

Chapter 1

Geology and Chemistry at the Surface

1.1 The Geological Framework of Surface Geochemistry

In the mid-sixteenth century Bernard Palissy (1563) mused upon the characteristics of rocks and water and the interaction of the two. He was interested in the movement of water within the surface of the earth and the relations of water and rocks. In his publication *Discours Admirables*, presented in published and verbal form for the royal court in France, he was interested in the durability of rocks and the eventual transfer of material at the surface of the earth. Since at this time the earth was said, dogmatically, to have been created and unchanged since biblical times, he wondered if it was in fact true, being strongly influenced by the thinkers of the Renaissance. He contemplated caves and caverns in rock. Here he saw cavities produced by water–rock interaction and precipitation of matter from aqueous solution. In his account concerning rocks (*pierres*) he noted that water can enter a rock, move within extremely small cavities, and when it comes out, deposit crystalline material. Here rock–water interaction and dissolution is clearly evoked, which is the basis of surface geochemistry. It took a long time, but eventually modern science caught up with his ideas, and those of others, concerning surface geochemical interactions. However no name was given to the phenomenon at the time. Nevertheless the phenomenon of water–rock interaction was realized to be a significant event in the structure of the earth and its history. In Fig. 1.1 one sees the representation of such an event, somewhat romanticized, in the grotto of the Pitti Palace in Florence. Here it is evident that there is dissolution and precipitation of matter, which are the fundamentals of surface geochemistry.

The use of the name Geochemistry applied to the study of chemical relations in different geological situations in or on the earth is somewhat recent, coming into full vogue in the 1950s. It has its roots in the application of chemical principles (what was often termed mineral chemistry, dating to the origins of chemical investigation in the eighteenth to nineteenth centuries). Most of the elements of major abundance were discovered and defined in the period 1750–1850 (Correns 1969). Although the idea of geochemistry is rather old, mid-nineteenth century

Fig. 1.1 Grotto of the Pitti Palace, Florence showing dissolution and re-crystallisation phenomena, which are the basis of surface geochemistry



(Correns 1969), the concept was not made popular until the fundamental text of Goldschmidt was published (Goldschmidt 1954) followed by several other fundamental texts which opened the realm of chemistry in the geological sphere (Mason 1958; Krauskopf 1967, among others). This set the stage for a new era of geological investigation using well-defined and modern scientific principles borrowed from another field, chemistry. With time geologists became more and more interested in the distribution and affinities of element isotopes as they reflected different chemical and physical properties that formed rocks and minerals. In the twenty-first century one often thinks of this part of the chemical world of geology more than the distribution of chemical elements and the chemical causes of these distributions. Surface geochemistry, as we wish to treat it here, will be uniquely considered from the standpoint of chemical occurrence and the causes of the presence of the different elements found in different surface environments and materials. Isotope geochemistry certainly has an important role to play in understanding the processes that affect the surface of the earth, but it is not our preoccupation here.

We will treat the basic affinities of elements as they experience different chemical environments where earth surface materials are transformed and transported. The geochemistry of the surface reflects the changing chemical environment which leads to an instability of rock forming minerals at the surface and it

reflects the forces of nature: plants, rain, gravity, which affect and move surface materials from one site to another.

The most important concept and reality of surface geochemistry is that elements can enter or leave a given mass of matter, forming what thermodynamicists call an open system (see Korshinski 1959). Further the chemical constraints on the material in the system can come from outside. The passage of water into and through a rock will change its chemistry, but in a large part of the reactions the chemical constraints, which change mineral phases, come at least partially from outside of the rock. The interaction of biologic agents, bacteria and others, can influence the chemistry of the rock or geo-materials so that they have different properties and mineral phases. Surface geochemistry is the study of multiple influences, coming from outside of the geologic system (air and water) or from within but where the products of reactions can often be released outside of the initial material considered. This is the case for chemical constraints, but one must consider the physical movement of masses of matter also.

1.1.1 Movement of Materials

As all geologists know, Geology is a four-dimensional problem. The earth has three dimensions, all of which play a major role in the dynamics of the earth. Using the word dynamics implies the dimension of time. Hence the four dimensions. If a mountain is built by rock material being moved upward, the problem is three dimensional since the rock has to come from somewhere and is usually moved by forces described in x , y , z coordinates. The mountain is not build in a day, and hence the dimension of time is extremely important. The movement of materials at the surface of the earth implies an understanding of the four dimensions of geology (see Birkland 1999).

Surface geological materials are composed, to simplify, of rocks and the products of their alteration through the interaction of water and rocks. The thickness of the alteration zone can vary from several centimeters to tens of meters depending upon the length of time of exposure of the rocks to the surface chemical forces and the intensity of alteration, i.e., the amount of water coming into contact with the rocks. Rocks can be moved by gravitational forces, as well as can the alterite material. However the distance of rock transport is relatively small, hundreds of meters, whereas the distance of transportation of altered rock can be hundreds of kilometers. Movement is the key to understanding the surface of the earth.

The earth is in constant movement at the surface with mountain building and the erosion of these mountains. The leveling of geographic highs is done in different manners and the eventual transport of altered materials from one site to another is extremely important. The relative amounts of matter moved by different physical processes have been estimated as follows (Milliman and Meade 1983; Gorsline 1984) in billions of tons/year:

Particles in rivers	13.5
Dissolved in rivers	4.2
Ice transport	3
Dust transport	0.6
Volcanic ejecta	0.15

In looking at these numbers it is clear that the largest part of alteration products due to rock–water interactions moved from mountains to lower areas is displaced as particulate material in rivers. This is the nature of longer distance movement of surface alteration materials, which eventually end up as sediment, which becomes rock as it is buried, hardened, and recrystallized by pressure and temperature.

The movement of mountains to the final “resting place,” sediments, is complex and depends upon many factors. The rate at which rocks alter to new materials, essentially oxides and clays, depends upon such factors as climate, rate of mountain building or elevation, and plant interactions, among others. In order to better understand these processes, we will go from large scale to small scale which allows us to consider the mechanisms and impact of geological forces on the geochemistry of the earth’s surface. The questions are: how do surface materials form, what are they, and where do they go as they interact with the physical forces of the surface (gravitational forces, aqueous, or wind transport)? These questions define the basic setting for surface geochemistry, which has been and is geological.

Geology is a nonlinear sequence of events. Mountains are built by infrequent vertical movements, signaled by earthquakes. Landslides occur during earthquakes and periods of exceptionally high and episodic rainfall, bringing the materials moved upwards by tectonic action to a lower geographic level of deposition. The movement of most of the surface material occurs during events that are widely spaced in time. However the daily input of fine material into the oceans by major rivers is very important in that it is the system of major transit to the eventual final residence of material moved by surface erosion. This transport is also episodic but less so than major massive short-distance transportation (landslides), which occurs on a smaller geographic scale.

1.1.2 Physical Constraints

It is initially important to understand the physical setting of surface geochemistry. The surface the earth is in a state of continual change, on a geological scale, thousands or hundreds of thousands of years, or periods much shorter, tens of years, when biological activity is involved. In fact the dominant trend of surface geochemistry is change of place.

1.1.2.1 Slope Failure and Transport

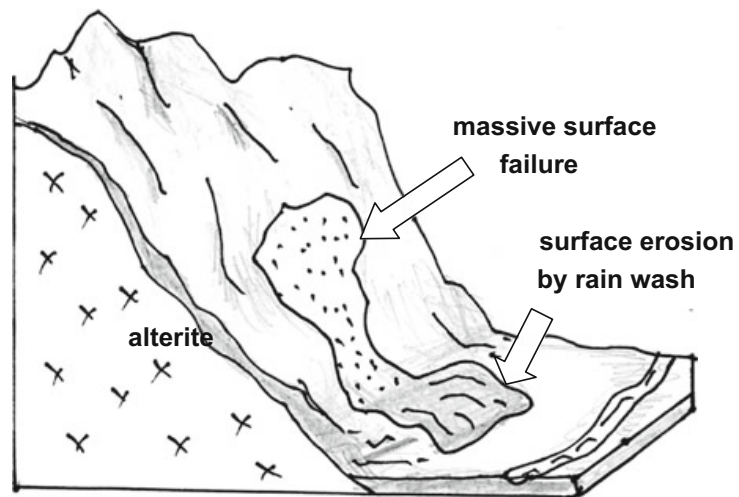
The basic paradigm of surface geochemistry is one where rocks formed at higher than surface temperatures are brought in contact with the atmosphere of the earth's surface and its chemical constraints. The reasons for this contact are the upward movement of rock masses by tectonic forces to form mountains. Surface geomorphologic relief produces instability. Here rocks are placed in two unstable situations: physical and chemical. The physical constraint is that the rock mass is higher than the lowest residence point, the ocean, and it is therefore subjected to the forces of erosion directed by gravitational movement of solids. What goes up must come down. A brief illustration of massive transport of surface materials is given in Fig. 1.2. In the case of massive erosion due to structural failure on highly sloped surfaces, the major force is gravitational which, under conditions of exceptional stress such as high rainfall or earthquake tremors, accelerates the inherent unstable materials into downward movement. This produces landslide, rockslide, and slumps of surface material, which is rocks and soils. This type of movement is by far the most important in surface movement as far as the mass of materials is concerned when relief is significant. However the effect is local to a large extent, essentially stopping at the foot of the slope that caused the instability of the rock-soil masses.

Once the slide material is deposited it in turn is subjected to rainwater transport where the small particles, which are newly exposed at the surface, are subject to displacement and eventually find their way into a stream or river. Massive displacement is followed by more small-scale erosion, which continues the movement of materials to lower levels.

1.1.2.2 Resistance to Erosion

One might think that the hardest rocks resist erosion more than others and that those most resistant to chemical dissolution will be also more resistant to transformation and erosion. This is true and not true. In looking at mountains, one sees very clearly that sandstones and carbonates tend to make salient features while granites, basalts, and other eruptive rocks tend to be eroded as well as are shales, and different aluminous schistose metamorphic rocks. Normally carbonate minerals are strongly affected by the acidity of atmospheric aqueous solutions, tending to dissolve with a much greater coefficient of dissolution than silicate minerals. Quartz is the most resistant mineral, even though thermodynamically it should dissolve readily, it resists water attack with great efficiency. In the observations noted above, the sandstones should resist chemical attack and remain chemically stable. They are brittle under differential tectonic stresses, tending to fracture, but not to a great extent. Granites and basalts are more soluble than sandstones, but the soluble elements are less soluble than calcium carbonate. Thus in the sequence of chemical stability one should put sandstone > granite, basalt, shales, and metamorphic rocks

Fig. 1.2 Massive slope failure showing displacement of unstable material on slopes which is deposited at the foot of the slope to be eventually moved by the action of rainwater toward streams by surface erosion



> carbonates. Yet one sees that the most chemically stable and least chemically stable rock types both form resistant ridges and massifs in mountain ranges. The anomaly is the carbonate rock.

If we consider the mechanism of chemical alteration, it is clear that the agent of dissolution is rainwater, which is slightly acidic (pH around 5.2). For rainwater to have a chemical effect it must stay in contact with the rock and mineral matrix it should alter. Mineral dissolution takes a certain time. In mountain ranges, the rocks have been recently subjected to anisotropic forces and confining constraints, which lead to local failure and the development of cracks. These cracks can be large enough to be called faults, hundreds of meters long, or of smaller dimensions down to the size seen in thin section under the optical microscope, several millimeters in length. These failure planes are open to water flow when the confining pressure is released as the mountain finds its final position, at least for hundreds or thousands of years. If all rocks responded to tectonic forces in a similar manner one would expect to find similar patterns of faulting and fracturing in them. However this is not the case. The resistant rocks, forming ridges and peaks in mountain edifices, sandstones, and carbonates, show fewer micro-fractures than do granites, basalts, and to a certain extent metamorphic and sedimentary rocks. In fact carbonates are more resistant to fracturing because they deform in a ductile way, being semi-plastic under great pressures and pressure differentials. Hence they show fewer brittle fractures in their macro- and microstructures. As a result there are fewer small cracks in a carbonate rock than in a granite for example. The micro-fractures are passageways for water entry and hence for chemical interactions, i.e., dissolution and minerals transformation.

