potassium nor ammonium in that the ionic radii are relatively large and the charge small, plus one. Calcium is about the same diameter in ionic size but it has a charge of plus two, hence a significantly higher charge density. This gives it an advantage in the cation exchange process. Ca and Mg are selected before the large mono-valent cations. But since these potassium and ammonium ions are vital to plants some mechanism must be available to sustain their needs. As it turns out this mechanism is the formation of anhydrous ionic interlayers resulting in illite – like clays. Liu et al. (2008) have demonstrated that in soils which had a long history of potassium fetilization, with a creation of a significant amount of illite clays, ammonium is more easily fixed in the interlayer sites of the clays as "non-extractable" ions. In other words, it takes illite, a supposedly closed mineral, to fix ammonium ions, by cation exchange with the anhydrous potassium in the illite structures. It appears that the ammonium is more easily extractable than the potassium in these minerals. There is then a relation between potassium fixation and ammonium fixation in the more permanent interlayer ion sites. The more illite that is "created" by ion exchange in highly potassic soil solutions, the more ammonium can be accommodated. Plants that bring an excess of potassium to the surface which is in its turn fixed to make illite then create a mineral capable of fixing more ammonium.

The stabilization of 2:1 clays, such as high charge smectites, is a decisive step in forming means of conserving the fertilizing agents of potassium and ammonium (nitrogen). As one can expect, there is a certain amount of these elements which escapes into stream water which represents the free pore water flow through soils. This material, essentially lost to the plant cycle, must be replenished. Ammonium (nitrogen) comes from the air, and is fixed by bacterial action. Destruction of roots by other bacteria releases this nitrogen in the form of ammonium compounds to the plant. Potassium must be sought either in the unaltered minerals in the soil or in the zones below this zone where water – rock interaction occurs to produce potassium ion sin solution. Some deep roots, through the agents of micorrhize can undoubtedly extract this element directly from the un-altered silicate minerals.

The problem is to conserve these elements in the soil zone throughout a growing season, or for several seasons. Fixing potassium, then ammonium in the anhydrous interlayer sites of high charge 2:1 minerals seems to be the method used. These "non-exchangeable" ions can be extracted by plants, but not by normal ion exchange mechanism under the chemical conditions of most soil pore waters. Field experiments have shown that there is a build up of potassium, and eventually ammonium in systems where the supply exceeds the demand of the plant regimes. This is a sort of "holding" mode of clays where the vital elements are kept in a situation which allows extraction by plants but not by soil solution chemistry (dilution or cation exchange). One can envision a system whereby plants bring more elements into the clays than needed but when for diverse reasons the plans cannot furnish these elements, the stock in the clays can be used for some period of time, i.e. several growing seasons. This is a sort of a pantry system, dear to our great grandmothers, whose living and lively hood at times depended upon a supply in reserve for an unforeseeable future.

One of the roles of clays is then to provide a reserve of fertilizing elements or future use due to fluctuations in supply from one year to the next.

## 5.2 Organic Matter, Clay Minerals and Soil Aggregation (Water Resources for Plants)

### *5.2.1 Clay Minerals and Organic Molecules Interactions: Soil Structure Development*

Soil profiles most commonly show an increase in organic carbon in the A horizon, due to the presence of plants. Plants more or less define the formation of soils as a matter of fact. Thus the measure of carbon content is an index of the amount of carbon that remains in the soil after plant deposition (root or aerial material) and bacteriological action. In Fig. 5.11 one sees a typical profile of carbon content, in this case in two un-plowed prairie soils from a slightly hilly situation, one on a plateau and the other in a valley bottom from Missouri (USA). Combination of organic and clays results in what is called soil structure or the capacity to form clay-organic aggregates.

The soil structure corresponds to the three dimensional organisation of solid particles and pore space. In soils, solid particles (mineral particles and organic molecules) are associated in aggregates. These aggregates are the "negative part" of the porosity. Clay minerals, due to their high reactivity, interact strongly with

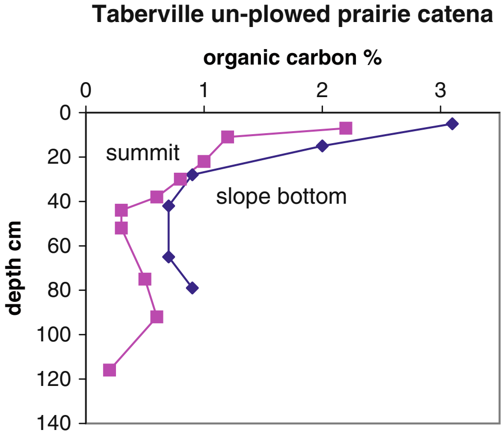


**Fig. 5.11** Relations between organic carbon content and depth in a catena sequence of soils in Missouri (Fenton et al., 1999). The carbon content increases towards the surface in the upland and slope bottom prairies soils but there is more present in the slope bottom prairie soils where humidity is greater, plant growth is probably greater and possibly bacterial action is less intense

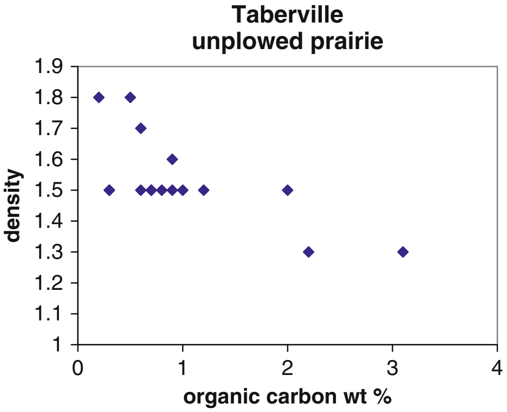


**Fig. 5.12** Relationship between the density of the soils in the Catena sequence of Figure 5.9 from Missouri and the organic carbon content (Fenton et al., 1999). Higher organic carbons forms more soil aggregates which have a capillary porosity filled with water in humid periods

organic molecules and are very efficient at building aggregates. Virto et al. (2008) showed that the clay fractions (<2 μm) of silt-size aggregates are enriched in clay minerals compared to the "free" clays in the soil. Among organic molecules, polysaccharides exuded by micro-organisms or roots have a central role for aggregate formation and stability.

For healthy plant growth, a soil should possess aggregates with both pores larger than 75 μm to remain aerobic and it should have a sufficient number of pores 30–0.2 μm diameter to retain water by capillarity and large pores between aggregates to allow rapid infiltration and drainage (Tisdall and Oades, 1982). Such ideal structure would provide available water to plants and a suitable environment for micro-organisms whose activity is crucial for nutrient cycling are living on pore surfaces. A demonstration of the results of aggregate formation related to organic – clay interaction can be seen in the density of soils related to organic matter content. Fenton et al. (1999) cite data concerning several soil profiles in un-plowed prairie Missouri (USA). In Fig. 5.12 one sees a good correlation between density (measured in oven dried samples) and organic carbon content of soils. The higher the carbon content, up to near 3 wt%, one approaches a density of near one. Since clays have a density of near 2.5, this means that with a relatively small amount of organic matter one creates structures of low density, where the voids are filled with air. These voids will contain water in a natural state in most soils. This is one of the major reasons that agricultural specialists insist on determining the organic carbon content of soils. It is a rough measure of water holding capacity (capillary sites) and hence a ready receive of water for plants.

Due to its crucial role, soil structure has stimulated much research. This effort can be separated into several complementary approaches:

#### 5.2.1.1 Soil Structure Stability and Dynamics

Soil structure is largely related to the intimate association of organic matter and clays. The organic materials tend to fix clay particles together and to form aggregates of particles. The size and stability of these aggregates is vital to the existence of plants in soils. Thus it is important to understand

- The underlying mechanisms of soil structure development and stability and the means by which the soil aggregates form
- Aggregation related to the biologically mediated structure modification in the rhizosphere

Soil structure is highly dynamic because of the dynamics of organic matter stability. It is important to be able to follow and to quantify soil structure evolution. Several tests have been designed to test the stability of soil structure. They are all performed on aggregates.

#### 5.2.1.2 Understanding the Underlying Mechanisms of Soil Structure Development and Stability

Numerous studies have made observations on the effects of different organic molecules on the formation of aggregates. It is clear that root exudates are highly important in this action (Troare et al., 2000 for instance). Also other secondary products of bacterial action can be important as well as the residual humic material (Dinel et al., 1991; Cornejo and Hermosin, 1996). Much of the interactions appear to occur at crystal edges (Varadachari et al., 1995) but the interaction of organic material and clays can be observed on clay surfaces and these more humic organo – clay complexes are bound by lighter molecule materials (such as polysaccharides) to one another (Chenu, 1993). Despite the complexity of the systems observations allow us to understand the fundamentals of the process.

##### Aggregate Formation at the Molecular Scale

Aggregation begins when two mineral particles or a mineral particle and an organic molecule are bonded together. Due to their high reactivity clay minerals interact with each others and with organic molecules. They are therefore of primary importance for aggregate formation. Many authors studied more precisely the interactions between clay minerals and organic molecules. Usually, such experiments were conducted in dilute suspension with pure clay minerals and model organic molecules. These studies gave interesting insights on the mechanisms of aggregate formation. It has been observed that the adsorption of negatively charged organic molecules on clay minerals increase colloidal stability, that is, reduces interaction between particles. The authors proposed the edge site reversal mechanism. They postulated that the adsorption of negatively charged molecules on the positively charged edge-site of clay layers reverses the charge from positive to negative and prevents edge-to-face clay mineral interactions.

This mechanism may occur for 1:1 clay minerals (Kretzschmar et al., 1993, 1997) and 2:1 clay minerals (Heil and Sposito, 1993; Tarchitzky and Chen, 2002a and b). The edge-site reversal mechanism does not lead to any colloidal stabilization when polyvalent cations are added to the suspension. In this case, polyvalent cations establish bridges between negatively charged particles leading to flocculation. Majzik and Tombacz (2007) established that the aggregation of mineral particle is enhanced by the joint effect of negatively charged organic molecules and calcium ions. Concerning neutral molecules, it has been reported than small neutral molecules do not really influence colloidal stability whereas larger neutral molecules, on the contrary, dramatically decreased colloidal stability of montmorillonite (i.e. diagenetically formed pure smectites mineral) suspension (Tarchitzky and Chen, 2002b). In this case, the bridging occurs through hydrogen bonding between the planar oxygen on the clay surfaces and the hydroxyl groups in the polymer.

### Polysaccharide-Induced Aggregate Stabilisation

According to soil structure models soil organic matter acts as a cementing agent between mineral particles (e.g. Tisdall and Oades, 1982). Among organic molecules, polysaccharides have been described as very efficient binding agents. This has been illustrated in the previous part for neutral polysaccharides and negatively charged polysaccharides in presence of polyvalent ions. In several studies authors attempted to establish whether or not polysaccharides also increase the stability of aggregates. Chenu and Guérif (1991) showed that scleroglucan (a fungal polysaccharide) increased tensile strength of pure clay samples. Czarnes et al. (2000) observed the same trend with polygalacturonic acid, PGA (a root mucilage analogue) on natural soil.

### Importance of Clay Mineralogy in Aggregate Formation and Stability

Although the importance of clay minerals on aggregate formation is of course recognized the importance of clay mineralogy, i.e. the type of clay present, on aggregate formation and dynamics have been less studied. Denef and Six (2002, 2004, 2005) and Six et al. (2000) observed that aggregate stability in 2:1 dominated soil depends more on organic molecules than in 1:1 dominated soil. These authors proposed that organic molecules are needed to cement negatively charged 2:1 particles whereas electrostatic interaction between kaolinite particles and iron oxides can occur without a cementing agent. However, they only studied two soils (one kaolinite dominated and the other illite dominated). It is difficult therefore to generalize their results.

Barré and Hallett (2009) studied the effect of the intensity of the organic – clay bond using rheological measurements of clay – organic mixtures in different water concentration solutions. These experiments were designed to describe the intensity of the bonds through the physical coherence in a fluid system subjected to physical shearing stress. They demonstrate that the effect of bonding increases shear strength on all soils studied and variably affected it depending upon the type of organic molecule in contact with the clay and upon the type of clay mineral present, 2:1 or 1:1 mineral. Hence it appears that the intensity of bonding depends upon several factors which can vary of course in a complex natural system such as a soil.

The stability of aggregates, i.e. their presence over a growing season or more, is determined by the rate of destruction of the organic material which binds the particles together. The smaller the molecules, less humic material dominated by C-C bonds, the more rapidly they will be destroyed by bacterial action. Hence the root exudates and bacterial exudation products, of lower molecular weight and less humic in nature, are fundamental for aggregate formation but liable to a short half life due to their vulnerability to bacterial action. The aggregates and their structure in soils then form a very dynamic system, dependent upon renewal by the living materials present, roots and bacteria which degrade plant detritus. Constant renewal is the rule, and since most matter is supplied by plants in one way or another, they are the major agents of aggregate formation and maintenance.

A simplified vision of the organic – clay processes in soils can be given as follows: organic matter is transformed by bacterial into gases and high carbon content molecules (humic matter). The most efficient bonding agents are less humic molecules produced by plants by root exudation or bacterial action; However these less carbon – rich molecules, chemically active by their external functional groups, have a shorter life span due to eventual bacterial action. The cementing agents need to be renewed in the soils in order to maintain a strong clay – organic structure to form aggregates.

### *5.2.2 Consequences of Clay – Organic Interactions: Soil Structure and Aggregation*

There is nothing as rock – like as a clay mass that has dried. This is true for clay lumps or surfaces of clay deposits such as those found in deserts or along sea coasts on mud flats. Clays dry to a very hard and coherent mass. Yet when wetted they become more supple, and one can find aggregates in them which are individual masses of clays separated from others in the clay sample. In soils one often looks at the dried surface, for example in a plowed field. Here the soil is relatively dry, otherwise one would not be walking in it unless with stout rubber boots on. One is familiar with cracked surfaces of soils as they have dried. These cracks are a manifestation of contraction of the material due to loss of free water. When wetted, clay masses usually expand about 30% or so due to adsorbed water and absorbed water in the case of smectites. Interlayer water, two layers associated with a cation, expands the mineral by 50%. In extreme cases the major cracks can be quite wide, several centimetres.

#### 5.2.2.1 Soil Pore Structures, Aggregation and Fractures

##### Soil Structure Observation

Soil structure is obviously not directly visible in three dimensions in that soil materials are largely opaque. Thus its observation is challenging in itself. Some methods have been used in the past which have given useful results. More are needed in the future. The first method that provides soil structure visualization is by the thin section method. A soil core is impregnated by a resin which penetrates the pore system to different size domains depending upon its viscosity. It is then cut with and treated to produce either flat surfaces or in the form of a thin section which is on the order of 15 μm thickness. The thin sections are then observed and photographed using a petrographic microscope. The image is reduced to a black and white figure and methods of image analyses of the pictures allow one to quantify the porosity of the soil core. Usually this method is limited to pore spaces on the order of 25 μm width or diameter. Serial cuts of a block can be used to give the same effect, taking pictures at each stage of evolution (See Moreau et al., 1999 for example). However, soil structure is a 3-D object. In particular, more than porosity, the key property is the continuity of the poral network. The continuity of the poral network can only be studied using a 3-D visualization of the soil structure.

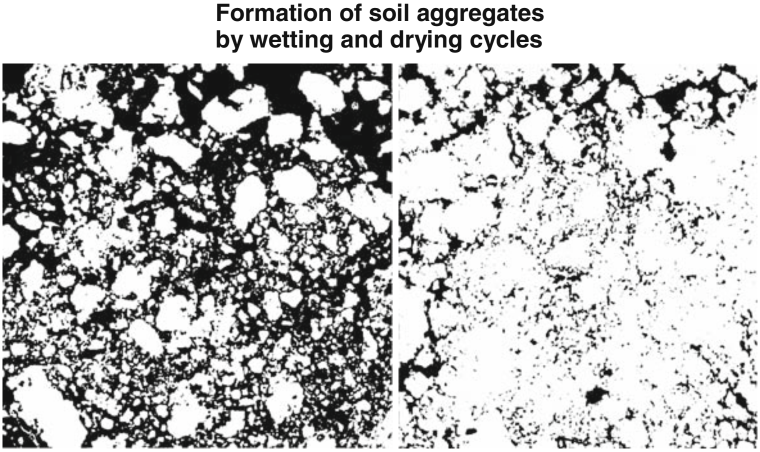
This visualization was first obtained by doing several parallel cuts in an embedded soil core. Several parallel thin sections were obtained and analyzed. The 3-D structure was interpreted from these images. This technique that is particularly time consuming has now been replaced by the direct observation of the soil core using C-T scanners (Perth et al., 2008). These scanners coupled with more and more powerful imaging programs allow looking inside the soil core and provide direct measurements on soil structure. For instance, data processing programs allow quantification of porosity and the connectivity of the poral networks.

##### Surface Features

Soils have holes and passageways in them as well as cracks. For a pedologist and above all a farmer, a primary criterion for assessment of a soil is its structure, i.e. the extensions and discontinuities in three dimensions. Cracks, holes and passageways due to animal activity are the characteristics of soils. In between these pores are the solid parts, or at least the parts with only micro porosity. The "reason" for the presence of macro porous structure of soils (the organic surface horizon) is that most plants cannot live in a water saturated environment. Air is a necessity for roots and plant growth. Most plants cannot survive in an anoxic soil environment. Some do but they are specialized to say the least. One of the reasons for this is the need to have a source of air to extract nitrogen from. Most of the nitrogen exchange between the air and plants occurs in the soil zone. Thus soils have pores, i.e. passages in which air is present. As it turns out these pores are also a vehicle for water flow, out of the soil system and hence they evacuate water to let air into the system. Pores are then vital to the well being of most plants. Certainly some plants have adapted to the total wetting of their roots and anoxic conditions of soils. Such are the plants that thrive in swamps and bogs. However, in surface environments if clays have no plant – soil interaction, i.e. organic content, they tend to have almost no macro – porosity or passageways for air circulation. Organic matter interacts with clays to form aggregates or self contracting units which as they release water form pore spaces between themselves. This occurs by wetting – drying cycles (Li and Velde, 2003). The structures, spatial distribution of these pores, can be quite varied.

### Internal Features and Porosity

Porosity is due to the disposition of the solids in a soil. Most soils, those at the surface with some organic matter content have soil aggregate formation. This is a state where the clay particles are bound or fixed together to form a more or less dissociable mass of roughly equant dimensions. The finer the aggregate sizes, the smaller the pores. The more irregular the aggregates, the greater will be the range in size distribution of the pores, from fine to large. Aggregate formation is affected by cycles of wetting or drying (Fig. 5.13). In this figure one sees samples of roughly broken soils in the dried state loosely packed in a cylinder (0 cycles of wetting and drying) and a second stage after nine cycles of wet – dry after the methods described in Li and Velde (2003). There is a clear tendency to form large aggregates with wet – dry cycles and pore sizes become somewhat smaller as the soil particles settle downward in the cylinder. This settling effect is common to plowed and cultivated fields under agriculture use. One can see that the aggregation process



**Formation of soil aggregates by wetting and drying cycles**

LaTouche Rendzina 0 cycles
Wetting and drying
3 cm depth

LaTouche Rendzina 9 cycles
Wetting and drying
3 cm depth

**Fig. 5.13** Illustration of the effects of wetting and drying on soil aggregates. The same soil material is shown in an initial roughly broken state and after nine cycles of wetting and drying. The tendency to form larger aggregates at the expense of smaller ones is quite evident (data after Li and Velde, 2003) tends to maintain more or less equant soil aggregates. Eventually the aggregates are sufficiently large to be unable to shrink homogeneously and they are cracked. One can see the beginning of such a process in Fig. 5.13 in the lower left hand corner.

The existence and nature of soil aggregates is normally attributed to the organic matter present and a relation between clay particles and organic matter is assumed to be largely responsible for aggregation. However these are not necessarily the only variables affecting pore sizes and aggregates.

Figure 5.14 shows the differences in pore spaces developed in the same Mollisol soils by three different regimes of plants growth. In the figure one sees the differences between pores and their distribution over a 6 cm depth in cores from an experimental farm in central Iowa, USA (samples courtesy of David Laird NSTL, Ames Iowa). The variations are not extreme but one sees the influence of the depth on soil porosity due to the type of plants grown in the soils. The natural prairie shows the deepest zone of macroporosity distributed in various pore sizes. The continuous soybean cropping shows a more or less homogeneous pore distribution with an abrupt loss of macropores near 10 cm depth while the rotation of corn and soybeans shows a more inhomogeneous distribution towards the surface with larger and smaller pores present and an abrupt of more or less evenly dsitributed macroporosity at 7 cm depth. In the lower zone one sees evidence of cracking, shown by the linear macropore. In these examples the soil type and physical characteristics of

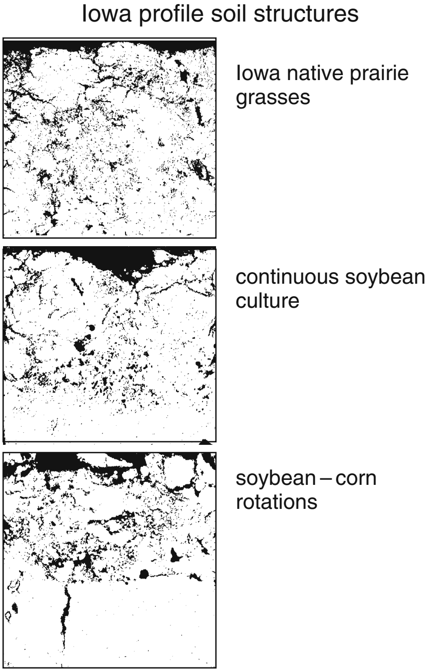


**Fig. 5.14** Example of the effect of crop types on soil texture (aggregation) as a function of depth in cultivated soils after harvesting (samples courtesy of D Laird, USTL Ames IA USA). The depth of disseminated pores (in *black*), indicating aggregation is quite variable depending upon cropping management. The zone of low aggregation and sporadic cracking rises to the surface as cropping is more important and the presence of corn increases the effect. The soils with the greatest distribution of soil aggregates are those of native prairie followed by soybean cropping and the least aggregates soils are those where corn (*zea mais*) was grown. Vertical cuts are near 7 cm in depth

grain size distribution (clay and sand content) are almost identical but the influence of the type of plant present affects the surface macropore sizes and distribution and the depth to which it extends. The most irregular distribution of porosity, variety of pore sizes, is found in that of the native prairie soil. Is this an advantage? Most likely yes. The problem for roots is to find a place to live and develop in a macropore. Roots can penetrate soil masses (aggregates) but it is easier to grow around the soil aggregates where they are in contact with the solid phases, which have microporosity which is usually filled with water and where they also have access to air.

In Fig. 5.15 we can see a two dimensional distribution of porosity and aggregate type as a function of depth in a soil, in this instance a Mollisol from central Illinois taken at the end of the growing season and numerous cycles of wetting and

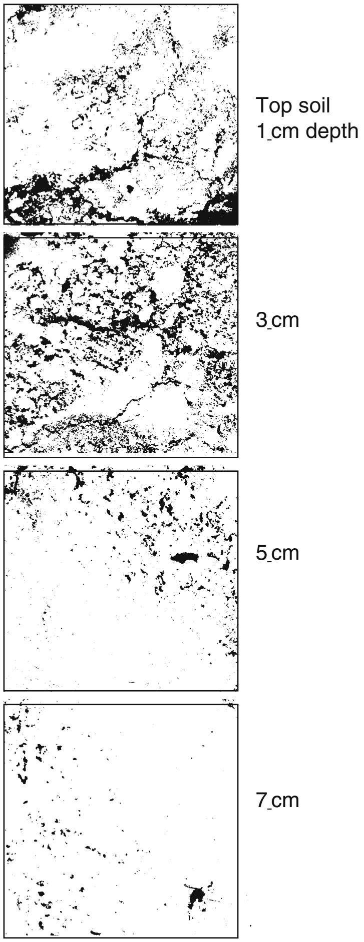


**Fig. 5.15** Sequence of pore structures in sequential cuts at different depths for a corn field in Central Illinois. The aggregates are quite similar down to the depth of around four centimetres where cracking is the only form of pore structure except for worm holes (round pore in the lower figure) Dimension of the soils shown is 6 cm on a side

drying since the tilling and planting of the corn crop. In each section the porosity type changes, from an initial fine pore size distribution at 2 cm depth, to a more coarse distribution at 3 cm, and below 5 cm one finds a loss of macropore size distributions and the presence of cracks. It is interesting to note the trace of a worm burrow (round pore) in the upper right hand portion of the 5 and 7 cm depth figures. This shows that aggregate formation is not the only cause of soil porosity.

In Fig. 5.15 one can follow the change in macropore structure by horizontal sections as a function of depth in a profile of a soil which had been strongly watered, by rainfall and the formation of standing pools for several days, with subsequent formation of surface cracks. Here the fine clays were moved towards the pools by surface erosion, on a minor scale, and formed a strong clay, low organic and silt – sand, textured material. This material formed cracks with little or no aggregation. This is the type of soil cracking that is most often remarked when on walks in fields or open spaces. However the surface cracks quickly give way to the underlying aggregate structure it the soil due the clay – organic interactions (Fig. 5.16). At less than 2 cm depth one sees the trace of the surface cracks but already much smaller porosity is apparent. At 3 cm depth there is no trace of this surface crack expression.

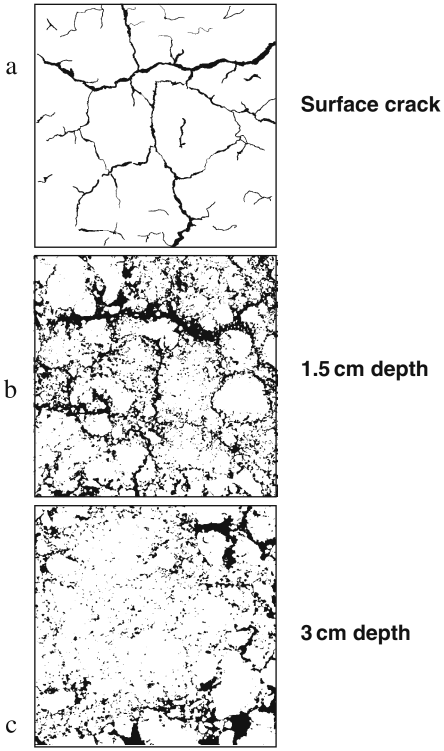


**Fig. 5.16** Illustration of surface cracking on a soil and the effects it has in the organization of cracks and aggregate porosity as a function of depth. Sample is from a rendzina soil in center western France (see Velde, 2001a). The obvious cracks at the surface are quickly dissipated into the soil aggregate structure at minimal depth

This example illustrates the importance of having a soil of balanced components: clay, silt, sand and organic matter. Such material promotes “good” soil structures with a variety of irregularly distributed pores created by soil aggregates, i.e. association of organic matter and clay minerals.

### Deep Fissures

Some soil types are reputed for their strong cracking and fissure formation. Often they are classified as Vertisols or when having such characteristics they are designated by a vertic adjective. Such materials are clay – rich, but often not excessively so, in the 20–35% range. However if the organic matter is of low content or poorly fixed in the clay-organic complexing system, aggregation is not sufficient to prevent the formation of deep and persistent cracks. Surface cracking is seen in the presence of wide cracks which descend to significant depths. Well below the plant – soil interaction zone one finds very wide and deep cracks extending to several meters depth. An example is seen in Fig. 5.17.

The surface of the soil is under prairie, as shown in the figure. Here cracks are apparent on a large scale (4–5 cm large). In fact they are not just the expression of

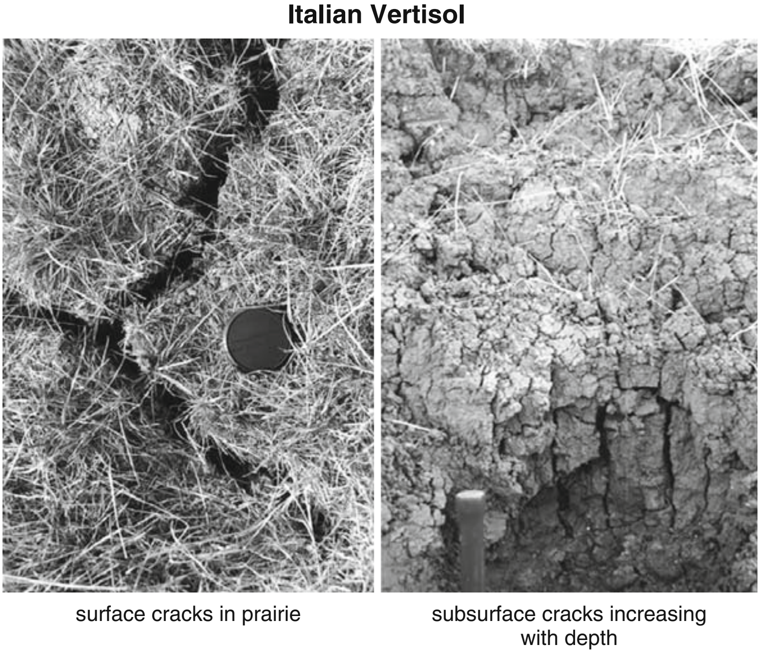


**Fig. 5.17** Example of the succession of crack features in an Italian Vertisol (Moreau et al., 1999) showing the importance at eh surface, tehe formation of aggregates in the soil (plant – clay zone) and the formation of larger cracks at depth in the C horizon of the alterite material (photos BV)

drying in an organic – poor and clay – rich medium. As one can see, prairie has installed on the soil surface and on can expect a relatively significant content of organic matter. Still, the high smectite content and the significant clay content of the soil (near 30%) produce a vertic structure. Low organic matter content allows the full expression of water loss from the smectites which is moderated by clay – organic associations (personal communication, F Terrible, Univ Frederico II, Naples). In the adjacent photograph one can see the extent of the crack formation. In fact the large cracks are more apparent at depth than at the surface. In the photograph (the geologist's hammer is a scale factor at the bottom left) below a meter, one finds the development of very large cracks or fissures. In fact it appears that the soil horizon (plant – silicate interaction zone) has mitigated, again, the effect of fissure creation and such activity has resumed at depth below the A horizon.

However, the internal soil structure, i.e. crack and aggregate structure, can be important concerning the properties of a soil (Velde, 2001a; Logsdon, 1995).

### 5.2.2.2 The Importance of Soil Structure (Organic Matter and Clays) on Some Soil Properties

Aggregate Formation

Aggregate formation essentially divides the soil water into two compartments, that found in large passages where water can flow and air can enter when gravity has emptied the pore space and that water present in only small capillary sized pores which can contain water but where the water is much more tightly held (Coppola et al., 2008). The micro pore structure can be visualized and treated numerically using high energy scanning devises (Perth et al., 2008). Such features as average path length, pore size distribution and so forth for the micropore network are values that are now available to modern research. The micropore structure is vital to plants in that it is the major reservoir for water under normal growing conditions in most climates. The two compartments of pores in soils, intra and inter aggregate rhythm the life of the soil – organic structures. Low organic matter content or soil clays that do not aggregate well (kaolinite) limit the capacity of the soils to retain water and hence the growing capacity of the soil.

Smagin et al. (2004) show the importance of organic matter on the water retention capacity of soils from a macroscopic point of view. Using measurements on long term field studies and laboratory experiments they demonstrate the strength of retention of water depending upon the carbon content of the soils and hence the organic – clay contacts forming soil aggregates. This sustains the age old adage that organic matter content is important for soil fertility, in the sense of water availability. Thus on of the foremost functions of soil aggregates is to hold water in the micropore positions which is a reservoir for plants throughout the growing season.

Figure 5.18 indicates the structure of such soil – organic complexes with micropore space and macropore, inter-aggregate space.

The decoupling of macropore water, which moves through gravitational forces from the aggregate micropore water which is strongly retained in the soil is the

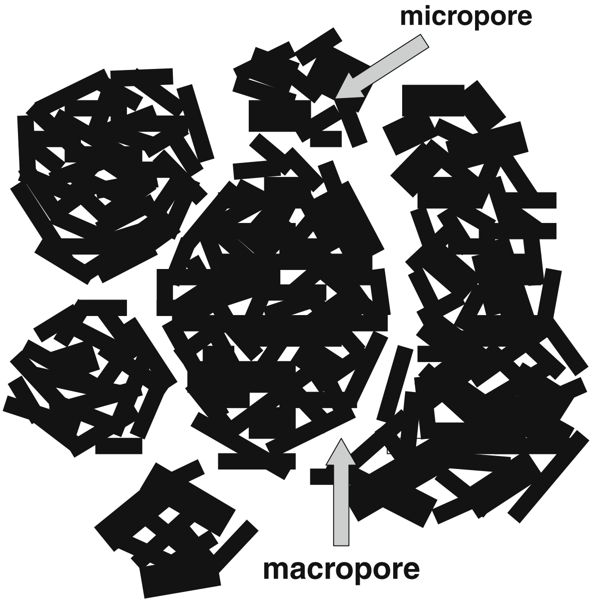


**Fig. 5.18** Diagram indicating the organization of clay particles forming aggregates with micropore sites and inter – aggregate porosity

key to understanding the chemical hydrology of soils. The water in the pores of aggregates will come into chemical equilibrium with that of the soil clays and the organic matter while the water in the macropore solutions will be less influenced by the solids. Data from a forest soil where certain mineral elements were analyzed in fluids coming from macropores and micropores (Ranger, 2002) shows a decided difference depending on the site where the water is found for certain elements and for others no significant difference can be noted. Potassium and Si are notably higher in the capillary, micropore water whereas Al seems to be present in roughly the same amounts in either case. Hydrogen ions seem to be more concentrated in the capillary, aggregate water. This is just one example for one situation, a conifer forest soil, which does indicate different levels of saturation for the different types of water. Such studies would be valuable in order to understand which mineral elements are controlled by the clays present and which are more likely to be extracted from the system by water flow through the macropore structure.

The existence of aggregates, controlling water flow and retention then not only controls water availability in the soil but also the flow of mineral elements from the solids in the soil into free flowing water due to rainfall.

### Importance of Aggregate Formation on Physical Properties

The aggregate structure in soils is not only of chemical importance but can also play a role in the structure of the soil in a physical sense. Aragon et al. (2000)

show the importance of organic matter, and hence aggregate structure, in the overall resistance of soil to compaction. The more organic matter in the soil, the more aggregates are formed and these aggregates resist re-organization which determines compaction. Such resistance to compaction pressure is important for agricultural practice, especially when heavy wheeled vehicles are used to treat the soil. But in a general sense it is better to have a compaction -resistant soil structure which will hold its aggregate structure under heavy rainfall for example, and maintain the pore microstructure and almost as important the inter-aggregate macropores which convey oxygen to the roots when the free – flowing water content diminishes.

Higher bulk densities of soil aggregates, i.e. lower abundance of micropores, impede root growth (Logsdon et al., 1987). This reflects the resistance to root pressures made by high density, low porosity soil material. An organic rich soil of good aggregate structure is less resistant to root penetration.

Yet another effect of the organic – clay aggregation is that of maintaining soil clays in place. The more tightly bound, in the assemblage, the more resistant to transport in runoff water by suspension of soil clays (Rhoton et al., 2002). This study is oriented to show the effects of different types of soil tillage practices, no till and conventional tillage. The no till practices leave a maximum of organic matter in the field after harvesting which is incorporated into the soil as clay organic complexes upon bacterial reduction. Normally in plant covered terrains, runoff loss of clays is not important. However in agricultural terrains, the soil is left without plant cover during the non-growing season and hence subject to runoff of soil clays. The same situation exists in arid and semi-arid climate terrains when plant cover is not complete and bare zones without plant cover can be easily attacked by rainwater carrying clay and other material in suspension. Aggregate stability under conditions of wetting is greatly increased by overall organic matter content and as such the soils are more stable. Water dispersible clay content in run off and streams decreases as a result of aggregate stability. Hence the presence of organic matter stabilizes and conserves clay content of soils.

The inter-relation of organic matter and clays is fundamental to the environment that plants grow in. The formation of soil aggregates, which are essentially sponges for the storage of water, is an extremely important of the functioning of soils (the A horizon). This structure is strongly dependent on the presence of 2:1 clay minerals which are more chemically active than are the 1:1 kaolinites. The stability of the aggregates depends upon the presence of smaller organic molecules which are more chemically active. However these smaller molecules are more easily degraded or mineralized by bacteria due to the presence of C–O and other bonds instead of the predominance of C–C bonds in larger molecule humic material which are resistant to bio degradation. Thus the continued activity of plant deposition of their aerial parts and decay of roots is necessary to microbial action which produces some low molecular weight material. Also, the roots themselves exude this low molecular weight organic material which also maintains the aggregate structures. Loss of input, from aerial deposit, decreases the content of the low molecular weight material. Hence the cropping and exportation of plant bio mass impoverishes the soil in its organic content and destabilizes the aggregate structures. This leads to more difficult conditions of plant growth and to a loss of clays due to surface rainwater transport. The organic – mineral relationship is fundamental to plant growth.

## 5.3 Plants and Soil Chemistry

### *5.3.1 Plant Compositions and Chemical Needs*

Plants do not live on air and pure water. There has to be something in the water. The reason is that plants are not composed uniquely of components found in the air, though largely so. Most of plant substance is found in the air, water, carbon dioxide and to a lesser extent nitrogen. These major components are freely available to all and with sunshine as a source of energy plants do very well. However, minor mineral elements are necessary for the proper growth and well being of vegetal matter. For terrestrial plants these elements are found in the soil they develop in or on the rocks that they colonize. Agricultural science has developed around the needs of the mineral elements found in soils and nitrogen which is to a large extent transmitted in the soil zone from air to plant via bacterial action. It has been found that certain elements are especially important. They are potassium and phosphorous for the mineral parts. Traditional fertilizer contains nitrogen, phosphorus and potassium. Other cations such as Ca, Fe and Mg are usually sufficiently available in soils as to pose little problem in limiting plant growth. However some cases show a lack of these elements which needs to remedied by application of a mineral supplement.

One of the functions of plant roots is to gather the necessary mineral elements needed for proper growth and development and to prospect for water. The methods of obtaining the necessary mineral components appear to be varied and at times complex. Often plants use or encourage micro-organisms to provide the mineral resources via actions of mineral dissolution or elemental extraction certain elements from minerals. There is a strong interchange between root exudates material and microbiological activity in soils which promotes the extraction of mineral elements form the soil, rock and mineral substrate. The concentrations of different mineral elements is not constant in the plant, roots, stems or trunks, branches and leaves (Gain, 1895) indicating their involvement with different metabolic functions in the plants. However, in general mineral substances are important though present in much lower concentrations than $CO_2$ and $H_2O$ which make up about 90% of plant matter. Mineral elements vary from one plant species to another. As an indication of the relative importance of each component, Bormann and Lichens (1994) give the following ratios for an active hardwood forest in Northeastern United States: Ca 10, Mg 1, Na 0.02, K 0.6, P 0.2, Fe 0.3, N 0.8. The relative importance of potassium and nitrogen as far as their influence on plant growth is much greater than their relative ponderal importance.

#### 5.3.1.1 Silica

Among the mineral elements that the roots gather one finds silica. The role of silicon is usually not mentioned in studies of plant physiology except that it is present in most species. The presence of Si is higher in more primitive species (Hodson et al., 2005) such as horse tails, liverworts and club mosses. Non-woody plant parts show up to 1.5 wt% of Si of the total plant material (i.e. including water components or "wet" weight). The silica is present in plants as phytoliths, concentrations of amorphous silica in a pure form. These silica aggregates can persist in soils for significant periods of time. Borrelli et al. (2008) indicate that the phytolith populations can remain un-changed for at least 50 in soils subjected to different vegetal cover in Argentina. However it is generally considered that the phytoliths control the silica content in soil pore by their dissolution water and in the water that eventually drains in to rivers and the sea (Farmer et al., 2005; Derry et al., 2005). Thus the concentration of silica in soil pore solutions appears to be controlled by plant action, in the form of phytolith concentrations of pure amorphous silica. Amorphous silica is far more reactive, i.e. can dissolve much faster and at higher concentration that most silicates and especially quartz, the pure crystalline form of silica. Quartz has a very low dissolution constant and rarely controls the silica activity of pore water solutions. Hence with one form of silica, phytolith, the silica concentration is solution is very high and the other, quartz, it would be very low. The impact of the activity of silica in solution is very important to the stability of the different types of clay minerals present which we will seen below.

Data from Gain (1895) shown in Fig. 5.19 indicate that the different parts of crop plants contain different proportions of potassium and silica. The silica content of the structural parts, stems of grasses, is particularly high in that it forms a structural element within the stems. This is one of the reasons why we like to eat the fruits of plants and not the stems, most often.

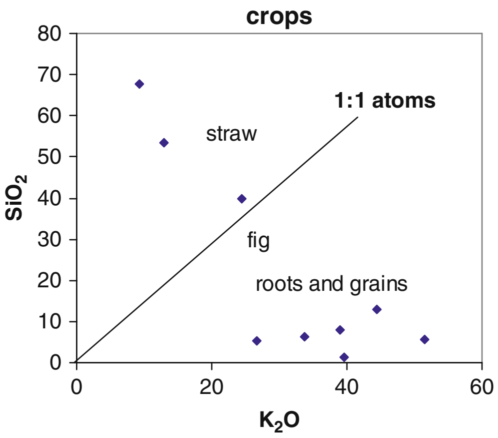


**Fig. 5.19** Relative atomic proportions of potassium and silica in several examples of grain crops comparing straw and other portions of the above ground plant (data from Gain, 1895)

#### 5.3.1.2 Calcium and Magnesium

Calcium and magnesium are present in plants, but seem rarely growth limiting. However they have been used as fertilizers (Larbaletrier, 1891) but they are more rarely used as fertilizers today but instead used to correct the soil pH. The common presence of calcium in rock silicate minerals and carbonates is such that calcium is almost ubiquitous. However Ca is largely present in plant compositions, equal to or about half that of potassium. Knecht and Göransson (2004) report similar abundances for a large variety of plant types but Broadley et al. (2004) indicate lower values for angiosperms, and especially herbaceous plant types. Magnesium is present in plants in much lower proportions, about 10–20% of Ca weight content. Calcium seems to be equally present in coniferous, deciduous and herbaceous plants.

Hence calcium being almost omni – present soils is hence rarely critical to plant development. The importance of magnesium is less well documented.

#### 5.3.1.3 Potassium

Potassium is another story. Very much of agricultural practice has been focused on the availability of potassium for terrestrial plants. It is one of the more abundant mineral elements in these plants. Plants fixed nearer the sea, or in arid areas of salt deposition are much more dependent on sodium, because of it s relative availability. For terrestrial plants potassium is an element which changes their growth factors greatly, as seen in demonstrations of the use of fertilizers in 19th century texts. Potassium is frequently a limiting factor in plant growth. However although potassium is found in most parts of plants its metabolic and functional role is poorly known (Treshaw, 1970, p. 182). It does not appear to be fixed in plant tissue units. Since the 1860s in Europe the use of potassium chloride has been know as a major element that could be used in synthetic fertilizer agricultural use (Larbaletrier, 1891). The material could be mined in essentially the pure state. It replaced the use of wood ash as a source of potassium. In fact such ash materials were imported to Europe from Russia and the United States as a fertilizing agent before this time. The use of potassium has been much studied and its consequences on plants, not only crops but tree growth has been well documented.

From the assembled data of Knecht and Göransson (2004) herbaceous plants contain more potassium than trees on a nitrogen based comparative scale. Gain (1895) indicates that in agricultural crops, grains have less potassium in roots than do legumes and cotton. Stems and grains have two times as much potassium present than do roots but there is a strong variation from one crop to another. Usually the material harvested is the most potassium rich. However the needs and plant composition do not remain constant as a function of maturity stage. Clark et al. (1980) show that the potassium content in grasses and legumes can change by a factor of about three during different stages of growth. Potassium uptake is strongest in the early stages of maturity. Thus the exportation by agriculture of potassium is critical to the soil – plant balance. The ratio of potassium to calcium in different parts of trees can vary to a large extent, oak for example can have 25% of calcium content in the wood and 17% in the leaves of the tree. By contrast beech and confiers show a lower potassium content in leaves and wood than in calcium. These differences are important in the short term in that trees seem to stock more calcium than potassium especially in the wood whereas perennial plants appear to stock more potassium in the plants. Thus the annual return of mineral elements to the soil shows a higher return of potassium for herbaceous plants and oaks (leaves) than trees. Overall herbaceous plants take out more potassium (and return it to the surface in the soil if left to mature) than do most trees. The herbaceous plants can be seen as potassium storers and gatherers more than are trees.