There is thus a paradox of the normal laws of chemical reaction and rock stability, which is due to the mechanical properties of the rocks involved. Carbonates are more reactive chemically but less accessible to rainwater chemical interaction, while granites and other rigid macro-crystalline rocks present more passageways to water infiltration increasing the residence time of aqueous solutions which promotes chemical reaction that destroys the mechanical coherence of the

rock. Here we see that the weakest can be the strongest. The most chemically fragile and least mechanically resistant rocks are least transformed by aqueous solution attack and fracture failure due to mechanical stress. Despite their inherent weaknesses, carbonate rocks resist the effects of alteration and tectonic weakening and remain among the most stable rock types forming mountains.

1.1.2.3 Water Transport of Dissolved and Suspended Material

The chemical transformation of minerals, where minerals formed at high temperature become out of chemical equilibrium with the chemical conditions of the surface, is that dominated by an abundance of water. The transformation of rock minerals to more stable phases is accomplished by the interaction of water with rocks in an oxidizing atmosphere which promotes the recrystallization of the minerals and at the same time removes some of the elements present from the solids. Generally this process is accompanied by the incorporation of hydrogen or water molecules into the new mineral phases. Surface chemical interaction is essentially one of hydration. Materials are dissolved either integrally or incongruently, forming “residual” alteration minerals. More importantly, the new minerals formed are of smaller dimensions than those of high temperature origin. This change in size allows the new minerals to be transported more easily by moving water down to lower geographic levels, and eventually into the sea. Of course larger chunks of rock are moved as well as particles of mineral grains (sand and silt). The larger the particle, the faster it will be deposited in the trajectory of the water carrying it toward the sea. The principle of faster deposition of larger particles (particle size sorting) can be illustrated by taking a handful of soil material and dispersing into water in a beaker. The finer materials stay in suspension while the larger ones settle out rapidly. The larger they are the more rapidly they settle. This is illustrated in Fig. 1.3.

The further the materials are transported, the lower the transport gradient, and the less energy available for moving particles. Thus the larger grains tend to be deposited along the slopes of mountains, or deposited at their bases. The lower gradient areas, along rivers and streams, are where sand-sized materials and clays are deposited along slow moving and less energetic water. Clay materials are gradually deposited until they reach the ocean where the finest material held in suspension is flocculated in the saltwater and moved along the seacoasts. A significant portion of the fine material reaches the greater depth of the ocean continental platforms where they become buried by materials of subsequent sedimentation.

As the slopes are less important, fluctuations of rain inputs can vary the energy of transport and at times local deposition occurs as the streams overflow or become less active. The deposited material, along streams for instance, before final deposition in seawater can be chemically altered further if exposed again to the rain and plant interactions of the earth's surface along the river banks or on flood plains. With each cycle of alteration some matter is lost from the solids to the solution and the material that remains becomes finer grained.

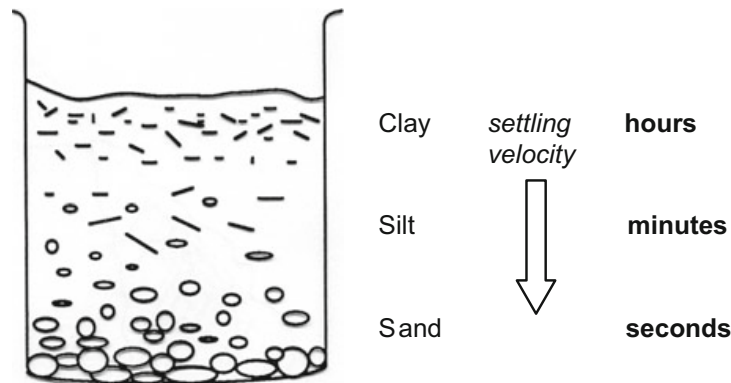


Fig. 1.3 Beaker experiment where heterogeneous alterite material is dispersed in water and allowed to settle. The largest grains are deposited first and the smallest last. Eventually the small grains can be held in suspension for very long periods of time if the water is moving and turbulent

In Fig. 1.4 the relations of slope and grain size for some major rivers are indicated. In general the larger the river, the larger the drainage basin the more fine particles (clay size or $<2 \mu\text{m}$ in diameter) are transported. These are the fundamental variables of surface geomorphology, which determines the types of material transported. In general, the further from a mountain chain one is, the more fine particles the rivers will carry.

Figure 1.5 indicates situations where material can be transported and deposited locally, from the slope of a stream bank for example, and deposited, along the flood plain of the stream. Streams are at the same time vehicles of transportation and deposition. When a stream has a high sediment charge under conditions of high intensity flow, material is transported that would not otherwise be carried due to the high energy of the moving water. The importance of floods to the transport of clay-sized material is emphasized by the fact that many rivers transport more than half of their annual sediment load in only 5–10 days of the year (Meade and Parker 1985). When the period of high flow is less important, or when the stream overflows its normal channel, the transport energy decreases and material is deposited along the edges of the stream channel. This deposition is very important in that it is a temporary holding area for fine-grained material, which will eventually reach the sea. However, during its period of temporary deposition, the newly deposited material forms a substrate for plant life and biological activity, which modifies the chemistry of the sediments. This secondary soil forming process is or has been very important to mankind in that many ancient civilizations were founded on stream or river deposits along the major channels of water movement. A classic example is the Egyptian civilization built upon soil renewal through deposition of the fine-grained sediments of the Nile river. The formidable Near Eastern civilizations of the same period were based upon sediments in the Tigris–Euphrates river basin. These holding areas of deposition essentially of soil materials have been a key in the development of agricultural mankind.

Not only is the height of the mountain important as a factor of transport, but also the climate, measured by temperature and rainfall which are the agents of alteration,

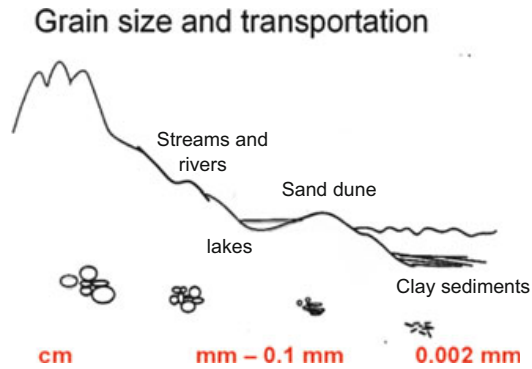


Fig. 1.4 Illustration of transport distance as a function of grains size in a landscape situation

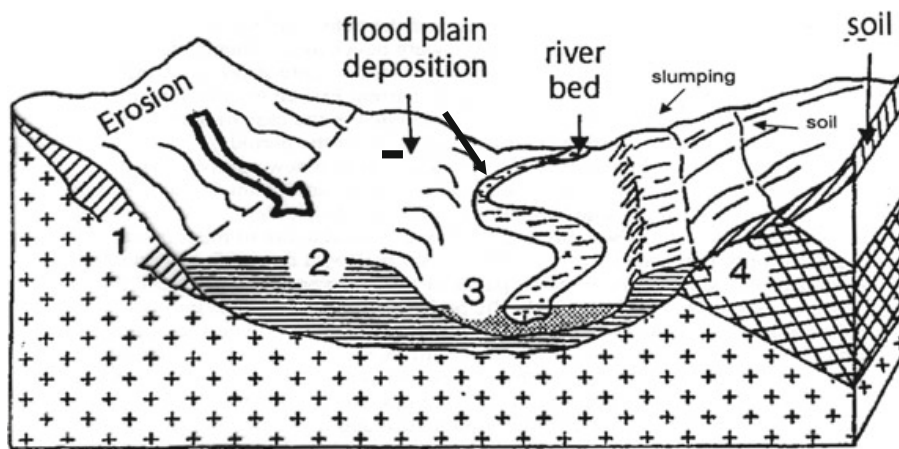


Fig. 1.5 Illustration of massive transport erosion and re-deposition along a river. 1 Surface erosion and slump movement of soil surface material, 2 temporary deposition of slump material which is eroded in its turn by rainfall erosion, 3 deposition of the overflow material from the stream when it reaches low energy water movement, 4 slump movement of poorly consolidated rock material

is an important factor. The more rain and the higher the temperature, the more small particles formed from unstable minerals in rocks and the more fine material there is in the rivers. Sediment yields on a basin scale vary greatly, and there is no correlation between basin size and yield (Fig. 1.6). Nor is there any statistical relationship between variables such as runoff and yield (Selby 1984). The two factors that are important are geomorphologic relief and climate. Gibbs studied the variation of sediment yield in the Amazon Basin which showed that 80 % of the sediment is derived from only 12 % of the basin area comprising the Andean mountains. Gorsline (1984) pointed out that the land use by man since late Pleistocene times also greatly affected sediment yields.

To a large extent the fine materials (clays) are moved by rivers into the oceans and deposited offshore, i.e., several hundreds of meters or kilometers from the shoreline. This action depends upon the configuration of the ocean bottom, depth and rugosity, and the intensity of the river flow which can move material to greater or smaller distances depending on its flow rate (energy). However not all of the

Source and supply of mud

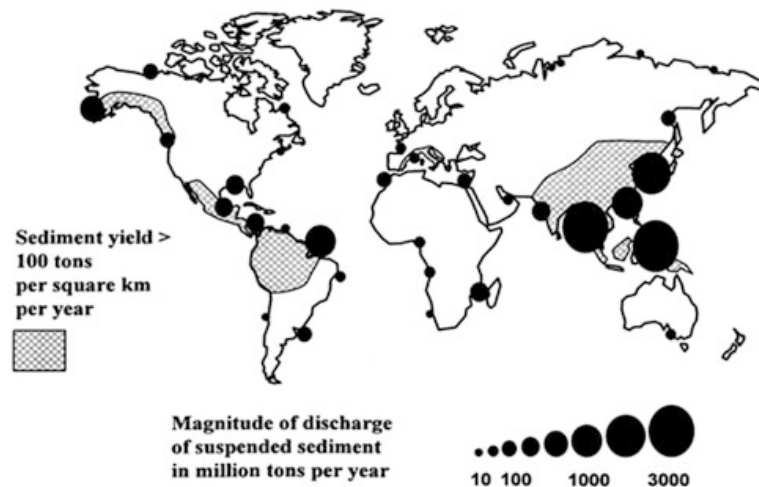


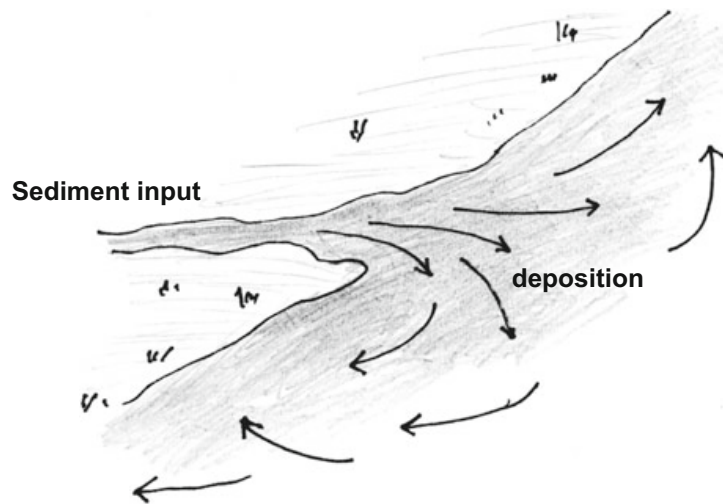
Fig. 1.6 Sediment yield map for major geographic areas [adapted from Hillier (1995)]. The Western Pacific Islands are combined. Highest yield occurs in areas of high relief and/or high rainfall

material finds its way to deep repositories off the coasts. Some is moved along the shore, laterally from the mouth of the river, which brings the sediment to the sea. The clay (or mud) deposits and movement are generally termed wetlands. Slightly more coarse material is often moved by coastal currents on or near the shore forming deposits of sand-sized material, usually composed of quartz (silica) and refractory minerals little affected by the alteration processes of the surface forming sand dunes. In areas of high relief, movement of these un-transformed grains will include minerals less stable or refractory to alteration, such as olivines and pyroxenes in areas of volcanic activity or garnets and amphiboles coming from metamorphic rocks. Sand reflects at the same time chemical resistance to weathering and the importance of slope and gravitational movement of alterite material.

This transport of the finer materials and their deposition occurs along coastlines of large lakes or seas. Initially, suspended or deposited material can be moved by shore currents parallel to the coastline and deposited material through strong turbulent wave action can re-suspend material deposited at some distance from the coast, depending upon the depth of the continental shelf. These zones are of importance to humans in that they concern a large portion of the aquatic life used as a food source. Most often sedentary shore or shallow marine life depends upon the sediments (clays) and adhering organic matter for sustenance. The chemistry of this material is thus involved in the nearshore food chain. These “wetlands” are considered as being very important to ecological balances (Fig. 1.7).

As we all know, one finds sand deposits, as beaches or dunes, along the edges of large water masses as well as deposits of clay rock sediments. The reason why one or the other type of deposit forms, usually well-defined grain size categories, is undoubtedly due to the energy of the movement of water masses along the edges of land. However it is not easy to see why there is such a bi-polar selection of grain sizes as to select grains from rocks that have not reacted with the surface

Fig. 1.7 Illustration of deposition of fine-grained stream-borne material, which becomes littoral deposits



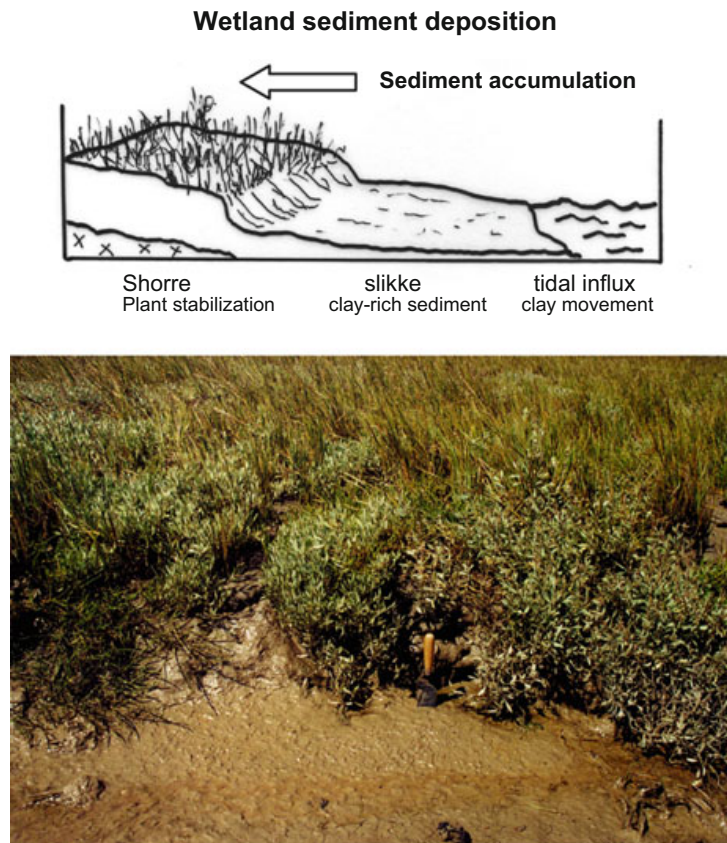
environment (essentially quartz) and the newly formed materials that have been the result of water–rock interaction (clays and mud). In any event most clays are detrital, probably more than 90 %. They are supplied to the sedimentary systems from two main sources. One source is rocks, and the other is the soils that develop on them by weathering. Sandstone and shales are usually rather well defined, with some intermediate mixture material, but for the most part there is a strong difference between these sedimentary rock facies.

In any event concerning the clay-rich material deposited and re-worked along a coastline, it forms two types of structures, the *slikke* and the *shorre*, i.e., the clay-rich newly deposited and mobile material moved by tidal action (*slikke*) and this same material which can be fixed in place by plants where the newly arrived clays are stabilized to become wetland deposits or remain mobile along the coast tidal zones (*shorre*, see Fig. 1.8).

The roots and stems of the peri-maritime plants (grasses and small shrubs) provide a catchment for sediments, clays, moved by tidal action. As they are fixed they form an advancing front of sediment, stabilized by plants, which extends the dimensions of the wetland and hence the continent into the sea. Such structures are often very useful to farmers forming fertile zones where soil clays filled with nutrients and organic matter can be exploited by mankind. When these zones are protected from further intrusion by tidal movements (diking) they become prime land for farming as demonstrated by the Dutch and others in coastal areas. Plant growth fixes clays and as they are fixed plants roots advance seaward forming deposits of stable clays. This is an advance of the land into the sea by plant action.

Thus in general the farther from the mountains and the lower the slopes, the smaller the particles will be which are transported by rivers. Deposition of more coarse materials occurs along the trajectory as a function of slope and river flow intensity. Exceptions are sand-sized material transported under periods of high stream flow intensity, which can be moved along the coastline through coastal currents, forming sand dunes and beaches. When this material is deposited in a deep-water environment, it is buried successively to form a sandstone.

Fig. 1.8 Illustration of the stabilization of fine-grained, clay-sized material along coastlines. The shore is the area of plant fixation of the deposits stabilized by plant roots and the slikke is the area of recent and continued movement of clay-sized material by tidal and wave action. The stabilization by plants allows more sediment accumulation and an advance of the land area into the tidal deposition area (photo)



1.1.2.4 Wind Transport

Another means of moving matter at the surface is by wind action. In certain areas of the world wind is an important agent of erosion, transport, and deposition of sediments. Dust storms, which are some of most frequent natural hazards in desert regions, can be a quite important source of deep-sea sediments. Impressive pictures of dust storm from the space can be found, for example, at the NASA earth observatory (<http://earthobservatory.nasa.gov>). The grain size effect is quite limited, mostly in the clay fraction ($<2 \mu\text{m}$ diameter for long-distance transport, hundreds of kilometers). The source of dust material or loess is usually in desert areas where previous or infrequent current movement by water has left the fine material without plant cover and thus vulnerable to the action of wind erosion. Sand seas occur throughout the interior. The large deserts are on either side of the tropical, high rainfall zones near the equator except where the Himalaya Mountains have deviated the normal weather circulation belts moving them to the north and the case of the Americas where the mountains have changed the weather circulation directions especially rainfall patterns. For the most part the transport of loess today is toward the oceans from the deserts except for the case of China where the western deserts at the foot of the Himalayas move dust to the east over the Chinese mainland. In Xian the rate of accumulation is near 2 mm/year, enough to renew the agricultural soil zone in 100 years. Nevertheless smaller amounts of dust move

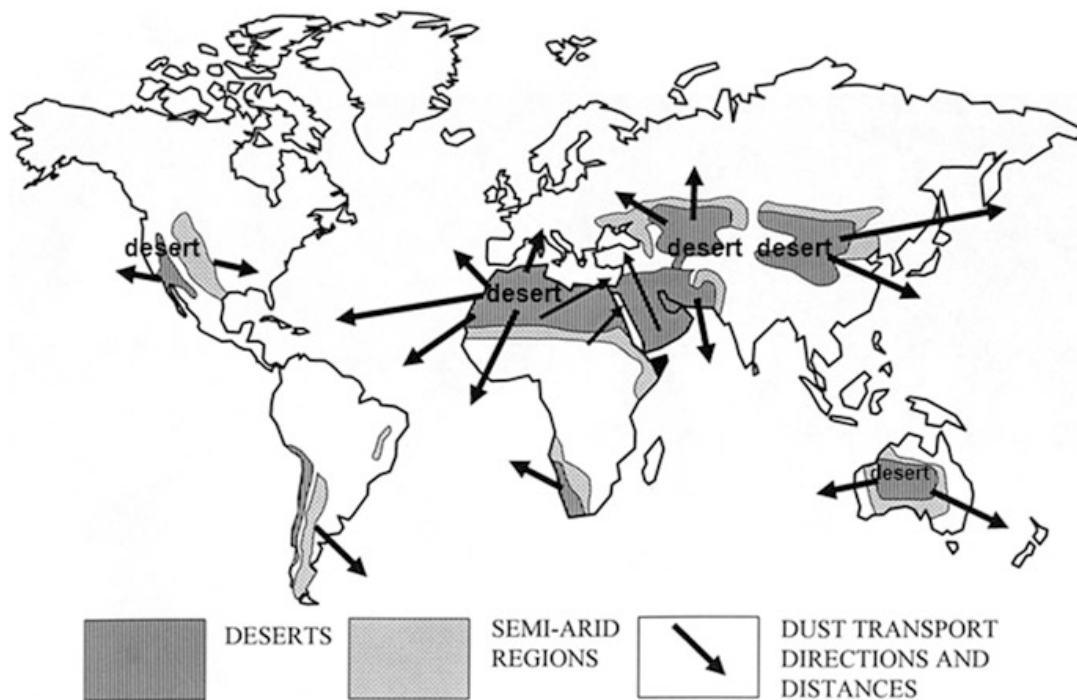


Fig. 1.9 Illustration of major movement patterns and transport distances of dust material and loess. Loess (dust borne by wind currents) originates in desertic areas on either side of the tropical zones of high rainfall. Long-distance transport involves particles with grain sizes of $<20 \mu\text{m}$ [adapted from Hillier (1995) after data in Pye (1987)]

to the north from the Sahara into Europe and eastward across the central United States. Figure 1.9 indicates the major movements of dust over the globe.

Wind transport is often not considered in studies of soils, for example, but the input to the surface environment can be very important especially concerning the minor element content of wind-borne material. It is a very important aspect of modern surface geochemistry in that wind-borne material from industrial sites can become an important factor in surface geochemical interactions.

1.1.3 Chemical Effects

Along the coastlines and in deep oceanic waters, one finds effects of biological activity which can extract materials from the dissolved part of transported materials, especially calcium and magnesium which can be combined with CO_2 which were dissolved in the water to produce carbonate material. These deposits are most often dominated by the carbonates, which become sedimentary rocks concentrating the dissolved part of the sediment load (Ca and Mg notably).

In some instances stream water is concentrated in closed basin lakes (i.e., without an outlet to the sea) where it is evaporated depositing dissolved material as sulphates, chlorites, and borates. Evaporate deposits are very important

for human activity in that they often contain life-sustaining sodium chloride, as well as potassium chloride which is essential to aid in plant growth. Other useful elements such as boron are found in such deposits also.