Potassium is found in clay minerals and some high temperature minerals (feldspars) which are found in the soil zone. The major source of potassium in soils is from clay minerals. Potassium can be extracted from high temperature minerals in the water – rock interaction portion of alteration profiles, and deeper plant roots surely use this as a source of potassium renewal as this rather soluble element is leached out of the plant soil horizons. The potassium is transferred from root zone to plant and plant to soil by leaf and other plant decay mechanisms. Then the potassium is incorporated into the clays as illite, an anhydrous layer of potassium ions in the 2:1 structures. Release of potassium from leaf matter can be rapid, where leaf decay and transformation by bacteria is not necessary to release the K in the leaves (Lupwayi et al., 2006). Potassium is not held in the plant structural elements.

#### 5.3.1.4 Phosphorous

The use of phosphorous as a fertilizing agent was known and practiced in Europe from the 1840's (Gain, 1895). It is relatively abundant in many countries as reasonably concentrated calcium phosphate deposits, usually found in sedimentary rocks. Since most agriculture is accomplished on sedimentary terrains, this availability was quickly exploited. Phosphorous is, as is potassium, fundamental to good plant growth and lack gives poor plant growth. However the chemical path of phosphorous in soils is not well understood. Phosphorous is fixed strongly to amorphous silicate materials (allophone) and oxy-hydroxides especially those of iron. This capacity to fix phosphorous is a definition for Andosols in soil classification (Dixon and Weed, 1989). However the chemical path of phosphorous in soils with crystallized silicate materials is less sure. It is apparent that phosphorous is little available in the organic matter. Thus one must presume that a large portion of available phosphorous is associated with clays somehow. The major source of mineral phosphorous is from apatite, a calcium phosphate. This mineral is strongly affected by low pH solutions. The source of phosphorous in rocks is often that of animal concentrations, as bones and teeth deposited in phosphate deposits, made mainly from fish remains. Some phosphorous is found in igneous rock, especially granitic type materials but is some basic volcanics it can be abundant, especially in eruptive rocks of high potassium content. Such are found in the Roman co-magmatic province and have given rise to the rather fertile material around Naples and Rome. It is not an accident that this reliable source of soil fertility and hence crop production gave rise to a strong and independent nation in the distant past.

It is proposed by many authors that the phosphorous is fixed by the Al and Fe hydroxyl bonds on the amorphous materials in such soils (Dixon and Weed, 1989). Such bonds exist, in smaller numbers per mineral mass, on clays at the edges of crystals. It would seem possible that such electronically active bonds could also fix phosphorous. The amount and intensity of bonding on clay edges, according the type, 1:1 or 2:1 structure would determine the phosphorous availability for plants. At present we do not know about the relative values of these bonds and their intensity but it is perhaps a fruitful avenue for future research.

#### 5.3.1.5 Nitrogen

Nitrogen is the major component of air. However, as far as one can see now, most nitrogen in the bio-cycle passes through soils before entering into the plants, initially. Thus the air in soil, in the pores at the surface is the vector of nitrogen fixation in the life cycle of plants. The importance of nitrogen and the nitrogen cycle has been the subject of much research and discussion. There is a very large body of data on the subject, related to the growth of domestic plants (crops) and forest growth. Essentially, nitrogen is a large component of air, about 80% by volume. It is found in many components of plants. It has been known for a long time that nitrogen containing components can be used to facilitate plant growth. Nitrogen seems to be a sort of catalyst for plant growth being present in relatively low concentrations in many parts of a plant. The basis of farm manure use is based upon a knowledge of the management of this essential fertilizing agent. Ninteenth century texts on agricultural practice, preceded by those of other practitioners of the art (de Serres, 1600 for example) who quote ancient Greek authors, all acknowledge the importance of recuperation and proper treatment of animal excrement in the nitrogen cycle. The problem in agriculture is to avoid the “mineralization” or reduction to a gas state of the nitrogen by bacteria in the soil. Nitrate is a useful form of nitrogen for plants as is ammonia. The ammonia state is often found directly produced by bacterial action in manure accumulations and in animal urine. Hence the barn yard was an important cite of recuperation and fixation of nitrogen for fertilizer use. Today, barn yards no longer exist. Animal excrement is considered to be a noxious by-product and mostly misused by direct application to the earth where it is very largely mineralized by bacteria being lost for about 80% to plant use. The intermediate step of mixture of excrement and urine with straw or other plant materials fixes and develops a more stable form of nitrogen – bearing substances. Russell (1945, p. 237) illustrates this effect as one lasting for at least four years which increases crop productivity by a factor of two. Of course synthetic sources of nitrogen can be more powerful but are not as long lasting.

Plants most often extract nitrogen from organic matter via bacterial action on such detritus as provided by the plants themselves. Further sources of nitrogen are accumulated in soils via bacterial action associated with plant roots forming nitrogen – bearing nodules, especially prevalent on legume plants roots. The ultimate source of nitrogen for plant growth is in the air present in the pores of soils. This transfer replaces the nitrogen lost from the biomass through bacterial action producing gasses and nitrogen – bearing molecules dissolved in aqueous pore solutions which drain from the soils eventually into the water table and stream sources.

#### 5.3.1.6 Distribution of Elements in the Plant

As might be expected, elemental distribution is different in different plants and is variable within the plant itself. These variations have been used by farmers for some time, perhaps from the beginning. Basically one can consider the roots, the stems and woody parts and the leaves of plants. Overall woody plants appear to store much K and Ca in stems, trunks and branches. Some specialists (personal communication D Righi, Univ Poitiers) attribute the acidity of forest soils in large part to the exchange of the bases, Mg, Ca, K for hydrogen ions as the mineral elements are taken up across the root membranes. Since a great mass of these elements is permanently stored in a forest, the overall effect is to permanently acidify the soil as the bases are taken from the soil and acids left behind in an electro – neutral exchange. Overall it appears that deciduous trees and forest plants take up more potassium than do coniferous trees (Knecht and Gôransson, 2004). Herbaceous plants have even more present than woody plants. Forest floor plants such as ferns have roughly twice as much potassium present in their leaves that beech trees for example (Larbaletrier, 1891). It appears that much potassium can be stored, above and beyond incorporation in cellular material in the leaves of herbaceous plants leading to “luxury consumption” by certain species (Broadley et al., 2004). This potassium is readily available to the soil solutions either by rainfall washing or rapid release from fallen leaves.

Root compositions of “old prairie” given by Larbaletrier (1891) are comparatively less potassic that shoot material of herbaceous angiosperms (Broadley et al., 2004). However compositions of root crops and grain from traditional agriculture (Fig. 5.11) indicate high potassium levels. Thus all depends upon the plant concerned and this will have an impact on the chemical balance in a given soil setting.

For the most part, modern agricultural practice is focused on the NKP fertilizing agents, while other mineral elements are used in cases of special deficiencies due to specific local soil, and substrate conditions. The fundamental necessity of these three elements and their use in encouraging plant crop growth have led to what has been called the green revolution in changing the productivity of agriculture in developing countries in the period 1960–1980. The systematic use of these chemical fertilizing agents gave rise to an unprecedented increase in agricultural productivity in less developed countries as was the case earlier in developed countries. The importance of these chemical agents was of course not unknown before the use of synthetic agents. The traditional agricultural practices used conservation and concentration practices which enhanced or preserved such element sin the soil horizons. Thus the modern agricultural practices have not discovered new truths, as far as the chemistry of plant growth is concerned, but they did use such information in a scientific way to concentrate the effects in crop science. More on this subject in Chap. 6.

### *5.3.2 Chemical Profiles in Soils and Alterites Engendered by Plant Activity and Resulting Clay Mineralogy*

The chemical effect where plants have been seen to transfer certain elements from the alterite zone to the soil zone has been known for some time (Duvigneaud and Denoyer – DeSmet, 1970 for instance). These authors indicate that the uptake of potassium the alterite and soil zones is greater than that retained in the soil zone. The transfer and fixation are dependent upon several factors, not the least the type of plants present such as conifer versus deciduous tree for example (Homann et al., 1992; Quideau et al., 1996). Nevertheless, in many instances, one can clearly see a trend of potassium increase at the surface (soil horizons) and frequently an increase in silica where free quartz is not present (Fig. 5.20).

This is true for alteration profiles in temperate climates on basalts (Chesworth et al., 1981) serpentinites (Rabenhorst et al., 1982; Bonifaccio et al., 1997) and various eruptive rocks under humid and tropical climates (Leumbe et al., 1993; Meijer and Buurman, 2003; Pion J-C, 1979; Mohr and Van Baren, 1959, p. 147; Zarin and Johnson A, 1995; Nguetnkam et al., 2007; Jahn and Asio, 1998) highly weathered podzolic soils in Alabama (Bryant and Dixon, 1964) for contrasted season semi

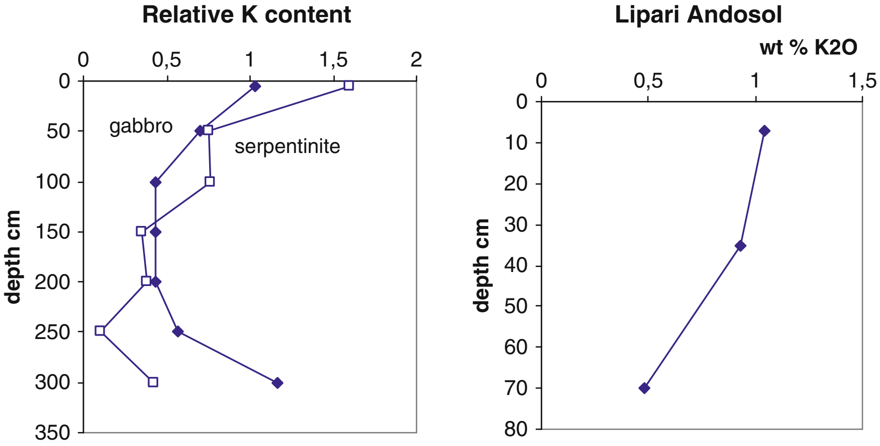


**Fig. 5.20** Representations of the variation of potassium and silica contents of several soils, where the presence of metastable quartz does not perturb the estimations, The evident increase at the surface, essentially the A horizon, of these elements is apparent (Pion, 1979 and Mirabella et al., 2005)

tropical forest soils on terrace deposits (Ahmed et al., 1971) and on a basalt in New South Wales, Australia (Loughnan, 1969, p. 89).

Silica is found in plants as a pure, amorphous phase, phytoliths, which has been considered to be the major controlling phase of silica activity in soil solutions (Farmer et al., 2005). This effect has been modelled comparing the results to long term observations on soil pore solutions under conifer forest in a temperate climate (Gérard et al., 2008). Similar observations have been made by Derry et al. (2005) for soils with various plant covers on the Island of Hawaii. Potassium is found in most parts of the plant. Plant decay by leaf shedding or loss of branches and eventually the entire tree deposit these mineral elements at the surface (Fig. 5.19). De Connick et al. (1987) show data demonstrating that the transfer effect can be concentrated in the fine fraction of the soils in the a horizons. The presence of phytolith material is the controlling factor of silica activity in solutions because phytoliths are highly reactive materials susceptible to dissolve much more rapidly than other forms of crystalline silica such as quartz (Fraysse et al., 2006).

Righi et al. (1999) give data showing the rapidity with which this uplift or plant engendered chemical transfer can occur in young montane soils. One compares the A (plant influenced) horizon to the C horizon where the major activity is due to water rock interaction. In Fig. 5.21 given above one sees that potassium is lost in both horizons but much less in the A horizon with perhaps a stabilizing composition near 4% $K_2O$. However potassium is lost in the C horizon regularly with time. The same effect is seen for silica for the two horizons. The time span is 6,000 years, and one sees the effect of plant transfer in the very early stages of development of the soil profile, probably less than 400 years. It is clear that plants can control the silica activity, which determines mineral stability, in soils.

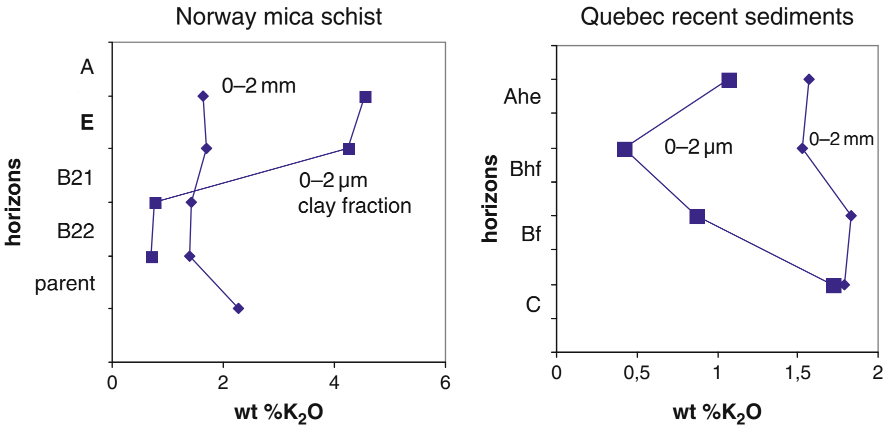


**Fig. 5.21** Illustration of the relative increase of potassium as a function of size fraction in two sandy till and loess based soils. Data from De Connick et al. (1987)

#### 5.3.2.1 Clay Minerals

Lucas et al. (1993) and Lucas (2001) have emphasized the importance of the phytolith uplift of silica to the stability of kaolinite, the alumino-silicate 1:1 clay, compared to gibbsite, the alumium hydroxide clay mineral. The maintenance of silica activity at the surface favors the presence of kaolinite in tropical soils. The normal weathering trend is to lose alkalis then silica (Pedro, 1966).

However the stabilization of other clay minerals is possible and numerous studies suggest their presence due to the silica activity engendered by plant phytoliths. This is a sort of reverse weathering.

Reverse weathering would occur as follows:

| | |
|---|---|
| Gibbsite | Al |
| to | |
| Kaolinite | Al-Si |
| to | |
| 2:1 mineral | Si-Al-Si |

The 2:1 portion of the minerals can vary from muscovite composition with an Al:Si ratio of one as is the case of kaolinte, to aluminous interlayered ion hydroxyl vermiculite where the Al:Si ratio is slightly greater than one due to a lower substitution of Al for Si in the tetrahadreal sites, to a smectites where the charge is low due to more silica in the tetrahedral site. The mineral formulae are something like the following:

It is clear that the Si/Al ratio will be quite different if one takes into account the interlayer ion population of Al in the hydroxyl interlayered minerals. In the case of accounting for these Al atoms one changes the Si/Al ratio from 1.45 to 0.8, below that of either kaolinite or muscovite, placing it chemically between kaolinite and gibbsite. This seems to hardly be the case in that hydroxyl vermiculites are not usually associated with gibbsite in soils. On the contrary they are found with kaolinite. Thus it appears that the essential chemistry of the clay minerals, comparing 1:1 to 2:1 structural types, should be based upon the covalently bonded cations in tetrahedral and octahedral sites and not the interlayer ion population. Interlayer ion occupancy will be determined by the general ambient chemical conditions of the soil pore solution while the same solutions will determine the stability of either silica-poor kaolinite or silica deficient gibbsite, compared to the silica – rich 2:1 minerals such as smectites, HI minerals or illite.

The chemistry of the soil profiles shown in Fig. 5.22 indicats that for the Red Bay series, Mississippi oxysoils developed on Mesozoic sedimentary rocks (Glenn and Nash, 1964) where one finds kaolinite – gibbsite in the lower horizons and vermiculite in the soil A horizon. The presence of more silica at the surface is reflected

| | *Interlayer* | *oct* | *tet* | *Si/Al in 2:1 unit* |
|---|---|---|---|---|
| Muscovite | K | $Al_2$ | $Si_3Al$ | 1 |
| Al hydroxyl vermiculite | $Al_{1.6}$ | $Al_2$ | $Si_{3.5}Al_{0.7}$ | 1.45 |
| Smectite | Ca, Mg | $Al_2$ | $Si_{3.7}Al_{0.3}$ | 1.6 |

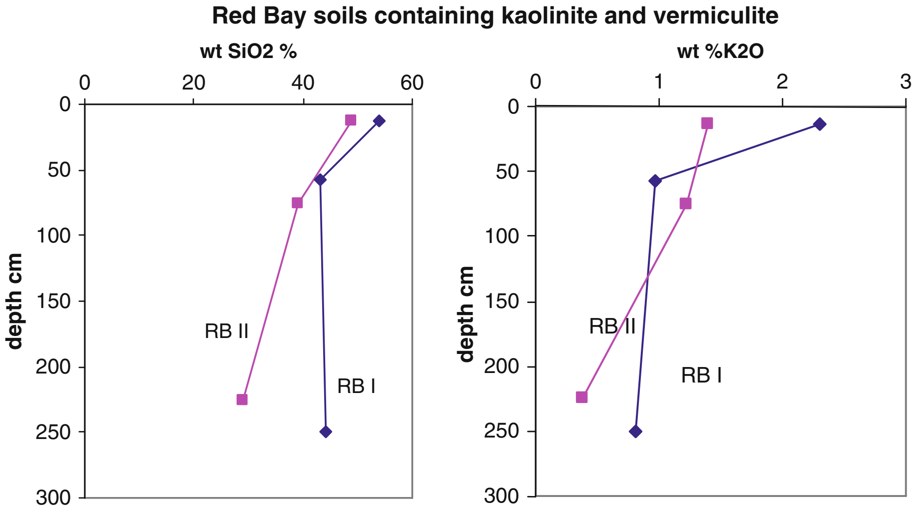


**Fig. 5.22** Red Bay series of soils from the Mississippi Bay region showing the increase in potassium and silica in soils where gibbsite and kaolinite are dominant in the C horizons and HI minerals and illite in the A horizon. (Glenn and Nash, 1964)

in the change in soil clay mineralogy from a silica – poor type at depth to a more silica – rich one at the surface where plants have a greater influence on the soil clay minerals.

An example of the influence on the filling of interlayer ion sites in soil clay minerals effected by plant enrichment of the surface horizons, can be seen in the chemistry of the clays present in the various horizon, as is shown in Fig. 5.23 (data from Glenn et al., 1960). Here the clays are essentially illite-smectite interlayered minerals with some illite and kaolinite present. For different size fractions of the clay sized particles there is a significant increase in potassium content in the A (plant) horizon. Here it is clear that the clays are affected by the presence of plants and that the interlayer ion sites are impacted by the availability of potassium in the soil zone.

The higher availability of potassium at the surface fills the interlayer ion sites of the clays, increasing it by about 1 wt% or around 25–30% of the clay $K_2O$ content. This clearly demonstrates the importance of plant uplift of potassium seen within the same family of clays, where the interlayer ion sites fix more $K_2O$. Ahmed et al. (1971) indicate that illite is favored and possibly formed at the surface in soils formed on terraces under conditions of strongly contrasted humid climate.

### 5.3.2.2 Fixation and Loss of Translocated Elements

If there is a strong tendency to increase potassium and silica in the surface A horizons of alteration profiles, one cannot assume that the potassium and silica transfered to the surface are permanently captured. Duvigneaud and DeSmet (1970) have

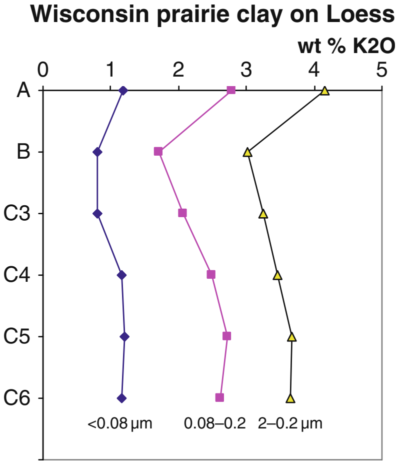


**Fig. 5.23** Plot of potassium content of various clay fractions in a Wisconsin loess soil (Glenn et al., 1960) as a function of depth. The higher potassium content in the more coarse fraction of the surface indicates the illite content, often found in the coarse clays of soils

studied the net change in these elements under forest growth in very old forest land (from 1,836 to the present day). Different elements are moved upward in different proportions for different tree species. However in this study on two oak forests in Belgium, the ratio of MgO:CaO:$K_2O$ is on the order of 1:5:4. In a larger geographic comparison, these authors find that the potassium transfered is retained in a ratio of 3:1 of uptake to retention in the Belgian forests, but 5:1 in German and Russian oak forests. Beech retains potassium in a 1:3 ratio of retention to loss, and pine in a 2:1 ratio. Depending upon the tree species more or less of the uplifted potassium is retained in the A soil horizon. But in any case more potassium is lost than retained.

Walker and del Moral (2003, p. 106) show how important vegetation is to the stabilization of alteration processes as seen in the composition of stream water. After landslide event, forest recovery significantly decreases the loss of potassium from the land area as seen in stream water compositions. Thus forest vegetation fixes potassium but there is still loss compared to the uplift or transfer of potassium from mineral to vegetal sources (Fig. 5.24).

The balance between translocation of mineral elements will depend upon the rainfall and vegetation type. Some plants bring up more of these elements than others, some have higher turn over than others and the different types of soils and water retention along with the overall rainfall will determine the amount of material fixed and re-cycled by plants at the surface.

### 5.3.2.3 Climate, Plants and A Horizon Clays

If we can identify a transfer effect where plants bring mineral elements to the surface and if we accept that this will affect the surface clay mineralogy, can we identify effects according to broad type of vegetation and climate? Our investigation to answer this question includes information for soils of different age and hence most likely different stages of evolution. The more humid the climate, the older the soils. This is a general rule due to happenstance to a certain extent. As it turns out,

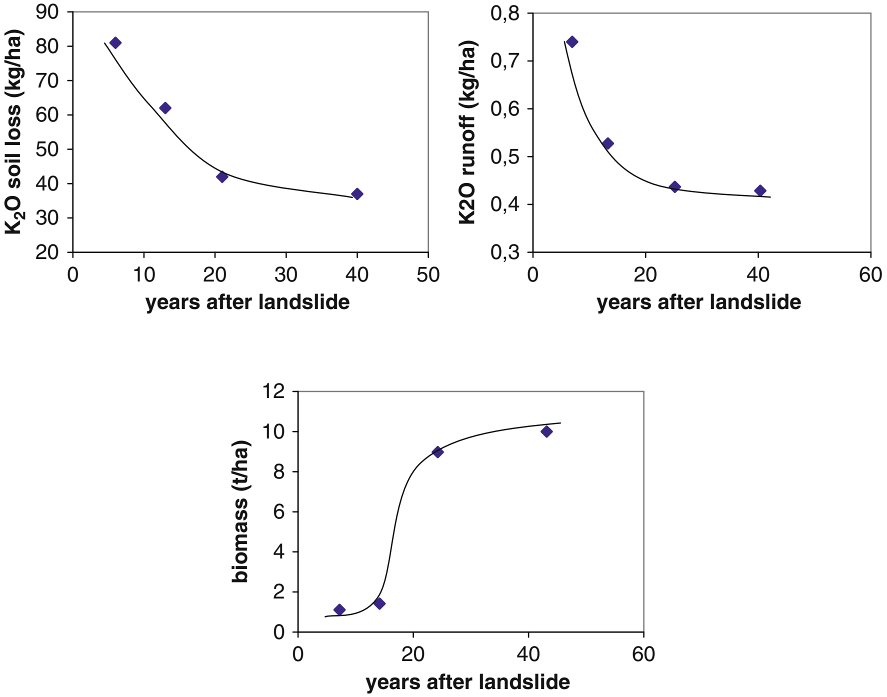


**Fig. 5.24** Relations of potassium loss form water – rock interactions after a landslide in a forest area. Potassium in stream water decreases with time as does the amount of potassium present in soils. The biomass increases in a reciprocal manner showing the stabilization of potassium in the surface portions of the alterites due to plant activity. Data from Walker and del Moral (2003, p. 160)

the tropical areas and areas of high rainfall are frequently based upon old cratons where tectonic renewal of surface material is small. However in some areas, the south Pacific for example, significant new deposits of volcanic material are present and thus one can find younger soils and older soils (see Mohr and Van Baren, 1959). These authors indicate the different stages of chemical alteration from juvenile to laterite stage induced by heavy rainfall. Chemical alteration is attested by the color of the earth, going from brown to red and also by the amount of organic matter in the surface layer of the alteration profile. This organic content is also a testimony of the fertility of the soils and the plant growth activity. There is then an evolution of plant action and capacity to modify the surface chemistry as a function of time. He et al. (2008) indicate this for clays formed on basalt substrates under sub tropical conditions. In the initial stages of alteration (60,000 years) the surface clays contain 2:1 minerals with the presence of illite, in small quantity. With time the2:1 clays change in character and diminish in relative quantity. The longer periods of alteration indicate that the translocation of certain elements is not sufficient to modify the clay mineralogy: illite is lost and replaced by and HI mineral.

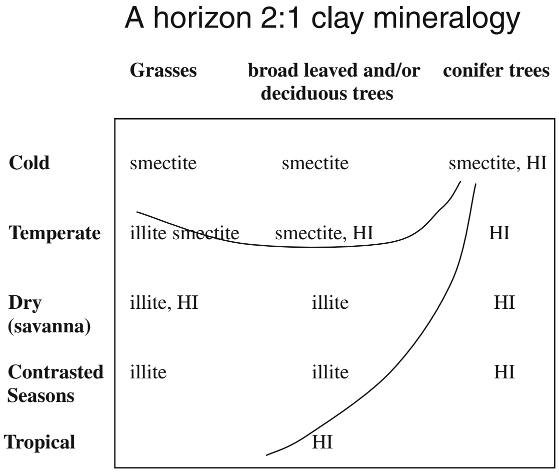
Huang and Uehara (1968) demonstrate thet climate (rainfall) can have a significant impact on the transfer of elements to the surface. This effect is of course indirect in that the agent of uplift is the vegetation present and with increased rainfall the intensity of plant activity increases. The study observes the change in clay mineralogy in A horizon soils on Hawaii where the rock substrate is similar, a basalt of rather low alkali content ($K_2O = 0.23$ wt%). The formation of illite in the plant – silicate interaction zone is a direct function of the rainfall parameter, increasing from near zero percent with 800 mm rainfall to being the dominant clay present at rainfall values of 6,000 mm per year. No information is given for the vegetation regime but one can consider that it changes from steppe – like prairie to heavy tropical forests in the range studied. The presence of illite, when no phyllosilicates are present in the basalt is striking. Here the uplift effect, transport of potassium necessary to form illite, creates a new mineral in the soil clay assemblage which co-exists with a diminishing amount of kaolinite. The change with depth is from illite – kaolinite in the A horizon to kaolinite – gibbsite in the deeper horizons.

Thus the plant – clay mineral alteration system is a function of time to a certain extent, possible governed by the relative biomass produced which reflects the total available resources. In the case of basalt, there is little potassium available in the rock and gradually some is lost to rain water percolation even though plants attempt to bring it to the surface.

In the brief review of surface 2:1 clay mineralogy given here, we attempt to give data for the younger soils in a given situation.

In Fig. 5.25 we indicate the topsoil (A horizon) mineralogy for the 2:1 minerals when present. Data are from Netttleton et al. (1973), Ruhe (1984), Barré et al. (2007), Graham and Southard (1983), Boettinger and Southard (1995), Righi et al. (1999), Mirabella and Egli (2003), April and Keller (1990), April et al. (2004), Gillot et al. (2001), Fichter et al. (1998), Pevear et al. (1984), Teveldal et al. (1990), Tice et al. (1996), Ahmed et al. (1971), Bryant and Dixon (1964) and Graham et al. (1990). Birkeland et al., (2003), Huang and Uehara (1968)

Some points should be reiterated: cold climates are associated with glacial events which are recent, on a continental scale or in mountain ranges. Hence soils associated with cold climates today are by nature young and may not represent a stable clay assemblage. Tropical climates are biased toward old, stable craton geological features and have been active for a long time, hundreds of thousands of years or more. This is the case for African craton soils or those in certain areas of the Amazon regions. Here the time factor would lead one to think that most of the material has come to an equilibrium with the climatic elements. However, if one allows a cold climate to come to ultimate equilibrium it might well converge in its mineralogy with that of a warm and humid climate. The overall trend in weathering is to lose alkalies and silica, no matter how much plants work to overcome this inevitable fact. The soils will become impoverished in the long run. The end assemblage of a very old soil would be iron oxide plus gibbsite and perhaps some kaolinite. This means that what we see in soils today is part of a dynamic system, one that will change with time. This is no surprise to a geologist but perhaps unsettling to a biologist or ecologist.



A horizon 2:1 clay mineralogy

| | Grasses | broad leaved and/or deciduous trees | conifer trees |
|---|---|---|---|
| Cold | smectite | smectite | smectite, HI |
| Temperate | illite smectite | smectite, HI | HI |
| Dry (savanna) | illite, HI | illite | HI |
| Contrasted Seasons | illite | illite | HI |
| Tropical | | HI | |

**Fig. 5.25** Relations between climate and vegetation as they determine the dominant 2:1 clay minerals types in the A horizons of the soils. Different vegetation types under similar climatic conditions affect the soil solutions differently producing different interlayer ion site occupations. Conifer trees tend to produce HI (Al hydroxyl complex) clays, while grasses and deciduous forests favour potassium as the interlayer ions. Under conditions of lower temperatures smectites are favored. Data are from Nettleton et al. (1973), Ruhe (1984), Barré et al. (2008), Graham and Southard (1983), Boettinger and Southard (1995), Righi et al. (1999), Mirabella and Egli (2003), April and Keller (1990), April et al. (2004), Gillot et al. (2001), Fichter et al. (1998), Pevear et al. (1984), Tedeval et al. (1990), Tice et al. (1996), Ahmed et al. (1971), Bryant and Dixon (1964), and Graham et al. (1990). Birkeland et al. (2003), Huang and Uehara (1968)

In looking at the assembled observations in Fig. 5.25 one sees a tendency to have HI minerals present as 2:1 minerals under conifer trees for various climates. The HI mineral listed under tropical climate is perhaps misleading in that most broad leaved trees in tropical forests are in fact evergreen and not true deciduous types. Smectites seem to be more or less restricted to cold climate regimes. Here one must be careful in that the young soils may evolve over slightly longer periods of time. Data from Mahaney and Halverson (1986) for soils of Holocene and Pleistocene soils in montane regions of the Rocky Mountains (USA) indicate that the older soils would tend to have HI minerals present after 8,000 years instead of smectites for shorter periods of 3–4,000 years, similar to those reported by Righi et al. (1999) and Mirabella and Egli (2003). It is not sure then whether or not smectites would be the stable 2:1 mineral phase in older A horizons of soils. These authors do describe the change in octahedral site occupancy. In the stage of smectites formation one finds a gradual change from trioctahedral occupancy to diocthahedral occupancy changing the clays from ferro – magnesian to aluminous in character. The aluminisation of the clays is a general characteristic, well documented by these authors.

The presence of illite in grass or prairie soils as well as deciduous forests under temperate to drier climates seems to be rather universal. Here the tendency to stock potassium in the clays is quite apparent.

Overall then one finds that the 2:1 clays in the A horizons of soils are largely of two types, both of high charge. HI and illite fix cations in the interlayer site which can most often be extracted by plants. Some illite is of a very high charge where it will be difficult to remove the potassium as is the case for the strongly polymerized Al-OH in HI minerals. In a general way, conifer forests produce the HI minerals while prairies and deciduous forest produce illites. Younger soils will show important amounts of smectites forming in the surface horizons especially in cold climates.

These are that clay minerals “useful” to plants in that they can store potassium and eventually ammonium in the interlayer site. There are however other clays present, such as kaolinite, which are less useful but with time become omni-present. In a number of cases of advanced weathering the 2:1 clays are present only in the A horizons.

Overall, the presence of kaolinite, and eventually gibbsite is a function of rainfall, age and to a certain extent temperature. The kaolinite is found in the initial stages of mineral weathering under water – rock interactions. It is more and more important as climate provides more rain and more dilute pore water solutions. With time the kaolinite content increases further. Old soils show high kaolinite and often gibbsite in the C horizons. In soils of the Coastal Southeastern United States one finds a loss of A horizon 2:1 minerals, essentially HI minerals, after 1 My, where the soils of older age show, rather abruptly, a loss of significant amounts of 2:1 minerals, a change which was accompanied by a change in bulk composition of the soils (Howard et al., 1993). The 2:1 minerals are replaced by kaolinite and gibbsite. In soils of semi tropical Hainan Island (China) clays formed from basalts have a very low, but persistent 2:1 mineral content which is reduced with time changing from an initial illite facies, to a smectites – illite and eventually HI mineral facies (He et al., 2008). The ratio of kaolinite to gibbsite changes in favor of gibbsite (aluminium hydroxide) with time affecting the interlayer ion of the 2:1 minerals changing from a potassic form to an Al-OH form. In these cases the plant regime cannot maintain the necessary elements in the A horizon for stabilization of potassic minerals due to the gradual loss of this element in the total alteration profile.

## 5.4 Impact of Plants on Clay Minerals and Soil Formation According to Biome Type

Numerous studies have given results showing the specific change in clay mineralogy from the source rock to the surface (A) horizons (Drever, 1994 for example). If one correlates these different results with the type of plant regime, and hence climate, a general pattern can be initially observed. There are many questions to be asked and specific situations not yet studied, but nevertheless a certain pattern emerges. In Fig. 5.26 we represent the general characteristics usually attributed to prairie and forest soils in manuals of pedology. It is important to note tht the point of view of most pedologists is of their local surroundings, and hence the inhabited Northern

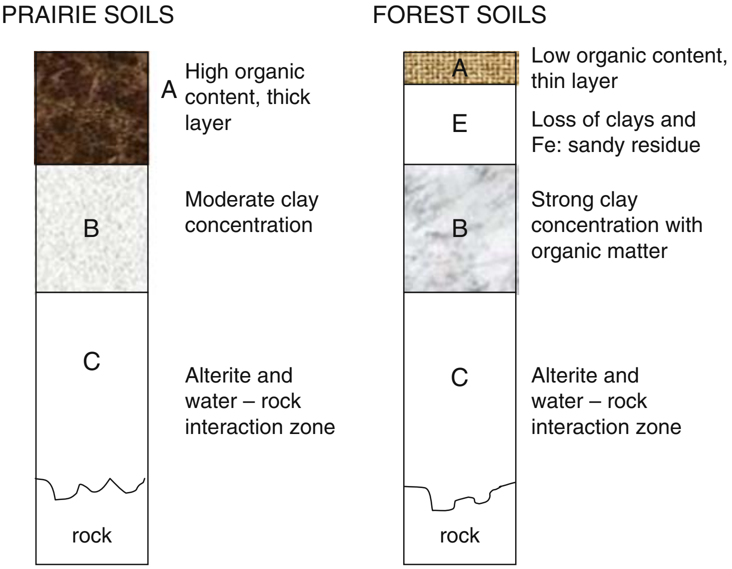


**Fig. 5.26** Comparison of some of the major characteristics of forest (especially conifer) and prairie alteration profiles. Notable are the differences in the thickness of the layer of organic matter and the presence of the low clay E horizon of the forest soils

Hemisphere in middle latitudes. These generalisations are valid for temperate climate biomes to a large extent (see Duchaufour, 1977). In fact one can find certain characteristics of these two type profiles in other biomes and climate alteration situations. Further, the rock substrate can alter the profile characteristics by influencing the pH and clay – organic matter stabilities.

## *5.4.1 Prairie and Forest Type Profiles*

We will use the temperate climate vegetation as a model or starting point for the description of the two major and often competing types of plant regimes. Much work has been done on these types of plant – soil interaction regimes because they concern a large part of the environments in which human activity has evolved and manipulated the two plant regimes.

### 5.4.1.1 Prairie

In prairie soil profiles one finds the epitome of a rather continuous change from a highly transformed mineral matrix, rich in clays and organic matter with a gradual decrease in clay content, to an increase in mineral debris and rock fragments until one finds the bedrock. Usually, as in most more mature profiles, one finds clay accumulation below the organic horizon (see Sect. 2.4.2). There is transport of clays and organic matter in a humic state well below the dense root mat characteristic of grasses. Normally prairie soils are of neutral to basic pH characteristics. However, in mountain or tundra prairies the pH is most often acidic. The difference is due to the relative activity of bacteria. In colder climates there is a stronger accumulation of organic matter in a less evolved state which leads to acidic conditions. This is true for swamps or lowland situations also where anoxic conditions lead to incomplete bacterial action. The organic mater in most prairie soils lends a black color to the soil and alterite. (Fig. 5.26).

Jenny (1994) has assembled much data concerning soil properties across the United States. If one considers the data correlated to rainfall, one of his major variables, values up to about 35 in. of rain (about 85 cm) per year on average covers the dry land and prairie range where grass dominates or dominated before agricultural practices became universal in prairie lands, between 180 and 100 years ago in the region of study. Clay content, organic carbon content, nitrogen content and the depth of concentration of these components in the A horizon, presence of large soil aggregates found in the alteration profile are all correlated with rainfall. There is a strong correlation of pH and rainfall, changing two units from 5.5 under conditions of more abundant rainfall to 7.5 under conditions of arid conditions. In general, the more rain the greater the biological activity in the A horizon. Thus under the same general biome conditions there can be strong changes in the physical and chemical characteristics of prairie soils.

Ruhe (1984) demonstrates the importance of time as a factor in controlling the different effects of plant – soil interaction. In looking at soils based on the same starting material, loessic depositions, as a function of age, <9,000 and 14,000 years. In particular the clay content of the B horizons of the prairie soils in a transect from western Iowa to eastern Nebraska, shows that the B horizon, clay accumulation zone is on the order of 80 cm in older soils, whereas in the younger soils the thickness of the B horizon varies from 80 cm to less than 50 cm. Jenny (1994, p. 138) shows in data from soil profiles from different points in these sequences that in all cases the Si/Al ratio increases in the A horizon, indicating the influence of grasses in extracting silica from depth and depositing it on the surface.

Prairie soils in temperate climates then are rich in organic matter and clays in the surface horizons. Soil color changes from grey in more arid soils to very dark grey or black in full prairie regimes bordering on forest biome areas. Acidity in soil A horizons tends to be slightly acid to basic in well to moderately drained situations of prairie growth.

#### 5.4.1.2 Forest

In forest soils the organic layer is less developed, brown in color and it often has a low amount of clay material present. The layer just below the organic zone is typically sandy, i.e. where few clays are present, and devoid of organic matter. Below this zone (called the E horizon) the accumulation of clays and some organic matter is apparent. The stark contrast between the surface A horizon and the sandy E hori-

| | mmole/litre Al |
|---|---|
| Pine, oak, birch | 0.8 |
| Spruce, fir | 0.3 |
| Poplar | 0.1 |

| | |
|---|---|
| Wheat | 0.02 |
| Barley | 0.015 |
| Cotton | 0.0015 |
| Graminae | <0.0009 |

zon is the characteristic which is used to describe these soils as Podzols. These soils are typically acid, with pH in the 5–4 range or less.

Miles (1985) gives a detailed review of the effects of various types of tree regimes on soil properties. He indicates that confiers are the most acidifying and deciduous trees less so and further these trees have different effects depending upon the soil substrate. Acidity is identified with the formation of a clay – poor E horizon just below the humic zone of organic activity. The intensity of this effect (podsolization) is variable depending upon the climate, nature of the substrate and type of tree present. Overall, deciduous trees have a less strong podzolization effect, with higher pH values than those of confier forests. Some shrubs, such as heather, show even stronger effects of acidification and podzolization. Quideau et al. (1996) conclude that depending upon the vegetation type, deciduous or conifer trees, the weathering reactions are different in that they produce different concentrations of and relations between elements in pore solutions associated with the two types of plants. Thus not all forests are the same.

Low pH (acidity) is assumed to be the cause of the loss of clays in the E horizon by dissolution of silicates due to organic acids. This description best fits the forest soils developed under coniferous forests but can be seen under other types of plant regimes. Alumina in soil solutions is relatively high in acidic soils. This is reflected in the aluminium toxicity threshold levels for several types of trees (Wolt, 1994, p. 235).

One can compare this to graminae and similar food crops where the toxicity tolerance is much lower:

There is an obvious antagonism between the chemistry of forest species and prairie species tolerance. The soil solutions typical of forests, are of course tolerated by trees but not by prairie plants. Robert (1996, p. 85) indicates that the alumina content of soil solutions is related to acidity and that the pH or alumina content of soil solutions affects crop plant growth such that of corn (*zea mais*) and soybean plants.

It is obvious that a forest tree, especially conifer, is subject to destruction by fire and relatively slow re-growth. Prairies burn but are green again in the following spring. The time lag in re-establishing vegetation is greater for forests than prairies.

If there is no retarding mechanism, the forests will be covered in prairie after a fire. However this does not happen. Taking the example of Yellowstone National park where forests were allowed to burn in the 1980s, the re-growth of the pine forests fifteen years later can be traced to within several meters of the old stumps without invasion by the adjacent prairies in the high country meadows inter fingering the forests (personal observation of BV). The adjacent grass biome could not invade the old conifer forest soils. The answer can lie in the inherent pH and more importantly free alumina content of the soils which impedes the installation of grasses and non-woody plants. A deficit in clays in the E horizon will also hamper the installation of the dense grass root system usually found at these depths in grass soils. Thus the structure of a forest soil (often classified as a Podsol) is such that it is antagonistic to the installation of grasses.

## *5.4.2 Comparing Forest and Prairie Soils*

### 5.4.2.1 Temperate and Semi Arid Climates

Comparisons of different properties in forest and prairie soils in proximity to one another indicate consistent differences. Jenny (1994, p. 223) compares acidity in forest soil profiles and prairie profiles showing a strong difference in the E horizon (Fig. 5.27) for soils in the temperate climate area of Illinois. This data can be compared for prairie and forest (oak) soil in semi-arid Utah (Graham and Southard, 1983). The differences in pH are found in the E horizon, below the A organic-rich horizon in both examples. The A horizon pH is similar in the two sets of soils. However the pH values in the semi-arid soils is higher than those of the temperate, more organic – rich soils of Illinois. In general one can correlate the pH of the soil A horizon with the amount of organic matter present which is a function of climate, in these cases in biomass production, greater under conditions of higher rainfall.

Jenny (p. 148) also shows systematic differences in nitrogen content, a measure of humic content in A horizons as a function of climate. In general the prairie soils have two to three times the nitrogen content and hence humic matter. Both diminish as a function of latitude from Wisconsin to Mississippi (USA) showing the influence of humification and lower bacterial activity in colder climates.

The organic – rich layer in forest soils is less thick than that in prairies, the color is not grey to black but different colors of brown. Brown acid soil is a typical description of forest soils. However, it is necessary to distinguish between the two major types of trees present, confier and deciduous, in forests under conditions of temperate climate growth. Confiers develop more acid soils while deciduous forests are closer in their soil development characteristics to prairies. Both forest plant regimes do however develop the E horizon structure where clays are absent and sand (chemically resistant quartz) predominates. Acidity is usually greater than in prairie soils, especially below the humic A horizon. The difference in soil chemistry and the resulting stability of silicate minerals is due to the difference in the organic mater and the mummification of this material in the soil horizon by bacterial

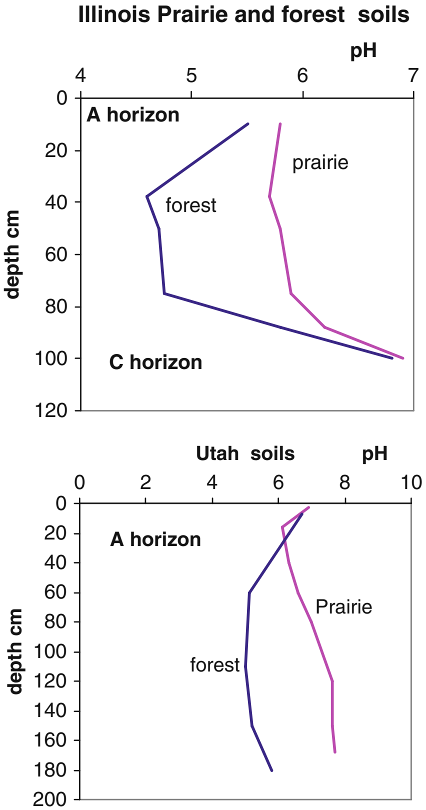


**Fig. 5.27** Comparison of forest and prairie soil pH values in two different climate areas, one in the Midwest prairies of Illinois (USA) and the other in the semi arid climate of Utah (USA)

action. The fixation of alumina by organic matter is known, but poorly understood in a specific manner. However the free alumina is lower in prairie soils than in forest soils, especially confier soils. This difference allows the change in clay interlayer ion occupation where fixed alumina allows potassium to be fixed by 2:1 clays whereas free alumina produces HI minerals typical of forest (conifer) soils.

### Cold Climate Prairie and Forest Soils

Cold climates usually lead to the accumulation of organic matter in the A horizon. Biologic activity is reduced and the humification process is slower as well as the mineralization of the organic litter. This effect is important for the pH of the soils. In general, cold climate soils have a lower pH. The relationship between pH and organic content of cold climate soils is indicated in Fig. 5.28.