The coastal concentration of sand, which is essentially un-reacted rock material refractory to surface chemical processes such as quartz, the deposition of clays in the nearshore area, and the formation of carbonates produce the strong chemical segregation of materials found in sedimentary rocks; shales which are potassium, iron, and alumina-rich, sandstones silica-rich, and calcium, magnesium-rich carbonate materials.

Magmatic materials →	Al, Fe, K	Shale (essentially altered rock material)
	Si	Sandstone (refractory non-altered minerals)
	Ca, Mg	Carbonate (mostly biological deposits)
	S, Cl, Br, S	Evaporite deposits
	Na	Seawater
	P	Shallow sea deposits

Other elements found in rocks will follow these major mineralogical, sedimentary groups as a function of their chemical affinities with the minerals present in these sediments. This is the fundamental geochemical effect of surface interaction of rocks with the chemistry of weathering and alteration of rocks which dissolves the rock materials, and forms new minerals of different compositions.

1.1.4 Alteration: Rock to Soil Transformation

1.1.4.1 Alteration and the Development of Alteration Profiles: Water Rock Interaction

The initial framework of surface geochemistry is that of a chemically unstable assemblage of minerals in a compact material (rock), which will re-adjust to the chemistry of the surface producing small, new minerals, which are the product of mineral–water reactions under conditions of oxidation. The chemical alteration process occurs at two distinct levels in nature: the water–rock interaction zone and the plant–soil interaction zone. The second level is in fact the surface of the contact between mineral and atmosphere where plant and other biological forces control and modify the chemistry and physical presence of alteration materials. The initiation of alteration can be of either mineral or biological interaction. Bare rocks, in areas of some moisture, usually show the presence of some form of living material, such as moss or lichens, where the interaction begins through, either integral dissolution or partial dissolution and formation as new phases. The initial interactions are initiated by the fixation of lichens on the rock, and then the development of mosses. A gradual accumulation of wind-borne dust (clay and silt) material allows the formation of grasses and the development of a very thin soil zone (Fig. 1.10).

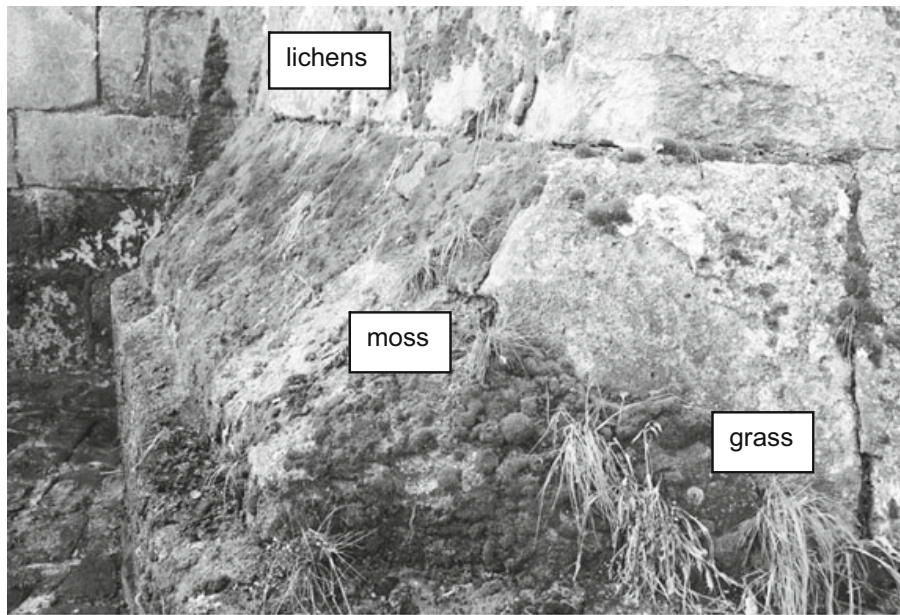


Fig. 1.10 Thirteenth-century church wall (Ile de France) made of limestone where lichens, moss, and eventually grasses fix clays and begin the development of soil formation

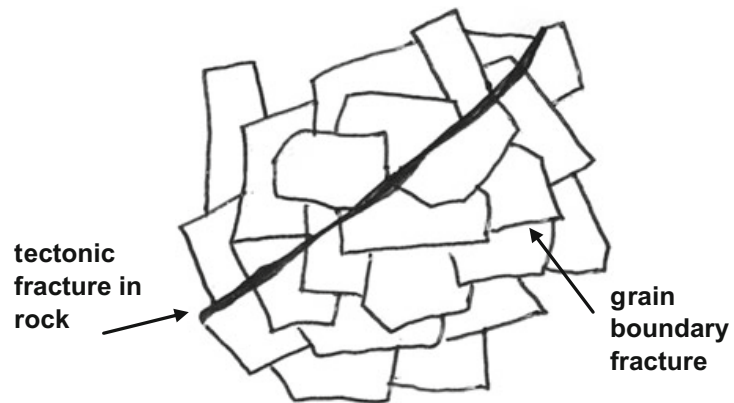
In some instances these contacts produce new silicate minerals (Adamo and Violante 2000), but most often they show a layer of calcium oxalate without the production of new silicate minerals. (Arocena, Univ. North BC personal communication). At water–rock interfaces, within the rock itself, alteration occurs when water, under-saturated with elements in the rock minerals, interacts dissolving the solids present. One can find congruent dissolution, total assimilation of the solids into the water, such as is the case for water–carbonate interaction, or incongruent dissolution where more soluble elements are taken into solution and less soluble elements reorganize to form new mineral phases.

1.1.4.2 Physical–Chemical Interactions

The interaction of water and rock follows physical pathways in the rock, cracks and fissures, opened by release of pressure (geological forces due to burial and asymmetric tectonic pressures) that occurs as the rocks are moved to the surface by tectonic forces. Several types of passageways can be described, according to size and resulting passage of water (Fig. 1.11).

Major tectonic movement produces fractures which transect mineral grains and which leave a passageway of several tens of microns to millimeters and more. Here the water moves rapidly, and in many cases it reaches the water table, zone of saturation of the pores, which then moves laterally toward a stream or river. The residence time of this aqueous fluid in contact with the rock is variable depending upon fracture size, but it can be relatively short in wide cracks and the interaction of rock minerals and water is limited. The water that remains which is far from

Fig. 1.11 Illustration of small infiltration passageways in a rock along grain to grain boundaries or along fractures induced by previous tectonic forces which transverse mineral grains in a rock

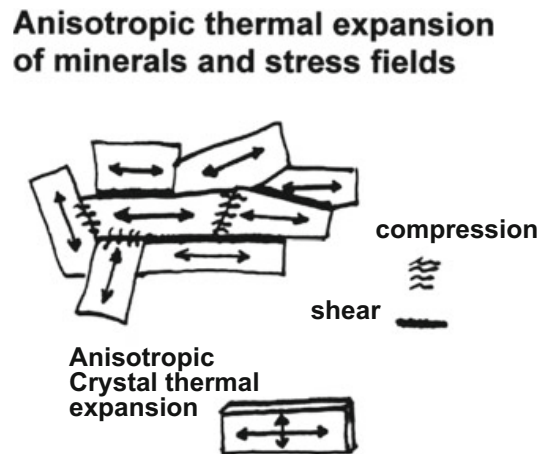


saturation with the minerals in the rock integrally dissolves the minerals on the edges of its passage widening them for increased water flow (see Meunier and Velde 2008).

Another important cause of small pores and cracks in rocks forming passageways for water flow is due to differential thermal expansion and contraction. Most minerals in rocks have a strong anisotropic thermal expansion coefficient following the different crystallographic directions of the crystal. This creates strong contrasts at grain boundaries, causing cracks to form between phases where water can pass and alter the adjoining mineral grains. If no water is present, in a desert for example, the grains will nevertheless be disjointed and the rock will gradually become unstable as a unit and become a mass of small grains (Fig. 1.12).

Slower movement, along fractures and cracks of less width, allows aqueous fluids to interact more with the minerals and produce more dissolution leaving alteration minerals in the rocks while transporting the more soluble elements from the high temperature minerals. However the fluids are far from chemical equilibrium with the rock and the minerals formed by incongruent dissolution are composed of the most insoluble elements combined with oxygen. As the pores are smaller, and the pathways more tortuous, the alteration minerals are less depleted in soluble elements forming more complex minerals, which eventually represent the phases, which would be in equilibrium with the rock under static hydrous conditions. At times material from one destabilized mineral can be incorporated into another mineral, which is forming at the same time. Hence the minerals formed in a rock under the initial stages of alteration will be heterogeneous in the sense that different minerals represent different types of interaction, or stages of disequilibrium between rock minerals and aqueous solutions. The rock–water interaction zone produces minerals that are not all in chemical thermodynamic equilibrium with each other. Although they are all stable under surface conditions as isolated phases, i.e., aqueous solution in an oxidizing atmosphere, they are not necessarily stable as an assemblage in aqueous solution, some containing elements that would otherwise be present in another phase which are released in solution to be incorporated into other phases [see Brantley et al. (2008), for a discussion of such kinetic effects].

Fig. 1.12 Illustration of the effect thermal expansion on minerals in a rock. Most minerals have anisotropic expansion, which creates strong interface tensions that create grain contact fractures. At some interfaces compressive forces occur while at others extensive (shearing) forces occur



The amount of alteration of a rock can be roughly gauged by considering the clay content (the fine-grained material present), which represents the new material produced by the interaction. Most of the new minerals are hydrous, i.e., containing hydrogen ions in the form of H_2O but more prevalently OH units. This is the trademark of surface alteration. Overall the rate of interaction is not very great, at least on the scale of human life. Egli et al. (2001) indicate less than 5 % clay for alpine soils on granitic materials of 700 years exposure. Oh and Richter (2005) report clay content for granite and phyllite (low-grade argillaceous metamorphic rock) as being < 20 % for what they describe materials from the oldest soils in the world. The climate for these series of soils is humid to moderate in the South-eastern United States. Lowe (1986) indicates that the time necessary to totally transform volcanic tephra (highly unstable materials) in subtropical climates is near 800,000 years. It is clear that the transformation of unstable high temperature minerals into new surface-stable clay-sized particles is a slow process.

The result of chemical alteration then is that in the initial stages the rock is transformed along cracks and fissures, weakening it and allowing it to lose some of its initial structure through the dislocation and loss of material. This produces what is called saprock. With a complete loss of physical competence, collapse of dissolved zones, and displacement of clays, the material becomes incoherent and is called a saprolite. The extent of development of these zones depends upon the alterability of the rock and the length of time that alteration has occurred. Of course the major variable in such interactions is the amount of rainwater, which moves through the rock. Alteration in tropical zones will be more intense than that on alpine meadows. The end result is that the greatest part of the alterite material (partially transformed rocks) is a mixture of reacted and un-reacted minerals. Frequently portions of un-altered or little altered rock can be found in a matrix of altered material, ranging in size and concentration depending upon the stage of alteration of the materials. Throughout this zone, which can be several tens of centimeters in thickness to tens of meters, the interaction of moving water and unstable minerals occurs to produce new minerals or integrally dissolving preexisting phases. The more rainwater and the higher the temperature (wet tropical

climate) the more water flow and the more dissolution, and a greater proportion of the new, alteration phases will be formed.

1.1.5 Alteration Profile

Looking in more detail at the structure of alteration at the surface, i.e., the interaction of rocks with the surface chemical environment, one can define two major critical interaction zones responsible for the transformation of rocks into surface minerals: one is that of water–rock interaction, which usually begins with a gradual disaggregation of rocks through alteration processes or physical fragmentation and the development of new low temperature, hydrous minerals and the plant–soil interaction zone (Fig. 1.13) where biological interaction with the alterite minerals occurs.