In general the forests have a lower soil pH as in other climates. Cold climate soils are usually poorly developed because of recent glaciation and hence their young age and the slower chemical activity due to temperature when water is ice, little chemical activity can occur. Biological activity is equally slowed by lower temperatures. Conifer forest soils are more acidic, and have more organic matter present. In

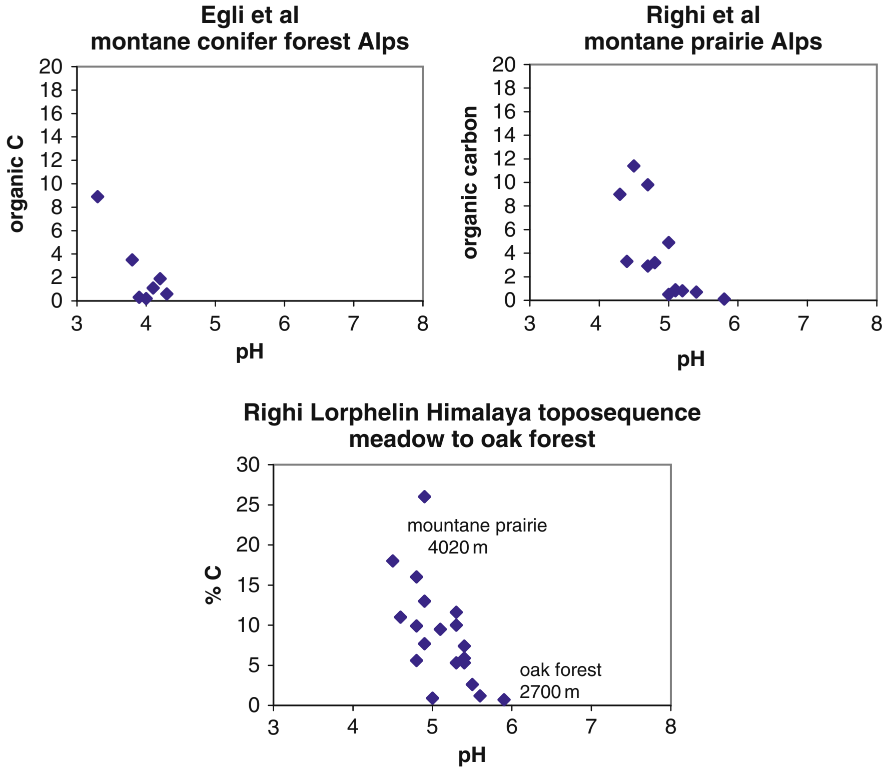


**Fig. 5.28** Relations between organic carbon content % of soils and pH in forest – prairie situations in colder climates. Righi et al. (1999), Egli et al. (2002), Righi and Lorphelin (1986). Notice the tendency to higher pH values corresponding to the type of vegetation and altitude

Fig. 5.28 one also sees data for a toposequence in the Himalayas from an oak forest soils at lower altitudes to high altitude a prairie soil. Here the prairie is more acidic and the carbon content is higher than that in the oak forest.

The major difference in properties of the humic zone, organic content and resulting pH are then controlled by the type of vegetation and the climate, the colder and wetter the more the organic matter tends to be retained in the soil giving it specific chemical characteristics. In these regimes the soil is not well developed, usually less than a meter deep due to the relatively short periods of time that have elapsed since the rock substrate was colonized by plants.

### 5.4.2.2 *Hot Wet Climates:* Laterites and Plant Regimes

These climates are conducive to laterite formation, i.e. strong oxidation of the iron in soil materials. The term oxidation intimates a change of state of the iron from incorporation silicate minerals to free oxide phases and hence a dismantling of silicates either the initial rock minerals or at times clay minerals formed deeper in the alteration profile by water rock interaction processes. There is often a strong association with plant regime. Laterites are not restricted to hot wet climate areas today because former climates changed during the glacial periods of the recent past, have left traces of former climatic and plant regimes in areas today less humid. The expression of iron oxides as a reddish color is not restricted to the tropics of today but covers a rather larger band extending from the equator (See p. 26, Segalen, 1971). Govinda Rajan and Murthy (1971) demonstrate the relationship between intensity of laterite formation and vegetation, of course guided by climate, in southern India. The strong laterite soils are found under broad leaved evergreen forests.

The problem of iron accumulation and the formation of laterite crusts in alteration profiles is very important in areas of the world where the tropical rain forests border savanna climates. Due to recent climatic fluctuations, the stronger accumulations of iron observed today are frequently not active but relict. (Bardossy and Aleva, 1990, p. 81; Temgoua, 2002, p. 5; Mohr and Van Baren, 1959, Chap. 13). However, in many regions laterite accumulation is still active. The movement of laterite iron oxide crusts towards the surface is of great importance in many areas. The formation of a hard pan of oxide renders the soils very difficult to work. Laterite formation indicates the last stages of chemical alteration (water – rock interaction) where silica content is very low and there is a strong accumulation of iron and aluminium hydroxy – oxides.

Numerous authors have indicated a relation between present day plant regime (biome) and the accumulation of iron oxide in particular. Essentially authors coming to these conclusions have looked at forest and savanna situations under conditions of warm and humid climates. The importance of such biomes in many regions of lateritic accumulation is that the relations of forest to grasslands are constantly perturbed by the action of agricultural or pastoral man. This changes the equilibrium which affects the accumulation and dispersion of iron oxides. This is a problem concerning natural equilibrium and those attained by perturbation due to human action.

Forests are considered to be conducive to the formation of lateritic soils (iron – rich) and the accumulation of a lateritic crust (duricrust) at depth, below most of the tree root masses (Maignien,1958, p. 65). The soils are friable near the surface with an increase in iron oxide nodules at depth in many cases. The entire alteration zone is of course oxidized to a large extent but the accumulation of iron is found at depth relative to the active soil zone. By contrast grass biomes (tropical savannas) near the forest areas are known to have iron crusts closer to the surface than those found in forests. This can be illustrated by a toposequence (Maignien, 1968; Bowden, 1987) where forests on slopes or hill tops have an iron accumulation at depth and prairies landscapes down slope show iron accumulations nearer the surface (Fig. 5.29). Under forests the deeper crusts have both Fe and Al accumulations whereas the prairie accumulations are richer in iron. Bardossy and Aleva (1990) have observed that iron is more likely to migrate, down slope or down an alteration profile, than alumina.

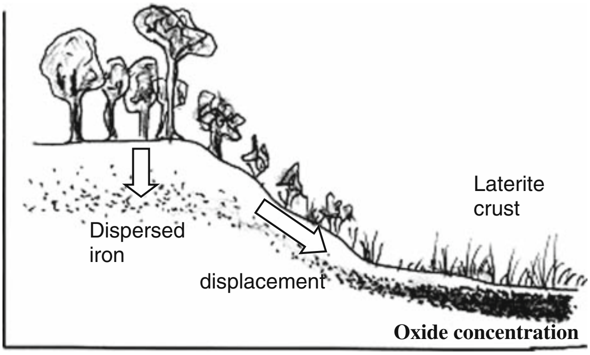


**Fig. 5.29** Illustration of the movement of iron oxide in soils with a tendency to produce laterite crusts. The oxidation is greatest on the uplands under forests where the iron oxide accumulation is below the A horizon. Lateral movement down slope moves iron oxides to accumulate in thicker crusts nearer the surface in grassland soils

Figure 5.29 indicates the extent of development of the different soil horizons of temperate to tropical soils and the dominant clay minerals present over the depth of the profile. In general, the clays in the A horizon are more silica – rich than those in the C horizons.

These observations have led authors to imagine a migration of iron down slope to form the duricrusts under prairie biomes. The formation of iron duricrusts is then often considered to be a function of topography. However, along with the topography factor one finds a change in plant occupation where forests are on hill tops and the upper slopes whereas grasses are found along the slope base and flat down slope bottoms, nearer rivers and other water resources.

McFarlane (1978, p. 50) has made further observations on the relations between vetegal cover and duricrust (laterite) formation. He has observed the relations of forest to duricrust under forests formed on old laterite surfaces or stable biome situations. Here the iron is concentrated well below the tree root zone. It has been observed that in many instances the inrtroduction of trees on duricrust (laterite crust) has softened them and contributed to a downward movement fo the iron oxides. Trees break up duricrusts. However when trees are replaced by grasses with change in landscape hydrodynamics, the iron oxides have been observed to "move" upward or at least be more present towards the surface. Temgoua (2002, p. 101) proposes that the initial formation of laterites in Cameroon was due to a general savanna biome during the Cretaceous which was gradually replaced by trees. The iron oxide masses were broken up under the forest regime and moved down slope to be found frequently under prairie.

It seems that in the case of iron accumulation trees are more efficient in moving iron oxide downward from the root zone whereas grasses do not do this to such an extent. McFarlane (1978) suggests that forest organic litter and root exudates are more efficient at moving the iron to lower levels where it accumulates, one imagines due to the loss of biotic activity and stability of iron complexing agents associated with the litter of the trees. The difference in depth in accumulation of iron oxides associated with the toposequences or catena of hill and valleys show the strong inter-relations between plant and mineral regimes which are often controlled by local climatic or microclimatic variations such as water availability and depth of the water table (Fig. 5.29). The needs of one plant regime are not those of another and the manipulation of the local chemistry by plant litter and root exudation change according to the local circumstances.

### *5.4.3 Successions and Soil Properties Influenced by Change in Plant Regime*

The action of change in plant regimes has been observed in several cases. For the most part the observations have concentrated upon the chemistry and soil properties such as the formation of aggregates and presence of organic matter. An initial consideration is to follow the changes in soil chemistry when plants invade clay rich substrate of water – rock alterite. These conditions occur after landslides. Zarin and Johnson (1995) give data concerning the chemistry of the soils re-colonized by plants over a 60 year period in a region of Puerto Rico normally covered by a montane tropical forest. Potassium is particularly interesting in that it follows a rather regular sequence of change in above ground biomass, roots and soil. Figure 5.30 indicates the changes in concentration of this element in biomass and surface soil (upper 60 cm). The accumulation of potassium in the biomass follows the classical S shaped curve, with a possible decrease after an optimum is reached. The loss of potassium from the soil appears to decrease gradually and becomes, probably more or less stabilized to a lower steady state after 100 years or so. Potassium uptake in plants is of the same order of magnitude as the exchangeable K in the soil and follows the same dynamics. There is an obvious inter-relation between K in the solutions that is fixed on the clays and the change in biomass and hence activity of the plants which bring potassium to the surface and re-cycle it into the upper part of the alteration zone.

From these data it is clear that the plant regime in the montane forests not only stabilizes potassium loss but brings it to the surface from depth below the plant – soil interaction zone.

Bormann and Likens (1994) give information concerning a de-forestation experiment in northern New Hampshire. Loss of mineral elements from the soil was measured as concentration of elements in stream water. The initial stages of forest recovery over 4 years showed a strong increase in potassium and calcium concentrations from 10 to 85 kg/ha equivalent which decreased to a near initial value 6 years after the de-forestation event. This indicates that the tree cutting event is much less dramatic to chemical balances in that roots are still present and most likely plant re-growth much more rapid than in the case of a landslide event where the soil cover and chemical structure is totally taken away. Nevertheless the loss of tree cover and growth leads to significant leaching of mineral elements for a period of time. The comparison of the two data sets indicates that the loss of vegetation and re-growth

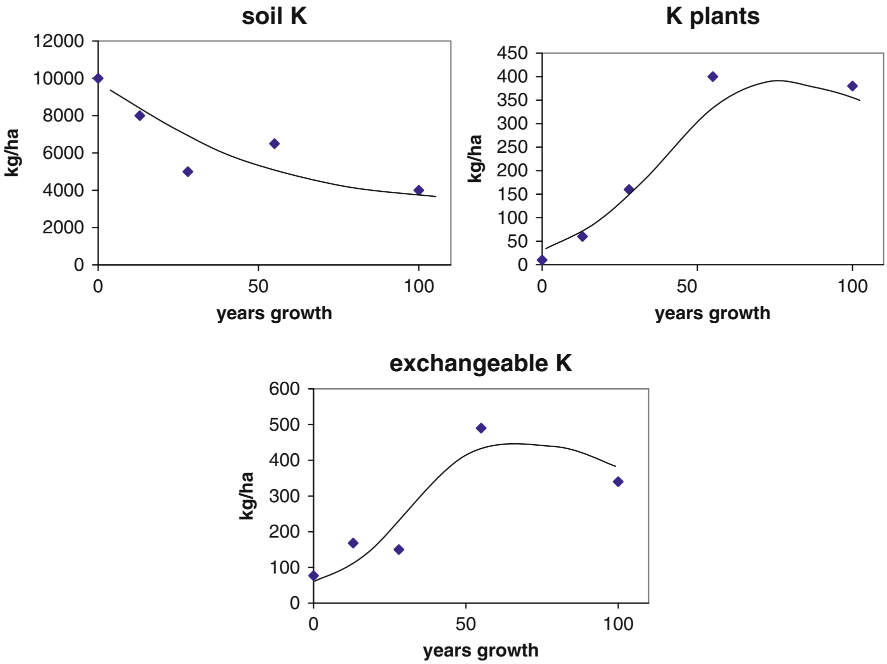


**Fig. 5.30** Effects of the re-establishment of forest vegetation on soil potassium balances after 100 years in Puerto Rico (Zarin and Johnson, 1995). Loss of potassium from soil is found to be resident in the plants as growth proceeds. The result of plant litter fall can be seen in the amount of exchangeable potassium in the soils (CEC exchangeable) which can be re-used by the plants

is less important for mineral element transport than the loss of topsoil and alterite and subsequent slower re-establishment of a vegetal cover. The root structures and soils structure play a role of absorbing the shock of plant loss.

#### 5.4.3.1 Effect on Soils of Changing Vegetal Cover

The change in vegetal cover can be of importance to the chemical and physical characteristics of a soil. Such effects are important when considering human intervention is land use. Miles (1985) discusses the changes effected by major change in plant species under conditions of a temperate climate. The examples given by this author concern the change in podzolic soils, developed under confier, heather and juniper stands which are acid, have low clay content below the top organic – rich A horizon and are generally of poor agricultural quality. One step to change is accomplished by deciduous trees which change pH by a unit or so and favor the decomposition of organic litter on the surface, which is at the origin of the low pH values of coniferous tree soils. Of course the reverse is true. When heather is introduced it will decrease pH by several units over periods as short as 10 years. Nielsen et al. (1987) show the effects of an oak invasion of a previous heather soil. The oak invasion of the over story cover is accompanied by a cover of grass in the understory. The type of organic matter changes from black to brown, indicating more transformation by bacteria, and pH increases.

Herbaceous species (grass and prairie vegetation) raise the pH by a unit over several decades of influence. The studies cited are instances of the introduction of grazing animals which destroy shrubs (heather) and favour grasses. This is an important concept which will be discussed in some more detail in Chap. 6. The higher the pH the easier it is for other graminae species to prosper such as grain crops.

It is evident that the change in plants affects the humic layer first and this determines the pH of the soil. This in turn influences the types of clays present, especially

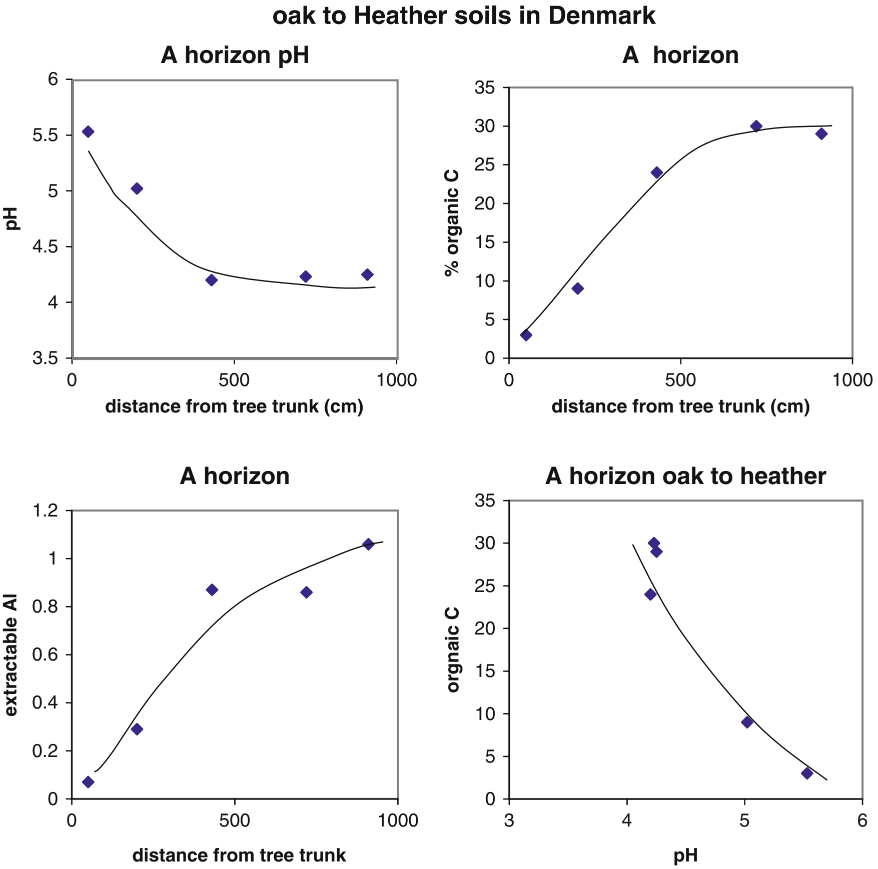


**Fig. 5.31** Effect of plant types on soils. An example used here is of soil characteristics under a large oak and moving to the surrounding heather growth seen in Denmark. Changes in pH, organic carbon % and Al content % of soil solutions are compared showing the effect of vegetation on the same soil substrate (data from Nielsen et al., 1987). The oak tree promotes higher pH in the soil, lower extractable Al in the soil solutions but a lower organic content of the soils. Heather is an acidifier, resulting in increased available aluminium, often a limiting factor for plant survival

the occupation of the interlayer ion sites. Such changes can occur in relatively short periods and are thus susceptible to manipulation by human activity.

Graham and Wood (1991) suggest that the effect of the introduction of oak on a chaparral and pine developed soil is to increase the clay content at the surface. The mechanism of this change, visible over 41 year period, is attributed to earth work activity. The increase in faunal activity is due to the change in leaf litter, and subsequent pH change. Organic matter is lighter and more brown indicating a higher bacterial activity and with a change in these parameters it is assumed that earth worms move upward and with them clay particles in their soil bio-perturbation activities.

The increase in faunal activity is due to the change in leaf litter, and subsequent pH change. Nielsen et al. (1987) present data to document such a change where samples were taken under a large oak tree and at distances from the tree trunk into a heath cover in Denmark. Figure 5.31 shows the changes in organic content, pH and extractable aluminium from the A horizons. As one might expect organic matter decreases under the oak due to better microbial action, and thus pH increases. The change in extractable alumina is very interesting in that it shows the inter-relations between organic matter and pH as they affect the critical content of alumina which determines the limits of chemical tolerance for many plants. Also the availability of alumina will determine the interlayer ion occupation in many cases for charged 2:1 layer minerals. Under conditions of heather one would expect to find HI (soil vermiculite) minerals while under oak, illite or smectite as demonstrated by the mineralogy of an oak on pine soil experiment by Tice et al. (1996).

## 5.5 Mineral Element Transfer in Soils: The Translocation Effect

### *5.5.1 Chemical Variability as a Function of Alteration Profiles*

The transfer of mineral elements from depth to the surface was understood long ago, and considered as a fundamental part of plant growth and soil fertility (see for example Larbaletrier, 1891, p. 104). However the overall effects and importance in a general sense have been ignored for much of the recent past in soil science circles. For some time the observation has been made that the chemical composition of the upper parts of soil profiles does not follow the accepted alteration scheme which would be produced by simple water – rock alteration. The interaction of silicates and dilute water (rain) will initially hydrate the minerals present, exchanging hydrogen cations for alkali and alkaline earth cations:

$$\mathrm{nH^+ = Ca^{2+},\ K^+, etc.}$$

The second step or stage of alteration is the systematic loss of silica. Most clay minerals are less silica – rich than their precursor tectosilicates (feldspars) and hence the formation of clays such as illite, smectite or kaolinite from these minerals releases silica into solution. Micas of course are near the clay compositions in terms of silica balance, to those of clays. Other silicate minerals in rocks tend to be as siliceous as clays that form from them. However, the most common clays are dioctahedral, and hence aluminous. Thus the silicate minerals with low alumina content, such as olivine, tend to form non-clay minerals, or tend to combine dissolved elements in solution with released alumina from other altering minerals (see Velde and Meunier, 2008, Chap. 5).

Continued alteration favors the low silica clay kaolinite. Eventually this mineral loses its silica content to be transformed into the aluminous hydroxide gibbsite.

1. $\underset{\text{Illite}}{K_{0.8}(Al_2)(Si_{3.2}Al_{0.8})O_{10}(OH)_2} \Rightarrow \underset{\text{kaolinite}}{1.4Al_2Si_2O_5(OH)_4} + 0.4SiO_{2(aq)}$
2. $\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \Rightarrow \underset{\text{gibbsite}}{2Al(OH)_3} + 2SiO_{2(aq)}$

These are the classical steps of de – silicification. The clay assemblage of kaolinite and gibbsite is typical of soils in regions of very high rainfall (Keller, 1967 for example). The normal trends of chemical alteration in surface environments would affect clay minerals as shown diagrammatically in Fig. 5.32 where aluminium content is constant.

In principle the part of the alteration profile which has been subjected to the most water – rock interaction, the A horizon (surface) one should find the most altered and hence the most potassium poor materials.

Some examples of chemical data reported in the literature are quite persuasive in indicating that the strict chemical alteration of soils is not always obeyed. Several cases are given in Fig. 5.33 for soils developed on rocks containing little potassium and being low in silica content. In these examples one sees a decided increase in potassium content in the A horizons of the profiles. In the example based upon andesitic volcanic rock where the profiles were observed at different altitudes, the

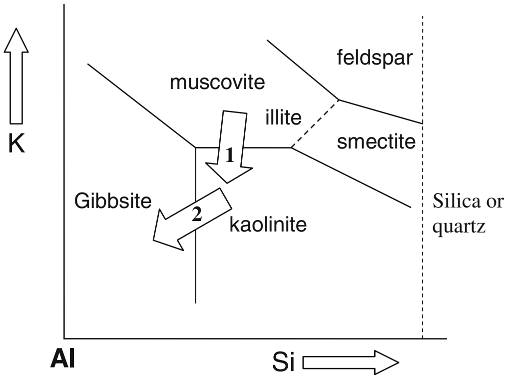


**Fig. 5.32** Diagram indicating the chemical relations of clays and magmatic minerals (muscovite and feldspar) as a function of the activity of Si and K in a soil or alteration zone. Alumina is considered to be of constant content in the system. *Arrows* indicate the path taken by the chemical system in a soil under normal conditions of water – rock interaction. The first step is loss of potassium and the second is loss of silica

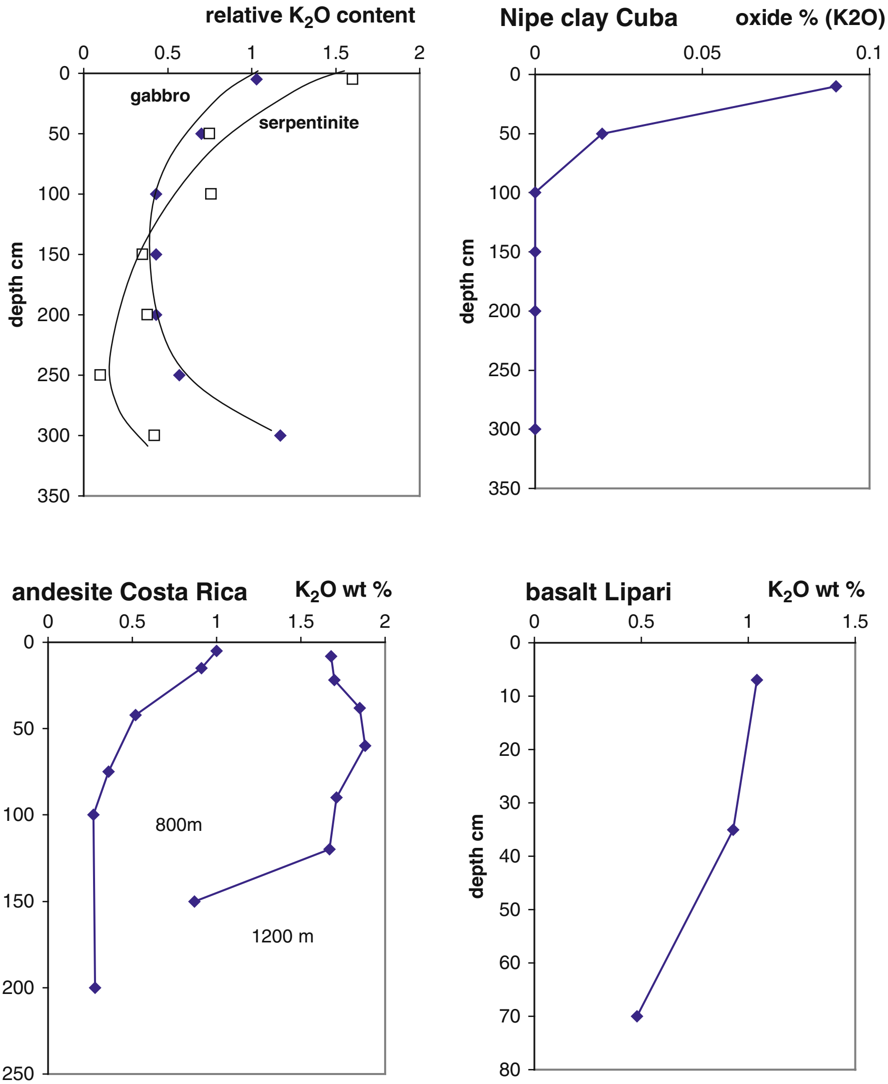


**Fig. 5.33** Illustration of concentrations of potassium in various profiles based upon parent material of low potassium content; gabbro and serpentinite (Pion, 1979), Nipe clay from Cuba (Mohr and Van Baren, 1959) volcanic andesite deposit forming a mountain in Costa Rica (Meijer and Buurmann, 2003) and basic volcanic rocks on the island of Lipari Italy (Mirabella et al., 2005). The andesite example shows soil compositions under forest at two altitudes, the 800 m soil shows a greater effect of potassium loss and relative gain at the surface

effect is accentuated at lower altitudes where plants are more abundant and alteration profiles are deeper and chemical weathering more advanced. The same observations can be made concerning silica content (Fig. 5.34).

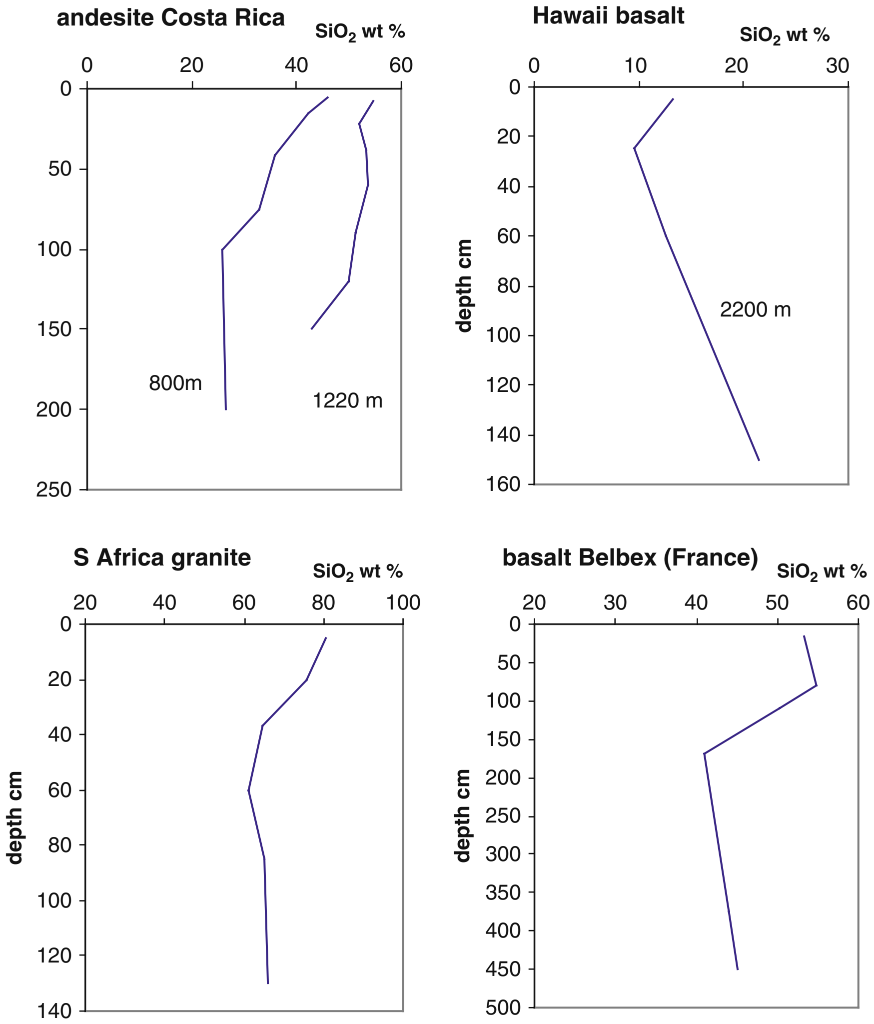


**Fig. 5.34** Changes in silica content of profiles on low silica rocks, most without initial quartz mineralogy. Andesite in Costa Rica shows values for two altitudes of forest growth where the lower altitude has a stronger effect of silica loss and gain at the surface due othogher rainfall and greater biomass production. Data from Meijer and Burmann (2003), Mohr and Van Baren (1959). This indicates that under various conditions of climate and plant growth, it is clear that the transfer of silica to the surface is an important factor in the overall chemistry of alteration profiles

These chemical surface anomalies can be attributed to the effects of plants which transport potassium and silica to their living parts, especially the aerial parts. Leaves, stems and woody parts of plants contain potassium and silica. Schactmann and Schroeder (1994), Zairn and Johnson (1995), Nettleton et al. (1973), Juang and

Uehara (1968), Ahmed et al. (1971) among others observed the formation of potassium – bearing minerals in the surface horizons (A) of soils under different climatic conditions, ranging from dryland to semi tropical. These authors attributed the presence of this potassic mineral to plant action where the concentration of this element occurs at the surface. However, these authors did not find a general audience for their conclusions, and most clay mineralogists and soil chemists ignore in fact that the minerals found in the soil in the A horizon can be influenced by plant action. Most authors and generalizations presented in text books indicate or state that plants tend to destroy clay minerals by interaction with organic acids especially when the presence of potassium minerals is concerned.

As mentioned before, it has been recognized for some time that there can be a translocation of elements from depth to the surface, alkalis and other cations (Larbaletrier, 1891 to Jobaggy and Jackson, 2004). The translocation of silica has also been recognized and considered to be a fundamental factor in forming or stabilizing more silica – rich minerals (Lucas et al., 1993; Lucas, 2001; Kleber et al., 2007 for example). The cycle of silica in soils has been considered from the standpoint of a geochemical model based upon the deposition of this element in the form of amorphous phase, the phytolith (Derry et al., 2005; Farmer et al., 2005; Gerard et al., 2008).

Interestingly, the silica content (phytolith) in plants can reflect the silica availability in the soil in which the plant grows (Henriet et al., 2008).

Plant action then affects the A horizon by a translocation of key elements which are fundamental for the stability and perhaps formation of certain clay minerals. The most important element is silica, which determines the present of the type of clay mineral in the soil: either the silica – rich 2:1 minerals (illite, smectite, HI) 1:1 minerals (kaolinite, halloysite) and eventually the silica – free gibbsite. One can consider this situation as a function of the presence of either K or Si which is the reverse of the water – rock weathering sequence of Fig. 5.32. This transfer or translocation effect is shown in Fig. 5.35 where again Al content is considered to be constant.

In this representation of the impact of chemical variables, engendered by plant activity, the final clay mineral can be smectite or illite, depending upon the potassium content of the solutions. However, in reality, the representation does not take into account fully the variability of the 2:1 soil clay mineral. We do not know what the chemical parameters are that determine the charge on the 2:1 mineral, smectite (low charge) or illite – HI mineral (high charge). It could very well be the amount of available silica in solution which would form the more silica – rich and low charge smectite mineral. Perhaps the presence of smectite and 2:1 minerals is initially determined by the silica activity in the soil solution and then the interlayer ion occupancy is determined by potassium availability and alumina availability. In any event, there must be a certain amount of potassium present in soil solutions to saturate the interlayer sites with the anhydrous potassium layer characteristic of illite. Further it seems that he presence of HI minerals depends upon a relatively high charge on the 2:1 mineral. This is normally due to a higher alumina content compared to silica for the dioctahedral, aluminous minerals.

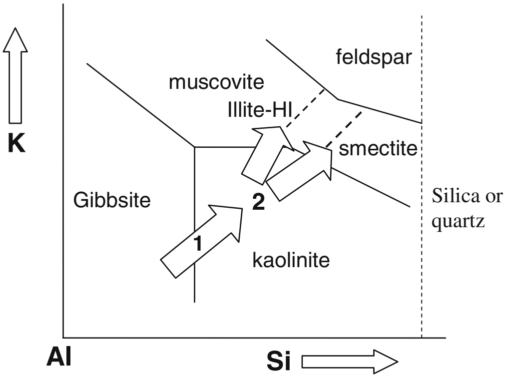


**Fig. 5.35** Diagram of mineral relations as a function of chemical parameter of their stability. The arrows indicate the general change in A horizon chemistry as a function of plant (biomass) deposition. Deepest level clay assemblages in highly altered rock profiles often show gibbsite (aluminium hydroxide) which is replaced by kaolinite and eventually 2:1 minerals HI or illite of high charge and smectite of low charge

Translocation then has the major effect of stabilizing, anr/or creating 2:1 minerals in the A horizon of alteration sequences. One can pose the question of its durability.

#### 5.5.1.1 Dynamics of the Translocation Effect

Initially plant regimes must stabilize the soil chemistry in order to create a translocated mass of nutrients in the soil (A horizon). In order to do this they need to create an A horizon, i.e. a layer with organic matter renewal, a stable clay fraction and so forth. How long does this take? One can give a tentative response using data from two sources, one for a landslide area in New Hampshire USA (Walker and del Moral, 2003) and another analogous situation in Puerto Rico (Zairn and Johnson, 1995). Both studies show that the potassium content appears to stabilize after a hundred years or so (Fig. 5.36). This indicates that the dynamics of plant action is rather rapid in establishing a steady return of soluble elements to the surface of an alteration sequence.

Studies in areas of semi-tropical to tropical climates (Howard et al., 1993: He 2008) show that there is an initial maintenance of higher Si content in soils with plant growth but after a certain period of time the transfer of silica from depth cannot compensate the water – rock interaction and dissolution of silicate minerals. On the Atlantic Coast of the South eastern United States the soils have a strong 2:1 mineral (HI) content in the A horizon for periods of up to about one million years, and after this period the presence of these silica – rich minerals decreases notably. In the Hainan basalt sequence (southern China) the period where the presence of 2:1 minerals can be detected is on the order of 600,000 years. Given that the climate in Hainan is now, and perhaps was, one of more rainfall than that of the south Atlantic Coast of the United States, one can assume that rainfall and hence climate

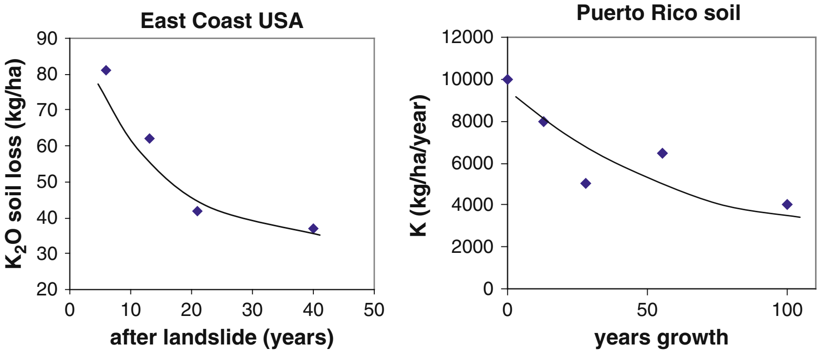


**Fig. 5.36** Illustration of the effects of plant growth on landslide areas in stabilizing the soil chemical balance. Potassium loss from the soils is slowed significantly after a period of about 100 years in two different areas after the re-establishment of forest cover

determine the time period of 2:1 mineral stability in soils. The relative proportions of 2:1 minerals are greatly different in the two cases, largely due to the initial lack of alumina in the basalts compared to the mica schist substrate for the American soils. However, even though the chemistry is quite different (seen in the difference in Al./Si ratios for the two horizons, A and C shown in Fig. 5.37). It appears that the effect is the same. Also the potassium content of the A horizon is shown by the presence of illite in the youngest soil sampled (Fig. 5.38). One can conclude that the effect of chemical transfer by plants can overcome the forces of high rainfall for about a million years after which the chemical context of the soils changes to the disfavour of the more siliceous 2:1 clays. The 2:1 clays respond to the changes

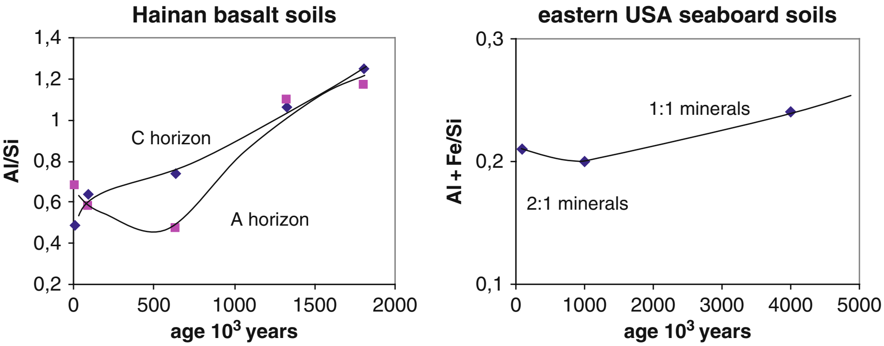


**Fig. 5.37** Ratios of Al and Si in two soils series where weathering and plant growth have occurred over periods of more than a million years. In both series there is a lowering of the Al/Si ratio in the initial stages of plant implantation indicating the transfer of silica to the surface but after 500,000 years or more this effect is lost and silica loss dominates in the soils. In both instances the climate is of rather high to high rainfall and the plant regime is of strong growth. Data from He et al. (2008) and Howard et al. (1990)

in general chemistry as shown in the Hainan series (Fig. 5.37) where the first mineral formed is a mica, then a smectite – illite mixed layer mineral, and eventually an HI mineral, even though it is of very, very low abundance. The prevailing pore water chemistry determines the interlayer ion content of the 2:1 minerals which are present. The high intensity of the gibbsite peak in Fig. 5.38 for the older A horizon clay assemblage shows that the overall chemical equilibrium will be of high alumina activity in solution, where the aluminium hydroxyl mineral becomes a very important part of the mineralogy.

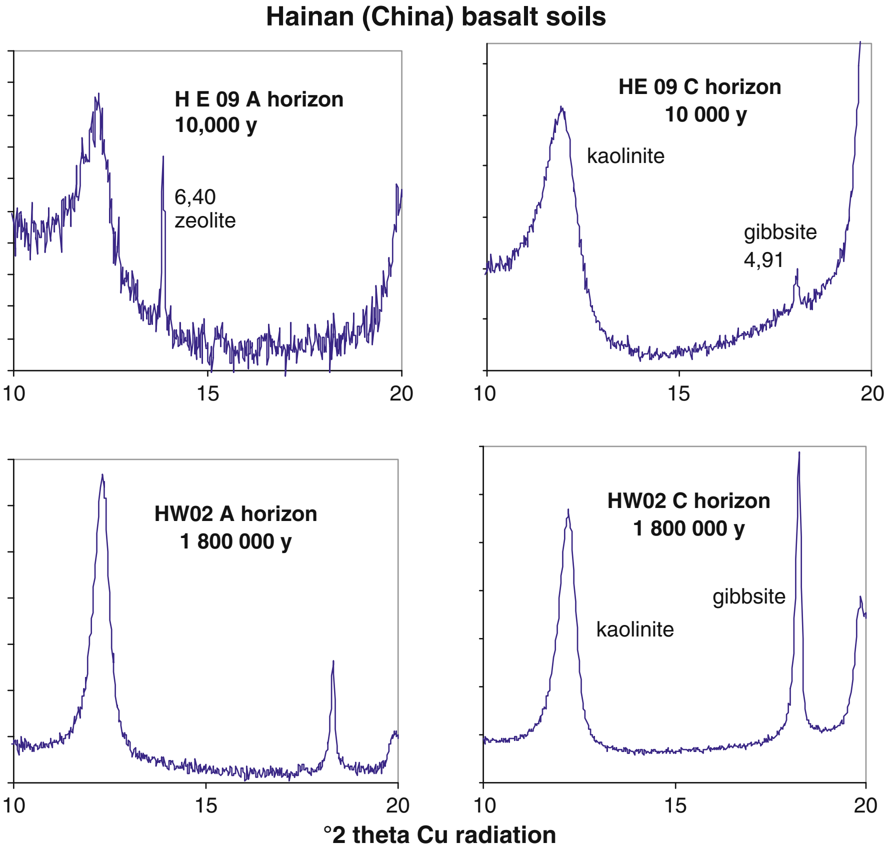


**Fig. 5.38** (**a**) Hainan (China) soils based upon basalt substrates showing the differences between the A and C horizons. In the younger to older samples one sees a strong increase in the gibbsite clay mineral component in the C horizon, especially marked in the deeper part of the alteration sequence. This indicates that the silica transfer mechanism functions even though the ratio of Al to Si has begun to change significantly in the A horizons (see Fig. 5.37). Data from He et al. (2008). (**b**) Diffractograms of the A horizon soils in the Hainan basalt soils showing the changes in the 2:1 mineral fraction of the clays. Initially the phase is a mica, changing to a smectite mixed layer mineral and eventually an HI mineral, with aluminium hydroxide interlayer ions

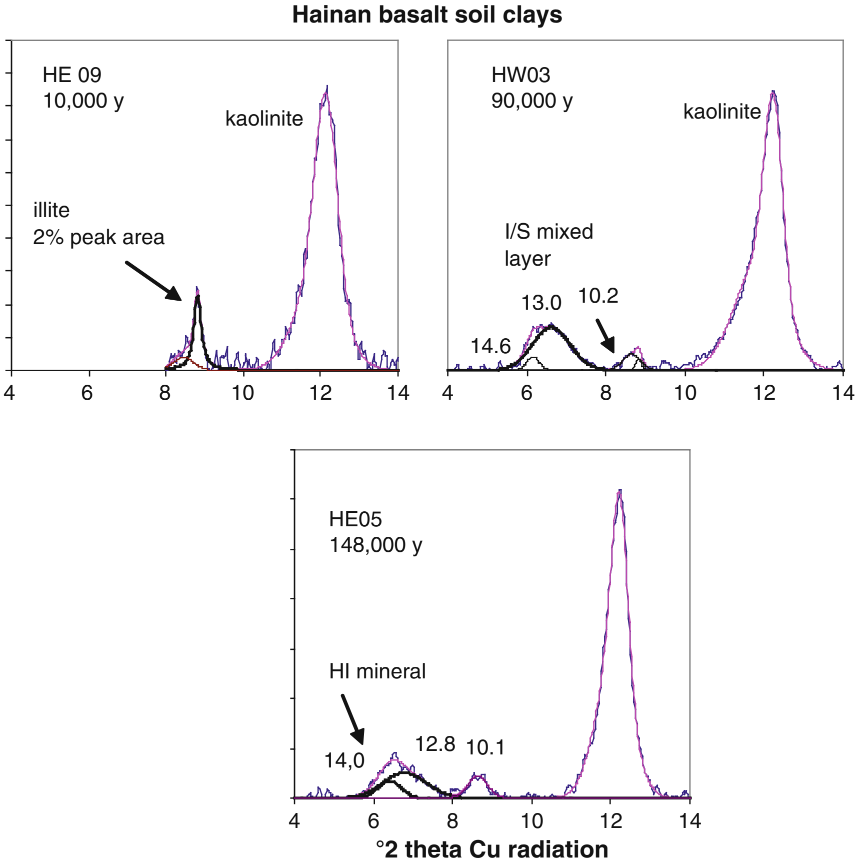


**Fig. 5.38** (continued)

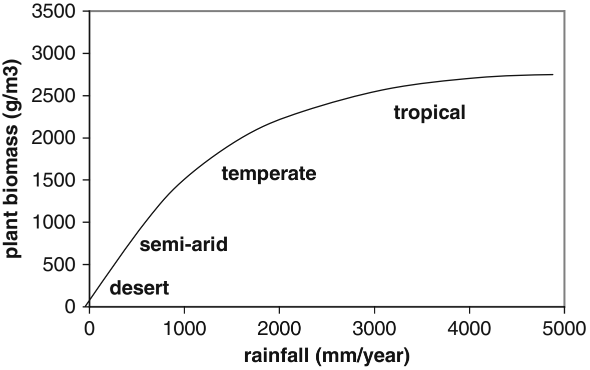


**Fig. 5.39** Data from Lieth (1975) on biomass production as a function of average annual rainfall

The limits of the efficiency of the transfer mechanism operated by plants seem to be within the range of several tens to a hundred years to establish the system and stabilize an effective 2:1 clay mineral A horizon and near a million years under high rainfall conditions when the uplift effect can no longer compensate for the loss of alkalis and silica.