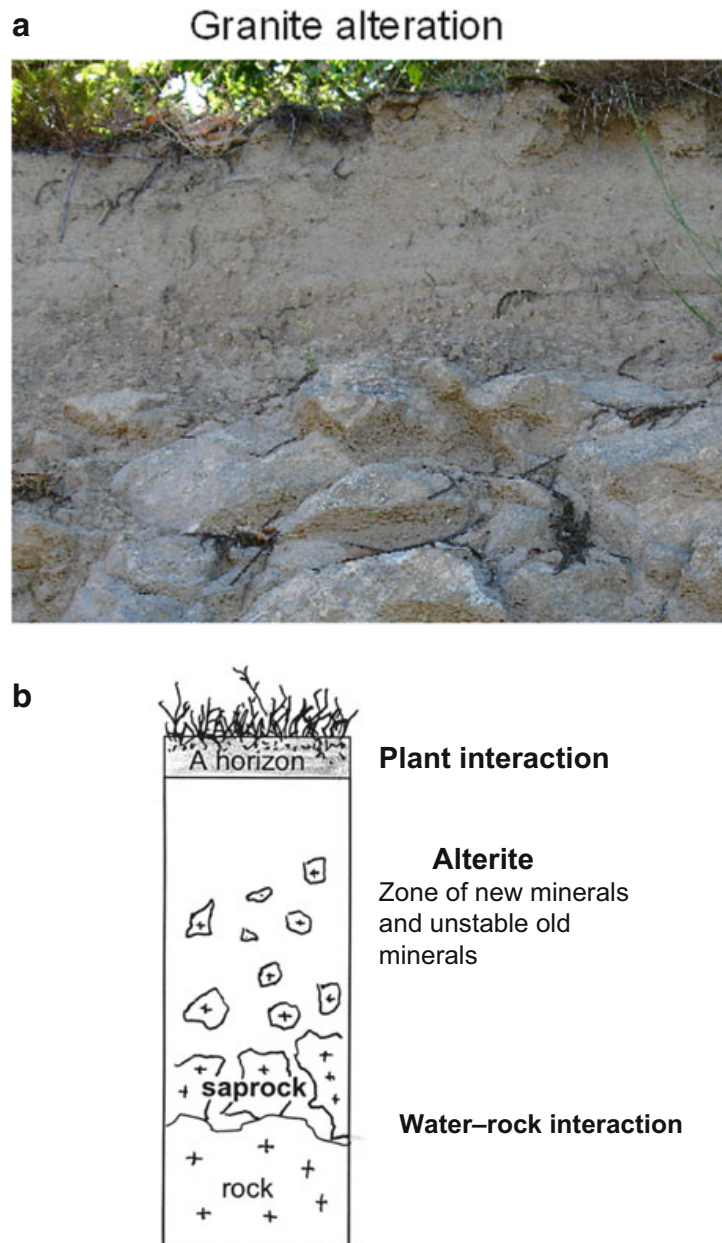
1.1.5.1 Water–Rock Interface

The water–rock zone is the first major step in chemical change where rocks of high temperature origin come toward chemical equilibrium with surface chemical conditions. The ambient hydrous state and oxygen-rich atmosphere effect hydration and oxidation of minerals in the rocks of higher temperature origin. New minerals form along fractures in the rock where water can pass and evacuate dissolved material. The relations of chemical potential and the consequent production of mineral phases in these stages of alteration are detailed in Velde and Meunier (2008, Chap. 2). The fundamental point to realize is that the initial stages of alteration of a rock will give heterogeneous results, following planes of physical weakness, and will contain new minerals of different type and composition. The mineralogical heterogeneity remains through most stages of alteration until the forces of hydration and dissolution reduce the initial materials to more simple chemical configurations, essentially hydrous oxide materials with a more simple chemistry.

1.1.5.2 Alterite Zone

As the rocks are altered to a greater degree, a zone of alteration material is formed, thickening with time of exposure. Here one finds new phases and un-reacted older mineral grains or rock fragments. Accumulation of this material can be called the alterite zone. The chemical forces operating on this material tend to be more homogeneous in that the rate of passage of rainwater is regulated by a more homogeneous material with fewer differences in flow rate due to a more homogeneous pore system. In general there is a re-adjustment of the minerals present which become more homogeneous in their composition and structures.

Fig. 1.13 (a) Alteration of granite near LaMastre (Ardeche, France). Granite alterite is seen in the large boulders at the *bottom* of the photograph, alterite material above, and a thin soil zone developed by grasses at the *top*. Larger roots penetrate into the alterite zone. (b) Illustration of alteration zones in a profile where the rock is altered at the water–rock interface producing new fine-grained minerals and rock and grain fragments which form the alterite. This material (alterite) is continually transformed by water interaction forming more fine-grained material. At the surface one finds the plant interaction zone (soil) where fine-grained material is to a large extent conserved by the action of plant roots, plant exudates, and deposition of mineral elements and formation of the clay-organic aggregate material



Nevertheless the mineralogy of this part of the alteration profiles remains multiphase in most cases.

The amount of new mineral material in the alterite zone depends upon several factors. Initially the amount of transformed material is a function of the amount of water–rock interaction. This is obviously a function of time, the older the alteration profile the more mineral transformation will have occurred, and the amount of water that interacts with the system. Climates with high rainfall will show more alteration in the alterite zone. The clay or alterite content can vary from several percent of the material to well above 60 % in the tropics. This indicates that the alterite is very rarely uniquely composed of new, surface-equilibrated minerals. This is because some of the minerals in the initial rocks are only very slowly reacted

and remain in a state of metastable equilibrium. One notable case is quartz, which is not stable under weathering conditions but remains present metastably for very long periods of time being very un-reactive in its chemical context. The alterite zone is typically composed of old minerals and portions of un-reacted rock and new surface formed minerals, usually called clays due to their fine particle size.

The alterite zone usually shows a chemical progression from the bottom, rock–water contact zone, to the soil area of plant—alterite zone where the amount of interaction with the percolating rainwater interacts as a function of its degree of saturation with rock materials. The rainwater closer to the surface is less saturated with dissolved elements, especially of the unstable high temperature rock minerals and as a consequence it will transform the relict minerals present rapidly. Lower in the profile the percolating solutions, on average, are more saturated with the unstable mineral components due to dissolution–precipitation reactions and the reaction rate is lower. This general schema is of course conditioned by the rate of flow of water. The larger pathways, cracks and fractures, in the alterite will allow water to pass more rapidly and this water will be less saturated with dissolving elements. In this way one observes that the alterite zone is heterogeneous in the amount of new material present with high rates or reaction close to pathways of rapid percolation and lower rates of reaction in zones of small passageways such as soil micropores.

1.1.5.3 Soil Zone

At the atmosphere–solid interface one usually finds plant life, as well as that of animals and different types of micro-organisms. This is the soil part of the alteration profile, marked strongly by organic matter and plant–soil interactions. Frequently the fluid chemistry in the soil zone is different from that lying below, due to plant induced uplift of mineral elements such as potassium, calcium, magnesium, phosphorous and silica (see Velde and Barré 2010). Plants also move minor elements and thus change the chemistry for major and minor elements in the soil zone compared to that in the alterite zone.

A new variable occurs in the soil zone, that of pH. Decaying organic matter or lack thereof can vary the pH significantly. This is largely determined by the type of plants present at the surface. Forests tend to form more acidic soils, with conifers producing the lowest pH. The acidity is variable depending upon the climate (rainfall, rainfall frequency, and temperature) and plant species present. These variables govern the biological activity in the soil. Prairies tend to form more basic soil contexts, usually several pH units higher than conifer forest soils. Deciduous forest soils are usually of intermediate pH values. Changes in pH can change the mineral stability forming new types, either oxides or silicate clay minerals.

An important vector of movement of fine material is within the soil profile itself. Macropores and cracks move rainwater to the groundwater level rapidly and in doing so can move clays, the fine particles of the soil, with the movement of water.

Such material accumulates in the subsoil horizon (named the B horizon), but it can also move outward to the groundwater table and eventually into stream or rivers. The movement is particularly important on slopes as one might suspect. An example is given in Fig. 1.13 where measurements of fine material, clay content, show an accumulation on the upland (some 3 m above the lake level, a loss of clay and no accumulation on the slope, and an accumulation near the foot of the slope.

In Fig. 1.14 one finds the clay content of profiles on uplands, a difference of tens of meters from the lowest zone, on the slope and at the bottom of the slope, near an irrigation rice paddy. In the upland profile under forest cover one sees a zone of clay accumulation below the major root zone (40–50 cm in depth). Clay movement is more or less vertical in the upper parts of the profile. On the slope there is no accumulation of clays, only a gradual increase in clay content into the alterite zone. At the foot of the slope, where water flow intensity decreases near the rice paddy, the clay content is greater at depth (60–80 cm in depth) than in the upland zone. This is a demonstration of the lateral movement of clays and their accumulation in the soils of the foot slope. Such movement has been described in a general sense, on the scale of a landscape in Millot (1970).

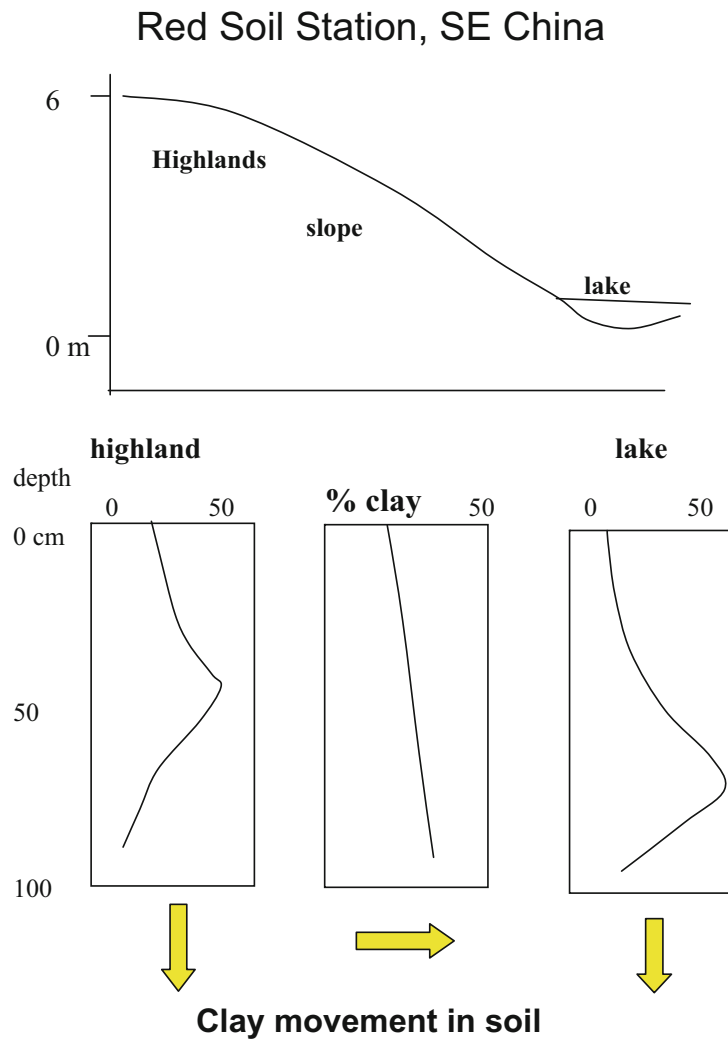
Such a vector of movement of fine particles is very important to consider in that often in areas covered with vegetation such as prairie grass, very little if any movement of particles comes from the plant-covered surface by erosion, but one finds that the streams draining the area have significant suspended clays in the waters during the rainy season due to transport within the soil zone. Soil clay particle movement is well documented from the soil horizon to the area just below it, forming the B horizon of clay enrichment. It is also the case that clays can move laterally, down slope into a zone of deposition or into ground water flow and hence into streams and rivers, thus exiting the local soil zones to be transported out of the immediate area.

1.1.5.4 Consequences of Alteration: Physical and Chemical Aspects

Smaller minerals, in the clay fraction, change the coherence of the rocks, as one would expect. The material becomes plastic and can be displaced by local differential gravitational forces. This produces slumps and landslides at the surface that are much more rare for rocks. One of the major reasons for this plasticity is the increased water content, water in the sense of H₂O. On any particle surface water adheres in the amount of one or several layers of molecules. This surface coating decreases the particle-to-particle friction factor and promotes plastic deformation in that the particles slide one over the other. Thus alteration promotes physical instability of surface materials.

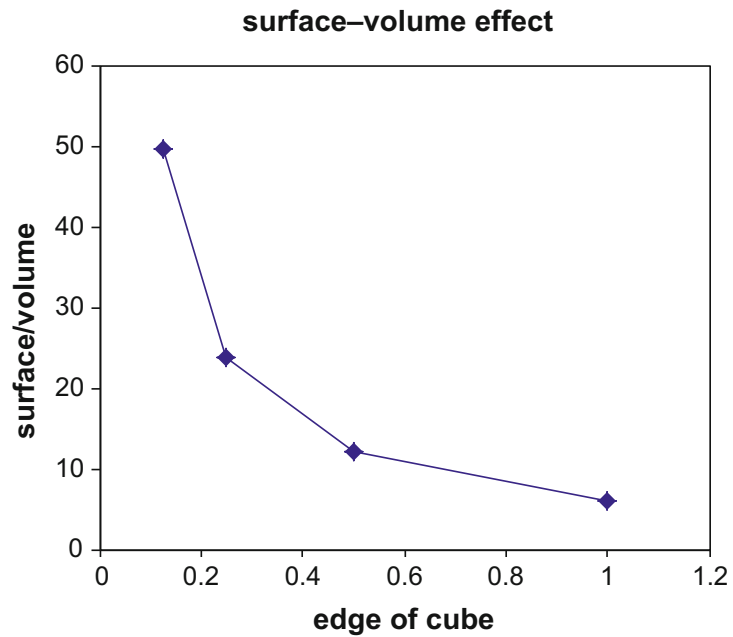
More important to geochemical considerations is the relative surface area of particles, which increases with the decrease in grain size. In Fig. 1.15 one sees that the total surface area produced by alteration increases as particle size (indicated by the dimension of the edge of a cube) decreases. As the dimensions of the particles

Fig. 1.14 Example of lateral soil clay transport within the soil zone down a slope. The site is at the Red Soil Station (Jiangxi Province, China; data kindly provided by Professor Bin Zhang, University Nanjing) where upland soil clay is transferred down slope to the edge of a rice paddy



decrease, the surface area compared to the volume of the particle increases very rapidly in a nonlinear fashion. This is important in that particle surfaces coated with a water layer permit the transfer and fixation of hydrated ions in the aqueous solutions that impregnate the soil and alterite zones (see Chap. 2). The solid–liquid interface is the zone of ionic contact and one of chemical importance. Hence the smaller the grain size the more chemically active surface areas are present concerning ions in solution. In contrast to rocks, alterite materials then have an enormous chemical activity by surface transfer and catalytic properties on these surfaces. For surface geochemists this is the primary factor in any study of the migration and fixation of elements under conditions of alteration and transport.

Fig. 1.15 Illustration of the relationship of surface to volume as a function of relative grain edge size. The smaller the edge or the grain size, the higher the surface area compared to the volume of the grain. Clays have a flat shape and are of small grain size, which produces a very high surface area compared to the volume of the particle

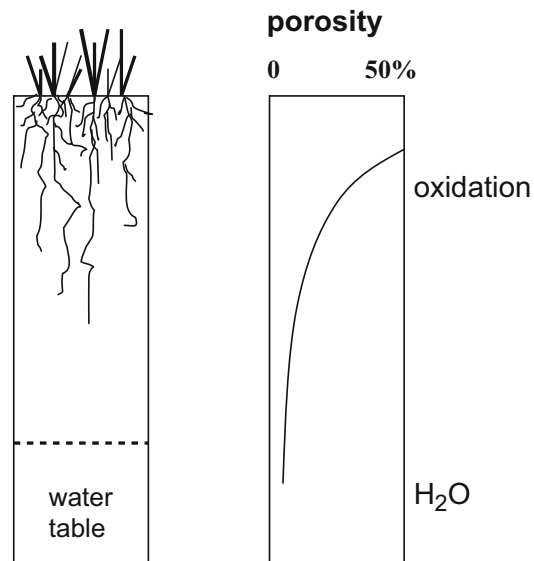


1.1.6 Plant and Soil

In the structure of alteration, there is a moderating factor at the top of the sequences. This is the biologic influence on the altered material issuing from water–rock interaction. Basically, plants need clay minerals for their biological cycle. The clays are storehouses of mineral elements, which can be extracted and exchanged at will (see Velde and Barré 2010). They form the aggregate structure of clay mineral particles fixed by organic matter into loose microporous volumes in soils that are the storehouse of water (in capillary sites). Clay minerals being vital to plant biotic processes, the plants attempt to keep them present in the root zone (that of plant–mineral interaction) so that the biological cycle is maintained. This is done by root action, which retains the clays and protects them from erosive processes. Typically clay concentrations are high in the upper parts of alteration profiles. One should note that if there are no plants present, there are no clays and there is no alteration profile. Without plants alterite material developed by physical fracturing (differential thermal expansion) and subsequent disaggregation of the rock is quickly eroded and the rock is constantly at the surface without its soil mantle.

In data of Huang et al. (2004) for Heinan (China) soils developed on basalt flows of different ages under subtropical conditions it is clear that the clay content in the profile increases toward the surface of the profiles and it increases in proportion as a function of time, but here again it is far from being a complete transformation despite the climate of humid tropical type. We can assume that in most cases soils and alterite will contain some minerals that have not yet transformed into surface materials. However, under tropical rainfall conditions, after very long periods of time, alteration can be almost complete with only the most refractory minerals resisting chemical alteration, such as quartz grains.

Fig. 1.16 Schematic illustration of the relationship of porosity and water content in an alteration profile where plant activity determines the porosity of the profile at the surface. In most soils, air is present in the surface porosity and oxidation potential is high. Most plants need oxygen for the soil system to function. Thus the soil root zone is one of a higher oxidation potential for alterite minerals

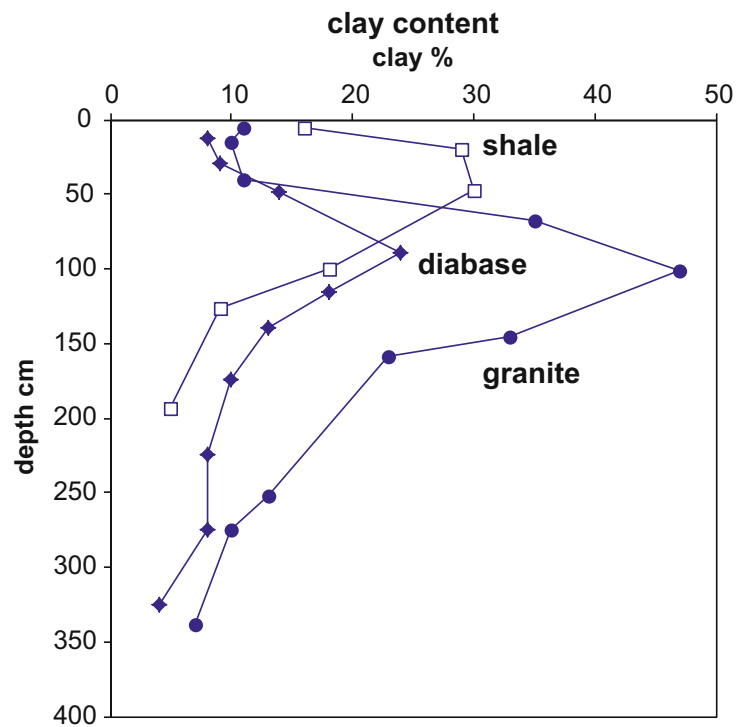


At the surface, biologic layers are conditioned by plants to be open to air infiltration in that most plants need oxygen to function in the root zone. Figure 1.16 indicates the structure of porosity and the effects on the infiltrations engendered by plant roots. As a result there is a stronger tendency to oxidation of minerals and materials in the root zones of alteration profiles than at greater depth. Thus the biologic factors in general complete and reinforce the chemical action of water and atmosphere as they affect the rock minerals of alteration.

The higher porosity in the soil surface zone (that where most of plants roots reside) is where there is a greater movement of fluids, keeping the pores open to air (oxygen) and where water can move downward easily. Such a physical structure has consequences on the movement of solids, clays, within the soil zone. In Fig. 1.17 it is apparent that the clay content increases from the bottom of the soil profiles, reaches a maximum at several tens of centimeters from the surface, and decreases into the soil zone. This is due to clay transport in the more porous zone, maintained by the plant regimes (in these cases forest and prairie) where fine particles are moved by moving aqueous fluids to a more less porous zone (the B horizon in terms of pedology) where clays accumulate.

Clay percent (amount of alteration reaction) increases with time and can be different depending upon the rock type. Also the biome can be important to soil clay movement. In Fig. 1.17 three rock types altered under similar conditions indicate the differences that one can find under oak–hickory forest cover in North Carolina [data from OH and Richter (2005)]. The topmost horizon, that of leaf litter and high organic content, is somewhat depleted of clays, which are found in high concentrations in the lower, B horizon. These are very old soils, and even so, they have not completely transformed to soil clay minerals. Some of the material is present in metastable form such as quartz, which would be found in the phyllite (shale in the figure) and granite based profiles, but in the basalt profile there would be little, if any, quartz and still one finds that the clay content is far from 100 %. In Fig. 1.17 for three rock types submitted to the same alteration conditions, the phyllite, low-grade

Fig. 1.17 Clay content as a function of depth for soils on different bedrocks in a sector of old soils [data from Oh and Richter (2005)]. Depending upon rock type the soil clay content varies and the transport of clays to moderate depth is more or less important



metamorphic rock which has a mineralogy similar to that of alterite products, the lower part of the rock is the least affected by water–rock alteration indicating that the minerals it contains are near chemical equilibrium with the altering fluids. Clay minerals are often recycled from one environment to another. As the product of alteration, clay minerals derived from a rock frequently pass through a soil with little or no obvious modification by soil process (Hillier 1995). Others are only partly modified (transformed). The changes for granite and basalt are greater than for phyllite. However, the increase to make clay-sized particles in the phyllite is accelerated in the plant–alterite zone where plants become the major chemical agent of change. This underlines the fact that the alteration profiles have two major parts. The water–rock interaction zone, which transforms solid material into lower density, has less structured material with a high clay size fraction. In the plant interaction zone the chemical forces are not the same as those in the rock–water interaction zone due to chemical control by plants and biological agents. New phases are formed in response to these solicitations.