## *5.5.2 Parameters of the Translocation Effect*

### 5.5.2.1 Primary Production of Biomass

The main parameters of the translocation effect are those of climate and plant species. Obviously both climate and plant species are inter-related. In the same way, climate and plant growth are inter-related. These inter-relations determine the effect or impact of plants on the chemistry of the surface, A horizon of the alteration zone of the earth's surface. If we postulate that the translocation of mineral elements to the surface is due to plant accumulations, the amount of plant material produced is an important part of the equation. The more plant growth, the more vegetal matter is deposited on the surface and as a result the more mineral elements are present. Thus the factor of climate can increase the translocation of elements from depth to the surface. However, the more plant growth, the greater the need for rainfall. Rainfall, precipitation, is the motor of dissolution and dispersion of the elements formerly in the bedrocks in pore solutions. The more rain, the more material is dissolved from the overall profile and the more is evacuated to rivers and eventually the sea. Thus at the same time rainfall promotes the translocation of material to the surface, and it engenders its dispersion and extraction from the soil zone. This is a sort of dilemma for plants as they try to keep the needed mineral resources present for the formation and stability of 2:1 clays.

On the one hand rainfall promotes translocation and enrichment of the surface layer in mineral elements and on the other it extracts these same elements from the soils. Lieth (1975) has given a compendium of plant productivity (primary biomass production) as a function of rainfall for various regions of the earth. In Fig. 5.39 one can see that the average line deduced from these data is not at all a linear function of rainfall. Initially primary production increases very rapidly with rainfall increase but then finds a sort of plateau value at high rainfall values. In fact in the original data presented by Leith there is significant scatter in the initial portion of the rainfall – productivity curve. This is precisely due to climate in the full sense of its meaning. The numbers most easy to deal with are those of average rainfall, which are used as a general measure of climate. However the frequency and duration of the rainfall affects the bio – productivity very greatly. For example, the average rainfall in much of France is similar to that of northern Morocco. The vegetation is quite different. Infrequent but abundant rainfall does not produce the same vegetation. This is the syndrome of the savanna alternating season climates near the tropical rainforest areas. There is water but it is not distributed evenly enough throughout the year to give consistent plant growth. Thus the measure of average rainfall is

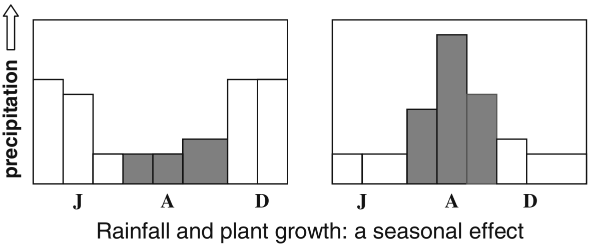


**Fig. 5.40** Illustration of the possible effects of rainfall distribution as a function of season where rainfall in the summer months produces much more biomass than that falling in the winter, low temperature, months

useful but does not tell the whole story. Nevertheless average rainfall is the most efficient tool to measure climatic effects, and relate this to plant growth and primary biomass production. Again if it rains very much during a short period, the overall effect on mineral dissolution will be less than a constant rainfall over the entire year. Since mineral dissolution is a slow process, it will occur during the periods of soil pore saturation where the solutions can eventually be drained from the soil.

#### 5.5.2.2 Mineral Elements and Biomass

Of course a second and very important variable in the transfer equation is that of the mineral content of different plant species. Silica and potassium can vary very much from one plant species to another, as well within different parts of the plant itself. Hodson et al. (2005) and Broadley et al. (2004) indicate the variations in silica content for plants of different orders. The variations can be very great. The same is true for potassium (Gain, 1895). Then as could be expected the ratio of potassium to silicon can vary from one plant or plant assemblage to another. The mass of mineral elements and the ratio of potassium to silicon is a very important part of the translocation effect.

#### 5.5.2.3 Rainfall and Biomass

Biomass responds to water input and the temperature when the water is available. Precipitation can be variable throughout the year (Oliver, 2007). For instance over much of the central and northeastern United States rainfall is rather constant throughout the year varying by about 15% from one month to another In other areas, Los Angeles or Oklahoma, the change is near 80%. In Singapore the change is near 80% month to month but the total rainfall is twice that of the American sites. The period of rainfall concentration is important in higher or lower latitude areas in that during colder periods vegetal activity is low, plant production is low and little transfer of mineral elements is accomplished. In Fig. 5.40 we suggest the potentials of rainfall frequency during a yearly cycle according to the temperature, warm in summer (A) and cool in winter (J,D). The greyed areas show monthly rainfall which is roughly proportional to plant growth and plant production of mineral element bearing substances.

Thus the biomass present under different climates will be controlled by total rainfall (precipitation) and the periods in which it occurs. It would be necessary to use a function of biomass linked to the climate; rainfall, frequency and temperature. This would give a better insight into the mineral input through biomass input.

#### 5.5.2.4 Rainfall and Pore Water

Rainfall is fundamental for the production of vegetal material and hence mineral elements transported to the surface. However rainfall has a second effect of first dissolving silicate matter and then transporting it out of the chemical system of the A horizon. The more rain, the more dissolution will occur due to the contact of under – saturated aqueous solutions with the silicates. All minerals come into equilibrium with their aqueous environment by dissolving into the solution. When a certain limit is reached dissolution no longer occurs and if one adds more of the mineral elements to solutions the minerals will increase in mass through mineral growth. Rain water is rarely saturated with mineral elements.

The variation in the amounts of rain per period in the year is a basic part of climate. If rainfall occurs in short periods, and in abundance, throughout the year the soil is essentially dry when it rains the effect will be dilution of any water present and low amounts of dissolution of silicates. The contact time of the aqueous solution would be short and little dissolution of minerals would occur. If rainfall is regularly spaced over the year, pore water will be more likely to come into equilibrium with the silicates in the soil. Upon release of mineral elements from vegetal input, the silicates could be stabilized or perhaps the input from plant matter would create new silicate minerals. High rainfall throughout the year would promote dissolution of silicate materials in the soils.

The above assumes that the pore space is equally distributed in the soil. However this is far from the case. Many studies have been performed to determine the water holding capacity of soils as it is related to the availability of water for plants. Much of the water held in soils is in the smaller pores and capillary pore spaces. This is the ultimately available water for plants. However, Coppola et al. (2008) demonstrate the importance of the two types of pore sites, in soil aggregates and in the inter-aggregate pores.

One can visualize this function using images of pore space in different soils and depths in soil profiles (Fig. 5.41).

The example is an agricultural soil, where horizontal cuts in the profile have been used to show porosity. The top zone has a range of aggregate sizes and pore sizes which are both more or less regularly distributed in the sample. At the base of the agricultural zone, one sees the development of more large scale pores and cracks. Below the agricultural horizon only crack and biologically caused (worm

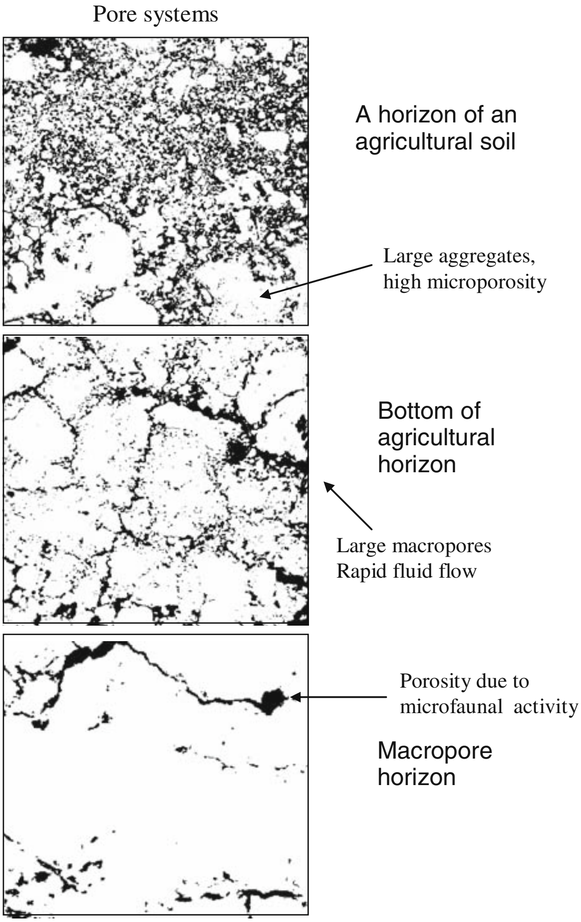


**Fig. 5.41** Illustration of soil porosity types as a function of depth in a profile of an agricultural soil. Horizontal soil cuts show that at the surface one finds large aggregates with capillary porosity and micropores with significant macroporosity developed between the aggregates. At the *bottom* of the agricultural horizon cracking macropore porosity begins to occur forming passageways of rapid fluid flow and the lower macropore zone where only fractures and biotic porosity occurs leaving little micropore spaces and allowing water to flow out of the system rapidly (images are 6 cm squares)

galleries in this case) pores. These large scale events are interconnected and allow rapid passage of rainwater downward into the soil to reach the water table. In the large aggregates one finds small pores and capillary porosity. Figure 5.42 shows a vertical cut of a native prairie soil where the aggregates are present throughout the soil and interconnected crack like pores are found also.

In both examples there are two sets of pore types, one where the aqueous solution is largely in equilibrium with the soil clay minerals, and the large inter-aggregate pores and cracks which become filled with air after rainfall events. The larger pores are zones where plant roots grow and develop.

Depending upon the frequency of rainfall, there will be a different average occupation level of the macropores, high in climatic zones of regular rainfall and low in zones of irregular rainfall events. The more fine pores and aggregates of smaller size, the more small pores and the more water will remain in the soil zone. The

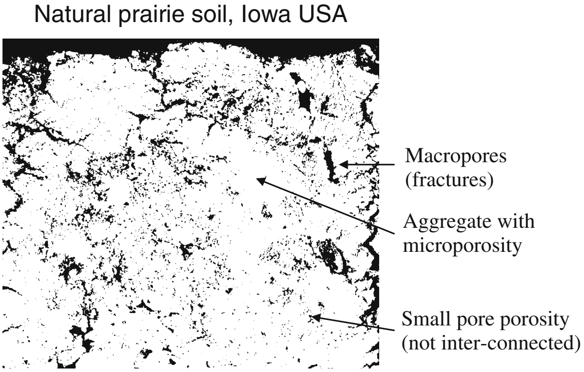


**Fig. 5.42** Example of soil porosity types under native prairie where large aggregates hold capillary water and micropore structures with less frequent fracture porosity. The system is relatively homogeneous through the vertical 6 cm depth shown

fewer aggregates and a higher proportion of macropores and cracks will leave the soil with less residual water.

Consequences of such pore size distributions can be seen in the chemical data of Ranger (2002) for residual macropore and capillary water in a forest soil (Fig. 5.43). The potassium is essentially in dis-equilibrium between the capillary pores in soil aggregates and the remaining macropore water and silica is significantly more concentrated in the capillary water. Since potassium is present as a mono – ionic species in solution, its mobility would be expected to be relatively important and one would expect it to diffuse into the macropore solutions rapidly. However, silica is a more strongly in dis – equilibrium in the two types of water indicating that the complex ion and has lower mobility remaining associated with the major source of silica in solution, the clays of the soil aggregates. These data indicate that in this case there

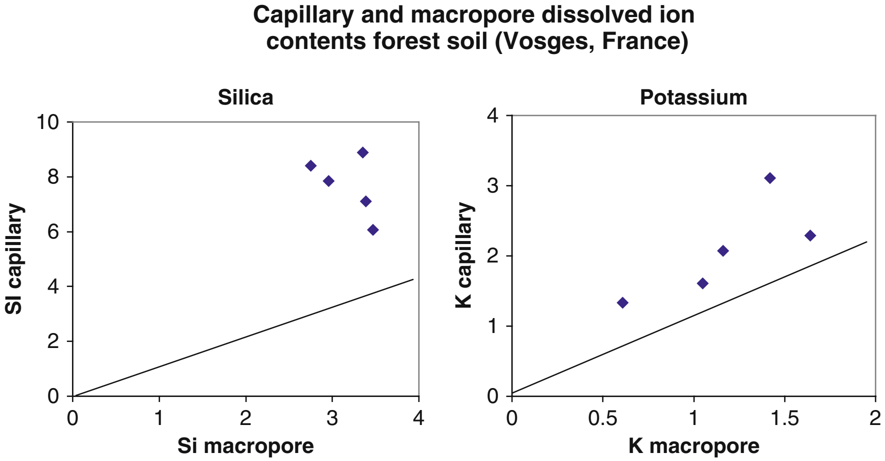


**Fig. 5.43** Dissolved ion contents (weight %) of micropore, capillary water solutions and macropore solutions. The line indicates chemical equilibrium between the two types of solutions in the same forest soil (data from Ranger, 2002) which is the more the case for potassium content than for silica

is not a balance between micro and macroporosity in soils for these elements but that the flow of water through the soil will control the amount of mineral material in solution and its residence time in the soil, potassium coming into closer equilibrium than silica. Higher rainfall, at constant amounts will tend to move out less dissolved material. Less frequent rain events will allow mineral elements which remain in the soil for longer periods of time to approach equilibrium to a greater extent, but there is a differential diffusion and certain elements will be selectively evacuated.

The presence of organic matter in soils enhances the stability of siliceous clays under the same porosity conditions (Karathanasis and Wells, 1989)

It is evident that the transfer effect operated by plants to move mineral elements to the surface A horizon will depend upon several factors:

1. Rainfall and frequency which influence primary production of *biomass* and hence the capture of mineral elements by plants,
2. Rainfall and frequency which effects the differential *movement of fluids* will determine the evacuation of elements from the aggregate environment or the inter-aggregate pore space through capillary or macropore space.

### *5.5.3 Modelling Mineral Stability*

Given the understanding that plants move key elements to the surface that stabilize certain clay minerals, one can attempt to model the effects of climate on biomass and mineral dissolution or crystallization (Barré et al., 2009). In a first approximation one can consider the relations of rainfall and biomass, one a dilution and destabilizing factor and the other a mineral forming factor. Taking simple assumptions of biomass as a function of annual rainfall and annual rainfall as an average dilution factor one can propose the mineral stability relations as a function of these two variables (Fig. 5.44).

There are several key points which confirm, in a general way, the model. One is at the low rainfall end of the curves. Nettleton et al. (1973) indicate that mica (illite) forms in semi-arid soils, near the low precipitation end of the diagram. Mahizhnan et al. (2006) give evidence for the formation of kaolinite in a very a rid desert in Australia. These two points are very closely related at the low rainfall end of the diagram, the semi-arid climate could be expected to produce some illite while the very arid climate should form kaolinite. In very low rainfall areas the stability of potassic, siliceous and 1:1 minerals (kaolinite) are not very fair apart in their regions of chemical stability.

The second area of interest is the high rainfall portion of the diagram where the stability of 2:1 minerals cedes to that of 1:1 and eventually silica – free minerals, gibbsite. In the initial stages of rock – plant interaction, 2:1 minerals can form but they are lost over period of high rainfall. This indicates that despite the high biomass productivity the effects of dissolution cannot be counteracted. The biomass productivity reaches a limit where increase in rainfall does not produce that much more

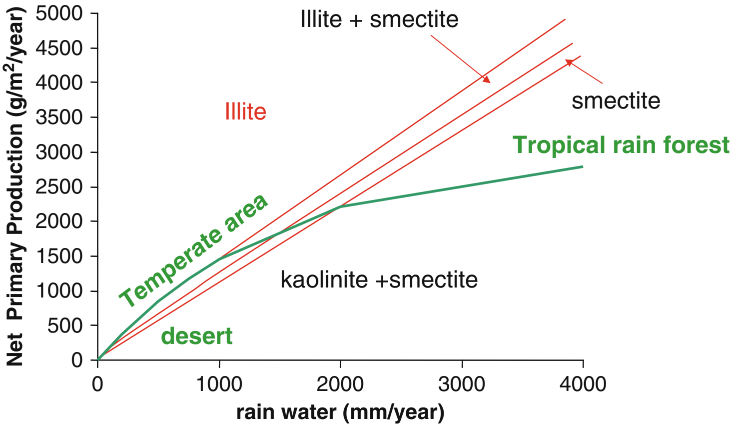


**Fig. 5.44** Results of equilibrium mineral calculations of aqueous solutions with different amounts of mineral elements from biomass input (net primary production) and annual average rainwater quantities (Barré et al., 2009). Net primary production averages (heavy line) taken from Lieth (1975)

plant material and the translocation effect of mineral elements cannot compensate for loss to percolating rainwater through the dissolution of the clays in the A horizon of the soil. This state exists well below the A horizon in older soils with high rainfall inputs. This is indicated by the data or Glenn and Nash (1964) for soils from the Mississippi (USA) costal plain (Fig. 5.45). Surface (A horizons) show the presence

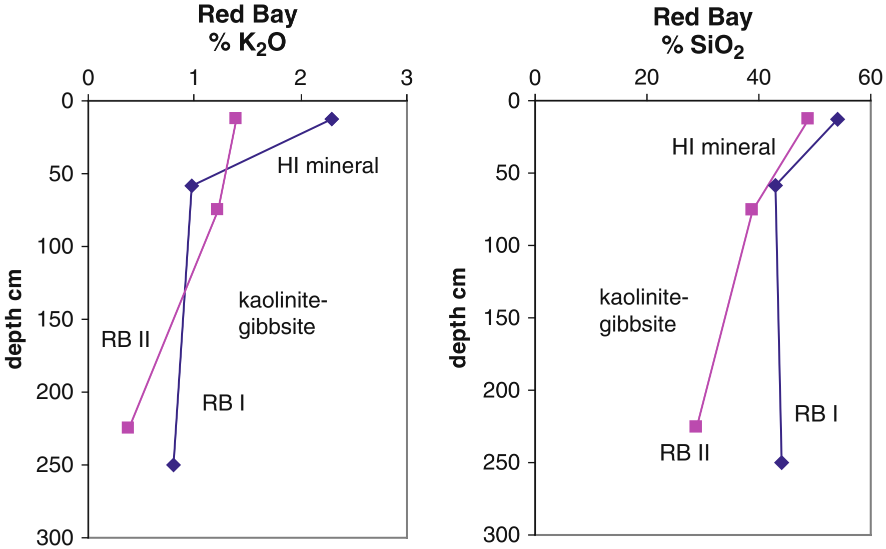


**Fig. 5.45** Comparison of clay mineralogy and potassium and silica contents of soils in a south east coastal plain soil sequence (Glenn and Nash, 1964)

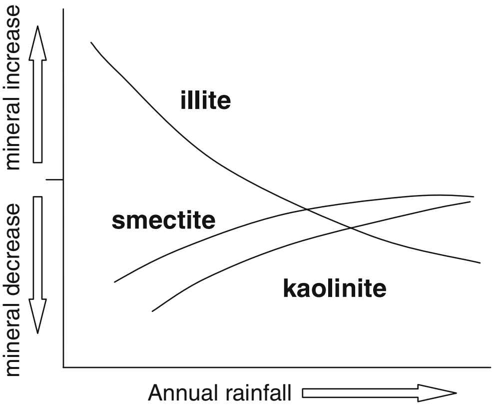


**Fig. 5.46** Comparison of relative stabilities of the minerals illite, smectite and kaolinte as a function of annual rainfall (adapted from Barré et al., 2009). Illite is strongly affected while smectite and kaolinite increase less rapidly in relative amount

of 2:1 minerals (HI phases) while less siliceous minerals (kaolinite and gibbsite) are present at depth. When the biomass cannot keep up the needed supply of Si at the surface, under conditions of high rainfall, or in older soils where resources have been exhausted, the 2:1 minerals in the A horizon are lost.

Given the parameters of biomass and rainfall, what are the components of these factors that affect mineral stability? Barré et al. (2009) give examples of the individual effects of the rainfall – biomass variables. For example, all other factors being constant, what is the effect of dilution or total water through put to a clay mineral assemblage? In Fig. 5.46 we indicate the relative changes in mineral abundance with change in average annual yearly rainfall. This does not take into account the frequency nor flow through the system. It is just an estimation of the dilution effect or the relative rates of mineral dissolution. The illite tends to decrease in content and smectite then kaolinite increase. This reflects the pore water compositions reported by Ranger (2002) for capillary and macropore fluids. The equilibration of K between the solutions indicates that it will be lost to the flowing solutions and that the Si and Al remain in the solid phases, kaolinite and smectites in the example given.

On the other hand net primary production of biomass, taken independently from rainfall shows a trend of favoring illite as more biomass, and more element transfer is effected to the surface. Figure 5.47 indicates these relations.

At a constant ratio of Si and K in the plant mass, 5% $K_2O$ and 0.75% $SiO_2$, the increase in plant biomass favors illite compared to smectite and kaolinite If one changes the relative amounts of Si and K in the plant biomass brought to the surface A horizon, the effects are such that increase in $K_2O$ favors illite, as would be expected, but if Si is increased relative to K then smectite is favored at the expense of both kaolinite and illite whose Al/Si ratios are similar, being near one (Fig. 5.48).

The inter-relations of elemental content of the critical elements potassium and silica are fundamental to the stability of illite, smectite and kaolinite. Of course a deficit of silica will in the end favor the aluminous mineral gibbsite, with the loss of silicate clay minerals.

**Fig. 5.47** Effect of annual biomass on relative mineral stabilities at constant amounts of Si and K in pore solutions (adapted from Barré et al., 2009)

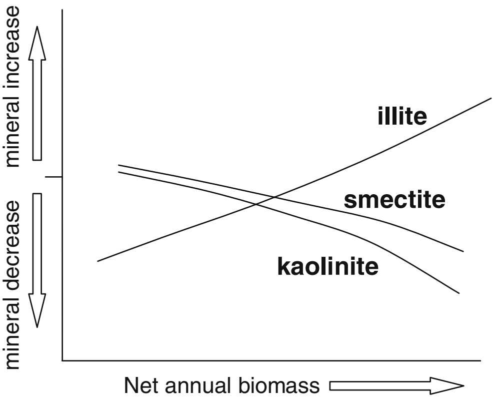
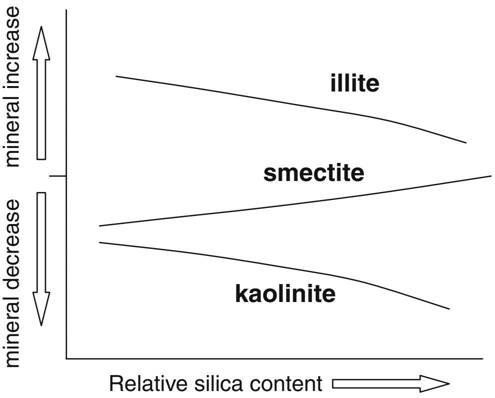


**Fig. 5.48** Effect of different silica to potassium ratios in the biomass affecting a soil system. Increase in silica increases smectite while it decreases relative to illite and kaolinite content



These simulations indicate that the simplified diagram of Fig. 5.44 should be considered as a general concept but not applicable to all specific situations. One factor is of course the relative amount of rain that moves through the soil in macropores compared to caplillary and micropores. The factor of dilution, rainfall in Fig. 5.46, is moderated by the soil structure, i.e. the rate of flow of rainwater for a given rainfall event. The plant productivity affects the clay mineralogy in the total of the matter brought to the surface but also, and perhaps more importantly, in the proportions of the mineral elements contained in it. Bacterial action and root exudate production can affect the acidity of the soil solutions in the A horizon so that some minerals are favored over others. The higher the acidity, the more hydrogen ions will be incorporated into the clays, (OH units) and hence kaolinite will be produced compared to illite or smectite. The ratio of OH ions in kaolinite compared to silica – alumina in illite is 1–3. Hence acid solutions favour kaolinite greatly. Thus the system is multidimensional but not impossible to understand.

The idea of translocation of mineral elements to the surface horizons by plants has been in the minds of agronomists and soil scientists for some time, even in the 19th century (Larbaletrier, 1891, p. 104 for example) but up until very recently no systematic attempt has been made to use numerical data to explain and eventually predict the minerals present in the A horizon of an alteration profile according to the variables of plant recycling and climate. The formulation of transfer as a function of mineral stabilities in equilibrium with aqueous solutions is certainly a progress in understanding the nature of the mineralogy of soils and the importance of plant interactions concerning their stabilities according to the parameters of climate and plant growth.

*What we need to know*

This chapter has presented much information which pertains to the possibility of building a chemical model which can be used to describe and eventually predict the effects of plants on clay mineralogy in the A surface horizons. Several points are inadequately known:

1. *What are the kinetics of mineral dissolution compared to mineral formation in the A horizon*? Studies must be done to establish realistic reaction rates for dissolution and crystallization of 2:1 minerals under surface conditions.
2. *What is the transit time of rainwater in different soils? What is the time constant of equilibration of the different elements dissolved within the micropore and macropore compartments*? This information can be used to estimate the effect of soil texture on the clay mineral stabilities.

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# Chapter 6
# Man and Agriculture: Manipulating Soil – Plant Interactions

## Contents

## 6.1 The Adventure of Agriculture: the Manipulation of Nature by Man

Plants manipulate soils and rocks debris to stabilize and produce clays that form good properties to their benefit. Without plant there would be no soil i.e. association of organic matter and clay minerals. This stabilizing influence and the ecological interactions between rocks, silicate minerals, clays, organic matter and micro-organisms is the basis of plant life on the surface of the earth. Animals live from plant material, either first hand (herbivores for example) or second hand (lions, jackals and other hunters). The trick is to use the ecology of plant actions to produce vegetal material for direct consumption (wheat for example) or for the production of meat (cattle and other meat animals). Man needed to understand how to manipulate

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_6,

the original manipulators, how to use the natural tendencies and inter-relations of plant and soil materials in order to become less dependent on the vagaries of nature. This chapter gives a brief resume of the steps of plant manipulation related to soils constraints and the eventual impact of agriculture on the soil materials, especially the clay minerals.

### *6.1.1 Introduction*

There are many books in most languages concerning the evolution of mankind. The use of natural materials and concentration of resources mark the evolution of mankind in general in the different regions of the inhabited earth. Most histories of this evolution are centred on the material and intellectual side of the evolution. Housing, graves, the written word, use of stone and metals as tools and so forth dominate books on the pre-history of mankind. These aspects are of course most important to an understanding of today's societies but they do not indicate much of the crucial developments that were accomplished and which shaped the life of mankind. One obvious reason for study of non-perishable artefact is that they are non-perishable and relatively abundant. Stone is well preserved in all archaeological sites as are ceramic materials, wood much less so and the remains of crops and grain even less so. It is not incuriosity on the part of archaeologist that leads to the concentration on durable goods. The biggest problem is to have representative populations of objects and artefacts which can be used to describe the life a given community in the distant past. One of the major if not the major transformations of human societies was the development of agriculture. This step in changing the local environment to the advantage of human sustenance represents a step from being submitted to the whims of nature to controlling the natural system necessary for human welfare. Here we would like to try to get an understanding of the problems faced and the uses of nature that were effected by early communities as they began to use the vegetal resources available in their environment.

One does not often think that agriculture is a manipulation of nature. However this was the case up to the mid – 1950 revolution of agricultural practice in the west. Before this period man was using nature to produce things in nature. The genius of farmers was to use the natural tendencies of plants and animals in order to control and regulate the productivity of vegetal and animal species. The basis for animal sustenance is plant matter, in one way or another. Cultivating plants is not only useful to produce food for humans but also for the animals he uses for traction and eventually food also. The idea of a factory product which could be used to increase the productivity of the earth was for the most part a dream for much of the agricultural world. However, the use of the tractor, factory produced ammonium and herbicide, insecticide products made in factories from petroleum changed the concept of the earth and the relations of man and the earth. The progress of this idea was not immediate nor was it done with conscience. The idea of progress due to Science is to a large extent a part of post – War culture; change is good, change is Science applied to everyday endeavors, change is progress (for the better of course). Yet the means of using nature to produce the material needs of food and clothing was practiced from time immemorial. This initial step we think of as the Neolithic Revolution, one where man became independent of the whims of nature and natural availability which permitted him to multiply enormously and become a more than major actor in the world of the living. Here in the distant past, some 11,000 years ago depending on where in man's past habitat one looks, there was a revolution. Instead of submitting to the laws and vagaries of nature, man became to a certain extent independent of yearly changes in climate and could ameliorate his future supplies of basic substances.

Man did not become a farmer first. The development of the human species passed through various stages of using natural resources for sustenance and comfort. Hunters became hunter – gatherers and eventually herdsmen. The gatherers became more specialized and developed into farmers. The process was long, covering many hundreds of thousands of years.

Earlier crucial steps in human development, pre-farming, included the invention of the shaped stone or flint which produced a cutting edge. The process of shaping flint to make the variety of tools we have found today was quite long, much more than a million years, By forming a strong cutting edge of a flint stone man made not only a useful penetrating weapon to kill game with thick hides but this sharp edge also allowed him (or her) to cut meat from a carcass and take off the skin with efficiency. One could transport and store the kill and further use part of it (the skin) for decent clothing. Heaven knows how one skinned a mammoth, bison or musk ox before that. In any event great material progress was made using simple tools and a lot of human ingenuity. Try to make a blade from a piece of flint.

However the true manipulation of natural resources seems to have come together in what is called the Neolithic revolution where not only selection of seeds and amelioration of the species for food sustenance was practiced, but there was a selection of heretofore wild animals and a development of specific characteristics of the animals. Roughly at the same time heating clays to the point of becoming artificial rocks (ceramics) came into use. Instead of chipping stones to make sharp edges the concept of stone polishing developed which allowed the production of a much more robust tool, useful to cut tree trunks or effectively dig in the earth. These various things came together in a surprising way and with relative rapidity in several centers of human experience, so that in cities or communal concentrations humans could live longer and more plentiful lives. In a sense man was re-born when he could manipulate his natural surrounding with success. His everyday life changed radically. For one thing specialization occurred, where one family or person could do what it did best and not have the necessity of doing all things necessary for sustenance. Potters, axe makers and other specializations could occur albeit we know little of just how nor by whom. In any event it is clear that life in a large community allows portions of it to specialize in their activities to the benefit of all. Providing food for a large stable population fixed in one location was a key to development of humankind.

The processes was not universal nor did it come at the same time nor in the same succession of events or mutations over all of the human (*homo sapiens sapien*s) inhabited earth. However the major changes occurred in a more or less parallel manner over a similar time period following the climate – controlled plant regimes which were presented to man as glaciers retreated. The control of climate over plant regime shaped the agricultural future for some peoples, others chose different paths to arrive at about the same stage of self sufficiency in the major areas of the world. Often times one dealt with things as they were. The radical changes and agricultural progress of the latter half of the 20th century have effaced these differences between developed cultures largely, putting different human cultures and climates on a more or less similar agricultural footing. One can make an argument for a better or poorer choice and future, assuming changes in human needs and conscience, but for better or worse we are in the post industrial agricultural world.

How did we get there or here? How can we use past experience to benefit from the fantastic evolution of human kind based upon the manipulation of natural processes? We will not answer these questions but propose a short, simplified history of the development of agriculture in order to understand the relations of plants and soils as they were understood and used by man over the millennia. We have used several texts as references to describe the general sequence of events in the agricultural adventure but many more texts can be found (Bell and Walker, 1992; Guilaine, 1989; Masurié de Keroualin, 2003; Clark, 1955; Shane and Cushing, 1991; Stamp, 1961; Chambers, 1993; Dalfes et al., 1994; Ruddiman, 2005; Duby and Wallon, 1975; Ferdiére et al., 2006).

#### 6.1.1.1 Multiple Centers and Multiple Problems

The spread of human communities was completed some millions of years before the time we wish to describe here. Most habitable zones we know today were colonized by the time of 10,000 years before our era. Arctic and sub arctic areas, tropical rain forests and the great steppes below the tundra stretching across climatic and geographic zones were known to the hunters and hunter – gatherers. If one were to use the natural vegetal sources of sustenance to develop a reliable food supply, the obstacles of natural vegetation had to be overcome. Gathering is fine but one rapidly runs out of resources at a given site and migration is necessary. The shift from migration to sedentary communal structures necessitates a greater concentration of food sources over a small area. One can only go so far to bring back food to a village each day or fortnight. Concentration of resources necessitated an intensification of exploitation of vegetal sources and an amelioration of their productivity. This is the story of agriculture.

Roughly four "centers" of agriculture can be identified; the Indo- Near East, Central China, the Meso and South American zone and the Southeast Asian and Polynesian areas. Concerning the climatic structures and hence vegetation biomes, the Chinese and Near Eastern areas were similar in these aspects at the end of the last major glacial period, around 11000 BC. Steppes supplied abundant food for foraging animals, and a certain sustenance for food gathering nomads who eventually became sedentarized in a general way. The landscape was dominated by grasses. This biome developed a specific type of soil and alteration structure with much organic matter preserved in the soil zone having a significant pH (usually above 6). Here the obvious plant types which could be used for agriculture were the grasses and associated legumes so abundantly present. Further climate change, increase in temperature and changes in rainfall in some areas, necessitated further adaptation of agricultural practice, irrigation in some instances and after several thousands of years eventual displacement of the major population centers occurred. The great development of agriculture took place during the climatic optimum, around 7000–2000 BC. However the exact time span varies depending on the location (Bell and Walker, 1992, p. 70)

The situation in Mezo and Andean South America is less well known but certain generalizations can be made. The introduction of agriculture as such was later than in the Chinese and Near Eastern areas and certainly more diverse. Significantly different types of crops were produced coming from both forest and prairie resources where rapid climate change occurred due to topography. Avocado along with squash can be found in the Andean zones while more grass – like plants were used in the Meso American area in the much more arid and steppe like areas. Valley bottoms were often preferred in initial stages of development. Overall the areas of agriculture seemed to be temperate and somewhat dry, dominated by grasses and prairie type vegetation.

A very interesting experience occurred in the South East Asian and Island areas of the Southwest Pacific. Here the climate was and is dominated by tropical or at least very dense forests. This is not where grasses such as the precursors of millet, rice and wheat would grow. However the forests did have abundant root resources, or at least they were discovered and used by the inhabitants as a source of food. Taro and Manioc became the stables of the vegetal part of diets here. Root culture is quite different from that of grasses and as such agricultural development was not the same. In such areas drainage of water is often more important than irrigation, totally unnecessary there. The forests provided fruit trees which eventually became domesticated. There is a strong contrast between the problems faced by rain forest farmers and those on the steppes. Nevertheless some of the oldest traces of agricultural manipulation of plant species are found in the rainforest areas. Essentially the agriculture here remained in the same biome throughout time whereas that in the old steppes moved to new areas by necessity or choice. The agricultural practice did not necessitate a complete change in biome as it did in other areas.

However in the European experience the needs of agriculture led to a major change in the vegetal cover. This very interesting manipulation of nature is the subject of the next chapter.

### 6.1.2 History of Traditional Agriculture in Europe: An Example of Soil – Plant Manipulation: Changing the Landscape Through Agriculture

Due to a reasonably complete body of information, the history of agriculture is exemplified here in using the European experience. The Neolithisation process occurred in different areas under different conditions and the response of mankind was adapted to these local conditions. One of the more striking examples of plant manipulation is seen in this conquest of the European continent where the relations of plants to climate and the development of soils had to be strongly modified in order to accommodate the ever increasing numbers of humans. It is not the only case to be sure but one of interest in that the manipulation of nature is rather striking.

#### 6.1.2.1 The Context of the First Steps in Agriculture: Steppe Plants and the Hunter-Gatherer Cultures

*Homo sapiens sapiens* emerged at the end of the last cold stage of the last ice age. Also the initial steps towards agriculture in the European area occurred on the Near East in what is often called the “fertile crescent”. The Palestinian – now Israeli – coast, Lebanon and the Tigris – Euphrates valleys descending to the Red Sea were the early centers of agriculture from what we know today. This is of course not what we consider to be Europe, but things started there. The Neolithic era marked by domestication of grazing animals, the development of new species or strains of wild grain plants, and the making of pottery all of which were practiced at different centers in the area at roughly the same times. Uncertainty is on the order of a thousand years. Different authors give slightly different dates and different sequences of use of the different elements of the Neolithic “package”. However a strong and recurrent use of these methods of food productions seems to have begun by the time of 9000 BC and firmly fixed in most areas of the Near East by about 8000 BC. The northern point of the crescent, in present – day Turkey seems to have been the zone of diffusion of the Neolithic methods toward more northern European areas.

Different types of wheat and oats were domesticated as were lentils and peas. Thus not only grasses were used and developed but also legumes. This is a very important step. As we know, legumes enrich the soil by symbiotic transfer of nitrogen to the soil via bacteria – root actions. Surely the initial farmers had observed the beneficial results of crop rotation as they had the two crops at hand. Animal husbandry occurred by the domestication of wild sheep, goats, pigs and cattle. These animals could be herded especially sheep and cattle or be kept in enclosures such as often was the case for pigs or goats. We do not have a very good idea of the spatial distribution of animals and farming practices relative to dwellings and other more distant areas. Perhaps the herders, who preceded the farmers stayed out in the larger spaces beyond the concentrations of the towns or other population concentrations bringing their produce home at different intervals. The information we have on animal use is of course from population centers, villages or towns, as is that for the use of plants, although palynology could be practiced in non-inhabited areas but there would be great problems in dating the materials outside of inhabited sectors. Hence we know about life in areas of human concentration but less in areas of temporary habitation or the “open spaces”. However the general landscape seems to have been one composed of grasses upon which the sheep and goats could graze.

The climate in this period of discovery was Pre boreal in Europe, with temperatures similar to those today but with slightly less rainfall (Calwe et al., 2007; Watson, 1991; Bell and Walker, 1992) following the end of the last glacial effects 134000–9000 BC. The boreal climate favored forest growth in Europe with cooler and wetter periods followed by a period of Atlantic climate type (warmer) in the period 7000–3800 BC. These climates reigned in Europe for the period which concerns us. The climate in the Near East was such that savanna with scattered oak patches dominated by grasses, becoming more or less humid as climatic patterns shifted. Thus there was a contrast between the Near Eastern area of Neolithic agricultural discovery and the European area. Somewhat minor climatic fluctuations appear to have affected the Near East slightly modifying the proportion of grass to scattered forest. Some authors feel that such fluctuations caused the migration of Neolithic practices (Maellart, 1975, p. 69). The area of interest to us is that of present day Greece and Turkey which is the obvious passage from the traditional Near East and the Fertile Crescent (Palestinian coast and Tigris – Euphrates river systems) culture to the forests of Europe.

In the Near East just where and how the initial settlements of hunter gatherers and herders settled down and why is open to question. Surely sedentarisation occurred during a time of abundance in food supply (Bell and Walker, 1992) both for animals and man. The economy was based upon a strong supply of prairie plant materials. Numerous archaeologists pose the question as to why man decided to settle down to farm, a seemingly more difficult task than roaming around to hunt and have the women gather. If one considers it, hunting is lots of fun, running around after game and killing for a living. Farming means staying at home, i.e. one place, and working each day in the same place. However, if one looks at it from the stand point of women, hunting means picking up all of your belongings almost daily, moving a lot and breaking things along the way. Sedentary living means that one is able to use and keep those nice ceramic vessels that one just recently learned how to make that do so well to cook the grains harvested and transformed into more nourishing food stuff. Perhaps the forces of civilisation were driven by feminine good sense.

In any event it happened, gradually over a period of several thousand years that Near Eastern communities formed and prospered based upon agriculture, vegetal and animal food production. Possibly as important, among the early crops were fiber bearing plants, hemp, cotton and flax, which could be used to make clothing and utilitarian articles such ropes, string and cords. The use of pottery was un-even in chronology compared to the agricultural process. Nevertheless it became a staple of the Neolithic civilisation centers by the time of its spread to other regions. In particular the fertile crescent area, Palestine-Syria and the Tigris Euphrates regions, the core areas of neolithic development, began to expand or diffuse the new technologies to the north and west into the area of present day Turkey. This in the period around 8000 BC and by 6500 BC or so had reached the eastern parts of Greece (Ruddiman, 2005; Masurié de Keroualin, 2003). At this point climate changed and forest began to encroach on prairie – steppe vegetation moving eastward, the boreal climatic period (Bell and Walker, 1992). Now things became more difficult in that expansion of the "method" faced a new biotope, the forest. Grasses do not like acid soils in that they most often allow a build up of aluminium ions in the soil pore solutions. Most of the cultivated species have a low toxicity limit (see Sect. 5.4). Of course not all trees are alike, nor are all soil substrates the same. Conifers tend to produce the lowest pH values in soils and show the presence of aluminium hydroxyl interlayer ion clays (HI minerals) which indicate high alumina content of soil solutions. Oaks tend to be less acidifying and so forth. Nevertheless, forest soils are typically of lower pH, lower organic content and less rich in clay minerals. The characteristics of the A horizon of forest and prairie soils are quite different. If Neolithic man wished to move further onto the European continent he had to find ways to change the basic soil characteristics of the forests that had recently established themselves there. This task was accomplished but only over significant periods of time. Progression was steady to the northwest (Fig. 6.1) where the conquest of the forested areas was probably guided by topographic – geomorphologic situations. Agriculture is most easily effected in areas where the soil contains few rocks and is relatively loose. Such is the case for loess soils, based upon fine grained dust deposits and sediments accumulated along stream or river valleys as terraces and along the shores of lakes. These were the zones or pathways of penetration for the Danubian civilisation moving northward around the alpine massif moving roughly at about 600 km/1,000 years. This rate of progress suggests cultural change more than conquest. Just why the daunting task of changing forest into prairie was adopted remains somewhat of a mystery. Archaeologists still debate the subject. In any event it happened and one should ask the question of how.

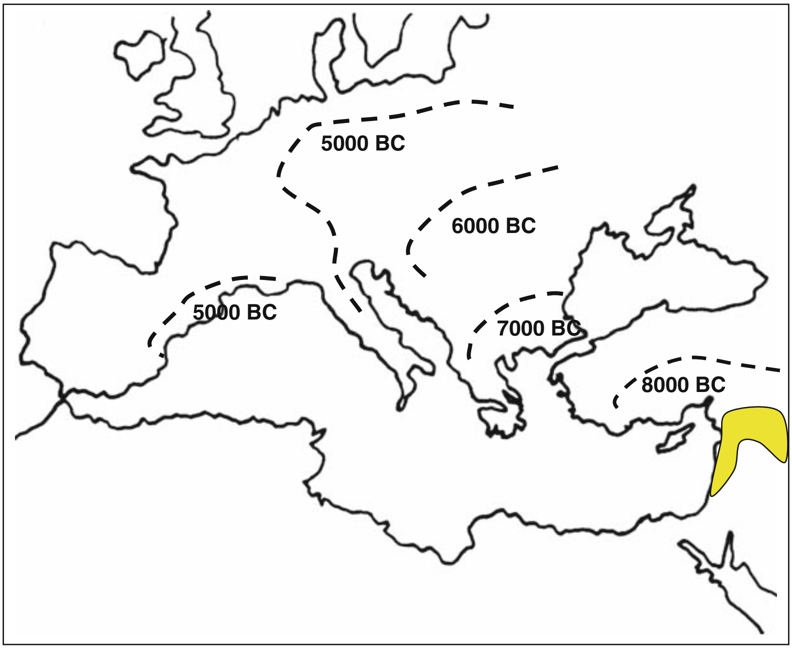
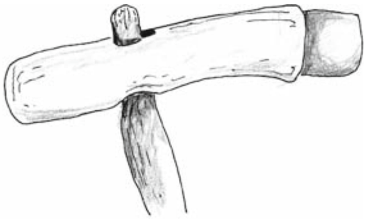


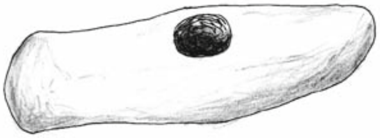
**Fig. 6.1** Spread of Neolithic culture across Europe (adapted from data and representations in Ruddiman, 2005; Masurié de Keroualin, 2003; Calwe et al., 2007; Watson, 1991; Bell and Walker, 1992; Maellart, 1975). Note the rather slow extension of the Neolithic culture, which was based upon agriculture. The movement to the north and west from the Near East was toward forested zones originating in the initial steppes of the Fertile crescent area of the Near East

#### 6.1.2.2 The European Experience: Changing Forest Soils into Prairie Soils and the Neolithic Revolution

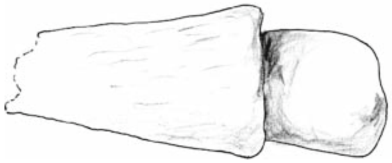
In the list of first plants domesticated from the prairie areas one finds grasses or *graminae* such as wheat and oats as well as lentils and peas. Thus at the same time Neolithic man domesticated grain producing grasses as well as the legumes which have the property of accumulating nitrogen in quantity in the soil zone. Thus a simple crop rotation will enhance the fertility of the soil. Undoubtedly this was not lost on these first farmers. The modern skills of eliminating trees and inducing prairie – based farming were acquired very early. The technological advance which made such forest clearing possible was the polished stone used as an axe. Thus the first major tool for the neolithisation of Europe was probably this instrument shown in Fig. 6.2. Simple enough but not all that easy to conceive. The idea of shaping stone was very old at this stage. Cutting instruments and spear or arrow



Stone axe head mounted in wooden holder with a wooden shaft



Stone axe head to be mounted on a shaft



Stone axe head mounted in antler base

**Fig. 6.2** Sketches of the different types of Neolithic axes one has found in different areas of Europe. The polished stone is the technical advance that allows one to chop down trees and to use the fallen wood to better advantage than by simple burning of the trees. Cutting and stacking allows a concentration of wood ash which can then be proe efficiently distributed on the land. Also cutting the branches and trunks allow one to build houses, cut firewood among other things. The stone axe was the key to de-forestation in a systematic manner and the eventual exploitation of the land for agriculture (sketch BV) points were quite common. But the smoothed surface on a more robust piece of stone was much better for the work of percussion. Such stones could not be shattered or chipped but needed to be smoothed and ground down into the shape desired. Thus the cutting edge was less sharp but much more robust against the impact of a tree trunk. Accessorily, the same instrument could be fixed on a longer handle to break and cultivate the earth. It is still used in some parts of the world. Cutting trees and breaking the ground was possible using the same type of instrument. The importance of cutting a tree down is that one can more efficiently burn it to a complete state of ash. If burned standing, most trees leave a charred trunk, which is not easy to farm around and which losses a great amount of potential ash material for fertilizing.