1.1.6.1 Erosion, the Movement of Matter and the Role of Plants

One usually thinks of movement of solids at the surface as being due to erosion, which is generally considered to occur during periods of intense rainfall removing solids from the surface, top of the soil zone. However, one of the major functions of plants is to retain soil materials which are basic to their survival. In fact the greatest mass of materials displaced at the surface by erosion occurs through the massive

failure of alterite materials on slopes through landslides and mass movement by creep mechanisms (see Fig. 1.2).

Probably the most important proportion of mountain “un-building” occurs this way. However when the material slides down slope its journey is not finished. Subsequent plant–soil interaction occurs, but in the initial stages the bare surface material is displaced by rain and subsequent by river movement. Here erosion of the finer grained material is important and the debris is moved further toward the sea, its final repository.

In agricultural areas, especially those where the soil is barren during the winter such as the North American continent, the erosion of fine-grained material by runoff of surface water into streams and eventually rivers is very important. Such runoff does not occur to a significant extent in areas of vegetal cover. The evolution of grasses during the Cretaceous or the development of agriculture had substantial impact on soil development and erosion. Plants use root structures at the surface to retain such clay material and preserve this as a soil base. If one looks at mountain streams there is still less material in suspension; clear water is more the rule than the exception. Hence the vegetal cover protects the soils from surface erosion, but massive displacement is more probable in areas of steeper slopes.

Basically plant retention of fine material at the surface in a root zone strengthens the surface material and rigidifies it to a certain extent. It is more resistant to lateral, and downhill movement. However, as alteration proceeds along the alterite–rock interface, the thickness of alterite increases. This material is more and more fine grained as water–rock alteration proceeds. Hence the alterite becomes less resistant to downhill movement through its increase in fine material while the soil plant–root zone becomes more rigid due to root retention and resistance to deformation. This system can eventually work to the disadvantage of plants in that by strengthening the surface and creating a contrast in mechanical resistance at the surface the interface between the alterite and the plant soil horizon is more and more contrasted increasing the likelihood of failure.

Overall the alteration process of unstable rock material forms small grains through chemical interaction of water and unstable minerals forming new small minerals grains. These grains are moved by various means (massive slope failures in mountains, stream, and river transport) under decreasing energy gradients where larger grains are deposited, and eventual deposition of the fine, clay-sized material, in lakes or more often the sea. The geographic slope gradient decides how far and where the different types of material are moved. The smallest goes furthest. This principle is extremely important for geochemical study in that the smallest grains have the greatest surface area per mass and are by this fact more chemically interactive, attracting different ions in solution to their surface. This activity of attraction is one of the key factors of movement of minor elements at the surface of the earth. Minor elements are those that do not make up a phase of their own and need to find a residence on another particle. Clays, fine-grained materials, are carriers of many elements, attracting them to their surfaces under certain chemical conditions and releasing them under others. This is the fundamental interplay of the geochemistry of the surface. We will pay particular attention to the components of

the clay fraction, clay minerals (silicates), and oxides which are the fundamental parameters of surface geochemistry governing the retention or loss and transport of minor elements which are important elements in considerations of environmental problems and hazards.

1.1.6.2 Chemical Conditions of the Rock–Alteration Transition

Rocks are composed of crystalline minerals or at times amorphous materials such as volcanic glass. Rocks are hard and dense, not those materials one finds at the surface of the earth in equilibrium with the atmospheric chemical forces. The contrast is striking when walking outside or digging in one's garden. Earth (dirt) is soft and mobile, changing its texture and structure with the amount of water present while rocks are immobile (on the scale of ones walk in the woods or digging a patch in the garden). The contrast is one of the physical conditions of the formation of rocks compared to soil or surface alteration products. Rocks have been formed under conditions of relatively high temperatures, those with enough thermal energy to change and recrystallize the mineral assemblage present compared to those present in the initial state of sedimentation. Magmatic rocks show high temperature minerals formed below the melting point of their mass; some show relicts of the molten state. Metamorphic rocks show the effects of temperature and tectonic forces, which changed the mineral content, creating new phases and changing their shapes. Sedimentary rocks retain for the most part relicts of the materials that were sediments, i.e., materials formed in equilibrium with surface chemistry. However, in most cases the minerals have been transformed chemically to a certain extent and the phases have been recrystallized to form a more rigid mass. In all cases, the minerals in rocks are unstable at the conditions of earth surface chemical forces. They have an origin of higher temperatures and pressures. They have chemical characteristics that are not those of minerals at the surface. For this reason they react with the atmospheric conditions of the surface, water, and an oxygen-rich atmosphere, which destabilize the initial phases to create new ones.

In contrast to the formation and re-formulation of minerals in sedimentary, metamorphic, and igneous rocks, the transformation of materials at the surface includes the separation of some of the initial material from the solids, forming a new material of a new composition. Rocks are formed in essentially closed systems, chemically conservative, or nearly closed systems, whereas the formation of surface materials is accompanied by a loss of material from the solids through the interaction with surface waters. In the geological cycle, this "lost" material is often re-deposited or concentrated in sedimentary deposits when the water of dissolution is re-concentrated through evaporation or biological action. The weathering process (interaction of rocks with surface chemical materials) is one of segregation and re-combination according to the chemical properties of the elements in the minerals of the rocks that interact. Some elements are relatively easily dissolved, calcium for instance, which is transported out of the surface systems in part, often to be re-combined with elements in the air (CO₂) through the action of animal life to

form carbonate material which in turn forms a new rock. On the other hand, quartz (SiO_2) is a mineral that remains metastably present, often concentrated through its grain size in contrast with smaller minerals of alteration origin, becoming sand deposits. Dissolved mineral elements that are not re-concentrated by evaporation of surface waters nor by organic interaction are transferred to the sea.

The rate at which the rocks interact with the surface chemical forces depends upon the difference in the conditions at which they were formed and those of the surface. Igneous rocks react relatively rapidly whereas sedimentary rocks interact relatively slowly. Generally speaking, sedimentary rocks will disaggregate into fine material through the action of physical forces, temperature differentials, but the minerals present will remain much the same. They are already the products of alteration.

There is a general hierarchy of instability for rock minerals, which is roughly related to the conditions of formation (temperature and pressure) and their chemistry. Concerning minerals in rocks at the surface, one can measure the rate of dissolution, which is the major factor in mineral reaction. The most soluble are the carbonates, not minerals formed at high temperature but those most affected by the exchange of a hydrogen ion for a cation in the structure. Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) show high rates of dissolution. These two minerals make up the greatest part of carbonate rocks, formed under sedimentary conditions. Next in order of instability are minerals from high temperature rocks, basalts for example, such as ferrosilite, an iron-rich olivine. Minerals from more acidic rocks, formed at somewhat lower temperatures, are less soluble (e.g., the plagioclase minerals anorthite and albite). Minerals found to form at the surface have lower dissolution rates, alumina, and iron oxyhydroxide. The high temperature mineral, muscovite, is the most stable of the composite minerals. It has a composition and structure very similar to one of the most common clay minerals formed at the surface, illite. The least soluble is quartz, which remains metastably present and is always a major component in surface materials.

It is evident that a rock will be composed of several minerals, which will have different rates of dissolution. This is a strong factor in the disintegration mechanism in that one phase dissolving differentially will create passageways in the rock that will favor differential fluid flow and subsequent dissolution due to the different amounts of rock–fluid interaction. The faster the flow rate, the more unsaturated the fluid and the greater will be the tendency to dissolve the surface of the minerals along the surface of the fracture pathway. Slower fluid movement will favor incongruent dissolution, i.e., reactions closer to chemical equilibrium which produce new phases and induct dissolved elements into solution. These reactions form clay minerals and oxides.

Another factor is the accessibility of water to the grain surfaces. In rocks fractured by thermal effects, those with heterogeneous grain types, water can infiltrate and remain present in the small capillary pores created in the rock. Here dissolution and mineral reaction will occur. In rocks that are more anisotropic, the thermal cracking factor is less important and less water penetrates the rock resulting in less water–rock chemical interaction.

The effects of differential dissolution rates on different minerals, the effects on desegregation, and enhanced alteration due to mineral heterogeneity and overall rock compositions determine the input of dissolved material into streams and rivers, which carry the geological elemental cortege to the sea. In doing so this material traverses the continents with interactions, some deposition, or halts in the movement of material (stream deposition, lake beds, etc.), which affect the chemistry of the surface. *Interaction of the alteration products with the changing chemistry of their transportation vectors is the basic interest of this book.* We wish to investigate not only the transformation of rocks to alteration minerals but also the effects of mixtures of this material as it moves from alteration site to final deposition site. Surface geochemistry is not only the formation of new minerals but also the effects of this initial interaction with changing chemical conditions during the transportation phase. For example, lakes can have different chemical constraints (pH, Eh, biological activity) than the soils that formed the clays and oxides of alteration, which are moved into lakes. The groundwater flowing from the rock–alterite zone can have different chemical constraints than those of the soils found above them. Streams and rivers will incorporate different materials from different setting of alteration and plant interaction as they flow to the sea and hence will have different chemical constraints imposed upon the suspended and dissolved material as it moves ocean-ward. These are the dynamics of surface geochemistry.

As has been mentioned above, geology is movement. The earth is in a constant state of change, albeit on a scale difficult for humans to comprehend. Nevertheless, the earth surface processes are such that they can be easily seen (landslide, muddy streams, mud flats, and sand beaches, etc.) as indicators of land surface change. These movements change the place of materials, in the dissolved state or in the particulate state. The new surface materials such as clays and oxides are moved in preference and carry dissolved elements on or with them in the process of adjustment to gravitational forces. This movement is the basic reality of surface geochemistry. Small particles move in aqueous solutions, and carry with them hydrated ionic materials, which can be easily exchanged with other elements when the chemistry of the solutions changes. Our task is to understand when the different ions released during alteration enter stably into newly formed alteration products or when they are fixed temporarily on the surface of a mineral due to inner-sphere or outer-sphere complexation or when the surface fixation forces change to release these elements into aqueous solution to be moved to a different site. Surface geochemistry is a study of the ephemeral.

1.2 Chemical Elements and Associations in Surface Environments

1.2.1 *Affinities of the Major Elements and Surface Geochemistry*

This book is not designed to give an exhaustive list of elements and their presence at the surface of the earth. The major reason for this is a lack of data for many of the less abundant elements found in the Mendeleev table compilation. There are chemical rules and deductions from these rules, which allow one to predict the behavior of elements, but often there is not much data available to test these hypotheses. We will thus focus our objectives on the better-known elements and their reactions to changing chemical conditions of the surface chemical environment. This approach is fraught with problems in that the influences of agents of chemical change are multiple in natural environments at the surface of the earth. Major factors are the chemistry of solutions, driven by variations in pH and Eh. The presence of different types of material with strongly differing chemical properties, silicates, oxides, and organic molecules, creates further difficulties in that each phase or chemical type of material exerts different attractions on the diverse chemical elements present. Our approach is to gather the available information on elemental abundance and association in order to describe the behavior of elements at the surface of the earth. The chemical differentiation and segregation at the surface occurs in the context of geological forces, which determine what we can call geochemistry. However there is always an underlying chemical reason for the dispersion and affinities of the elements in the geological environment.

Initially, we consider the relative abundance of elements. The classification of major and minor element used here is rather classical, and consequently not very precise. A major element is one that contributes more than several tenths of a percent (oxide weight) in a given sample. Minor elements are normally considered in the several tenths to one-tenth of a percent and trace elements are of lower abundance. This definition is of course subject to variation depending upon the geologic context. Ore bodies are typically composed of minor to trace elements, unusual concentrations, but nevertheless real and realizable in the geological context. In some rocks major elements might be rare. In ultrabasic rocks sodium and potassium become of minor abundance. However, if we consider the concentrations of elements in common, abundant rock types the major, minor, and trace element categories are valid. In problems of surface geochemistry one may find, through anthropogenic action, that a trace or minor element is present in major element proportions. Thus, one has to be careful to stipulate the context and occurrence when considering the nomenclature of the different elements found at the surface of the earth.