But how does one change the fundamental chemical parameters of forest soils, their chemistry, which hinder prairie plant growth? This was the fundamental problem of progression of farming into the European forest areas. The initial step is to eliminate the trees, by cutting them down. This act then gives light and eliminates competition for soil resources to low growing plants. Edwards (1993) and Clark (1955) indicate the steps used to eliminate the overgrowth and in certain circumstances use of the felled trees. When a forest is cleared, it is necessary to dispose of the fallen wood. The easiest method is to burn it. This produces alkali – rich wood ash which when spread over the cleared area increases the pH. Soil pH values were changed from 4.8 to 7.8 in an experiment by Firman (1986) when wood ash was spread on the forest soil from which they came. Also this method increases the potassium content of the soil zone. In the experiment exchangeable potassium (by cation exchange) changed from 38 to 1,200 milli equivalents of charge but dropped to 370 milli equivalents after the first year's harvest. This is a source of increased fertility for crops coming from prairie biomes, but it appears that it will be rapidly exhausted, usually after about 7 years of culture according to Clark (1955). This leads to the slash and burn type of agriculture where cleared areas are cultivated for relatively short periods and abandoned for new land, creating another type of nomadism. If the land is put into pasture, animals browsing on the vegetation, the plants which remain and grow are of the prairie type, grasses and various other low growing non-woody plants, which provide sustenance for domestic animals, sheep, goats and eventually cattle. Browsing maintains a higher pH level, decreases the high aluminium content of pore waters due to the forest type humic matter and builds up the soil type that fosters prairie type domestic plants. The key factor is the elimination of forest plants and the maintenance of prairie plants which will eventually build soil characteristics compatible with crops. Thus it would seem that the cutting and burning of trees is a first step to change in soil chemistry but the second fundamental and more long – lasting step is that of pasturage with a continued strengthening of the chemical properties of prairie soils necessary for cropping. Hence the initial stages of clearing the land were based upon the use of domestic animals to maintain the new biome. Clark (1955) shows that the system of cutting, burning and grazing to engender farmable land was successful for Neolithic farmers in deciduous forest situations but not strong enough to transform the conifer forests of the north in Norway and Sweden.

Miles (1985) gives examples of the effect of burning and browsing of forest soils, first creating a less acid Podsol and then forming a prairie – type soil. This is accomplished by the preservation and encouragement of grass and fern growth on the grazed forest soils. The pH increases and the type of organic matter changes being more like that of the prairie vegetation.

The initial, long term conquest of the forest to produce stable farmable land was not made just with the polished stone axe (see Fig. 6.2) but a judicious use of the wood ash and a succession of grazing which fostered the development of a prairie soil type. The advantage of such a system was that it was applied in areas of greater rainfall than the steppes, so that the planted crops would benefit more from their managed culture. A second advantage of farming in former forest land was that there was always the possibility of developing a wood lot. If one wishes to cook the food one produces and to make pots of ceramic materials to cook it in, one needs fuel, in the form of wood. In a natural wood land this is easy to do whereas in a steppe land it is more difficult. Thus it made sense to go to the forests to obtain a long lived sustenance for permanent communities. Not only did one have a supply of wood, forage for animals and eventually a good land for farming but the land was relatively un-exploited with a low intensity of habitation: the "open west" to a certain extent.

A very important technological innovation occurred in the late Neolithic, not very well documented in most cases but on some cave walls one finds a representation of the use of cattle to pull plows (Fig. 6.3).

The details of agricultural practice in the Neolithic (pre-historic) period are not well documented either, only the types of plants cultivated, the loss of forest trees (pollen records) and development of animals, mainly for food (carpology) can be stated with certainty. However the use of animals for traction can be determined by bone deformation. One can assume that use of oxen (cattle) could well have been for pulling a plow over the ground to replace human energy. The first evidence of such agrarian systems occurs some 3,000 years BC in Alpine cave paintings (Guilaine, 1989, p. 126). Such a step most likely created the necessity of keeping these animals close to the habitations, and hence created a ready source of manure. Clark (1955, p. 196) indicates this necessity and use for communities at a slightly later date (perhaps 1000 BC and later further north) for areas to the north of the Alps in the deeper forests. The earlier models seem to be present in the early bronze age in the Mediterranean area and iron age in northern Europe. It appears that there is an association of metal working with the appearance of the ox – drawn plow. This is reasonable enough in the problem of fixing a sufficiently resistant stone on a plow point was surely not a trivial problem.

The presence of work animals is of double importance, one for a multiplied capacity to work the earth, digging and conditioning it. A second is the presence of stabled animals and a source of manure. Manure as we know (or will see in Sect. 6.2.3) is a very powerful fertilizing agent and one that keeps fertility of the prairie soils at an optimum despite the extraction of soil resources in the proceeds of the activity. The use of animal manure to maintain or increase fertility is of course a major advance in agricultural practice. It is apparently of quite ancient use then,

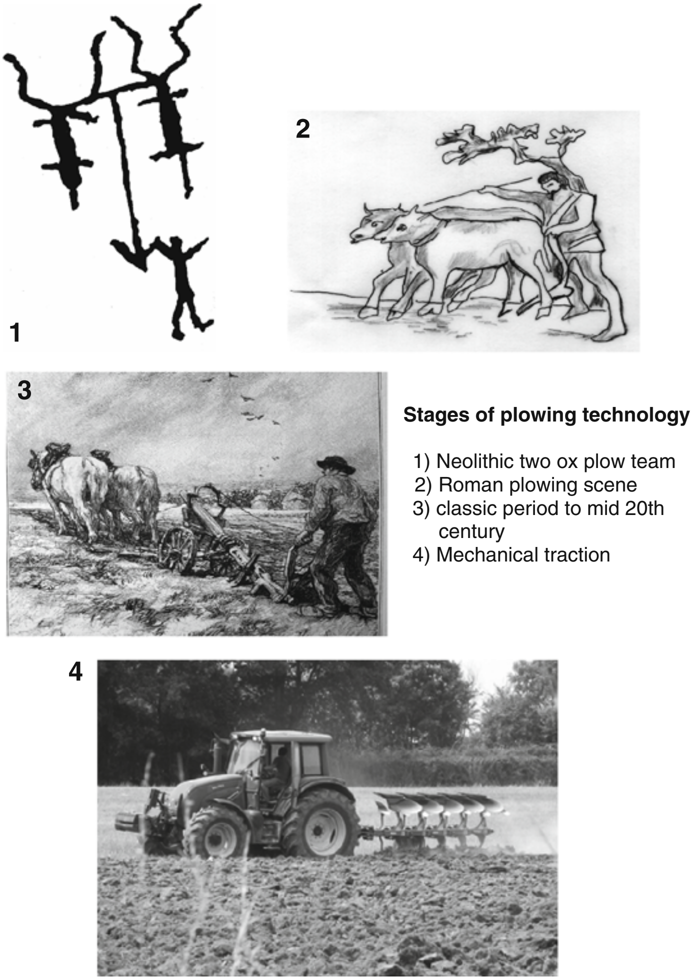


**Fig. 6.3** Stages in the methods of plowing the earth with a different types of traction. (1) Initial stages shown in a sketch of a late – Neolithic cave painting. Note the two oxen team used to pull the plow, adapted from Duby and Wallon (1975) (2) Sketch of a mosaic representation of Roman plowing techniques (sketch, BV, of a floor mosaic, National Museum of Antiquities Saint Germain-en – Laye, France (3) Plowing scene from the late 19th century in France, Leon Lhermite (4) advent of motorized agriculture, late 20th century (photo DV)

being practiced for 5,000 years or more. In this way the foundation of the renewal and maintenance of crop land fertility was established in Europe with the change in soil chemistry by forest cutting and the introduction of prairie growths using animals grazing. The use of animal traction and use of manure finished the gains made by potash fertilizer use, and crop rotation. The fundamentals of agriculture as we knew it up to the mid 20th century had been acquired.

A second vector of neolitithisation occurred. Instead of going north and turning around the alpine and associated massifs, a vector of Mediterranean coastal change occurred. along the Italian coast and along the French eventually reaching Spain. Phillips (1982) indicates the steps in this process along the French coast. Here the initial sites of settlement agriculture and domestication or use of domestic animals was first practiced along the coast and in river delta situations, and massif edges but not in the deeper forests. Initial lodgings were in caves and rock shelters. After some time dwellings expanded into open air sites. And around 3500 BC the Neolithic system was installed, farming, pottery, herding and the use of domestic animals. The process was less expansive but followed basically the same pattern as in north eastern Europe, except perhaps that the problem of forest soils was less evident, agriculture being implanted in less vegetated areas along stream bottoms and river deltas. Progress along the coast was clearly accomplished but penetration into the land mass was much slower that the corresponding movement to the north of the Alps.

Kleber et al. (2003) found that the best way to identify the agricultural activity of Neolithic farmers in loessic soils of Germany was to analyze the soils for potassium content and remains of charcoal. The mark of the new agriculture in forest soils was one of wood transformation to potash bearing ashes which was maintained in the surface horizons by the development of prairie soils through the use of grazing animals and then crop rottion.

#### 6.1.2.3 Agriculture in the Classical Age

The stage is now set for classical agriculture, that lasted in Europe roughly from a thousand years BC up until 1950. We have some written accounts of these systems in ancient Greek texts, quoted by de Serres (1600) and Toutain (1927) where Pline, Virgil, Columelle and Plutarch among others writing in the period of 300 BC 100 BC indicate that crop rotation and fallowing were approved practices, manure and green fertilizing was also important. Using lime is also mentioned. Burning in the fields in autumn was used as a control of weeds and pests. However by this time climate change, warmer and drier, and probable intensive agriculture made it necessary for the Greeks to resort to importation of grain from other Mediterranean regions and the Scythian plains.

North of the Alps and to the west, iron age agriculture was practiced in much the same way. It appears that fallow – cultivation cycles were practiced (Ferdiére et al., 2006). It also appears that planting legume type crops was not practiced as much as it was to the south. From archaeological evidence the use of an ox pulled plow was common, using a metal pointed plow shear. Also different types of hand tools probably used for hoeing and weed control have been unearthed. The initial heavy work done by animals and the more detailed and specific work being done by man. Animals became an intimate part of the daily farming practice. The use of fibre and animal skin was certainly of great importance. In the early Iron age (700–400 BC) it appears that a rather wide diversity of grains was used, perhaps to counter climatic influences on the success of a single type of crop. Later there is a tendency to have only one type of grain present. Here one finds evidence of cutting the prairie to make hay, which indicates the presence of animals in enclosures over the winter period. This reflects the writings of classical Greece which indicate the use of manure in the fields. Also the use of lime or carbonate rock on acid fields was practiced. The abundance of nitro – philic plants, or weeds (nettles for example) indicates the use of manure on agricultural fields.

Here we have a mastery of the concept of crop rotation and fallow, where the extraction of mineral resources from the soil is compensated in part by additions from below the soil zone (deeper root penetration and uplift of nutrients) and a period of time where plants and bio-agents could extract elements from mineral sources available but of slow release rate in the soil zone itself. Legumes were used to enhance the nitrogen content of the soils, and corrections for natural acidity were made using lime and calcareous rock. A portion of the plants taken from the soil were re-employed in the form of fertilizer, rich in potassium and also in ammonium which aided the bacterial increase in the soils. It appears that in the Classical age the means of plant manipulation were clearly mastered, using the resources of animal and other transformations of natural and plant material from the cultivated land.

Diversification and specialization occurred, trees and fruits were present and vineyards became the source of a large amount of commerce between different parts of the European world. Agriculture became a longer range commercial affair. Better transportation, using wheeled vehicles on paved roads (Roman) allowed and encouraged exchange and specialization of agriculture. Wine amphora of various regions found virtually all over the Empire attest to this. Instead of being tied to local conditions, use of the land in one area could influence the use of its products in another.

It seems that the mastery of plant manipulation and the use of animal by – products had become mastered techniques before our era. The transformation of forest soils into those useful for prairie plants was accomplished and maintained by grazing, prairie and fallow cycles, hay cutting and manure use. Wood ash was employed as a source of potassium and a means of increasing pH and lime was used to this effect also. These measures were adopted to change the chemistry of the soils so that plants of prairie origin could prosper. The forest lands were those of higher rainfall than that of the natural prairie – steppes, and thus the output of agricultural land was increased by installation in more northern areas than those of the Near East. The climate change of drier and warmer conditions experienced in the period of near 2000 BC in the Near East (1994) creating the collapse of the great bronze age civilization centers was a final push for development of these wetter northern sources which had already succumbed to the Neolithic revolution. The centers of power shifted as the Mediterranean was subjected to a more Mediterranean drier climate.

The agricultural cycles would then be gradually adapted and improved using different methods of manipulation of plant soil relations.

### 6.1.2.4 Agriculture in the Post Middle Ages in Europe

The continuation of agriculture was practised after some interruption during what are called the dark ages, the period of about 700–1000 AD. Significant re-organization and better practises were accomplished during the times of Charlemagne, but progress was slow. Fragmentation of land resources and markets did not encourage efficient production. For a long period land owners essentially owned the working class on their lands, the feudal system, which did not encourage production. However gradual sales of land to peasants and the use of money encouraged a surplus economy of agricultural production (Duby, 1962). In the 12–13th centuries things got better, land was reclaimed from forests developed on abandoned areas after economic stagnation and as a result agriculture progressed. Crops were more diversified, sale of animals and products in local markets gave a bit of relief to the limitations of isolated production and reliance on individual resources. Markets meant that a good crop would be stored for same at a later time, and not only at the profit of the land owner be it the local lord or the church, which owned and had much land farmed.

The structure of agriculture in the 16th century was one of diversity, relative, and a more market oriented economy. The following is based upon the account of agricultural practice given by Olivier de Serres in his study commissioned by King of France and published near the end of the 16th century as well as details of 17th century agricultural practice in Center Western France (Merle, 1958).

Movement of agricultural products was important in certain regions where an excess over consumption was possible as was generally the case after the periods of plague and ensuing wars of the 14th and 15th centuries. Wine was produced for export outside of the local consuming area, grain moved over some distances and useful items of manufacture found their ways into farm households. However, the farmer, and people writing in his stead, proposed numerous ways of managing natural forces and of manipulating nature. The old methods of crop rotation with fallow and prairie use were institutionalized. Cycles were established which often took into account the local vegetation and geological (soil chemistry) constraints. Here we have descriptions and reasons given for specific agricultural practices which have become lost to us to a large extent today.

#### Judicious Use of Fire

The use of fire was very important to farming in the period considered (Sigault, 1975). It had been practices in various ways before, clearing land, providing wood ash as fertilizer and a means of changing pH, and one of controlling insect, bacterial and other pests. Thus burning un-need straw and plant refuse in the fields was an advised practice. At times and when available understory plants such as ferns were gathered, placed over the fields and burned. Here the use of fire for prophylactic purposes was evident but also the understory growth in forests is well known as a source of potassium. In fact during these periods ferns were used as a source of potash in glass making in France. Burning these materials on the soil then served two ends addition of fertilizer and, equally important, pest control. Weed seeds were destroyed and pests were largely eliminated from the soil surface.

The practice of burning was also used in a slightly modified manner to another end. The use of prairies was common, one where land was but into prairie for 6 years or more in order to restore fertility for grain crops. The land was of course not left un-tended, animals were grazed which was an important source of income for the polyvalent farmer as most were. In these times specialization was rare except in mountain areas where grains could not be successfully grown. The problem with a prairie is that it leaves a very dense root mass and a lot of weed seeds behind. If this is plowed and seeded, most of the crop is unwanted material. The solution to this problem was fire. However one needed to reduce the root mass and disaggregate it. The method is called *ecoubouage* in French, practised in most European countries north of the Alps.

The system consists of stripping the sod from the prairie and reducing it to ash and charcoal by slow burning. The sod is piled into mounds and set fire slowly from the center. This is the same method used to produce charcoal. Here the root mass is reduced greatly and totally de-structured. The clays are heated to temperatures high enough to de-hydrate them and rupture the crystal structures thus releasing the potassium held in mica flakes. The roots that become charcoal present a highly active surface that can fix cations and release them increasing the cation exchange capacity of the soil. In recent "discoveries" based upon observation sin Brazilian steppe – forest areas, this system is called "biochar", where there is a distillation of organic matter to produce charcoal and recuperate the organic gasses to be used as fuel. This latter aspect of course escaped the farmers of the middle ages to modern times in that they had no vehicles that needed to be propelled using paleo – biofuels. Since petroleum and the internal combustion engine were to be found in the future, the farmers let the organic gasses escape, but as slowly as possible in order to gain a maximum of carbon in the residual matter.

Once burned, the residue is spread over the field and it is ready to be plowed for a grain crop. Numerous tools were developed for this process, starting with hand tools similar to flat hoes and eventually plow like wheeled tools were developed to slice under the root structures and loosen them for stripping.

Thus not only did one produce ash fertilizer, de-structured clays and charcoal but also the insects in the soil and bacterial and other diseases harboured there were destroyed. This soil could then be planted with significant hindrance due to the development of unwanted materials. One must remember that weeds were the greatest enemy of the classical farmer. This is why fallow fields were not left to the installation of new plants but were plowed during the year and weeded by successive cultivation.

Use of fire was then an integral part of agriculture for a long period, mentioned by classical Greek authors and continually practised until late modern times.

### Crop Rotations and Green Manuring

Again, the ancient Greeks (those of the classical period at least, around 300 BC) found that the use of leguminous plants to enrich the soil was a good idea. In fact the methods persisted into the 17th century where such use is clearly described. Flat beans (feves), alfalpha and peas were turned into the earth before maturity in order to enrich the soil. This of course increased the nitrogen content since these plants are known for their symbiotic use of bacterial to fix nitrogen in great quantities, but also the potassium content of the soil. Legumes and especially alfalfa are "luxury consumers" of potassium, bringing up more to the surface than they need for their proper growth. This practice was also used to increase fertility in vineyards where crop rotation is of course difficult. The legumes were sown between the rows of vines and plowed under in mid – season (de Serres, 1600, p. 209). The concept of green manuring is essentially that of using mineral resources brought to the surface by plants in order to increase the abundance of these elements when less efficient extractors are planted such as grain crops. The green manuring is simply the direct transfer of mineral and nitrogen into the A horizon of the soils. The elements concentrated in the plants are returned directly to the soil. Since much of the material in the plants has been taken from different parts of the soil but also alterite horizons, this represents an increase in the soil zone of nitrogen, potassium, calcium and so forth.

These methods were of course combined with various methods of crop rotation. The specifics of changes in plant cycles depended upon the type of terrain at hand and hence no one single crop rotation scheme was proposed in these times. However, it was proposed to plant a grain crop and alternate it with fallow (no plants growing in the fields) and gain several times and then a use of prairie established for more than seven years to increase the nutrients in the soil. Usually the cropping sequence was similar to or less than the time in prairie culture.

### Fertilizers

In this category the agricultural writers put mineral as well and vegetal materials. The use of wood ash was still practised, and a certain amount of importation occurred. This changed the pH and the potassium content of soils. Mineral components were mostly designed to change pH, lime and clay – rich carbonate rocks were used as modifying agents. The pH value was of course important for the well being of prairie plants, and the preservation of the organic matter which captured and fixed alumina.

The most important fertilizer was that of barnyard manure. This was the golden resource of a farm. Since the working animals and others were stabled in the winter, and some for other parts of the year such as milk cows, this material was abundant and extremely efficient in transferring ammonia and potassium to plants. Since animals do not retain potassium and not much nitrogen, the residue going through their systems is deposited on the stable floor. The easiest way to clean it up is to put a layer of straw down before the animals come in the stable. This mixture of straw and animal excretions is a very, very powerful agent when applied to soils with a reasonable cation fixing capacity. Its use of course dates from the post Neolithic times, roughly the beginning of the Bronze Age when oxen were used for pulling plows and farming had settled down for long periods of time in the same place. Returning much of the mineral resources to the soil and extracting only the grain was an important procedure. Russell (1945) shows that the effects of farmyard manures are strong in the first year after application diminishing some over the following four or more years. Fallowing increases nitrogen availability for the first year but the effect is negligible after that. In grain cropping one has an average yield 3.5 times greater using manure than not. Taking away all of the plant materials is of course not possible for a sustained agriculture system. One must remember that the farmland of Europe was used for agricultural purposes for about 6,000 years or more before modern methods managed to "wear it out" and exhaust its naturally maintained fertility.

The use of lime, calcium oxide, known from Greek times or earlier, can be associated with problems of pH in changing or modifying forest soil acidity to be more compatible with prairie soils. However, another aspect is or was known under traditional farming methods. Liming was used in conjunction with manuring, after the organic matter was deposed on the fields (Richeyre, 1884, p. 80; Cox, 1925). This action was reputed to make the manure more efficient, releasing ammonium from organics and probably potassium by cation exchange.

Use of wood ash as fertilizer was practiced from Greek times (Sigault, 1975, p. 102) which compensated the extraction of mineral elements taken away by crops. It was practiced until the 19th century.

### *6.1.3 Summary of Classical Farming Practice*

From the beginning much of European farming was concerned with maintaining a prairie type of soil where forests where converted into farming land. The process found its limits in the northern areas where dense conifer forests proved too much for the process uses (Clark, 1955). Crop rotation was used, using legumes (lentils or alfalfa) alternating with grain crops or by leaving the land fallow (plowing and cultivating but not planting it). Nevertheless long periods were needed to re-generate or maintain the soil characteristics of pH, and type of organic matter by putting the land into prairie which was grazed. As animals were used in greater numbers for traction, stabling increased and the resulting manure was spread, used as a re-generative method on all fields especially those that were cropped. Thus the manipulation of plants and use of animals and mineral materials changed the character of the soil from forest to prairie type where graminae plants could grow.

Further manipulation of plants was used in order to maintain a fertility of the soil which could then bear the extraction of natural soil resources, especially mineral ones. Fallow allowed clays to be slightly dissolved by rain water interaction. Prairie, grazed but not cropped, was used to bring mineral resources to the surface from depths by plant root extractions. Crop rotation allowed enrichment of different mineral resources or at least differences in extraction rates from one year to the next.

Manuring was a method of recuperation of a part of the mineral resources extracted and transported from the land. The return in a more assimilable material aided greatly to the renewal of soil fertility year in year out.

Control of pests was accomplished in part by the judicious use of fire to get rid of weed seeds and various pests in the soil. Liming had this effect to a certain extent also (Richeyre, 1884).

The practice of farming changed but little, in concept, from late Neolithic times until the 17th century in Europe. Tools were improved, had hoeing and ground breaking was replaced by ox drawn plows, different metallic tools for hoeing and cutting were developed in the iron age but the essential concept changed but little. Animal – plant relations remained much the same. Crops were much the same and crop rotation was similar depending upon the soil substrate and climate regime. Once the basic pattern was found during the Neolithic expansion the structure of farming and its concept were very similar over the ages. Agriculture was waiting for the scientific revolution.

## *6.1.4 Science and Agriculture*

### 6.1.4.1 Eighteenth Century Experimentation and Improvements in the Use of Plants

The big problem, for many agronomists in this period, was that the prairie cycle of crop rotation schemes was quite long. About half of the time a parcel of land was under grass and the rest in grain and fallow cycles. If the major product of meat was easily exported and sold, this was fine. But if one needed more durable goods, transportable over longer distances and capable of distribution throughout a year or several years, animals and meat were not practical. However wheat was. An effort was thus made to reduce the prairie regeneration cycle and deliver the agriculture of the period from the cycle of prairie and culture. The remedy was proposed by Henri Pattullo to Madame de Pompadour, a good friend of the French king, in 1763. Undoubtedly he was not alone in finding out the secret but he seems to have wished to have been. However his proposition was a concrete one, more tax money for the crown due to an increase in productivity. This was by no means a small thing, if it could be realized.

Two things needed to be reduced in the cycle of alternating, one the long period of prairie (6–10 years) roughly half of the time and the other the fallow periods alternating with grain crops. Often one had viable crops but only one quarter of the time. Pattullo proposed to reduce the prairie portion of the cycles by introducing new plants: clover, alfalfa or sainfoin. Three successive grain crops and fallow were followed by a crop of rye grass mixed with the above plants. The productivity of the non-grain artificial prairie crop was such that it could nourish more animals than the ordinary prairie. Here then the grain crops were present half of the time and artificial prairie and fallow half. This is an increase which doubles the periods of grain production on the same land. The use of clover, alfalfa or sainfoin depended upon the type of soil, clay – rich, intermediate or sandy. Thus the artificial prairie was adaptable to different types of soils and climates. This was very useful in France where climates change and the geology dictates different types of soil chemistry.

Henri Pattullo gives due credit to his predecessor, Olivier de Serres, in 1600, in that the use of clover, alfalfa and sainfoin was already prescribed but not in such a concentrated way and in such a short succession after grain crops.

This new method or revolution of agricultural practice, doubling the productive cycle for grain crops was one of using the natural resources in a prairie but in a concentrated manner. In the natural prairie one has grasses, legumes, and other plants of less nutritive value. Garola (1918) indicates the extreme variability of natural prairies which depend upon climate and soil substrate. Grasses dominate, but not always, with different proportions of deep rooted plants and legumes. In a natural prairie, and the artificial one of course, when animals are pastured, they leave behind them all of the mineral resources, taking away only nitrogen and of course carbon – hydrogen compounds. Thus grazing of the artificial prairie was recommended. One can compare the relative amounts of nitrogen and potassium in clover, alfalfa and grains (Richeyre, 1884, p. 23):

| | N% | $K_2O$% |
|---|---|---|
| Clover | 21 | 19 |
| Alfalfa | 22 | 15 |
| Grains | 4 | 5–6 |

In fact the new agriculture proposed by Pattullo (1758) was the selection of the deep – rooted, leguminous plants which were present in minor abundance in natural prairies. The selection of the nitrogen – rich and potassium – rich plants, those that concentrate these elements by different methods, was the innovation. Of course animals could well eat grass but the more deep – rooted plants brought more mineral elements to the surface soil zone. Here again one sees manipulation of natural elements to the overall goals of agriculture. Reduction of the long prairie cycle was effected by concentrating the useful plants in the prairie so that their benefit was concentrated and as such could be used to reduce the long period of non grain farming. Along with other uses of methods already known, such as liming, claimed by the English as a remedy to many problems of agricultural production, the system of agriculture was much the same up to the 19th century. However, at that time significant changes in agricultural practice occurred, if not on a massive scale, but on a philosophical scale.

#### 6.1.4.2 Nineteenth Century Innovation Through Chemical Investigation

In the 19th century modern science entered into the agricultural picture in Europe. Chemistry and plant husbandry joined forces in an attempt to ameliorate the economy in a rational and modern way. Agriculture was an early field of application of modern science. The method of investigation was by chemical analysis. First the composition of plants was determined, thus establishing their potential needs. When the different proportions of mineral elements were determined, an analysis of the soil components was made. Then depending upon the potential needs of plants, different fertilizer agents were dissolved and poured over soils. The amount of the different components retained by the soil was measured. Using these determinations the scientists determined what elements could be retained by soils and which could not. The consensus was that potassium, and ammonium (nitrogen) were retained as well as phosphorous. Thus soils could be reservoirs of the vital elements needed for plant growth. If traditional methods of fertilization did not fulfil the needs of a given soil and crop situation, one needed to remedy this by the use of concentrates of the needed elements.

This knowledge initiated the use of artificial fertilizers. Larbaletrier (1891, p. 55) notes that the elements which nourish plants (N, K, P) are fixed in the soil (A horizon or cultivated zone thereof). The logic is to replace those that lack by adding them from external sources. One needs only to analyze the soil chemically and add the needed materials to assure the growth of plants which extract these elements from the soil. This was of course understood implicitly by previous farmers who used plant alternation mechanisms to bring up nutrients to the surface and returned a maximum of nutrients after they had been cycled by animals. Use of ashes increases the potassium content of the soils also.

This being the case scientists began to search for sources of these elements found in nature and methods of rendering them more active chemically in soils (Larbaletrier, 1891). Two dates are important, the early 1840s when the source of phosphorous was associated with geological deposits rich in the mineral apatite, which was rendered chemically active by the Liebig process to make what is called superphosphate. One advantage of such sources is that such natural phosphate deposits (essentially concentrations of animal bones of different sorts often fish remains) are reasonably abundant and widespread in regions with sedimentary rocks of Mesozoic and Tertiary age. Chemical treatment using sulphuric acid in factories allowed widespread use of this fertilizing agent.

The second date is 1861 when the mineral sylvite or potassium chloride was discovered at Halle in Germany. Here no significant chemical treatment was necessary for use and the mineral could be shipped directly to the user. Other deposits were discovered in Europe, in Alsace notably, after this. Thus two of the major mineral fertilizers were made available in a large supply. Previously in the century wood ash from the United States and Russia was imported as fertilizer.

Earlier in the century sodium nitrate, “caliche” evaporate deposits were imported from South America but their price prohibited widespread use. Potassium nitrate, saltpetre, was also known for some time, the 17th century and before, but its relative scarcity made its use more restricted to industrial processes such as glass making.

The use of cheaper, more concentrated agricultural mineral chemical promised much for the development of agriculture. However, the availability of these products did not much change the average productivity curve, at least in France (Fig. 6.4). The trends of average production in one of Europe’s greater agricultural countries were not much changed by this new knowledge.

One of the major problems was the relative cost of the new chemicals. Most farmers were too traditional to invest systematically in chemical fertilizer when climatic differences from year to year could wipe out such investment. The gains were not seen as being worth the risk. Thus although the technology said a new way was

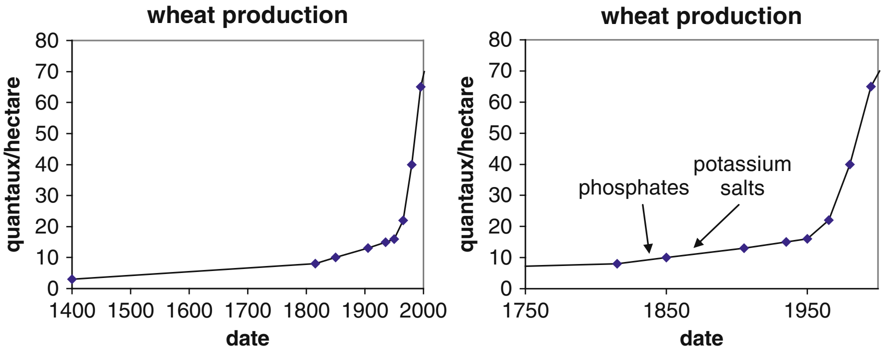


**Fig. 6.4** Wheat production in France (data from Duby and Wallon, 1975, 1976a, b). Overall the productivity per surface area changed gradually over the centuries from 1400 to 1900. The discovery and introduction of natural chemical fertilizers (potassium and phosphorous) did not the average productivity significantly in the 19th century. Major changes in productivity occurred in the latter half of the 20th century

possible, major change did not occur. The productivity increased by general better management over the period 1750–1950 by about 2.5 times all the same, in a gradual trend. There was no great incentive to invest more in the production of a crop if the value was not a significant compensation. Population pressures were not great yet.

#### 6.1.4.3 The Truly Revolutionary Agricultural Revolution

From the earliest times agriculture in Europe rested upon the same sets of knowledge, managing and manipulating plants and soils. The crop rotation system, the use of a fallow period and the re-generation of the basic prairie soil chemistry by alternating crops with prairie natural or artificial, were essentially natural practices. Recuperation of chemical elements by the use of manure was also in this tradition. In the United States mechanization in the form of replacing animals with motor driven vehicles began before the Second World War but in Europe the change took place massively in the 1950s. Perhaps the Marshall Plan had an influence in that money was available to buy American products, such as tractors. The effect was stunning for many reasons. In Fig. 6.5 one sees the change in the number of tractors in France.

The tractor population increased seven fold in 20 years while the cultivated surface area decreased by only 10%. Thus one sees an intensification of agricultural effort. The results are rather evident in looking at the average productivity for wheat in France over the period (Fig. 6.4).

Wheat productivity increases 4.5 times. Since the surface area did not increase but slightly decreased, gain in productivity is due to the use of machines but more so the use of artificial fertilizers. In Fig. 6.6 one sees that the use of ammonium was greatly increased also.

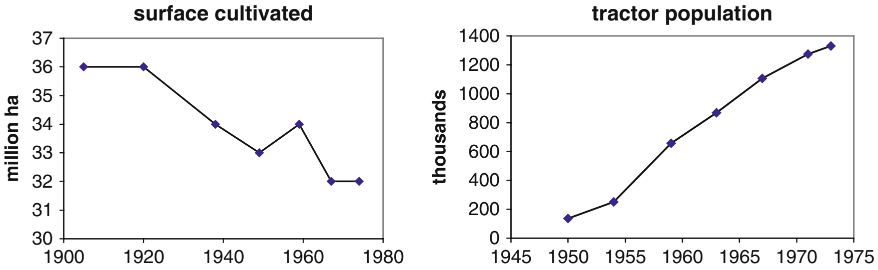


**Fig. 6.5** Graphs of tractor population and cultivated area in France (data from Duby and Wallon, 1975, 1976a, b)

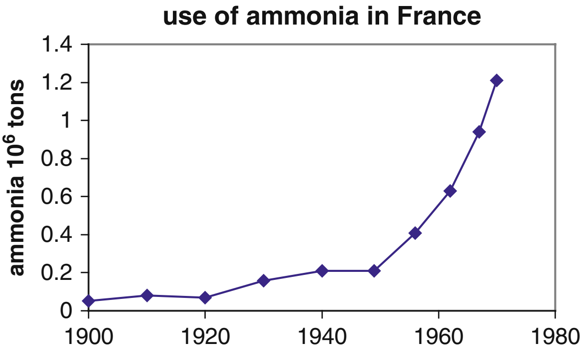


**Fig. 6.6** Use of ammonia in French agricultural practice

Artificially captured nitrogen was a necessary additive in that the traditional source, manure, essentially no longer existed in that traction animals, horses and oxen, were replaced by non-manure producing machines. Since draught animals used about 25% of the productivity of a farm before the mechanical revolution, this effectively increased the cultivated land areas but the fertilizer that they provided had to be replaced, and in this case it was by factory transformation of nitrogen from the atmosphere into a stable chemical form, ammonia or ammonium salts. All of these processes, mechanical traction and artificial fertilizers, were obtained by the use of fossil energy, or is some cases water driven electricity production such as in the Tennessee Valley Authority plants in the United States. Here the use of external materials and chemicals radically changed the relations of plants and soils. In a sense the modern world was born.

Looking again at data for agricultural France, one can compare the agricultural productivity with population growth. Traditionally since the 13th century of so the population of France held near 20 million people. However the 18th century saw a steady and eventually dramatic change in population (Fig. 6.7). The curve increases very dramatically only to be slightly interrupted by the period of 20th century wars but has resumed since that time, especially in the period 1950–1970. If one considers the productivity and populations in this period it is clear that the rather gradual

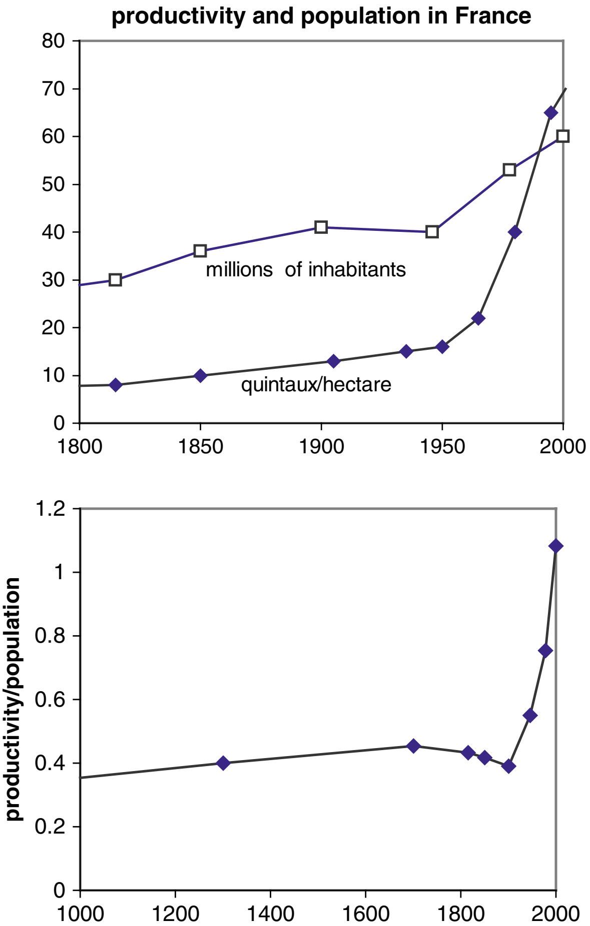


**Fig. 6.7** Comparison of the productivity of wheat and the population of France in the 20th century. (Duby and Wallon, 1976a, b)

increase in productivity before 1950 more or less kept up with population increase. The graph shows crop production divided by population. The explosive growth in production made it possible to eat differently. As is generally the case today, much of the crop production went to the production of meat. Thus diet changed as more was produced from the land.

The last part of the agricultural saga in Europe shifts out of the manipulation and fostering cycle of plant soil inter – relationships to one of a type of industrial use of the soil. Since the replacement of fertility usually practised using animal by – products, manure, was no longer possible and was replaced by powerful fertilizers, the increase in plant growth seemed boundless. Traditional grain production in the Middle Ages was on the order of 6 grains harvested for one planted. Today corn production in the United States in on the order of 280 grains harvested to one planted.

There seemed to be no reason to alter this type of development. Nature was and is essentially ignored in agricultural practise.

### *6.1.5 The American Experience: A Counter Example of Soil Use in the Classical Period*

The New World of the 17–18th centuries on the North American continent provided apparently unlimited fertile soil for farming. The major reason for immigration was for farming land which was in apparently short supply in the Old World. The methods of farming were initially probably relatively close to those practised in Europe but apparently rather rapidly they were modified. It seems that the several millennia of farming and apprentiship on European soil had been forgotten in the land of plenty. An English agronomist, Arthur Young wrote to George Washington concerning the economics of the American experience. He wanted to know what enticed or motivated the Americans to use so much land so quickly. The letters of George Washington (1801) are a fascinating response to the questions of Mr Young. Not only did Washington respond with accounts of his estate at Mount Vernon but he asked several of his colleagues, Thomas Jefferson, Alexander Hamilton, among others, about the economics of farming and we have these letters also. Young was interested to see if slavery, the cost of labor, had a role in the methods used, but Washington was convinced that the abundance of new and very cheap land was at fault.

From these letters we have a good description of farming methods on the East Coast of the United States. One must remember that the area farmed which Washington discusses was based upon deciduous forest soils. It was not until the 19th century that American farming got onto the very rich prairie land which responded differently to the farming practices of the period. On the East Coast, deciduous forest was dominant and gave rise to reasonable fertile soils. They were comparable to the types found in many places in England. Therefore the comparison sought by Arthur Young was an apt one.

Essentially Washington described what was going around him and had so for several generations. He describes the use of land from the time it was bought and then cleared for farming. This indicates essentially virgin land in many areas of his surroundings. Typically farmers used the land in three parts: cleared and farmed, parts being de-forested and land to be cleared. Initial farming of wheat gave roughly 20 bushels/acre (some 300 kg/ha). The land was cleared and the wood seems to have been used as such or burned but no mention is made of using wood ash as a fertilizing agent in the discussion of Washington. However he does mention slash and burn practices which indicate at least some return of wood ash materials to the land in the first stages of culture. This initial productivity of 20 bushels could be increased to 30 or 40 bushels with vigorous manuring and crop management.

The crops of most new farmers, the more recent immigrants of whom Washington did not especially approve, seemed to have been wheat and “indian” corn or in some places tobacco. All three were reputed to extract native fertility rapidly. Frequently the tobacco land was planted for two consecutive years followed by wheat or corn. After several cycles the productivity was reduced to 10 bushels an acre. The newly cleared land was then put into production. This wasteful method of farming seems to have been especially practised in the southern States (tobacco country) where as in Pennsylvania for example, more conservative farming practises were employed. The use of legume crops and artificial prairies was not practised on the tobacco lands. As Washington states, after this initial cycle of "scratch" farming, one has two choices: either resort to crop alternation and manuring or to move on, over the mountains to the west where more cheap and plentiful land awaited. Washington himself, in writing to Arthur Young asked for the best grades of clover and alternative prairie seed to be sent to him, and thanked his colleague when such was received. Animal manure was a vital part of his agricultural practices, green mauring also and grazing cattle on either natural prairie or planted prairie as part of the rotation scheme.

The practice of rapid clearing of virgin forest and apparent small use of the wood ash resource is mentioned by Hall (1829, p. 71) when he describes the spectre of girdled trees, dead and uncut in the farmlands of north western New York State. Land was cheap to new farmers accustomed to much higher prices in Europe, and as such its use was much neglected. A century later Cox (1925) devotes a Chap. to growing crops in well-planned rotations. Chap. VII tells how to Maintain the Fertility of the Soil by crop rotation, growing legumes (alfalfa, clover, etc.) use manure, lime and phosphate, potash and ammonium fertilizers. All but the last are of classical Neolithic practice, and rock or refined mineral resources from the 19th century.

However here in the early 19th century one is more worried about the fertility of the plains areas or woodland – prairie soils more than the deep oak forests of the East Coast. In looking at the maps of corn and wheat acreage planted in the United States in the 1920s it is clear that much of the agricultural land of the time of George Washington had been abandoned. Some land was put into production on the West Coast in California and especially Washington State and Oregon. Even though Washington demonstrated how to re-gain soil fertility, much of the land given to agriculture was abandoned on the East Coast and is now in forest. Curiously, the forests of the United States supplied wood ash to farmers in the early 19th century before mineral potash sources were used in the 1850s. This material did not appear to be used to re-generate fertility on American East Coast farms of low productivity, combined with manure of course for ammonium.

It seems clear that it is quite possible to reduce the fertility of land by using crops that extract much of the mineral nutrients. It is not that such land is no longer useful. Washington insists that by careful planning and use of manure, one can restore worn out tobacco land to a high fertility, three times that of the depleted state. In Table 6.1 we indicate the relative fertility in kg/ha in the time of George Washington.

It is interesting to note that virgin land can have a still higher productivity when using crop rotation and manure as agricultural practice. This suggests that the method developed by the Neolithic farmers in converting forest to grain agriculture

**Table 6.1** Production in kg/ha using different farming practices

| New land recently Cleared | Manured and crop rotations old or new land | High use without return to the land |
|---|---|---|
| 300 | 450 | 150 |
| Wheat 1 in 3 years | Wheat 1 in 2 years manure | Wheat 1 in 2 years |
| 300 | 220 | 150 |

was more efficient and productive than using just the steppe lands for grain farming. The necessity of moving into forests can possibly be explained by an increase in productivity over the initial farming on the steppes, without an intensive use of stabled animals which produce the much treasured manure. The important point is that poorly used land can be put back into normal productivity by traditional practices. Washington was adamant on this point. No need to move over the mountains to make a living. One just needed to do some hard work, or at least spend the resources necessary to keep up a decent rate of production.

### *6.1.6 Change in Agricultural Land Use*

Modern agriculture changes the landscape and the soil upon which it is based. Tractors become larger and larger with time and as such they are less manoeuvrable on the land. They cannot move up hill nor can they move along a slope with ease. More and more land is changed into pasture or wood lot. An example is given in land use in France between the mid 19th century and the 20th century (Figs. 6.8 and 6.9). On these sketch maps one finds cultivated, prairie and woods or other non-farm lands. Of course at the scale of the maps, many exceptions are excluded from the general trends, but overall the information is instructive. In fact the large areas of farmed lands indicate small farms of multi-crop traditions, where the crop rotation and prairie schemes prevailed. Draft animals were used on hill sides and slopes and thus the factor of topography was minimized. However the use of the tractor, especially important after 1950, had he effect of suppressing the smaller cultivated areas favoring the creation of large fields which were more efficiently farmed using motor vehicles.

Hence a new era was born and land geographic areas created based upon topography and geology (soil substrate type). If on looks at the map, the area of Normandy (central northern peninsula) changed from a multi – use agriculture area to one dominated by grazed prairies hence the importance of the camembert cheese today. The Brittany peninsula (western France) was converted from the same type of farming to an area of enclosed farming of chickens and pigs. Thus changes in overall patterns in farming practice have affected France but of course other countries. For example, the traditional beef cattle cycle between the Midwest and Western states in the United States is largely ended, that where cows were born and bred on the high planes grasslands of the west, shipped to the corn belt of the Midwest after several

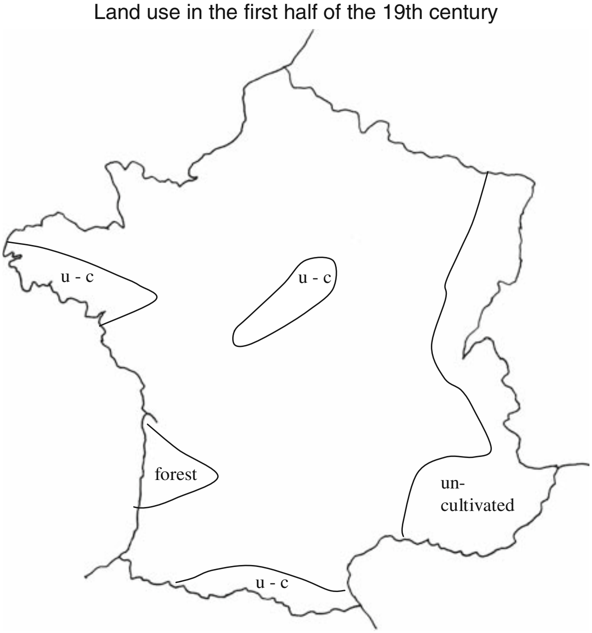
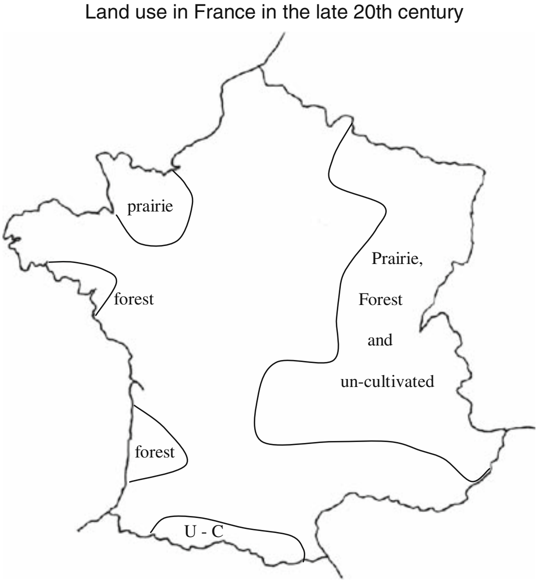


**Fig. 6.8** Land use in the first half of the 19th century. U-C indicates basically un-cultivated areas.(Ministère Agriculture, France 2001)

**Fig. 6.9** Land use in the last half of the 20th century in France. (Ministère Agriculture, France 2001)



years to be fattened and rounded out and then slaughtered in specialized units near or in the big cites of the Midwest such as Chicago.

In fact, the presence of farm animals has not decreased but probably greatly increased in the last half of the 20th century. Roughly 70% of the crops grown in Europe and the United States are destined as feed for animals. People in these areas surely eat more meat than people did in the preceding periods. Thus there is not a lack of potential manure for agriculture. Tractors have replaced horses, decreasing the numbers of farm animals used for traction but the numbers of pigs, cows and chickens has certainly increased. The problem is that the places of animal culture have been transferred from small units and dispersed areas to become more central and concentrated. Farm animal or meat production is now closer to the markets or performed on land less productive for grain and other food stuffs. In fact there is no reason that the manure of animal production cannot be used on the grain producing fields, except for its cost and difficulty in handling.

A particular disadvantage in intensive animal production is that the efficiency of such systems excludes the use of straw or other by products of grain farming. Moving animal dejection – laden straw (traditional animal barn yard manure) is very labor intensive, or at least enough so as to exclude it at present from common farming practice. When "raw" manure is spread on a field, it is mineralized by bacteria at a very rapid rate. However, traditional straw and dejection manure has a fertilizing effect which is useful for more than four years depending upon soil type (Larbaletrier, 1891). Of course George Washington was adamant concerning the use of manure fertilizer.

As a result of concentration and specialization in farming, the disposal of nitrogen – rich animal dejections causes water pollution problems where different forms nitrogen compounds find their way into drinking water resources. This is a paradox in that the intensive use of artificial nitrogen compounds as fertilizer also pollutes drinking water in grain growing area while the effluents from intensive animal production do the same thing. There is an over abundance of nitrogen on both sides of the food production structure in modern agriculture. It would seem reasonable to invest in some research to adjust these two agricultural systems so that a reasonable transfer could be obtained and that municipalities would not have to pay for expensive de-nitrogenating measures in the processing of water for human consumption.

The use of straw – based manure compost would also enrich the soil in a form of organic matter which appears to be more resistant to bacterial action than raw manure or green manure (Larbaletrier, 1891). The action of manure formation takes place over a period of several months where during this time there is most likely, a very high rate of bacterial action. One can attest this by looking at the steaming manure pile in the dead of winter. Manure is always over heated, due to bacterial action. This is one reason that it is applied on fragile plants in the ground during the coldest seasons. This bacterial action most likely produces a pre-humic material which is important to eventual clay – organic interactions when applied on the soil.

The major result of the new farming methods has been to increase productivity of a given land surface. The increase is so great that it more than compensates for the loss of some less productive types of land that have been abandoned to crop farming. Intensification of land use has led to dislocations of the two parts of agriculture, crop and animal husbandry which co-existed in many farm areas. Lack of natural fertilizing agents has led to the intense use of synthetic or mineral extracted fertilizing agents. Overall the system is immensely more productive than the traditional type of farming. However, there are several problems with such farming practices such as fertilizing agent pollution of water resources and pollution of the same water sources with chemical agents designed to protect the fast – growing plants from insect, mould and other attacks. These problems are beginning to be addressed by research at our major Agricultural institutes.

## 6.2 Effects of Modern Agriculture on Soil Properties: Organic and Clay Mineral Changes

As a reference point, we should compare classical agriculture effects, i.e. pre – 1950 in Europe and slightly before this in the United States with the changes that can be effected by intensive agriculture. There is not much data but one can refer to the results given by Kleber et al. (2003) who searched for methods to detect the presence of pre-historic agricultural activity. They found that in the A horizons of chernozemic (loess plain) soils in Germany, there was a distinct increase in illite in the A horizon compared to the C horizon. Illite peak height compared to smectite were clearly dominant in the A horizon and smectite appeared at 40–50 cm depth in the reference profiles whereas it was around at near 100 cm in the pre-historic farming sites. Other signs of old farming practice were found as traces of charred organic matter and a wider C/N ration in the surface horizons. These indicators can be predicted from the outline of the progress and practice in farming in Europe presented in Sect. 6.1. The efficient use of crop rotation, use of plant ash to increase potassium content and lower pH, lead to the efficient production of plants which bring potassium, and silica to the surface so that 2:1 clay minerals can be stabilized and so that potassium can be stored in these minerals when sources are sufficient to more than replenish the potassium is extracted in the form of crops.

Here it is clear that the traditional (from about 5,000 years ago) were efficient in stabilizing the potassium filled 2:1 clays. Thus one can use this as a reference for pre – 1950 farming.

On the other hand it is important to understand what will happen under the other extreme: water – rock interaction with a soil (i.e. formed under plant silicate interactions) an essentially fallow state. An interesting experiment in this sense was and is being carried out at the Agricultural Experimental Station of Versailles (France) reported by Pernes-Debuyser et al. (2003). Here experimental plots were kept plant free for 70 years and treated with different fertilizing agents. In the reference plot (no treatment and no plant interaction), there is a loss of organic carbon of 45% in the whole soil, and a similar loss in the clay fraction. Clay content decreases by 5%. Cation exchange capacity decreases by 43%. Exchangeable potassium is small in relative amount (1.5 % of CEC) but constant under the water – rock weathering conditions of the experiment. The initial clay assemblage, without chemical treatment, is dominated by illite/smectite interstratified minerals with some minor kaolinite and illite present in roughly equal proportions and a small amount of HI mineral. The water – rock interaction essentially decreases the illlite peak by about half, and shifts the illite/smectite peak to a higher (more smectie – rich and potassium poor) peak position. Hence the water – rock inter action over a 70 year period is essentially one of potassium extraction.

Fertilizer treatment with potassium salts and farm manure increase the illite content, decrease the HI mineral content and shift the illite/smectite position only slightly. Addition of potassium (and ammonium in the case of the manure treatment) then affect the illite content of the illite peaks more than the illite content of the illite/smectites mixed layer mineral.

Water rock interaction then decreases organic matter content, potassium content and decreases the clay content, most likely through the loss of the binding agent of the organic matter which fixes the clay fraction.

Given these data, one can attempt to understand the effects of modern agricultural practice on soil properties.

### 6.2.1 Organic Matter and Clay Content

Darmody and Norton (1994) indicate the relative effects of crop rotation or non-rotation on the organic content in mid western loess soils of the University of Illinois experimental plots. The study plots had all been farmed for some 50–80 years prior to the beginning of the observations. In all instances of cropping, 3 year, 2 year or no rotation, the soil organic content decreased. Analysis of the grass (sod) border of the plots showed an increase in organic content of about 30%. Thus all modern farming practices decrease the organic carbon content of the soil, non-rotation (*zea mais* cropping) showed the highest loss. Fenton and Lauterbach (1999) indicate that this effect is stronger on former forest soils than on prairie soils. In studies of various soil types where paired prairie and forest soils were observed, prairies were seen to lose roughly 30% of organic carbon under cultivation practiced for 100 years of less and forest soils lose some 60%.

One can conclude that modern agriculture, i.e. motorized, strongly influences the organic content of the soils, but not all that much more than the Versailles experiment of no cropping where similar amount of loss were observed. However, alternating crops with un-planted treatments (fallow) tended to increase the effect of loss of organic matter (Fenton and Lauterbach 1999).

### 6.2.2 Clay Content of Soils

Numerous studies report, though often make no comment, on the change in clay content of soils under cultivation. Darmody and Norton (1994) summarize published results on the importance of water stable aggregates in soils under different cropping practices. Compared to grassed soils, the stable aggregates are of course much less present, following the loss in organic matter. We give two examples here concerning two rather different situations, one in semi-arid alfalfa farming and the other in a rice paddy environment.

### 6.2.2.1 Lanzhou Alfalfa

In this semi-arid steppe province of northern China (Jiang et al., 2007) experimental plots have been observed for the changes in soil quality depending upon alfalfa cropping. The soils are based upon loess with a basic chlorite – illite mineralogy. The soil textural data indicates that, in general in all horizons, the clay content is related to organic carbon content (Figure 6.10). The range of organic matter is up to 3 wt%.

The amount of clay in the A horizon (0–20 cm) decreases with time. However the change is relatively small, 10%. This occurs when the organic content changes by nearly 10 but increases in the A horizon. Here the practice of agriculture does not impoverish the soil of organic matter but it decreases the clay content slightly.

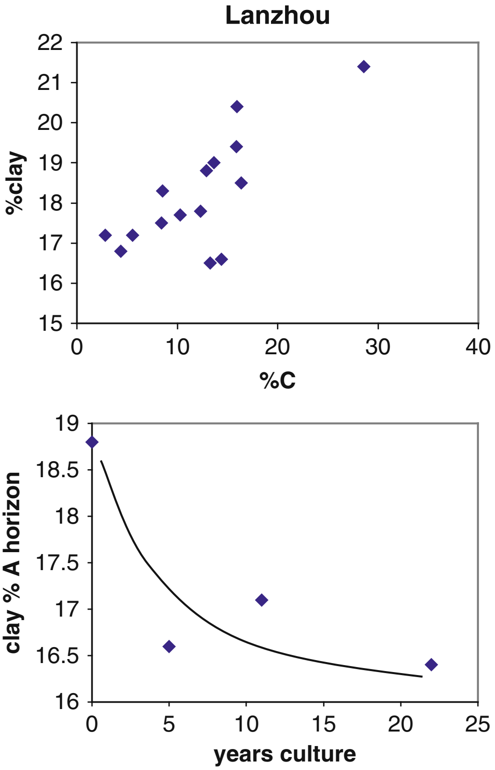


**Fig. 6.10** Relations between clay content and organic carbon in the Lanzhou (China) experimental plots, semi-arid climate where alfalfa is produced. The data is for the agricultural horizon of these soils (unpublished data of Yang Yanfang, Li Decheng, He Yue, Zhang Ganlin, and Hu Feng in Nanjing Agricultural Institutions, China)

#### 6.2.2.2 Rice Culture

Rice is grown in the Jiangxi province as in many parts of China, but here one has a red soil sequence based upon oxidized (red) Tertiary sediments. The clays are dominantly illite and chlorite. Iron content ranges from 5 to 3% varying inversely, after cultivation, with organic carbon content (Li et al., 2003). In the experimental plots of the Red Soil Station in this province, the system of flood irrigation has been used for periods ranging from 5 to 80 years. The clay content decreases rapidly with time, in the first 20 years or so, rising to above 1.5%. Here the system is basically anoxic where iron is reduced and organic matter is probably retained in a state of low maturation (bacterial action). The clay content decreases rapidly, when organic matter content is low, but stabilizes after 20 years of culture. Here the organic matter content stabilizes at near 2% and seems to fix the clay also. In the flood irrigation system it appears that high influxes of water can wash out much of the clay if it is not stabilized in organo – clay complexes (Fig. 6.11).

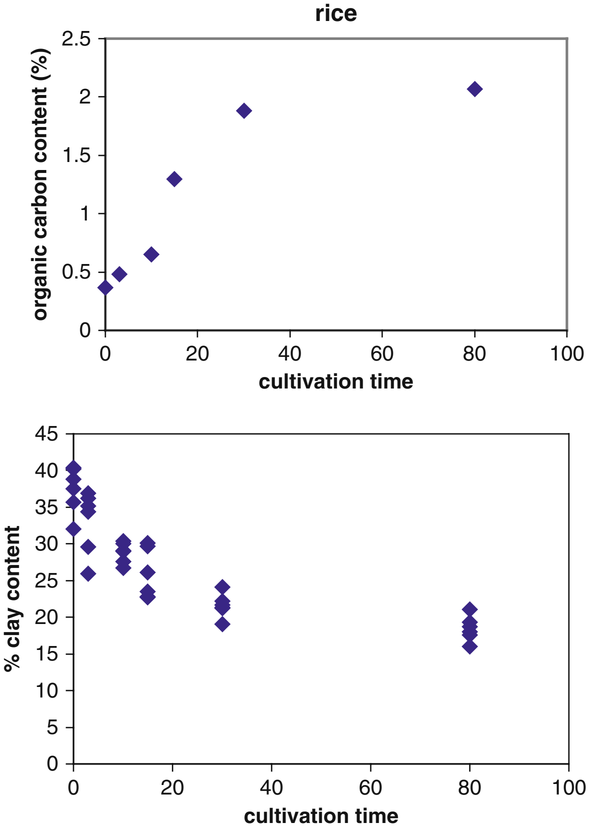


**Fig. 6.11** Relations between clay content and organic carbon as a function of time on an experimental Station in southern China (Li et al., 2003). The increase in organic matter in the flood irrigated soil plots appears to stabilize the clay content after a period of increase in organic content

The clays were stable in the initial soil, probably in part because of the cementing capacity of the iron oxides, but also because of the lower flux of water in the system.

## *6.2.3 Tillage Practice*

A study which sheds some light on the relations of organic matter and clay content under different tilling practices is rather instructive. Karathanasis and Wells (1989) give data on the effects of tilling practices, one of which, no till (NT), is designed to retain organic matter in the soil. Comparison is made of various soil properties using the two methods for 18 years in loess soils of Kentucky and Tennessee USA. The relations of soil clay content and organic matter content are interesting in that it is apparent that the tillage practice is not the only factor in determining retention of organic matter. In the soils with less clay, near 10%; the tillage practice is very important, where no till roughly doubles the organic content of the agricultural soil. However in soils with more clay the values seem to converge. Thus the organic matter will help bind the clays in clay poor soils but it is not as effective in the clay rich soils. Here one could predict that organic matter is important in forming clay complexes and aggregates when it is less abundant. The same study indicates that in soil pairs, NT and CT or no – till and conventional till, the illite content is slightly higher but other clays are very much the same. Hence there seems to be no strong selection of clays to form the aggregates or retain the organics and this does not significantly change the clay mineralogy from one tilling system to the other. However the authors do note a significant change in the chemical activity of mineral soil components in the pore solutions. Higher organic matter in the soils tends to increase the activity of Si and potassium in solutions. We can see the importance of this observation from the analysis of mineral stability and biomass (organic matter) given in Sect. 5.5.

These several examples of time studies under different conditions of agricultural practice indicate that the interaction of clays with organic matter is important in maintaining clays in the A horizon. However, the exact effects seem to be conditioned by the amount of clay and most likely also by the amount and type of organic matter (humic vs. low molecular weight substances). However, since the total of organic matter is not the only indicator of clay aggregation it seems that the system is somewhat multivariable in character. High influx of water tends to remove clays unless they are bound by the presence of several percent of soil organic matter. Higher clay content appears to decrease the importance of organo – complexion somewhat. It is clear that more work is needed to understand the relative importance of the variables.

## *6.2.4 Agricultural Practice and Its Results*

### 6.2.4.1 Prairie Soils

If the analysis in Sect. 5.5 is correct in that plants stabilize clays favourable to their needs (potassium reservoirs, formation of aggregates as water resources) one can ask what is the effect of farming practices and particularly modern methods of agriculture on clays. By modern methods we mean systems where motor traction has replaced animals and hence barnyard manure and animal dejections in an artificial prairie are lacking. As shown by Kleber et al. (2003) classical agriculture practiced in former forest soil areas in neolithic times sufficiently changed the chemistry of the soils as to allow them to be used as markers of man's conquest of loessic soils in Germany. These methods of farming were more or less maintained with some ameliorations, such as replacing natural prairie with artificial prairie which increases the potassium uplift effect. The general tendency was to use green manure, prairie roots and other means to maintain or increase the organic content of the A soil horizons and to replace potassium and other elements taken off through cropping. Manure was very important not only for the potassium and organic matter but also, and perhaps more so for the ammonium source of nitrogen for the plants. The liquid parts of a manure pile were carefully kept and dispersed with the solids (Larbaletrier, 1891). Loss of animals, through the introduction of motorized machinery, lost t his natural fertilizer source. Since the objective of modern farming, in the 20th century, was to reduce labor costs, machines were employed greatly as seen above in Fig. 6.5. in the case of French agriculture.

We can investigate some of these effects and changes in soil chemistry by observing the effects of potassium extraction on clay mineralogy, i.e., 2:1 clay loss and potential gain through the presence of more organic matter, or less loss of organics.

We will look at several examples of agriculture on prairie soils in a prairie plant regime where there is a natural tendency to form or conserve illite under conventional prairie grazing and the effects of intensive hay cropping. A time series study indicates the effects of alfalfa, the crop used in the 18th century to replace the natural prairie cycle as the alfalfa effect.

### Natural Prairie Development on Recent Sediments, Using Traditional Grazing Methods, Baie d'Authie (Somme, France)

The samples investigated represent the effects of natural prairie on sediments brought in from the coastal region of France near the Somme River. The zone investigated is just north of this large estuary where systematic poldering occurred for nearly 1,000 years (Velde et al., 2003). The poldering effects a well established time sequence which essentially isolates estuarine sedimentation which is put into prairie. In this region the oldest polder is dated at 1158. The sediments are essentially surface, soil based materials which are re-deposited on the surface and subjected to alteration processes (water – rock) and the interaction of plants as they establish themselves to form soils. Pasturage by cows and sheep was the agricultural practice in this region. No chemical products were added to the soils nor were they cultivated. In this instance we have a time series describing the installation of prairie interactions with as very clay-rich substrate, which contains quartz and calcite (shell material). The initial sediments are relatively illite – rich in that the illite mineral component is evident and the mixed layer minerals (illite/smectite) are proportionately smectite (S/I) and illite- rich (I/S). This is shown in Fig. 6.12. The

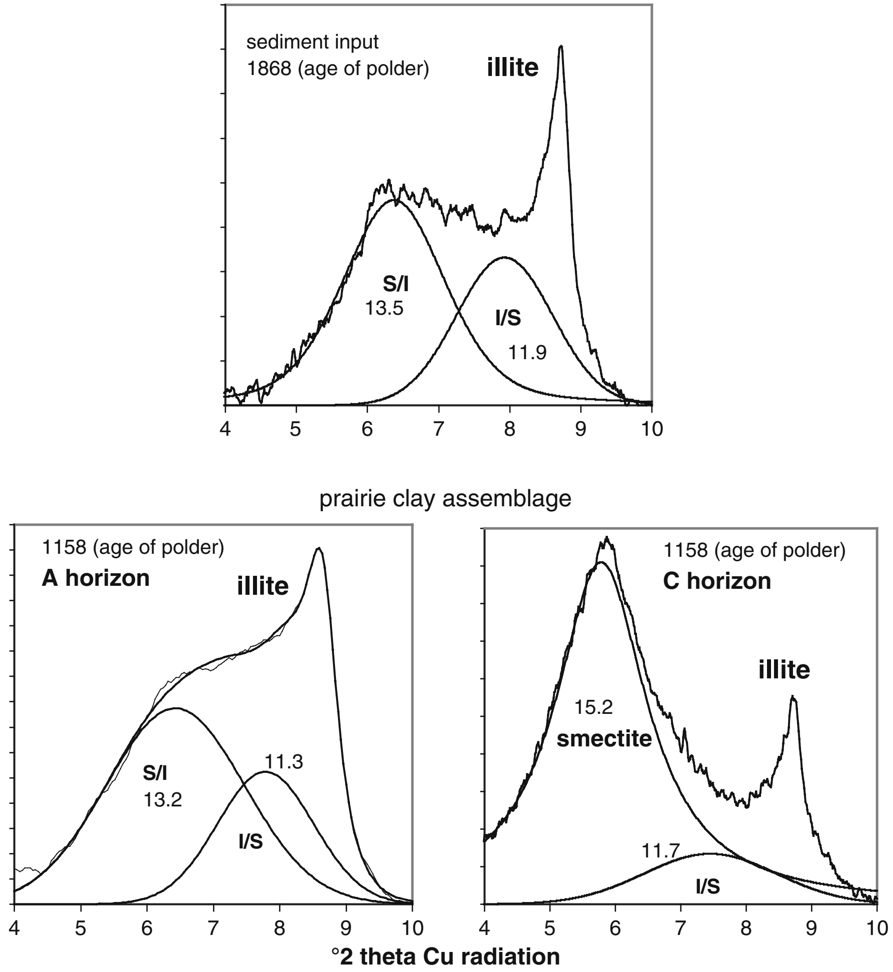


**Fig. 6.12** Baie de Authie grazing on poldered land since 1158 compared to sediments grazed since 1868. Background – subtracted X-ray diffractogram treated using decomposition methods. Illite content and mixed layered minerals are similar in new sediment and old poldered A horizon soil. However in the C horizon of the old poldered material significant illite has been lost to smectites. The prairie under traditional grazing maintains illite (potassic clay) content (Velde et al., 2003)

establishment of the prairie soil changes the assemblage into an illite – rich A horizon with a shift in illite/smectite peak positions toward illite (10Å) and the presence of a strong illite component. In the C horizon, below the organic activity one finds a strong, dominant smecite – rich mixed layer mineral and a much smaller illite peak intensity. The illite (potassium) component has been greatly reduced in the C horizon whereas the illite content (potassium) has been mostly preserved in the A horizon under prairie development. We can take this to be the natural development of a grass – dominated soil system.

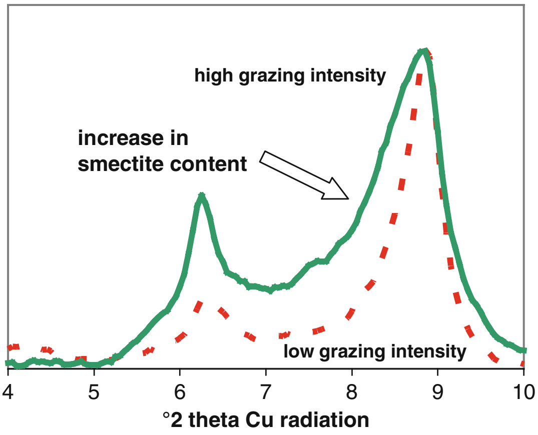


**Fig. 6.13** Data for two series of experimental plots on the Clermont Ferrand INRA station (France) station. X-ray diagrams are compilations of spectra for four different plots managed under the same conditions. Background – subtracted X-ray diffractogram is an average of clay spectra for four different experimental plots. Grazing, and hay cutting is the major difference in the two series, intensive five cutting per year and low intensity, one cutting per year with animals grazing throughout the period

### Intense Grazing on Prairie

An example of prairie clay systems under intensive, extractive culture is reported here by Barré (unpublished). This example is from an experimental area near INRA Clermont Ferrand Station in France. The experiment was to use the normal natural prairie system and to harvest it five times a year or one time with constant grazing. This was performed for 17 years. The impact on the clay assemblage is seen in Fig. 6.13. Essentially the illite peak is strongly affected by the intensive culture and exportation of the organic biomass. Mixed layer smectite/illite and illite/smectite mixed layer minerals are more important in the intensively farmed soils. The change is expected in that the major element which can come from the clays is potassium. This element is extracted and replaced by a divalent, bi-hydrated cation giving a peak position nearer to 15.2 Å. The importance of this experiment is to show that the extraction of potassium from the prairie soils is practically the reverse of the change which occurs in the establishment of the prairie on sediments in the baie d'Authie example given above. The process of potassium accumulation appears to be reversible in the extraction process.

### Alfalfa Cropping

Agronomists in the 18th century developed an efficient method of increasing soil fertility in using alfalfa plants. It is generally assumed that this fertility is due to the bacterial development of nitrogen-bearing nodules on the roots of the plants. This is of course a strong fertilizing agent. However it is also known that alfalfa is a "luxury consumer" of potassium, i.e. it accumulates more than it needs. How does this work? Data (Velde et al., unpublished) from a Chinese farm experiment in the northern province of Gansu at Lanzhou indicates what happens as alfalfa plants determine the chemistry of a loess soil in a semi-arid climate. The initial and final state of the clay mineralogy is not extremely different, being dominated by chlortie and illite minerals. Figure 6.14 Lanzhou indicates the initial soil clay mineralogy as a result of curve decomposition analysis. Without this method of observation it is virtually impossible to determine any changes in the X-ray diffraction spectra. Throughout the 22 year experiment the chlorite peak areas are almost constant compared to the illite components and the relative peak intensities of the chlorites are similar if not identical (7/14 Å peak ratios). Potassium saturation does not change the peak ratios significantly but the width of the 14 Å peak does change and hence although there is little of an HI component present it can be noticed. The potassium saturated sample shows a stronger PCI peak and a shift of the low intensity components of the

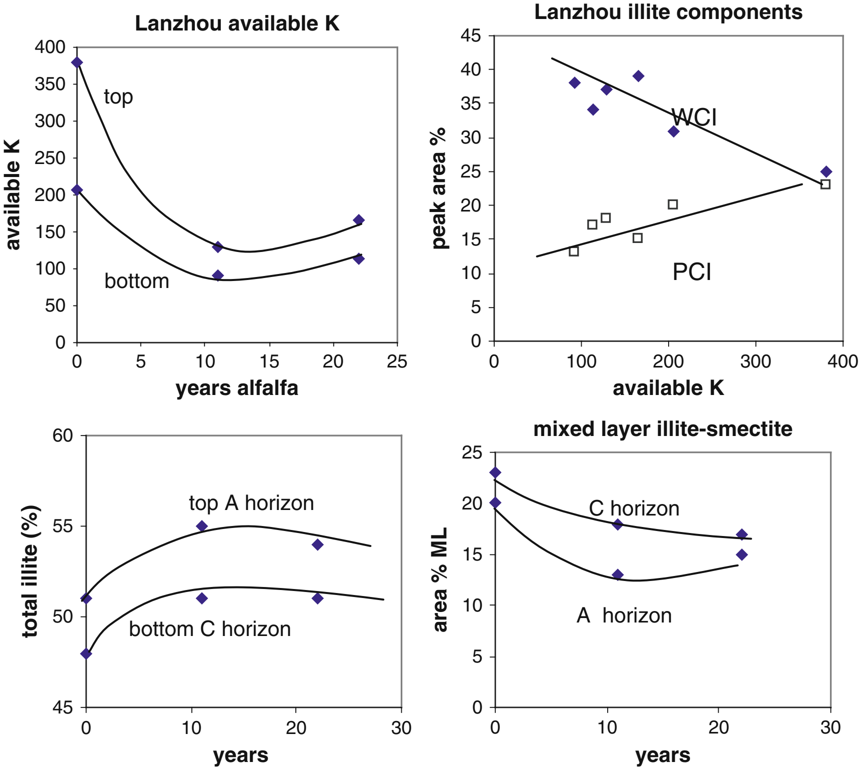


**Fig. 6.14** Comparisons are made or the A horizon (*top*) and C horizon of the profiles where potassium availability (extractable K, by ammonium acetate) is compared to the different mineralogical changes observed with time of alfalfa cropping. The amount of available K decreases, the amount of mixed layer illite-smectite decreases and the poorly crystallized illite (PCI) decreases with time and illite (WCI) increases. The change in clay content is small, and the relative amount of illite and smectite-illite change only slightly with time. Overall it appears tht the easily extracted potassium is exhausted y the cropping but the more firmly held potassium in illite increases. Alfalfa appears to build up reserves of long term potassium in the soil clays. Relations of X-ray diffraction decomposition determinations concerning the peak positions, and relative surface areas of the major phases in the Lanzhou alfalfa experimental plots (China, unpublished data of Yang Yanfang Li Decheng He Yue Zhang Ganlin Hu Feng in Nanjing and Lanzhou, China)

14 Å peak, those of an HI component. It appears that the increase of PCI illite peak intensity indicates a shift of this part of the mineral components to a form of HI or interstratified HI/illite mineral.

The major change with cultivation time of alfalfa is the relative intensities of the mixed layer mineral (I/S), the well crystallized illite (WCI) and the poorly crystallized illite (PCI). In the experiments the amounts of soluble potassium and available potassium (ammonium acetate treated and water treated) decreases as a function of experimental farming in both the upper A horizon and the C horizon of these loessic soils. This can be followed by the decrease in intensity of PCI and mixed layer mineral. Alfalfa growth, cropped and exportation of the aerial biomass, increases the relative illite content of the clay fraction in the A horizon. This means that even though the potassium available to plant growth decreases, the relative amount of illite (eventual potassium resource for plants) increases, by more than 50%. Potassium saturation of the samples increases the PCI, width was lost to plant growth.

This behaviour can explain a part of the increase in fertility in alfalfa planted soils. It would appear that the alfalfa exhausts the available potassium in the soils from the more easily extractable parts of the soil assemblage but leaves the illite component (WCI) essentially intact or increases it. In other plant experiments, using rye grass the WCI illite can be a source of potassium for the biomass (Barré et al., 2008).

In this series of experiments one sees that the prairie growth tends to reinforce the potassium – bearing mineralogy, forming or maintaining illite layers in the 2:1 structures, either the illite components or in the mixed layer minerals. Intensive exploitation of the prairie plant assemblages decrease the illite (WCI and PCI) content shifting the remaining 2:1 layers into the illite/smectite minerals. However, the alfalfa plants take out less of the potassium from illite (WCI) and extract potassium from the PCI and mixed layer minerals. This exchange of potassium in different mineral types (compartments) could very well explain the use of alfalfa as a plant which increases soil fertility, not only storage of nitrogen by bacterial nodules on the roots but also by an enrichment of potassium in the 2:1 mineral clay assemblage in an illite type mineral form. The soil – enriching effect of alfalfa is probably of two sorts, one for K and the other for N.

In general, the prairie soils tend to enrich the clays in potassium. This effect is a fundamental part of prairie plant growth and prosperity.

#### 6.2.4.2 Agriculture on Prairie Soils

Traditional Agriculture: Marais Poitevin (Center Western France)

In this region poldering was effected on aggrading sediments along the Atlantic coast. Here the newly conquered lands were put into agricultural use instead of grazing land as was the case of the Baie d'Authie example given above. The agricultural methods were undoubtedly traditional, crop rotation, prairie and manuring of the cultivated area. Sampling of the soils at the plow zone depth, near 20 cm, gave a

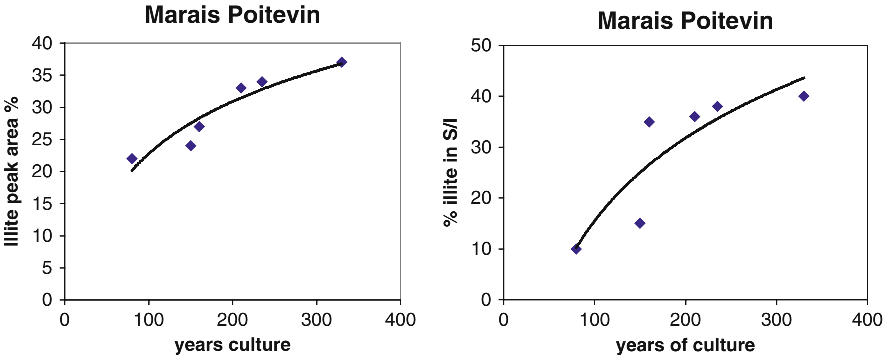


**Fig. 6.15** Clay mineralogical data for a sequence of poldered soils from center western France (Marais Poitevin, Righi et al. 1995). The overall evolution of the soil clays is one of increasing illite content in the mixed layer minerals as well as in the relative amount of the potassic illite mineral itself

sequence of clay mineralogies as a function of the time the new clays were affected by agriculture (Righi et al., 1995). The time period of agriculture is 350 years. The clay minerals are dominated by the typical mixed layer illite/smectite types with an illite and a smectite rich type. Illite is also present and kaolinite to a lesser extent. In this time series one finds that illite content increases as an individual phase and the illite content of the mixed layer minerals increases also. In both cases the illite (potassium mineral) doubles its presence relatively over the 350 year period of culture (Fig. 6.15). This result is similar to the observation of Neolithic farmers made by archaeologists to determine the presence of ancient agricultural activity (Kleber et al., 2003).

This information indicates that the traditional methods of farming on soil material developed fro eroded surface materials of illite – smectite mineralogies develop illite (potassium) – rich minerals as does the prairie soil developed on similar material.

## Intensive Agriculture on Prairie Soils: Illinois Loess

### Morrow plots University of Illinois (USA)

Velde and Peck (2002) have reported upon the changes in clay mineralogy engendered by the cropping of continuous corn for a period of 83 years on a Illinois Mollisol. The clay mineral suite is similar to most of the prairie soils clays in the Central part of the United states (see Velde, 2001). The observations are centered upon the effect of corn crop removal of mineral elements from clays, therefore potassium as related to illite content either as a distinct phase or as an interlayered part of the mixed layered minerals present. In these experimental plots over the course of the experiment, corn hybrids were introduced in the 1950s which dramatically increased corn productivity. Hence a plot of clay composition against time is not the whole picture. Peak positions for the illite, illite/smectite and smectite/illite minerals shift with time of the experiments where continuous corn production (CC) was employed, without additional fertilizer. There is a distinct overall trend in the CC soil clays to first show a decrease in peak position, increase in illite content, and with the introduction of high productivity hybrids one sees an impoverishment in illite (potassium) as the peak position increases. In the CC plots it is interesting to note that there is a clear tendency for all clay phases to become more illite – rich (peaks shifting towards 10 Å) with time as productivity decreases in the initial stages of the experiment due to lower availability of potassium and other resources. The use of hybrid corn varieties in the early 1950s increased production and increased the amount of potassium taken from the soil with the result that the clays show less illite (potassium) content. In Fig. 6.16. We plot clay mineral peak position against the time of the experiment for continuous corn and orn – oats – hay rotations. In this plot there is a general trend of change to a postion of higher spacing, one with more smectite present for the continuous corn plots and a slight change to higher illite content for the corn – oats – hay rotation. However, in the continuous corn plots clays initially there is a change to lower spacings, higher illite content. In Fig. 6.17 the corn production is plotted against the illite content of the clay assemblage. Here it is clear that there is a direct relation between the amount of material, potassium in corn, taken off of the land and clay mineral potassium content.

In the experiment the crop rotation program (COH, corn oats hay) appeared to have been little affected the clay minerals as far as illite (potassium) content is concerned, as indicated in Fig. 6.16 where the peak position change little with time whereas continuous corn decreases the illite content of the clay assemblages as a function of the amount of material taken from the soil zone.

The X-ray diffraction diagrams for three stages of the experiment, 1913, 1955 and 1996 show that the extraction of potassium occurs in the illite and illite/smectites mixed layered minerals which are shown in Fig. 6.18. A minor amount of kaolinite is present but it does not participate in the elemental exchange

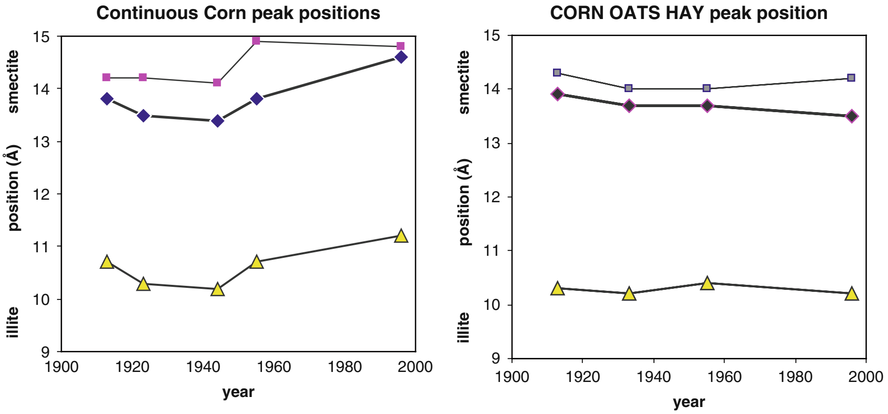


**Fig. 6.16** Peak positions of the various clays in the Morrow plot experiments as a function of time of culture without fertilizer amendements in a continuous corn production scheme

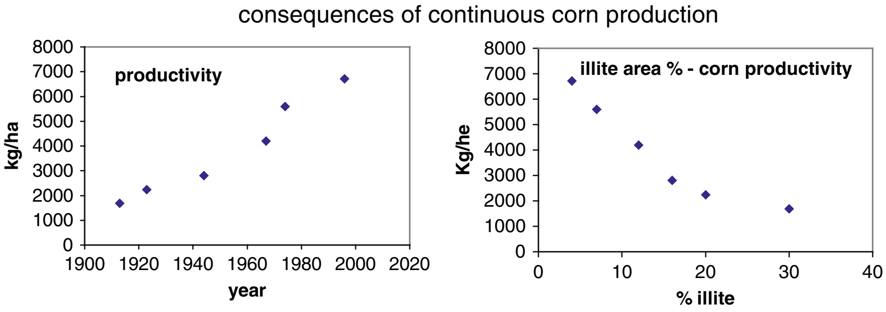


**Fig. 6.17** Relations between corn productivity and clay mineral potassium content (illite) in the Illinois Morrow plot experiments (Velde and Peck, 2002)

considered here. One sees the gradual decrease in the intensity of the illite peaks (WCI and PCI) where the well crystallized illite component (WCI) is decreased before the poorly crystallized component. This means that the decease in potassium potential in the soil solutions is first compensated by the larger illite crystallites. The PCI component is then decreased leaving a small WCI peak in the oldest experimental plots. The corn was grown without chemical fertilizer nor other amendments. The plot of corn productivity against mineral change (Fig. 6.17) indicates that the overall illite content is affected by corn production, i.e. the amount of potassium extracted from the soil. The presence of smectites/illite, lower in potassium content is evident, and hence it is also a source of potassium. The peak position of this mineral shifts, indicating a change in illite content of about 25% illite content. In fact the total potassium extracted from the soil is just 10% of the amount present in the soil itself, thus the clay fraction which is strongly affected is only a part of the total potassium reserves present. Since the corn productivity increased with time, one must feel that the corn plants were able to extract potassium from the more coarse, non-clay fraction minerals such as detrital mica or feldspars as well as from the clay fraction. They did not totally exhaust the potassium reserves of the clay fraction, in that the illite/smectite minerals maintain some potassium all the same, about 8% illite content. The loss in potassium from the clay fraction is only about 11% of the amount present.

In these experiments one sees the effects of extraction of potassium from the ready reserves of the soil. However these reserves seem not to be the only ones in the soil concerned in that corn production continues to increase with the introduction of new high productivity hybrid species in the 1950s. One can suspect that a certain amount of the potassium comes from greater depths than the sampling zone of the experiment, which was at the top 10 cm of soil. Nevertheless, the shift in interlayer cation type is seen to be directly related to the extraction (corn yield) of the potassium from the soil.

The Morrow plot experiment indicates that the direct impact of plant extraction can be seen in the illite minerals, those most rich in potassium. The total of potassium extracted is small compared to the total reserves in this particular soil.

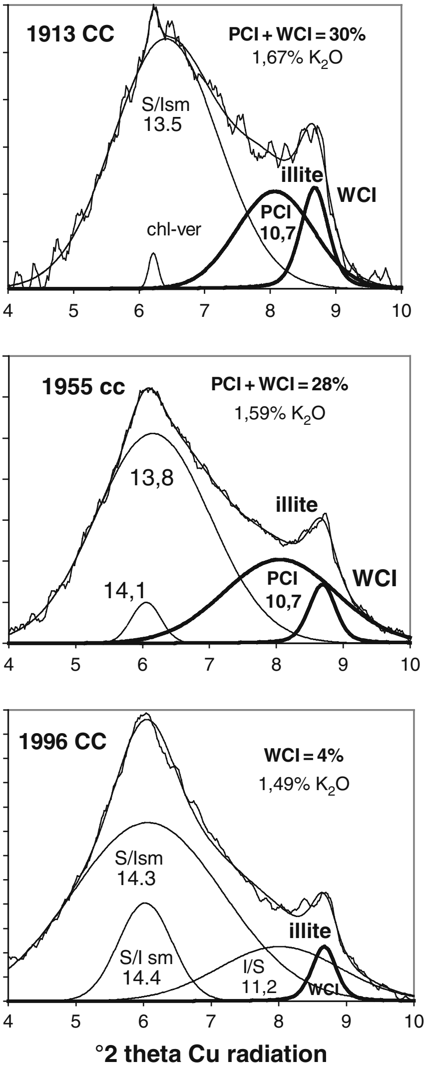


**Fig. 6.18** Decomposed X-ray diffraction diagrams of three stages in the Morrow plot experiment showing the change in illite peak intensity as a function of potassium content in the clay assemblage

### 6.2.4.3 Former Forest Soils

A perhaps exotic and special case of forest soil cultivation is reported by Li et al. (2003). Here a red, oxidized, forest soil from a near tropical region in China was used in a rice growing experiment where the soil was flood irrigated and cropped three times per year. In this experiment NKP fertilizer treatment was used with KCl at a rate of 1,500 kg/ha. The intensive agriculture for a period of 80 years changed the clay mineralogy greatly. Illite was especially affected. In Fig. 6.19 the average illite content is plotted against the period of rice cultivation. One sees a typical “S”

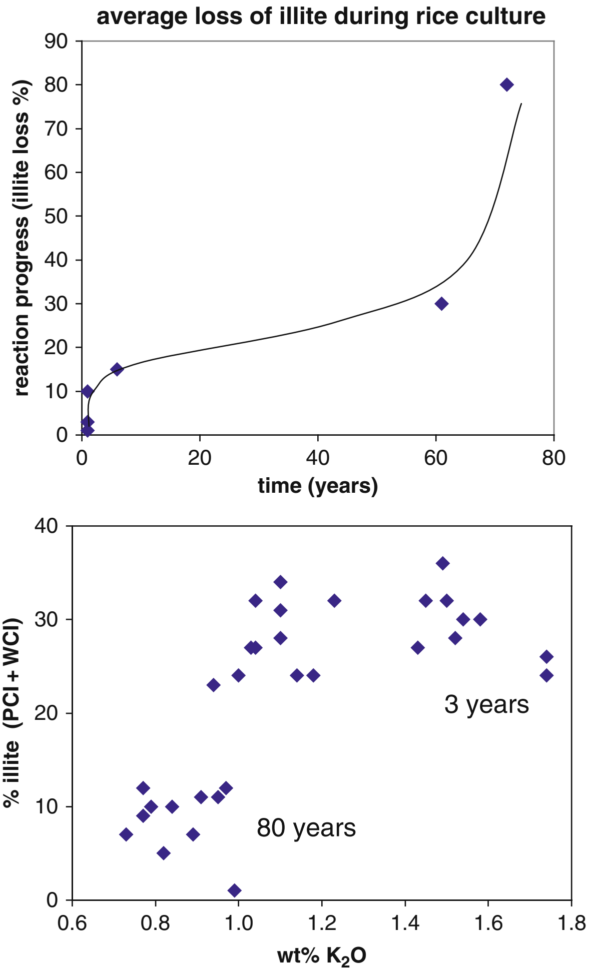


**Fig. 6.19** Irrigated rice plots in China (Li et al. 2003) where loss of illite (potassium bearing phase in the clays) and potassium content of the clays is compared to the time of the experiment. The typical "S" shaped curve can bee seen for the loss of illite

shaped curve of illite loss (reaction progress) due to bio-action on soils. There is a corresponding loss of illite from the soil clay fraction. Also the relative intensity of the mixed layer mineral chlorite/illite decreases. Thus one sees a direct relation between illite and potassium content in the soils, either as an independent phase or as layers in a mixed layered mineral. However there is a corresponding loss in clay content from the soil which may affect differentially the presence of illite to a certain extent. It is unlikely though that the illite was the only clay lost in that the other minerals were chlorite and an illite/chlorite mixed layer mineral one of which lost potassium content also.

The rice culture experiment indicates that even though potassium fertilizer was used, the overall exportation of potassium as greater than the ability of the clays to capture and store some potassium.

#### 6.2.4.4 Fertilizers

Studies by Singh and Goulding (1997) and Tributh et al. (1987) indicate the effects of potassium fertilizer use on clays on old forest soils in England. The case of rice cultivation on red soil sited above indicates that one needs a correlative amount of fertilizer to compensate the exportation of potassium from soils by crops. Barré et al. (2008) indicate the effect of different potassium treatments on soils where crops of different types were grown and harvested on the Versailles INRA experimental farm (France). The 50 year experiment using different amounts of potassium and other fertilizing agents was conducted to indicate the amount of potassium taken off of the plots as well as the amount supplied. In the case of un-fertilized plots, some 3,800 kg/ha was taken off. On a heavily fertilized series of plots an excess of 3,400 kg/ha $K_2O$ occurred.

Analysis of the average weighted peak position of the smectite-illite mixed layer mineral and illite assemblage indicates a difference between the net gain and net loss soils. Measured potassium content of the soil clay fraction indicates that a difference of 20% of potassium content (near 0.7 wt% $K_2O$) occurred between the extremes of treatment. The average weighted peak position changed by about 10% of mica content assuming a simple mixed layer illite/smectite mineralogy. Since the normal potassium content of an illite is about 7% the calculations and X-ray diffraction estimates seem quite reasonable. However, in the cases of high potassium fertilization, roughly seven times more potassium was added than fixed in the clays above the starting composition. Then it is clear that some fertilizer is necessary but it is quite possible to add too much, at least as far as the fixing capacity of the clays is concerned.

Here one can see that the excess of $K_2O$ can be stored in part in the clays, and that the systematic exportation of potassium impoverishes the clays. In the example presented the illite content is changed relative to the other phases; I/S, S/I, and HI. The excess ofpotassium and the extreaction by crops is basically found in the amount of illite present (Fig. 6.20).

It is thus apparent that the modern practices of agriculture diminish the basic properties of surface horizon (A) soils. The clay content decreases, the organic carbon content decreases, the soil structure is less aggregated and hence holds less water in reserve for plants. The clay minerals reflect the change in overall potassium availability showing loss of illite and illite layers in mixed layered minerals. This is a contrast compared to the effects of traditional farming, from the Neolithic period on to the 20th century where the organic carbon content was increased, where the potassium content was increased and where most likely the soil aggregation was reinforced. The potassium balance is one of the most studied aspects of soil change, although other aspects such as phosphorus content and capillary retention of water are also very important aspects of soil management. The factor of the loss of organic

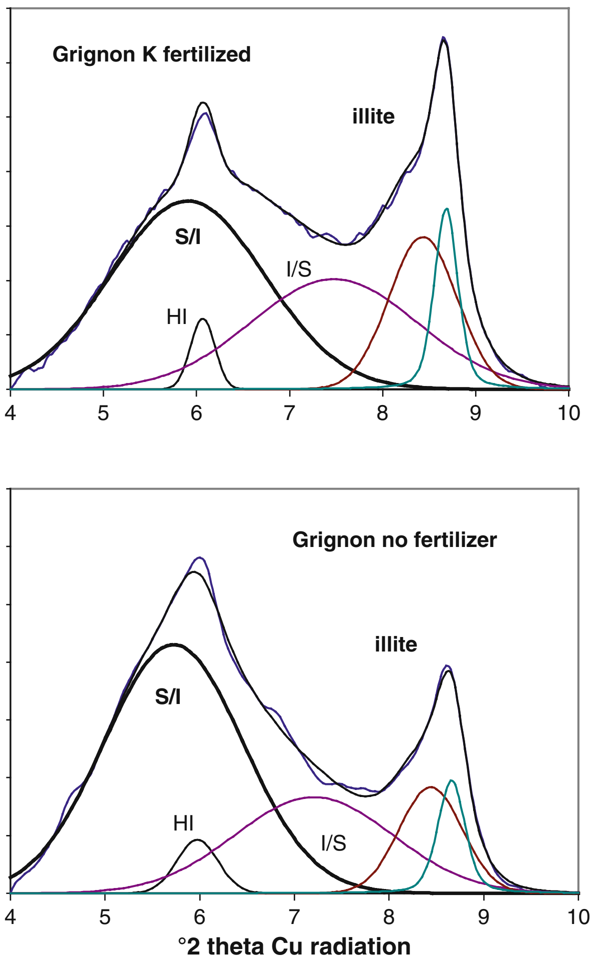


**Fig. 6.20** Decomposed X-ray diffraction data for the experimental plots at the Grignon INRA station (Yvelines, France). Spectra are averages of four plots with different treatments of high potassium application and non potassium fertilizer (Barré et al., 2008)

carbon from the soil horizon is reflected in the lower aggregation ability but also in the loss of clays from this horizon. The loss of clays diminishes the ability of a soil to retain potassium, water and provide a generally beneficial context for the growth of plants from the seeding stage onward.

The major change giving rise to these changes is the loss of organic matter in the form of manure applied regularly to the agricultural surface. This loss is due to the use of mechanical power which replaces animal traction. The use of machines is of course much more efficient in the production of plants, along with and largely because of the use of factory origin fertilizers. Without machines one could not have diminished the agricultural population of the western counties from near 70% to less than 5% today. Many changes have occurred during this process, mostly as by-products of the change in traction and fertilization methods. However, the apparently inevitable change to factory methods has its draw backs, notably in the loss of soil fertility which needs to be remedied by input from factories. Hydrophonic culture is of course possible, but perhaps it is not the best solution to the problem of providing food for humankind. The problems of natural resistance to the other parts of the natural system, bacterial action, moulds, insects and so forth, are intensified with the use of artificial support systems. It is perhaps time to look back to the past and re-invent the processes which have served to well for thousands of years to keep mankind alive and reasonably well.

### *6.2.5 Summary*

It seems that there are various results of agricultural practice depending upon the type of soil that pre-existed man's intervention of manipulating the regime of plants and soil clays. Depending upon the intensity of the extraction of plant material the soils can be more or less impoverished in their potassic components in the clay mineral assemblage. The classical regime of alternating of crops with grass – based plants (prairie) maintains or enhances the potassium resources of the soil clay minerals. Prairie grazing, on grasses, can be either an enriching mechanism or a loss of potassium depending upon the extraction rate. The same is true of grain cropping. All resides in the rate at which the mineral elements are extracted and the time or plant regime which is present to re-new the mineral resources. This concept is the key to renewable agricultural practice.

*What is needed*

*It is clear that a better understanding of the natural extraction of mineral elements by different plants is needed.*

*We have at present an idea of the kinetics of such changes but more work is necessary in order to predict the time frame of reaction rates so that one can use such information to guide agricultural practice in a realistic manner.*

*A better comprehension of the effectiveness and mechanisms of potassium – ammonium fixation in clays by manure treatment (animal excrement and vegetal matter) is of primordial importance. Such information can lead to an effective use of animal excrement on agricultural soils with a decrease in pollution and an effective addition to crop dynamic processes.*

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# Chapter 7
# Plants and Soils: The Ecological Paradigm of Plants and Clays

## Contents

The pages of text and figures which precede these notes are intended to show what is the reality (perceived as such today) of plant – mineral interaction. This effort is at the same time new and a re-working of old ideas and knowledge. We have not invented a new concept to say the least. The interactions of plants and soil minerals have been suspected since people could write it down. Perhaps the Neolithic agro-pioneers would have done so if they had had the tools of such expression. However, modern Science has obscured, gradually, these basic tenets of knowledge and now they might seem new to some experts and practitioners of agricultural practice, soil science and clay mineralogy. Ours is not to decry the vices of the past, nor to re-invent a "new" science. We wish to put things in perspective in order to allow a more fundamental approach to the investigation of plant growth in symbiosis with the mineral substrate of their existence. Such an effort has allowed us to investigate the past, through the tools of archaeology, the ancient texts of Greek and Roman authors and less distant books on agricultural practice from the more recent past, 19th–20th centuries. Basically, these sources converge on the evident conclusion of a strong interaction between plants and soil mineral resources. The key to understanding the inter-relations is to understand the chemical forces exerted by the different actors on the material found at the surface of the earth.

Basically the structure of the plant – earth situation is one of loss. The forces of rainfall and subsequent dissolution of minerals at the interface of atmosphere and rock are such that some of the major elements needed for the biological cycle

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2_7,

of plant life are inevitably lost. The initial interaction of rainwater, aqueous solutions essentially without mineral ionic charge, is one of dissolution of the existing solids found at the interface of atmosphere and rock. The fundamental chemical force is one of an exchange of hydrogen ions with ions in the rock minerals. This exchange is one of a type of "hydration" where $H^+$ is substituted for ionically bound cations. The result is a transformation of old, high temperature minerals, into new, hydrated forms, stable under conditions of earth surface chemistry. Exchange means that some ions, components of the pre-existing mineral, will be dissolved in the aqueous solutions whose inexorable mission is to find their way to the sea, the final repository of the earth, or at least that part which sticks up out of the sea. Chemical and gravitational forces move matter to the depths of the ocean.

The ions lost are those that stabilize some minerals containing elements vital for plant growth. Our story for the most part is one of potassium, the major element for terrestrial plant growth dynamics. The second part of the story is one of water retention. Rain wants to find its way to the sea or to be evaporated to become rain again. However, plants are largely composed of water. They need a ready and continual source of this material. Such resources need to be kept in the surface of the plant – earth interface. Here the problem is one of physical capture as much as chemical interaction. Water should be available during the growing and vegetation periods so that plants can develop.

The obvious repository for these two, among other, resources is that of the soil. The soil is a name given by scientists, according to the real practitioners, farmers, to the surface zone of plant earth interaction where organic matter and fine grained alteration products are present. The new minerals, formed by water – rock interaction, are called clay minerals, usually of small physical dimensions, $< 2\ \mu m$. The organic matter in soils is the result of vegetal life, either its exudate extension into the soil via roots, or the eventual decomposition of old debris which has been discarded from the life cycle of the plants themselves. Nothing is totally lost, and much is re-used. In the interactions of plant and soil materials one finds a great range of micro biotic materials such as bacteria, micorrhiza and other organisms. Thus one can easily call this situation one of ecological interaction. Such is the great variety of interactions between plants, micro-organisms and silicate materials from the rock substrate. The variety of actors is a response to changing conditions of climate and different chemical constraints imposed by rock substrates, temperature and rainfall variables that control the initial chemical configuration of water – rock interaction.

Plants have adapted to these constraints in, of course, a multitude of ways creating species and subspecies, communities of different plant types, symbiotic relationships with diverse microbiological communities and so forth. The complexity is staggering when one looks into it. However even though things are complicated they are not impossible to understand, to paraphrase the great 20th century scientific sage, "God is obscure, but not unkind". We have much information at hand, often more than is currently used to solve the ecological problems, but more is needed.

## 7.1 Stabilizing 2:1 Clays

One of the most striking examples of interaction in the soil zone is that between plants and clay minerals. Traditionally one thought of clays as a transient feature of soil zones, a stage between the surface alteration due to water – rock interaction. The soil clays are assumed to be inherited from underlying rocks either by the alteration of some high temperature minerals or by the transformation of the high temperature phyllosilicate minerals biotite; chlorite and muscovite. In all cases it was assumed that the clays would be destroyed by the chemical dissolution action of organic acids. Thus the plants make do with what is left to them.

However, in assembling existing published data and conclusions from certain studies, it is clear that plants can have an impact on the clay mineralogy of the surface, soil zone. Not only does this effect occur in tropical zones of high weathering intensity, but it also quite evident that the clay assemblage is conserved and perhaps renewed by crystallization of new minerals at the surface through the transfer of certain mineral elements, especially silica and potassium. The overall objective of the plant communities is to keep 2:1 (TOT) clay minerals present in the soil biozone. The type of clay mineral is determined by the ratios of silica, potassium, and perhaps calcium. The acidity ($H^+$ content) can also play a role in the stability of clay minerals. Natural water – rock interaction produces the following reaction series

Mica, feldspar => illite, smectites => kaolinite => gibbsite
2:1 1:1 hydroxy

In a sequence of lower silica content clays, logically, the lower silica minerals, such as gibbsite should be found in the zone of highest contact rate with un-saturated water, the surface horizon. Thus the sequence as presented is one from bottom to top of an alteration sequence.

In a number of instances in weathering sequences from temperate climates one finds somewhat the reverse where kaolinite and at times gibbsite are found at depth, near the water – rock interaction zone and 2:1 minerals are present at the surface. This is a clear reversal of the normal weathering trend, which can only be effected by the addition of silica to the surface clay materials. Such an effect is known through the deposition of phytollitic material from plans in the surface soil zones.

Mica, feldspar => illite, smectites => kaolinite => gibbsite => smectite, illite
2:1 1:1 hydroxy 2:1 potassic

This is a sequence from bottom to top of an alteration and plant intervention profile. The reversal can be called the translocation or transfer effect due to plant intervention. Figure 7.1 indicates these relations in a schematic manner.

Curiously enough, it appears that some bio-agents active in the root zone tend to preserve the phyllosilicate structure when present in the bedrock material (Arocena and Velde, in press). These bio-agents (micorrhize and bacteria) seem to preserve the phyllosilicates while destroying other silicate structural forms. Such an observation

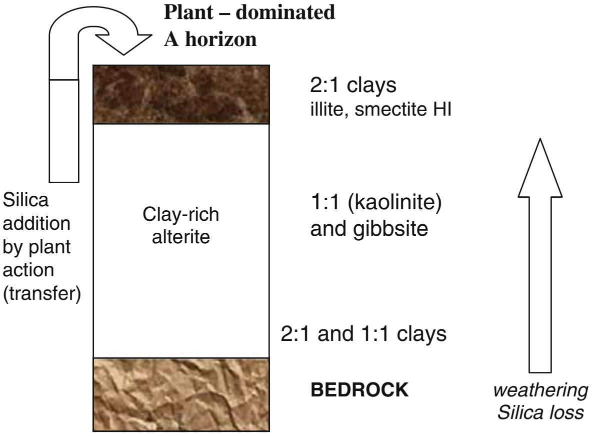

**Fig. 7.1** Schematic diagram of the effect of plant transfer of mineral elements from the alterite to soil horizons. Normal weathering trends are shown on the *right hand side* of the diagram and plant action on the *left side*

indicates that plants attempt to maintain the clay minerals in soils, either by sparing them under conditions of chemical attack or by forming them in the soil surface through the addition of silica.

## 7.2 Potassium Retention

This is all well and good, 2:1 clays are nice objects to study but of what use are they to plants?

As it turns out, these clays are the only ones which can fix and preserve potassium in significant concentrations. This is the only alkali ion present in terrestrial soils to any significant extent, sodium being only very loosely held in clays where Ca and K ions are preferred by the clay structures. Since potassium is primordial to plant growth dynamics at many stages of development, its presence is very important. The role of 2:1 clays is then to fix and store potassium as illustrated in Fig. 7.2. One can describe such actions as nutrient exchange, where potassium is absorbed and desorbed depending upon the chemical activity of mineral and bio-agents in the soil.

The 2:1 clays, smectites but especially illite and HI minerals are capable of fixing K ions from potassium – rich soil solutions within the structure (interlayer sites) and keeping them from being re-exchanged with dilute rainwater. This is the reservoir function. When plants or bio-agents exchange organic acid or other materials with these potassium ions in the interlayer mineral sites this extraction is like taking goods from a store room. The clay suite is one of a holding and sequestering action keeping a ready supply of potassium for plant use. It is probable that some ammonium can be fixed in this same manner in 2:1 mineral interlayer sites.

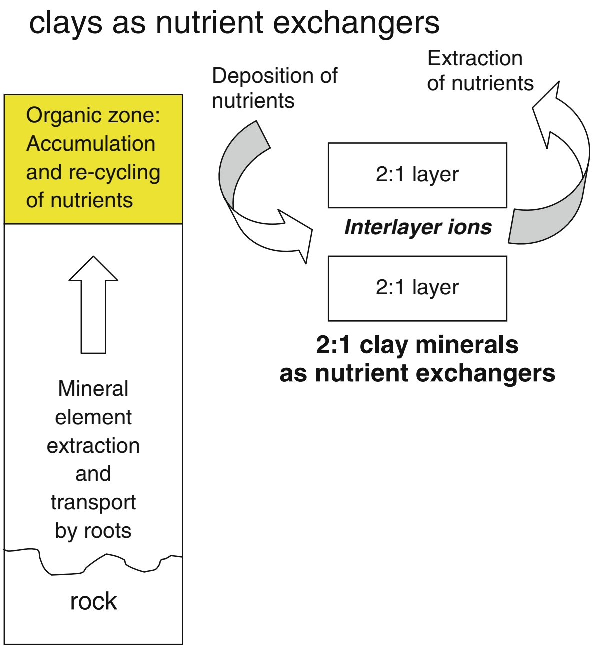

**Fig. 7.2** Clays as nutrient exchangers placed in the alteration schema. The 2:1 clay minerals are found or enriched in the soil zone where they play the role of retention and release of nutrient elements for plant growth, notably potassium

Much farming practice in the past has been designed to find ways of supplying these potassium ions, and possibly ammonium ions, to the clays. First crop rotation was practiced using legumes as potassium and nitrogen providers. Then animal manure was used to provide a more potent stock of potassium and ammonium. An example was given by G Washington, Chap. 6, where newly cleared deciduous forest land could produce 300 kg/ha with wheat grown one in three years. Using no crop rotation system, no manure and growing wheat one in two years dropped the productivity to 220 kg/ha. However using crop rotation and manuring the land gave results of 450 kg/ha when wheat was grown. It is clear that the availability of potassium and nitrogen give a high growth rate to crop cultures increasing productivity by 50% compared to cropping from the normal fertility of virgin land. Substitution of chemically derived potassium gives the same effect, and as shown in several studies, the potassium content of clays can be greatly enhanced by such practices. If the right clays are not present to hold the potassium throughout the growing season most is lost to rain water dilution and a very high amount must be applied to maintain plant growth. Kaolinite is a poor potassium fixing agent while high charge smectites (illite) is a good fixing agent.

One can conceive of using silica – rich plants, and returning much of the material to the soil as a means of maintaining or increasing the amount of 2:1 minerals in a soil.

## 7.3 Humic Matter, Soil Aggregates and Water Potential

A second and perhaps equally important role of 2:1 clays is their ability to combine with various forms of organic matter in soils, either the evolved humic matter or lighter molecule and more ephemeral root exudates, bacterial exudates or other material to form stable soil aggregates. The soil aggregate is in fact an assemblage of clay particles held together by organic matter which is largely micro-porous. Capillary pores are filed with water for much of the year and this water is then a reservoir for plant growth. The dark color of soil, due to humic substances, indicates the presence of soil aggregates. However, 2:1 clays are much more efficient at forming these structures and hence when present give an added water resource for plants. Use of appropriate manuring practices retains much of the needed organic matter and in fact builds it up in soils. Crop management can help to retain some of the un-used parts of plants such as straw and stalks in the eventual form of humic matter after bacteria have reduced it to the appropriate form. These are means of using the natural cycle of plant growth and reduction by bacteria to maintain a more natural soil structure which is beneficial to plant growth.

Very much effort has gone into an understanding of the water retention potential of soils by laboratory measurements but as yet much needs to be done to better understand the relations between soil clay mineral types, organic matter humification, bacterial action and plant root exudates in their role in creating micro-porosity.

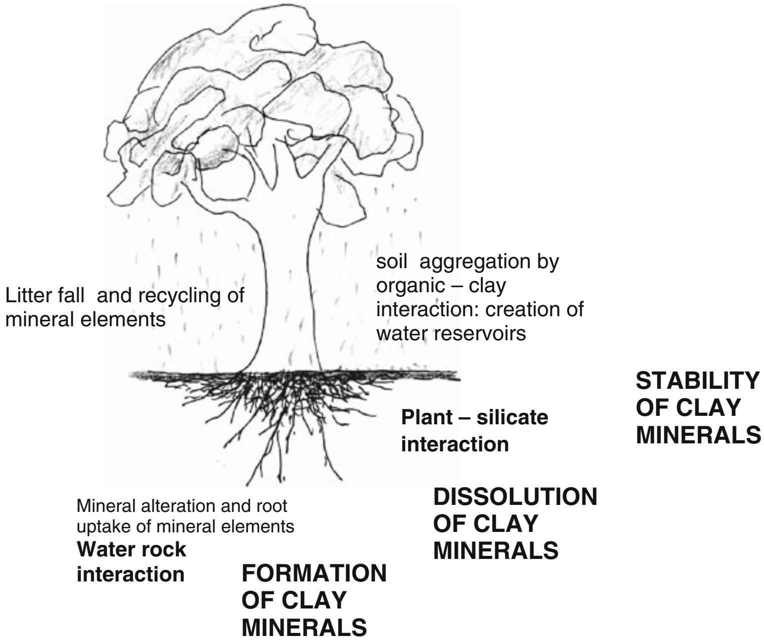

**Fig. 7.3** Overall schema of plant action and the major chemical actions of alteration and the effect of plants

The overall picture is presented in Fig. 7.3. The elements of clay formation in the water – rock interaction zone form clays, more contact with un-saturated rainwater dissolve clays or changes them to less siliceous forms, and at the interface of plant and mineral clays are stabilized by plant transfer mechanisms. The interaction of evolved plant debris (humic matter and other forms) with clays is another very important aspect of the surface zone.

In sum, the mineral sphere is used and manipulated by plant activity in order to maintain a suitable type of clay mineral structure which has various interactions providing needed resources for plants. In order to achieve this state of affairs the natural tendency of alkali and silica loss engendered by aqueous interaction with silicate materials crystallized under high temperature conditions must be countered. Such is the transfer effect or translocation of needed mineral elements from the lower parts of an alteration profile to the surface where a specific mineral assemblage is stabilized.

## 7.4 Modelling Chemical Stability

We have seen in Sect. 5.5 that it is possible to model the chemical interaction between plant transported mineral elements and silicate minerals, clays. The variables of the model are for the most part solution chemical components incorporated in the clay silicate minerals. The variables of K-Si proportions in the plant biomass, the pH developed by bacterial action or plant exudates, the amount of rain per year and its frequency can be used as input to establish the equilibrium clay assemblage under a series of conditions imposed by plant regimes. Such a model can be used to determine and explain the effects of certain plant regimes on a given type of alerite material. More important, there is a potential of prediction of the effects of plants introduced into a given soil situation under given climactic conditions. Should one introduce silica – rich plants into a given site? What will be the consequences of introducing a conifer forest on a grassland under dry conditions? Such are the types of questions one could hope to answer using the model of chemical equilibrium for clay assemblages. However, there are a great number of questions which need attention. Some of them concern kinetics of clay mineral formation. There are indications in several studies that the change in clays can be important over periods of years if one can take the liberty to extrapolate laboratory conditions of chemical variables and temperature that are outside of the normal range known for terrestrial soils. Producing new silicate minerals is the key to the predictive power of the model. Models must take into account the change in solution concentrations due to wetting and drying during a year. Drying increases the ionic potential of the pore solutions and hastens reaction rates. Wetting dilutes the solution and slows or stops reactions. The periods of chemical activity per year must be determined according to the fluctuations of water content in a soil. Thus there is a significant amount of work to be done before one can start a serious rate of change prediction. Nevertheless it is possible to use long term experimental sites to monitor change in clay compositions due to change in vegetation. If the parameters of climate can be assessed reasonably or at least be compared to other sites, such information can be used and fit to the model in order to establish rate constants. The potential of the model is such that further investigation is sure to be useful in the long run.

## 7.5 Roots and Landscapes

An aspect that has been only mentioned briefly in the text is that of root action concerning the retention of soils, the stability of landscapes and the overall importance on a long term basis for landscape stability. Engineers have been concerned with embankment stability and the consequences of changing the morphology of a landscape. Some work has been done to try to understand the importance and functioning of root systems as they relate to surface land mass stability. This work is extremely important and would deserve a serious effort in developing models based upon different types of root structures and distributions in soils formed under different climates. It is not just a problem for road engineers or housing development construction but also for the change in land use for agricultural purposes. In semi-arid regions the change in plant regime engenders a change is root structures and hence potential stability in land surfaces. Slopes, clay types, alterite depth, and other factors should probably be considered as factors of choice in using plants as stabilizing agents in a given situation. Perhaps more work could be done on this subject considering its potential importance for developing countries.

In agriculture, root densities are probably an important aspect in choosing a plant type in a given context, especially in areas of sporadic and intense rainfall. Stabilizing the surface to avoid clay surface erosion is one thing but prevention of mass movement by landslides, even on a small scale, can be an important part of agricultural consideration. Loss and disturbance of a landscape are important factors to consider.

In the same direction, one can consider the impact of introducing different types of forest plantations as a function of terrain and the risk of mass movement. This is of course a concern for foresters in mountainous areas and should always be kept in mind even in less steeply sloped areas. Roots are the conduit of mineral extraction from the earth but also the mainstay of stability for an individual plant and a group of plants under given conditions. The stability of a soil zone depends upon the plants present and the stage or advancement of alteration (thickness of the clay zone).

One should take into account plants, the alterite configuration and of course climate, when and how much rainfall there will be in a given environment. Factors of soil porosity (amount of water which can be incorporated) permeability (rapidity of evacuation of water) and change in physical properties with saturation (plasticity) are all part of the equation that links plants to their substrate.

## 7.6 New Pathways

Given this situation, and the all encompassing interest of mankind in the plant zone of continents (agriculture and forestry) it seems only natural that mankind has manipulated the manipulators (plants) to his benefit. Classical farming practice was designed to use the different effects of plant species in order to ameliorate the productivity of the surface for man's needs. New farming methods have largely ignored the lessons of the past preferring to substitute industrial know how for natural, time tested methods. Perhaps today with the new outlook on a foreseeable future similar to that known today, one can propose a new vision of the sciences concerning the interface between plants and the earth. This biosphere is in great need of being better understood. The means are available, modern methods of interpretation of X-ray diffraction spectra of clay minerals allows one to quantify changes observed natural settings. DNA sequencing methods can be used to identify more precisely the bio-world in a soil; bacteria; micorrhize and so forth. This can change our knowledge greatly by giving much more precision in determinations of the species present and allow one to un-ravel the extremely complicated inter-relations between the living and mineral world in soils. It is time to begin a new scientific endeavor, that of the ecology of soils concerning the mineral plant and microbiological world. It must be done together, as a whole system, or else it will be in vain.

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# Annex A
# Simplified Methods for the Interpretation of X-Ray Diffraction Diagrams of Soil Clay Assemblages

## Contents

## Annex I X-ray Diffraction Diagrams of Soil Clay Assemblages and a Simplified Method of their Interpretation

### *Decomposition Methods*

X-ray diffraction spectra of clay assemblages are the major means of identifying the mineral types present, and more importantly in measuring, quantitatively, the changes from one environment to another of the different components of the clay assemblages. This tool, now available routinely, via internet and by other means, is the key to any modern interpretation and assessment of clay mineral change and relative abundance. Identification is one thing, reasonably important in itself, but the change effected by different environments in clay abundance is the most important factor and tool which can be used to assess the use of different practices in using plants to effect changes in soils. Soil clays respond, rapidly, to changes in their local chemistry. This local chemistry is often, or can be, determined by the plants and bio – agents in the soils. The changes in clays are an indictor of their potential fertility, or infertility, for the eventual growth of other plants. Some plants need certain elements that are found stocked in clays, other plants other elements or perhaps none at all. The effects of plants on clays can be seen only through a quantitative and comparative analysis of X-ray diffraction spectra of the minerals present.

B. Velde, P. Barré, *Soils, Plants and Clay Minerals*,
DOI 10.1007/978-3-642-03499-2,

This has been demonstrated throughout the preceding chapters of this book, at least we hope so. Here we would like to present a short explanation of the principles of the interpretation of spectra using decomposition methods in order to obtain quantitative estimates of mineral type abundance. One must be careful in using such estimates in that the intensities of different minerals depends upon their composition, on their grain size and on the structure, inter-stratification of different layers, all of which change the peak surface for a given mass of material. Hence absolute abundance or mass is a difficult objective to attain. However, if one looks at a series of samples with approximately the same mineralogy, one can observe the changes of abundance in a relative manner and thus interpret the importance of the different chemical parameters affecting the clay assemblages. Relative change in mineral abundance is a very important estimate, especially in time series experiments, which are very common in agricultural practice. Comparing one sample against another is often more important than an absolute estimation of mineral abundance in a single sample.

The decomposition of complex spectra of electromagnetic signals is an old art. Problems arise when electro magnetic radiations interact with complex (often multiphase) materials. Here the individual bands of intensity, having each a specific intensity distribution, often overlap and present a vague distribution of intensities. Spectra of infrared interaction, Raman interaction, and different X-ray energy interactions have been the subject of efforts at extracting the individual components from the complex, overlapping series of bands in a spectrum. The use of relatively proven methods for an interpretation of X-ray diffraction data is not new (Lanson, 1997). However it is little employed at present in studies of clay minerals in soils. Nevertheless a certain number of studies have used such methods to interpret the spectra of soil mineral samples.

The problems of interpretation can be seen very clearly in the example of Fig. A.1.

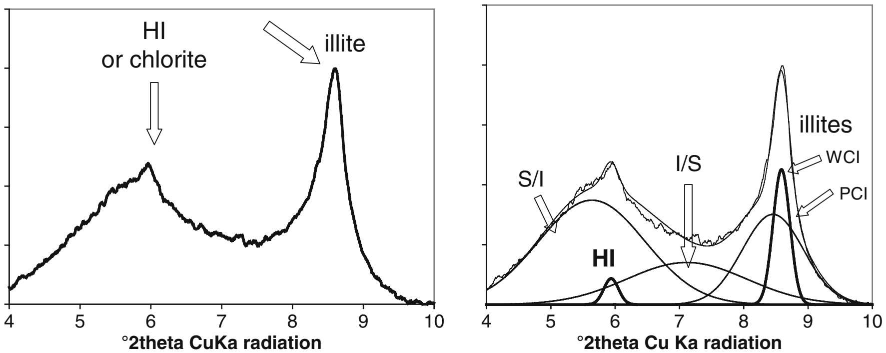


**Fig. A.1** Typical background subtracted X-ray diffraction spectrum where the obvious peaks are illite and HI – chlorite types. However decomposition shows that these peaks are of minor intensity compared to the others, especially the HI peak. Most of the diffraction intensity is found in the mixed layer smectite – illite (S/I), illite – smectite (I/S) and poorly crystallized illite (PCI) peaks

In this background subtracted spectrum of a soil clay mineral assemblage one sees two sharp peaks which can be interpreted as diffraction peaks of specific minerals in the soil, illite and HI – chlorite. The illite peak is in fact a major feature of the spectrum but the HI mineral is in reality a minor component. However the large majority of diffraction intensity is contributed to by other minerals, two types of illite – smectite mixed layer minerals and the poorly crystallized form of illite. An identification based solely upon identifiable sharp peaks is very misleading in interpreting X-ray diffraction spectra of soil clays. One would say illite plus HI or chlorite when most of the diffraction intensity is contributed by mixed layer minerals of different sorts. This has been the problem with the interpretation of X-ray diffractograms for the last 50 years. It is almost impossible to estimate the relative abundance of the less well characterisable minerals present. Clearly it is necessary to go into the problem on a different scale.

## *Some Fundamental Concepts of Decomposition Techniques*

### Background

X-ray diffraction diagrams of clays usually show a highly asymmetric background intensity which increases with decrease in diffraction angle (° 2 theta). This background must be subtracted in order to observe the diffraction maxima for the different components of the clay assemblage. Such subtraction methods are routine in most analysis programs. In Fig. A.2 one can see the effect of background and its subtraction in going from A to B.

In the example of a meta bentonite mono-mineral sample, background subtraction gives a peak that is almost symmetrical, at near 7° 2 theta Cu radiation which can be decomposed into one major Gaussian shaped peak and another minor one to the low angle side. The peak is slightly assymmetrical.

Given the need for decomposing the complex X-ray spectra of clay minerals, how can one go about the process without making too many errors? If one considers again the Fig. A.1 there are obviously two sharp maxima but other peaks are present which overlap and give difficult interpretations upon visual inspection. In Fig. A.1 in the lower figure it is clear that the large part of the diffraction intensity of the spectrum is made up of large peaks that often overlap, with the result of an apparent continuum of slightly varying diffraction intensity. How then can one go about identifying the different components of this diffraction intensity?

Initially there are several principals which must be recognized:

### Principles for Decomposition

*Principle number one*: in the region of interest for clay minerals, 4–14° 2 theta for copper radiation, or 16–7 Å, *some of the peaks appear to be slightly assymmetrical*, with a slight broadening to the low angle, high d value (Å) side. This can be an effect of peak broadening due to physical effects of X-ray diffraction as is the

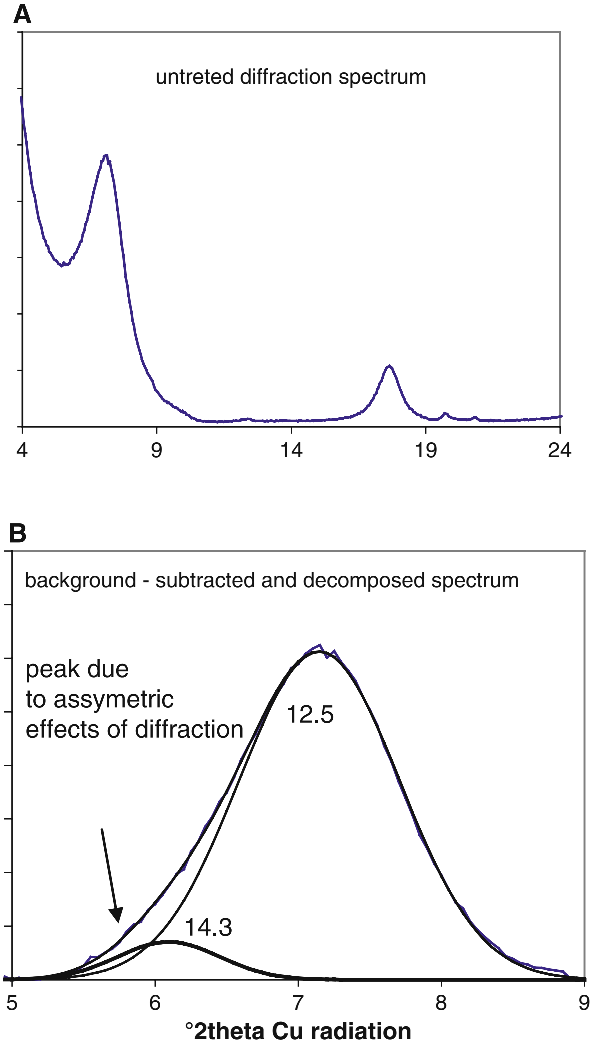


**Fig. A.2** Illustration of the effect of peak assymmetry on decomposition results. The un-treated spectrum of a bentonite clay is shown and the decomposition result treating the peak near 12.5 Å. The assymmetry gives a decomposable peak near 14.3 Å which is only of minor intensity, about 7% of the intensity of the 12.5 Å peak

case in Fig. A.2. The assymmetry can be defined by a second peak of minor peak area, usually below15% of the total peak surface area of the major reflection. Figure A.2 indicates this effect for a bentonite clay (smectite) from Sweden (Kinekulle deposits). The assymmetric part of the peak can be simulated using a small peak to the low angle, high d value side of the major peak. In the example, the peak is found at 12.5 Å and the simulation of the assymmetric part of peak can be simulated with a small band at 14.3 Å. The relative intensity of the small band, simulating the assymmetry of the large peak is 7% of the area of the large peak. Thus, the problem of assymmetry due to physical effect of diffraction is minor. However assymmetry of peak shape is usually far more important in most clay spectra and thus is due to other effects. *Thus when there appears to be a small peak widening at the base of a sharp peak, it is most likely due to the presence of another mineral phase.*

*Principle number two*: It is possible to "fit" or simulate any complex curve with a suitable number of individual band components. This is the principle of Fourier synthesis analysis. However, there is no use for such results in the identification of specific mineral in a complex assemblage without any basis in mineralogical reality. We are interested in identifying each species present. There are not an infinite number of species present, in fact only a limited number in most cases. We in fact wish to simulate a complex spectrum by using the minimum number of components. Hence principle number two is: *use the minimum number of bands possible to simulate a complex spectrum.*

*Principle number three* is: *use only bands that could represent a known mineral.* Initially this is difficult to follow in that one does not know, a priori, what is possible and what is not. Experience is the best teacher, and above all use of published, established diffraction components representing different soil clay minerals is recommended.

*Principle four* : *peak widths range from 0.2 to 2°2 theta at half height.* Wider peaks are un-realistic. Usually wide peaks are the result of an inter-stratification of different types of mineral layers in the same crystallite or small crystallite size. If one needs a very large peak to decompose a spectrum, it usually means that there in fact two peaks present. Peak widening from grain size effects is much less than 2° 2 theta (Fig. A.3).

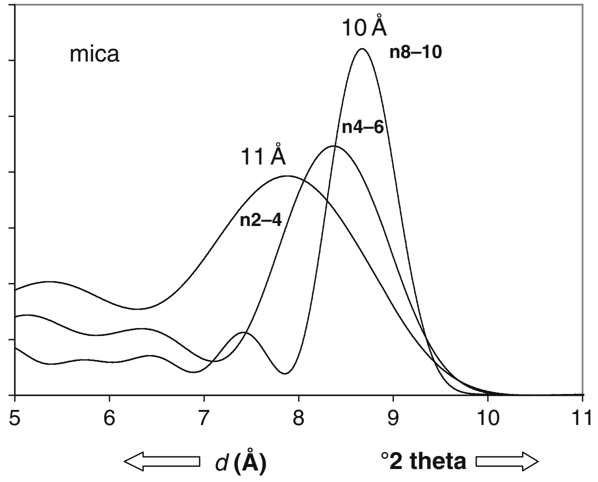


**Fig. A.3** Diagram showing calculations using the Reynolds NEWMOD program where a mica peak is modelled. The peak near 10 Å occurs for well crystallized illite, i.e. where crystallites have near 10 coherently diffracting crystallographic units present. Decreasing the number of layers in the crystallites shifts the peak to higher *d* spacings, from 10 to 11 Å, and widens the peak

In Fig. A.3 the effect of coherent diffracting domain, an approximate estimation of the grain size or order in a crystallite, is shown for illite. This widening effect is especially true of illites in soils. The reason is that the grain size is variable, and some material shows a narrow peak at low d spacings (higher ° 2 theta) and a larger peak at higher d and lower ° 2 theta. This effect is usually interpreted (see Meunier and Velde, 2003) as being due to a peak shift and peak broadening due to the dispersion of grain sizes, and perhaps composition of the illite particles. The effect of peak shift due to grain size (number of coherent layers diffracting in a crystallite) is shown in Fig. A.3.

The peak shift is not negligible and peak broadening contributes to the well known apparent asymmetricity of the illite peaks, called in the past illite crystallinity. To our knowledge, peak asymmetry, with a fitted band of more than 15% of the surface area of the major peak, is due to a population of different particle sizes of the same clay species. This is typical of illite and kaolinite but we have not identified it in cases of other minerals (Fig. A.4).

In the example shown for a diagenetically formed illite, there is a decided asymmetry of the peak at 10 Å with a width at half height of near 0.7° 2 theta caused by a peak centered near 10.7 Å which is significantly wider, 1.4° 2 theta. Hence it is common to need two peaks to fit the illite peaks at 10 Å and often the kaolinite peaks at 7.21 Å. In the case of illite the more narrow peak is called WCI, or well crystallized illite and the wider peak is PCI or poorly crystallized illite (PCI).

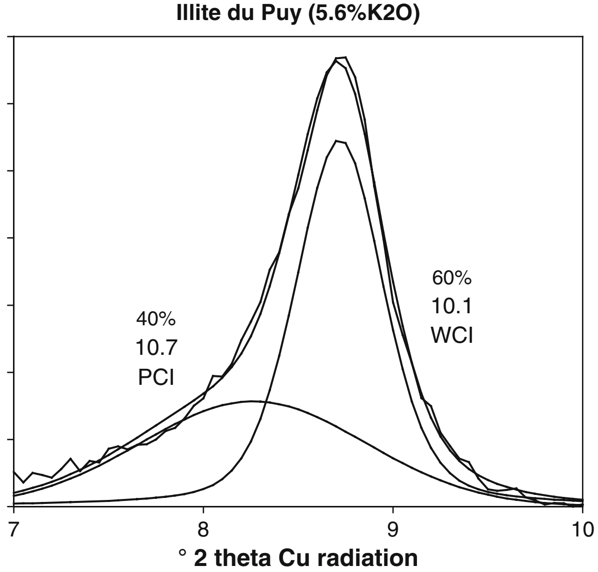


**Fig. A.4** Typical peak assemblage for illite with a relatively narrow peak near 10 Å (called WCI or well crystallized innite) and a wider peak near 10.7 Å (called poorly crystallized illite, PCI). The shift and widening is due to a smaller grain size (coherent diffracting domains in the crystallites)

## Decomposition Examples

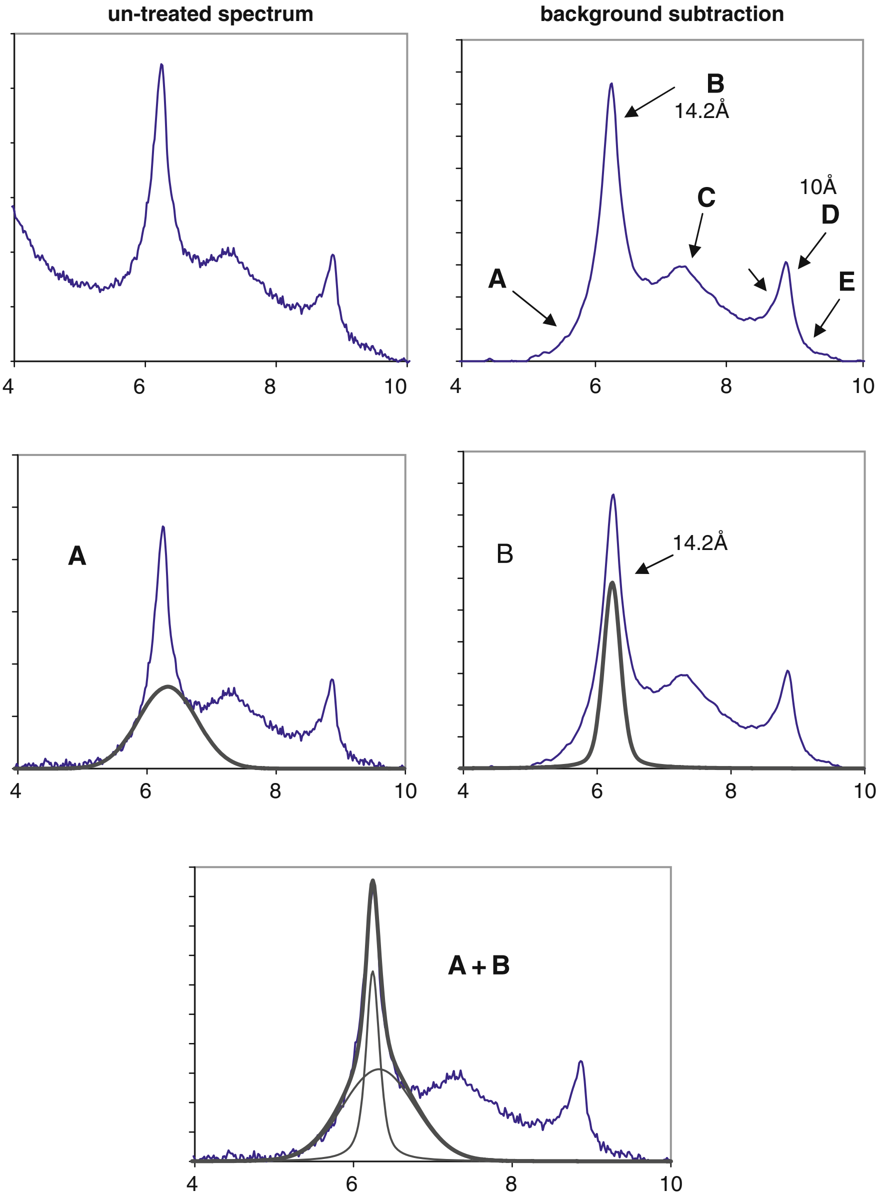
All spectra should be background subtracted before an attempt is made to decompose the complex spectrum into its components. In the examples below we show the un-treated spectrum before treatment, and begin the decomposition with the background – subtracted spectrum.

The easiest procedure for decomposing a complex spectrum is to work from the edges to the center, like eating a sandwich. Once the outermost peaks are defined, one can make an attempt to determine peaks in the center. This usually means going from the 10 Å illite peak to the 14–15 Å peaks representing the HI or smectites phases. We advise using the divalent ion air dried state for the initial determination of mineral species present. It is important to use a specific protocol for curve fitting (decomposition) in that the proposition one uses to establish the best fit of a series of peaks to a complex curve depends upon a knowledge of the phases (peaks) likely to be present. In most soils one finds kaolinite present, but the position of kaolinite is such that it is detached (little or no overlap with other peaks) and it can be treated as an isolated example, usually with two peaks as indicated above. We consider the 10–15 Å region (4–12° 2 theta using Cu radiation) as the most complicated and, for plants, the most critical part of an X-ray diffractogram necessary for the identification of the soil clay assemblages. It is here that one finds the 2:1 minerals, which can contain potassium Ca or Mg hydrated ions or Al-OH ions.

In Fig. A.5 we show a case of complex mineralogy where two peaks are evident in the spectrum, one at 10 Å and the other at 14.2 Å, indicated by arrows D and B in the figure. In between one sees a distinct but wide hump, arrow C. However there are one other point to be remarked, indicated by arrow A, which is where the slope to the low angle, high d value side of the 14.2 Å peak shows an apparent asymmetry, or spreading at the base. The 14.2 Å peak is sharp and well defined but its base is wider that a normal peak shape would allow. We use a proposition to fit the wide base of peak, B, with curve A. Then one can fit the sharp peak (B), to the 14.2 Å peak. The combined peaks A + B account for much of the diffraction in the region of the first peak.

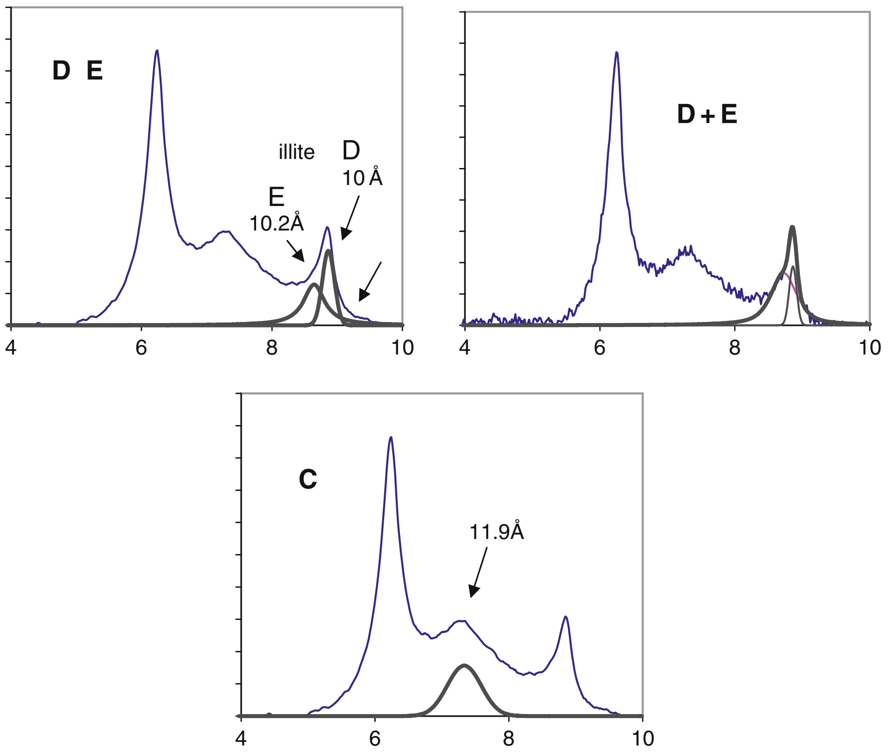
Now we can look at the high angle, lower d spacing side of the spectrum. Here the illite peak is evident and can be fitted with a band at 10 Å (peak D). However, there is a slight widening at the high angles side of the peak. Also there is some asymmetry to the low angle side of the 10 Å. This can be fitted using the peak E. As we have indicated above, illite is usually described by two peaks, one at 10 Å (called WCI or well crystallized illite) and the other slightly to lower angles 2 theta and higher *d* spacings (PCI or poorly crystallized illite). Thus a two peak proposition is most often necessary to describe the potassic illlite component in soils.

Having taken care of the exterior parts of the spectrum one can then look at the obvious peak at near 11.9 Å in the center of the spectrum (C). This can be simulated by a peak at 11.9 Å. However, there is still some diffraction intensity found between this peak C and the illite peaks (D and E). A peak at 11 Å is needed to complete the simulation. Here we have found two peaks at each end of the spectrum associated with a diffraction maximum, one in the center associated with another obvious


un-treated spectrum

background subtraction

**Fig. A.5** Example of decomposition of a complex spectrum. The initial spectrum is untreated and the following spectra are background subtracted. Background subtraction is the first step in decomposing spectra. One can readily identify peaks A through E visually. Peaks A and E are subtle but necessary. Peak A is fitted in order to take into account of the spread at the edge of the spectrum. Peak B is used to take into account the intense and sharp peak intensity near 6° 2 theta. On the right hand side of the spectrum, the same process is used but here the wide peak (E) which expands the spectrum base is on the inner side of the intense peak near 9° 2 theta (D). The peak near 11.9 Å is then fit into the spectrum and final decomposition shows a need for a peak at near 11 Å



**Decomposed spectrum after refinement**

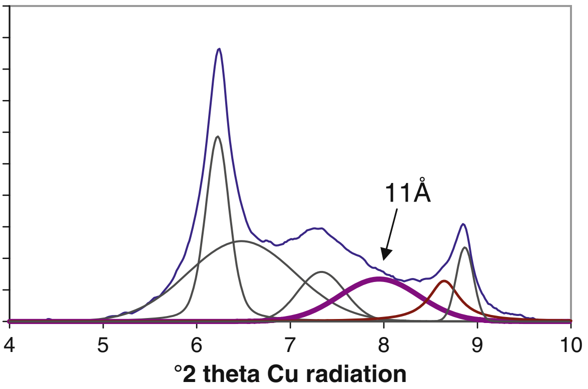


**Fig. A.5** (continued)

diffraction maximum and another which is found due to the incomplete description of the initial proposition. The last peak at 11 Å is not to be ignored in that it represents 15% of the total peak diffraction area. The sharp, clearly visible peaks represent only 25% of the surface in the example given. Therefore it is extremely important to use decomposition in order to have an idea of the total diffraction surface and phases present. The final least squares refinement of the spectrum, based upon the propositions we have proposed shifts some peaks slightly, for example peak A which is widened and moved to a higher position in ° 2 theta. This indicates that the whole spectrum must be considered when all elements are fitted to find the best solution to the problem.

In Fig. A.6 we indicate another example of similar mineralogy, but with different problems of decomposition. Here the peak at 14.2 Å is well expressed and dominant (B), while the peak at 10 Å (illite, peak D) is very small, in fact a shoulder on a larger, broader peak, indicated by arrow C.

Starting at the low angle (high *d* values) we can propose two peaks as before to fit the widening at the base of the sharp 14 Å peak. This is peak A which when completed by a sharper peak at 14.2 Å (B) completes this end of the spectrum. The necessity of peak A is seen at both sides of the sharper peak B.

The low d spacing, high angle side, of the spectrum is simulated by the double peaks of illite (D and C). In this case the illite peak of low crystallinity, (PCI, smaller number of diffracting layers), is significantly larger (greater peak area) than the 10 Å, WCI or well crystallized illite peak. However there is significant diffraction intensity between the 14 and 10 Å ends of the spectrum. This can be accounted for by a peak at 12.1 Å which is relatively wide (1.3° 2 theta).

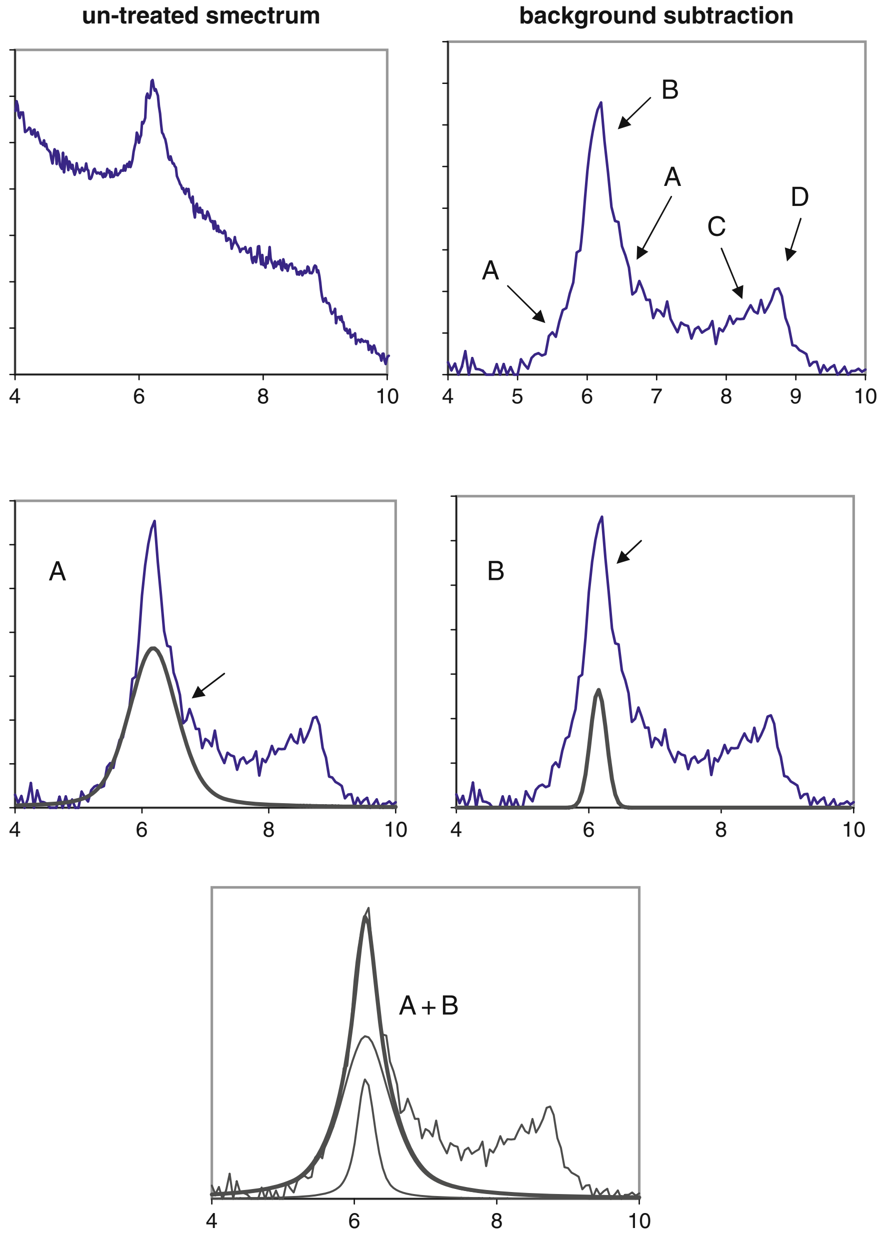
Again we see that the least squares refinement for a best fit changes the peak positions to a certain extent, again the peak A is shifted to higher ° 2 theta and widened slightly.

## Peak Shape and Intensity Change: The Comparative Method

The major use of decomposition is to identify the peaks present and to compare their relative areas in order to identify changes in mineral abundance and mineral type. This can be done for similar materials which have been subjected to different chemical changes.

An example of the use of decomposition to follow changes in spectra is given in Fig. A.7. A sample of agricultural prairie soil from Illinois is shown in the strontium – saturated state and in the potassium – saturated state. In the Sr-sat diagram, one finds two mixed layer illite – smectite peaks. The first is the smectite – rich phase (S/I) which is very close to smectite in composition, given its spacing at 15.5 Å. Another illite – smectite mixed layer mineral is present, whose peak is closer to 10 Å (12.8 Å). The two illite peaks (PCI and WCI) are present, with the poorly crystallized form (PCI) of larger peak area than the well crystallized form (WCI). The two illite peaks represent 34% of total peak areas.

Potassium saturation shifts the peaks to higher peak positions and lower *d* values, indicating an increase in potassium content as the peaks approach 10 Å. Potassium in the anhydrous form in the interlayer position, produces a 10 Å spacing. In the global experimental spectrum, irregular line above the component peaks, one sees an increase in the presence of the illite peak, indicated by the arrow. The combined area of the illite peaks now represents 55% of total peak area. Further, the smectite –


un-treated smectrum

background subtraction

**Fig. A.6** Example of the decomposition of an HI – bearing assemblage with a major peak near 6° 2 theta. The first peak on the left has a spread at its base on either side of the major peak B. this is fit with peak A. The second portion of the spectrum to be fit is on tD.he right hand side where two peaks are used to describe the illite material, one wide peak C (PCI) and a smaller illite peak (WCI). Final decomposition needs a peak to take into account of the intensity between the HI and illite peaks

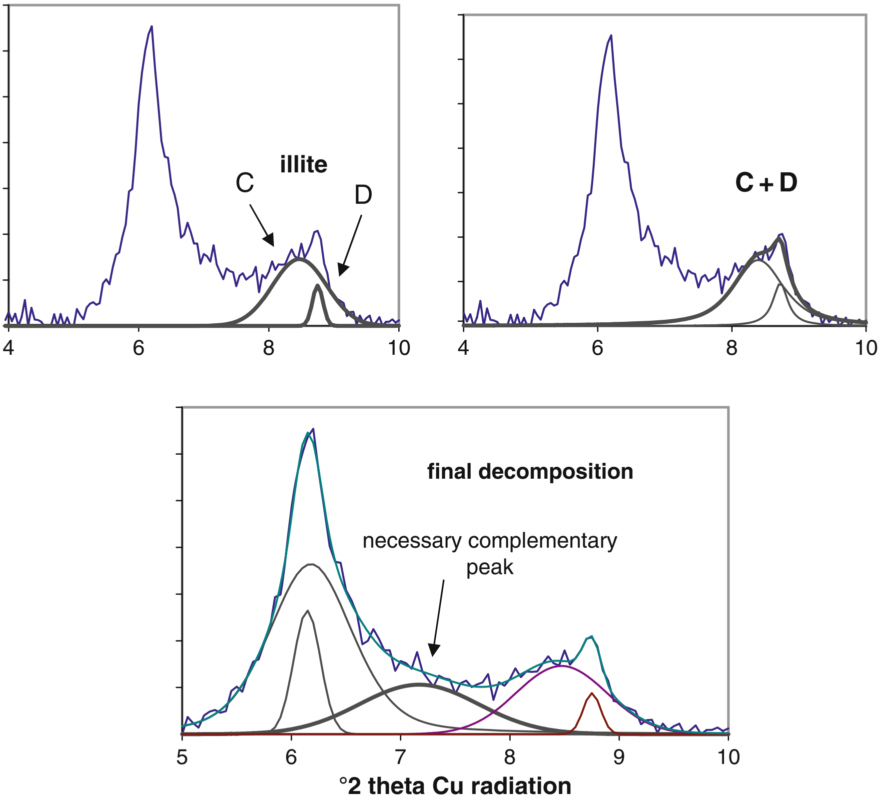


**Fig. A.6** (continued)

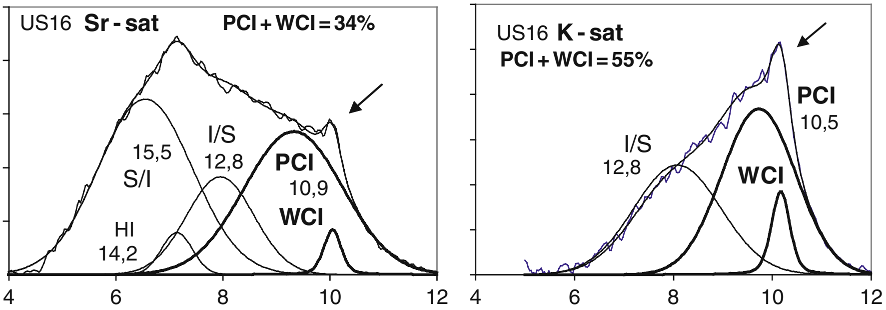


**Fig. A.7** Illustration of the effect of saturation saturation a clay assemblage of primarily illite – smectite clays. Potassium shifts the peaks toward an illite component of both greater PCI and WCI peaks. The peak areas can be calculated using the width at half height (WHH) in ° 2 theta multiplied by the peak intensity determined by the decomposition routines. All peak intensities (width times intensity) are added together and each is divided by the total of determined intensity in order to estimate a relative peak area rich mixed layer mineral peak has disappeared, with an important I/S phase present as in the initial spectrum. Note that the S/I and I/S peaks define the peak envelope in Sr and K – saturated states and that the PCI peaks define the other side of the peak envelope. By comparing the decomposition peaks in the two spectra one can numerically determine changes in the mineralogy (interlayer ion occupancy) of the samples under the two different treatments

### Surface Area

In this example we indicate the relative peak area of the different phases identified. The method of estimating the surface area for Gaussian peaks is simple, one multiplies the width at half height times the peak maximum value which defines a good approximation of the area. Summing the peaks and dividing the area of each by the total gives an estimation of the relative area for each phase.

Another example of the use of decomposition methods can be seen in a series of three soil samples (top of A horizon) under a sequoia tree near the trunk, at 2 m from the trunk and in the open prairie (lawn) around the 150 year old tree (park of the château Saint Fargeau, Vienne, France). The effect of the sequoia, grown on the same initial soil as that of the grass in the park, is to increase the potassium interlayer content of certain of the clays. One sees in Fig. A.8 that the smectite – rich phase (S/I in the figure) maintains its peak position and relative intensity. This peak, defining the left hand side of the peak envelope, is stable. The smectite – rich inter-layered mineral (S/I) appears to maintain its peak position also either in the grass or sequoia soils. However, one finds that there is a great increase in the intensity of a peak near 11 Å, an illite – rich inter-layered mineral (I/S) and in the intensity of the illite peak. Here it seems that the phases present initially remain essentially of the same composition (ratio of illite and smectite present in the crystallites) while a portion of the initial phases becomes either an illite – rich inter-layered mineral or illite.

### Center of gravity

If one multiplies the peak area of each phase (width at half height times intensity) and compares it to the total peak areas for all peaks, relative peak area, one can then multiply by the area by the peak position (in Å). This gives the contribution for each peak. By adding the contributions one makes a weighted average of the peaks in a spectrum. This is the center of gravity approach (Barré et al, 2009) to numerical comparisons. In the Fig. A.8 the center of gravity measurements (cg) are indicated for each spectrum. One sees that the center of gravity reflects directly the shift in peak intensities and peak positions described above. The cg shifts from a position of 14.2 Å under grass showing the predominance of smectite (two water layer hydration and a contribution at 15.2 Å) which is decreased under the influence of the sequoia tree where the cg value is 12.8 Å mid way between smectite and illite positions. This indicates the change in illite content of the mixed layered minerals and the amount of illite created by potassium saturation. This measure is very useful

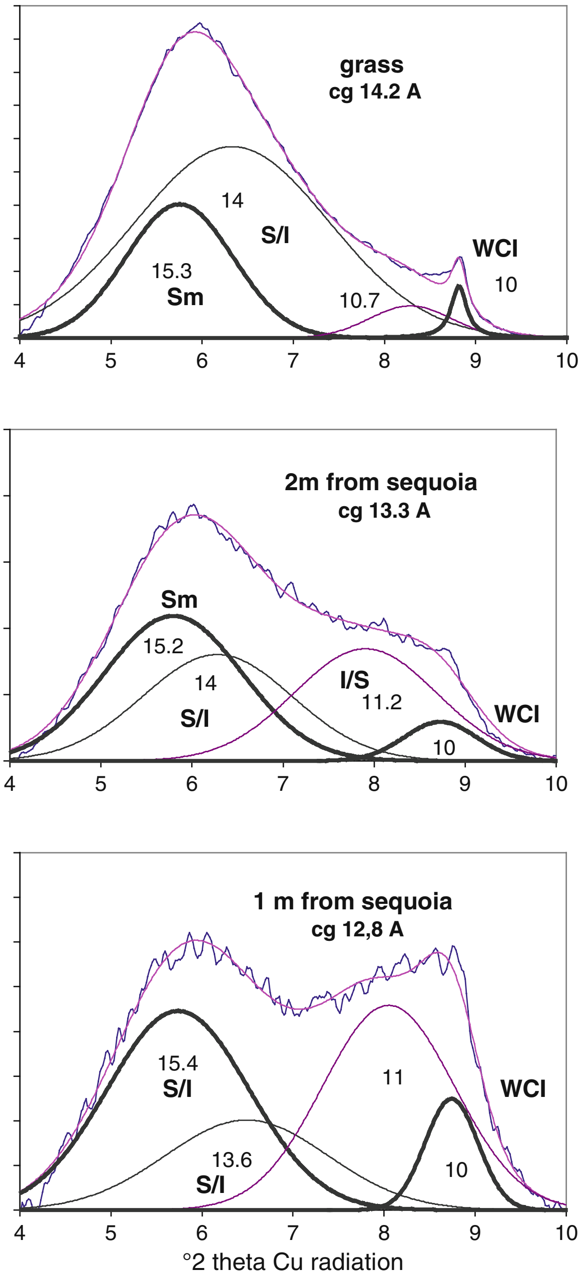


**Fig. A.8** Illustration of the effects of plants (sequoia vs. grass) on clay mineral type. Estimation of the effect can be made by estimating the center of gravity for the spectrum. This is obtained from an estimate of the individual relative peak intensity for each peak (width at half height times intensity, divided by the sum of peak intensities) multiplied by the peak position (in Å). The results are summed to give the center of gravity or average position considering the individual peak areas

as a comparative tool for soil assemblages which are similar but have experienced different histories.

Curve decomposition is in fact rather simple when one uses a minimum number of peaks to describe a complex spectrum. The most powerful use is to follow changes from one state to another of a clay assemblage which has been subjected to chemical changes either in the laboratory or those induced by plants in the soils themselves.

## Annex II Identification of the Major Groups of Clay Minerals

### *Major Mineral Types*

As described in the initial chapter (Chap. 1.3) clay minerals in soils can be classified into two groups;

*1:1 minerals* essentially kaolinite or hydrated kaolinite (halloysite)

*2:1 minerals* which include the groups of

Illite (anhydrous potassium interlayer ions)
Smectites with hydrous interlayer cations, essentially divalent forms (Ca, Mg)
HI minerals with hydroxy interlayer ions or complexes based essentially on Al forms.

*Hydroxyl – oxides* such as gibbsite, Al $(OH)_3$, iron oxides and hydroxyl, hydrous oxides. These area not silicate minerals and represent advanced stages of weathering even though they may occur in the initial stages of the water – rock interaction process.

X-ray diffraction sees essentially four phyllosilicate mineral types, based upon interlayer spacings of the sheet – like structures, the first near 7 Å, the kaolinite 1:1 structure. Another spacing, based upon a 2:1 structure, is near 10 Å which indicates a potassium interlayer without water molecules present. The third is a spacing at 14.2 Å, still a 2:1 type mineral, where the interlayer site is filled with hydroxyl ion (OH) units either as hydroxyl cations or fully polymerized hydroxy ion interlayer structures. These are HI minerals. The fourth and final type of spacing is near 15.2 Å, which indicates the presence of bi-hydrated divalent exchange cations. These are smectites.

Thus one has a relatively simple nomenclature to follow based upon X-ray diffraction characteristics as a function of laboratory treatments:

| *1:1 mineral* | *Hydrated* | *glycol treated* | *heated 200°C* |
|---|---|---|---|
| Kaolinite | 7 Å | 7 Å | 7 Å |
| *2:1 minerals* | | | |
| Illite (anhydrous K ions) | 10 Å | 10 Å | 10 Å |
| HI (hydroxy ions, OH + cation) | 14.2 Å | 14.2 Å | 14.2 Å |
| Smectite ($2H_2O$ + cation) | 15.2 Å | 17 Å | <15.2 Å |

From the above one can see that much of current laboratory treatment of conventional use is designed to identify the smectites type interlayer ions structure. Other more complicated treatments can be used to distinguish HI minerals, but essentially the peak position of HI structures is sufficient.

## *Inter-Layering of Structural Types*

There seem to be only rare cases of inter-layering between 1:1 kaolinite and smectite, although it is not unknown to say the least. We will designate this as K/S inter-layering. The principal characteristics are a peak to the high *d* spacing side of the 7.2 Å kaolinite peak and a peak at greater than 15.2 Å in the air dried state. Normal 2:1 mixed layered minerals and smectites give peaks at 15.2 Å

Interlayering between illite and smectite (ill/sm) is rather well know and has been thoroughly studied. The peak positions are between 10 and 15.2 Å in the hydrated, air-dried state.

Interlayering between illite and HI (HI/ill) minerals gives peaks between 14.2 and 10 Å. One can call this HI/illite.

Interlayering between HI and smectites (HI/Sm) will give a spacing between 15.2 and 14.2 Å in the hydrated state.

Thus there are three types of inter-layering between the three interlayer ion poles of 2:1 minerals, and one type of inter-layering between kaolinite and smectites, which gives us four inter-layered structures to identify. Using the possibility of identifying smectite components by glycol treatment, one can simplify the identification procedure as follows:

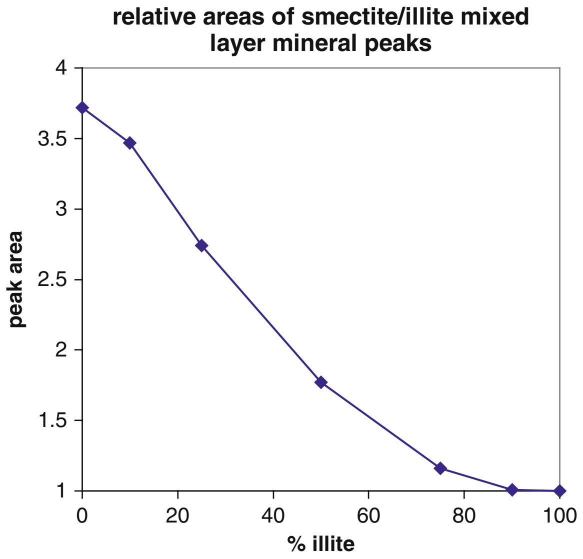
| *Peak position air dried* | *peak position glycol treated* | *inter-stratification type* |
|---|---|---|
| 10–14.2 Å | unchanged | HI/ill |
| 10–15.2 Å | increase in *d* spacing | ill/sm |
| 14.2–15.2 Å | increase in *d* spacing | HI/sm |

Peaks near the 10 Å illite position (between 10.5 and 10.0 Å) which do not change in position with glycol treatment are considered to be poorly crystallized (small diffraction domain) material called here PCI. Peaks that are un-affected by glycol and at the 10 Å position are WCI, illite. Thus for the illite pole there two peaks representing essentially the same mineral composition but of different crystallographic dimensions, PCI and WCI. The same is true for kaolinite. However we have not yet given the name of PCK and WCK to these forms.

### Illite/Smectites

Very much work has been done on the mixed layered minerals illite/smectite given their regular transformation with changes of temperature over different periods of time in diagenetically affected (burial and increase in temperature and pressure constraints) sediments. This information is useful to interpret the different X-ray

**Fig. A.9** Illustration of the relative intensities of mixed layer clay mineral species in the smectite – illite series. Coherent diffracting domain is constant and hence the only variable is the change in diffraction intensity which results from changing the interlayer cations from K to hydrated Ca ions in the case of smectite. Calculations were made using the Reynolds NEWMOD program (Reynolds, 1985)



diffraction characteristics of soil clay smectite/illite interstratifications and perhaps other types.

Several relations are of great importance for interpretation of the peak positions and the relative peak areas of the different forms. Initially, when a mineral becomes more hydrated in the interlayer site, the relative intensity of the peaks increases compared to a constant mass in the sample. In Fig. A.9 we show the changes in peak areas of smectites/illite mixed layer minerals as a function of their smectite – illite composition.

The smectite form with two layers of water in the interlayer ion position changes the surface area of the peaks by a factor 3.5 while the increase in cell dimension changes by 1.5. Thus one must be very careful to refer to relative change in peak area between series of samples before any estimation of absolute peak area can be made. Other differences in structural organisation can change the peak areas even further.

Another point which is extremely important is the fact that most smectite/illite inter-layer minerals have a disordered layer stacking structure. This means that the regular succession of smectite followed regularly by illite throughout the crystal is rare. This type of structure is known, especially in minerals found in hydrothermal alterations or in the transformation by water rock interaction of the trioctahedral minerals biotite and chlorite. Most soil clay minerals have a disordered, or non-ordered, succession of layers of the different components present. As a result one can consider that the majority of cases peaks will have a position between 10 and 15.2 Å that will change position upon glycol treatment will be of a disordered type, called R0. In Fig. A.10 we indicate the change in peak position and shape for changes in illite content relative to smectite content.

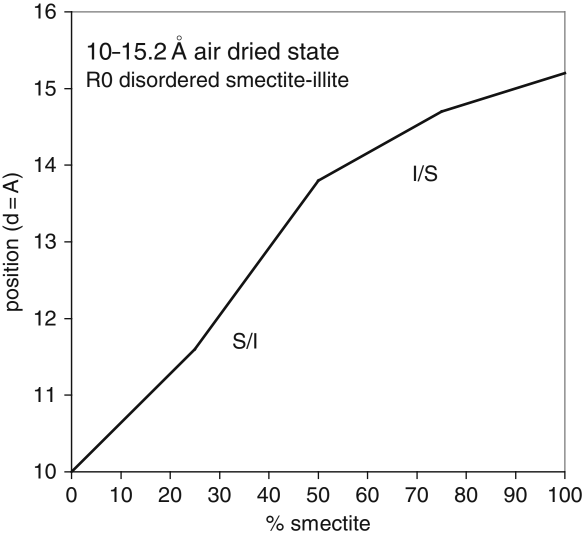


**Fig. A.10** Relations of peak position in Å and smectite content in mixed layer illite-smectites. This curve is valid for random (RO) type interstratification of the clay layer types which is typical of soil clay minerals except in rare instances. Calculations were made using the Reynolds NEWMOD program

The relation of position and smectite content is not exactly linear but nearly so. One must remember that this is valid for samples with the same number of coherently diffracting layers (crystal size) in the crystallites. On the diagram sm/ill is used to designate the smectite – rich minerals and ill/sm the illite – rich minerals. Thus using a normal hydration state, divalent ion saturated and observed in the air – dried state, one can determine the proportion of smectites and illite present in the average crystallites.

The spectra for mixed layer minerals (illite-smectite) in the air – dried state where hydrous cations are surrounded by two water layers, is shown in Fig. A.11a. There is a general shift in peak position, seen in Fig. A.10, with changes in peak width.

However this is not true for the minerals when they are in the glycol treated state. In Fig. A.11b one sees that the glycol treatment tends to shift all peaks to a position near 17 Å with varying peak widths.

Hence the glycol treatment loses the potential compositional information for a portion of the smectite-illite inter-layered minerals. It essentially effaces the difference between the S/I and I/S minerals. This is a very important point to remember. The use of a moderate concentration (0.5 M) divalent ion saturation (Sr ions are preferred) to determine the composition of a mixed layer illite-smectie mineral is essential. Since we are often interested in the potassium resources in clays (essentially the illite content) the peak position of the illite-smectite minerals is a very significant index to changes in chemical environment in soils.

The two aspects one should keep in mind in the assessment of illite-smectite mixed layer minerals is that the more smectite present the greater the peak area of the same mass of material. The second aspect is that the proper assessment and identification of illite-smectites as well as smectite – illites should be done in the air – dried state for a divalent cation exchanged sample.

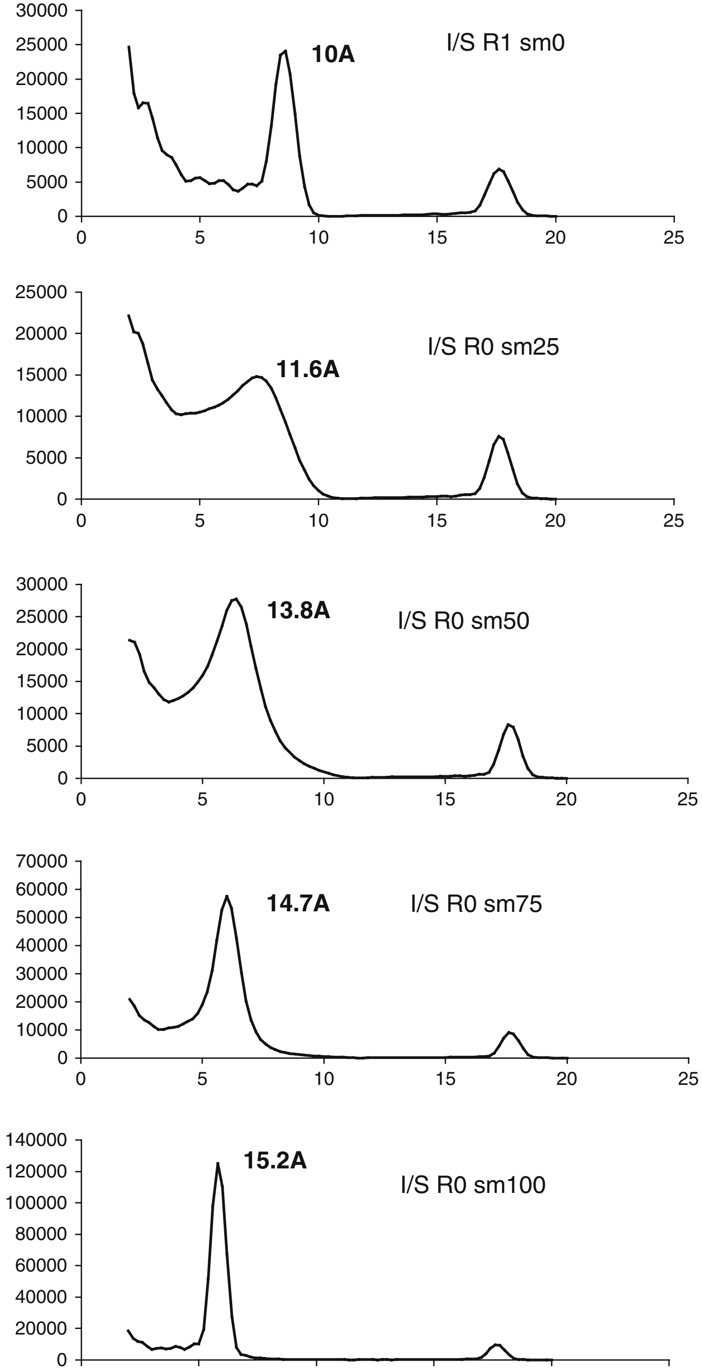


**Fig. A.11** Illustration of X-ray diffraction spectra calculated using the NEWMOD program for two types of interstratified illite-smectites, two layer ordered, R1 shown in (**a**) and without ordering, type R0 shown in (**b**)

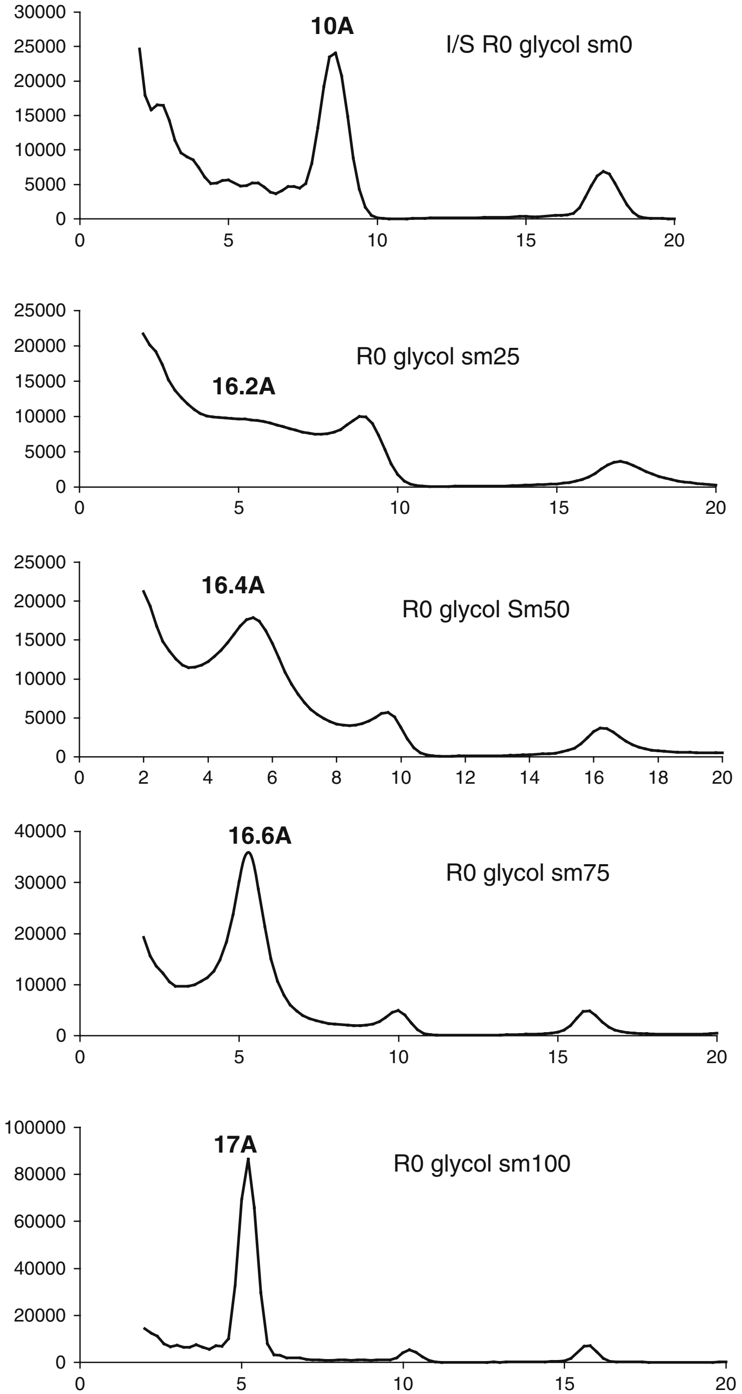


**Fig. A.11** (continued)

## HI – Illite Inter-Stratified Minerals

These minerals have been described many years ago (Millot and Camez, 1963). However their importance has perhaps been overlooked. Most authors consider that the HI mineral is the stable phase which can be interstratified with smectites. However, the exchangeability of Al-OH and perhaps Mg-OH interlayer ions with potassium is an important part of the mineralogy and chemistry of these soil clay minerals.

HI minerals have a basal spacing of 14.2 Å which does not change with glycol treatments or changes in air humidity. Heating changes the interlayer spacing in an irregular manner, tending to show a smaller basal spacing, moving towards illite. However, treatment with K ion solutions can, and does in most cases for soil clay minerals, change the spacing towards 10 Å and at the same time some now illite (increased peak intensity) appears. Thus there is a frequent, variable, tendency for an exchange of hydroxyl interlayer ions with potassium. These minerals can be identified by a wide peak between 14 and 10 Å of course, which does not change position with glycol treatment. Mixed layer illite – smectite minerals have a peak in this region, but it is strongly shifted to near 17 Å with glycol treatment.

This is a very brief introduction to the modern methods of treating X-ray diffraction spectra. Most new diffraction machines come equipped with decomposition programs. However, one must use them with care, so that a minimum number of peaks are defined and are well placed. Refinement by least squares methods can give good results or totally aberrant results depending upon the initial propositions that the operator defines. If one considers that in the air dried state, peaks will occur around 15.2, 14.2 and 10 Å and others at positions in between, one can eliminate many errors. The phases must correspond to true mineral possibilities as outlined above. Usually in soil clay assemblages one can have two illite-smectite minerals (S/I and I/S). The presence of an HI/illite mineral will occur with a strong HI phase. The three poles of illite, HI and smectites are the key to interpreting soil clay assemblages.

Calculations using the Reynolds NEWMOD program shown in Fig. A.12 indicate the position of this mixed layer peak and their width at half height, both values are affected by the composition (proportion of the interlayered components). Further, the number of coherent diffracting layers (*n* in the diagram) can shift the peak position and width making identification of these minerals rather difficult.

The above pages are designed to help the un-initiated to find their way in the difficult process of clay mineral identification based upon X-ray diffraction data. The only realistic method for soil clays must be based upon decomposition methods. Here one can identify peaks that are partly masked by others and in many cases one can estimate the relative proportion of these different components in the soil clay assemblage. Such estimates can help to understand changes in clay mineralogy which can be effected by plant regimes. This tool will allow one to see the effects of crop rotation or plantation of different trees on the clay mineral resources, especially the potassium present and available.

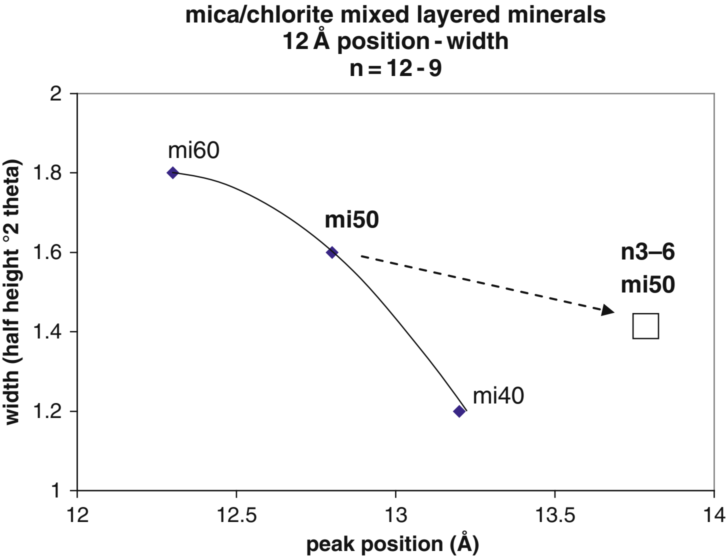


**Fig. A.12** Results of calculations using NEWMOD for HI (chlorite) illite randomly interlayered minerals in the range of 40–60% illite component. Coherent diffracting domain is near 10 layers for the diamond points and 4 layers for the square. The shift in peak position and width is significant due to coherent diffracting domain size as is the case for smectite – illite interlayer minerals

## References

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