Classification of the elements present in the earth's crust has been made numerous times over the past decades. McQueen (2008) gives a summary of the different

Table 1.1 Classification of chemical elements in the surface environment

I	II	III	IV			V	VI						
			Covalent with oxygen oxyanion complex formers			Covalent anions	Gasses						
Ionic charge (+1)	(+2)	Anions (-1)	(+3)	(+4)									
H													
Li	Be	F	B	C	N	O	He						
Na	Mg	Cl	Al	Si	P	S	Ne						
K	Ca	Br				Sc	A						
Rb	Sr	I				Te	Kr						
Cs	Ba						Xe						
VII													
Moderately covalent cations (forming oxides or oxyanion complexes)													
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Sc
Y	Zr	Cb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
								Au	Hg	Tl	Pb	Bi	
REE oxides and phosphates trans uraniumides													

The groups are based upon their behavior under surface conditions, the major differences being the valence of ions in aqueous solution. Cations are of positive valence, and anions are of negative valence, i.e., the relationship of completely filled electron orbitals compared to the ionized state where electrons are in lower or greater abundance than the normal equilibrium state. Association of elements with oxygen changes their behavior in many instances. Anions with a strong tendency to form strong electronic bonds with other elements, covalent ions, and those forming strong bonds with oxygen are extremely important to surface geochemistry [table based upon, data in Krauskopf (1967), Mason (1966), Pauling (1947) among others]

types of categories of elements as they are incorporated into mineral phases. General considerations range from whether an element is found in the atmosphere, in silicate minerals, in oxide minerals, or in sulfide minerals. These are the major criteria of Goldschmidt (1954), which have been useful over a long period of time. Our interest here is that these classification schemes are applicable to the rock as it is presented at the surface to be transformed by interaction with slightly acidic, oxygenated water. Here the criteria of elemental distribution in rocks and minerals are for the most part no longer applicable. Some minerals of the high temperature assemblages are still present but they are not stable, and given enough time will be transformed into different surface minerals. We will not use the terminology common to geochemistry texts in that it is not all that applicable to our problem of surface geochemistry (Table 1.1).

The elements of major abundance and many elements of lower abundance can be classified as to their behavior under aqueous conditions and different redox conditions. At either end of the periodic table one finds the elements that form gases, Ne, Xe, and so forth. These elements are not active at the surface of the earth and will therefore be ignored totally. We will start with the ions, which are found in solids and aqueous solution, the major solid phases, which are present, and the major components that affect the geochemistry of the surface. Our objective is to discuss the reactions due to aqueous conditions experienced at the interface of the

continents. Water is the major chemical agent and at the same time the physical agent causing movement of materials. Our discussion is oriented toward the reactions and associations of minerals and elements to aqueous chemical interaction at moderate temperature. Virtually all of the surface geochemical reactions pass through an aqueous stage. Ionic diffusion in solids is very slow at low temperatures. Thus in the absence of liquid water rock materials do not react or change significantly. The chemistry of elements in aqueous solutions is the key to understanding surface geochemistry.

1.2.2 Agents of Change

1.2.2.1 Oxygen

Oxygen is ubiquitous in the zone of surface interaction. This element is the predominant one present in geologic surface materials, as in most of the earth, at least from the crust outward. Oxygen commonly represents half of the atoms present in a rock or altered rock. This is in contrast to biologically related materials where oxygen usually represents < 20 % of the atoms in a molecule. It is the one of two elements that dominates aqueous solution and it is very present in the atmosphere. Oxygen is an anion of various properties, most important of which is the ability (or prevalence) to share electrons with other ions, which is the basis for covalent ionic associations. The relations of other elements with the divalent negatively charged oxygen ion are primordial to the structure and coherence of materials. It is the background in which geochemistry evolves. However, the tendency of oxygen bonding in solids is quite different from that of its bonding in fluids and in the air. In air oxygen tends to form its own gases (O_2 , O_3^{2-}), or be combined with carbon or nitrogen to form other gases. These molecules are quite stable especially CO_2 . In water oxygen is associated with hydrogen, either as H_2O , H_3O^+ , or OH^- ions. Some free oxygen (O_2) is dissolved and is a highly reactive substance. Oxygen in the air tends to combine with certain cations as they are released from rock minerals forming oxides. The activity of oxygen in the interaction with rock minerals in aqueous solutions is critical to mineral stability. When a constituent element (such as Fe) changes oxidation state, there is a change in the electronic balance of the original mineral which often causes the dissociation of the constituent elements resulting in the formation of new minerals. This action is frequently the initiation of alteration processes.

Oxygen is the primary oxidant for the degradation of organic matter in soils; in the absence of oxygen, however, other species oxidize organic matter following a thermodynamically predicated sequence of oxidants (oxygen \rightarrow manganese oxides \sim nitrate \rightarrow iron oxyhydroxides \rightarrow sulfate (Froelich et al. 1979).

1.2.2.2 Water

Probably the most important relation in surface geochemistry resides in the very unusual properties of water, H_2O . It is one of the most singular liquids we know, with a negative thermal expansion in the solid state, a capacity to accept cations, anions, and a significant array of charged ionic complexes in solution, inorganic as well as organic. It is composed of oxygen and hydrogen. In the water molecular structure hydrogen ions are present at 120° one from the other which results in an asymmetric molecule, with positive ions on one side and the underlying oxygen ion (negative) on the other side. The asymmetry leaves a portion of the oxygen without electronic compensation such that the water molecule has a tendency to attract cations to the “vacant” side of the molecule. This slightly ionic (polar) character gives water the capacity to attract and retain ionic species. Thus one can consider water to be a solvent, bringing other chemical materials into a stable state in the liquid. Also water is relatively easily dissociated in two components, H^+ ions and OH^- . Both are chemically active creating soluble units from solid materials. Both H^+ and OH^- units can associate with elements to form complex associations. The prevalence of one or the other depends upon the relative amount of H^+ or OH^- (pH), which is critical to most of aqueous solution chemistry.

Water is at the same time the prime altering agent by its chemical activity and thus the prime agent of movement of material in solution and of course it is the major medium of movement of particulate (non-dissolved and dissolved) material. Water is a chemical and a physical agent. The importance of water cannot be underestimated in surface geochemistry. Further it is the basic substance necessary for life on the surface, acting as a relay for dissolved substances to be moved into a plant and as a major part of the chemical functioning of plants. The “blue planet” is essentially governed chemically by the activity of water at the surface.

1.2.3 *Bonding Between Elements*

Rocks and alterite minerals, the products of incongruent mineral reaction in aqueous media, are largely found as silicates, which are covalent associations of oxygen with Si ions which form an oxyanion structure, such as carbonates, and oxides or hydroxy-oxides. The cation–oxygen associations are the primordial key to understanding the structure and chemistry of surface minerals.

The elements of earth material at the surface are for the most part linked by either covalent or ionic bonding forces or intermediate types. Ionic bonds and covalent bonds differ in their structure and properties. The exact definition of covalent and ionic bonding is difficult to determine in that there are different grades of intensity of the two opposing bonding types.

Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions. These ions have been produced as a result of a transfer of electrons between two atoms with a large difference in electronegativities. If a

compound is, for example, made from a metal and a nonmetal, its bonding will be ionic. For example, sodium and chloride form an ionic bond, to make NaCl, or table salt. For covalent bonding we distinguish between two types. The first type is nonpolar bonding with an equal sharing of electrons. But usually, an electron is more attracted to one atom than to another, forming a polar covalent bond. For example, the atoms in water, H₂O, are held together by polar covalent bonds. If a compound is made from two nonmetals, its bonding will be covalent. Whether two atoms can form a covalent bond depends upon their electronegativity, i.e., the power of an atom in a molecule to attract electrons to itself. If two atoms differ considerably in their electronegativity (measure of the attraction of an atom for the electrons in a chemical bond)—as sodium and chloride do—then one of the atoms will lose its electron to the other atom. This results in a positively charged ion (cation) and negatively charged ion (anion). The bond between these two ions is called an ionic bond.

The electron sharing links the atoms into a very stable chemical structure. It is difficult to extract one element from the others in covalently bonded compounds. A demonstration of this fact is the low solubility of covalently bonded structures in water. Ionically bonded atoms do not share electrons and are loosely held together. Materials composed of these bonded atoms are easily dissolved in water, such as is NaCl.

By contrast, in surface geo-materials, oxygen is the major anion present and bonding to oxygen is primordial. Two types of bonded materials are present. The first type is an oxyanion, where oxygen is bonded to a cation. The bonding is in a largely covalent mode, with a residual negative charge on the oxygen satisfied by bonding to a cation in a more ionically bonded form which is strongly covalent, silicates for example. Oxoanions are formed by a large majority of the chemical elements. The other type is an oxide where oxygen is bonded to cations directly to form a neutral compound. The equilibrated associations of quadrivalent cations occur when the cation is joined with two oxygen atoms (SiO₂, CO₂, SO₂).

Krauskopf (1967, p. 136) gives relations of bonding types for most of the common (major and some minor) elements found in surface geochemical situation. One can summarize this information as follows:

Type I: Ionic character of > 70 % with oxygen

Ca > K > Na > Li > Ba > Ca > Mg

Type II: Intermediate bonding character with oxygen 60–50 % ionic

Be > Al > B > Mn > Zn > Sn > Pb > Fe > Cu

Type III: Covalent bonding (< 50 % ionic character)

Si < C < P < N

Classically these values are based upon the electronegativity of the element ionic state, which can be found in tables of chemical character in many textbooks and reference works. The covalent bonds between Si, C, and P (type IV ions) with oxygen to form an oxoanion are very strong where the charged complex ion can be satisfied electronically by association with an ion of high ionic character (type I) or can be associated with ions in the intermediate category either in covalent or partly ionic bonding (type II). In some cases, oxoanion bonding with two types of cations in ionic or covalent bonds occurs (types I, II, and III) which is typical of silicate minerals. Hence within the same chemical compound ions can be present in different states of bonding. In such complex structures there is room for a significant amount of ionic substitution of one element for another. This “solid solution” is again typical of silicates.

Each ion has a general sphere of electron influence, which can be described by an ionic radius, in angstrom (\AA) dimensions. The radius essentially determines the number of oxygens, which can be closely associated with a cation in a crystalline structure. This number of ions is often referred to as a coordination number ranging from 12 to 4. Anions of course have the same ionic radii zones of electron influence. Figure 1.18 indicates the number of oxygens in association with different cations, which can change when the ion changes oxidation state such as is the case for iron. The most frequently observed ionic substitutions in a crystal occur when the ionic charge is the same and the ionic radius similar.

An important effect on bonding type is the oxidation state of the element concerned. In general monovalent cations are highly ionic in character. As oxidation state of an element increases the tendency to form oxyanions is greater. If an element can have several oxidation states under surface conditions, it can change its ionic form going from cation to an oxoanion. Arsenic is an example of oxygen–oxidation state interactions. (Arsenite (As[III]O_3^{3-}), Arsenate (As[V]O_4^{3-}). In aqueous environment the inorganic arsenic species arsenite (As^{3+}) and arsenate (As^{5+}) are the most abundant species. Some elements considered as metallic in type, chromium for example, can change ionic association in aqueous solution from cation to oxoanion. Chromium, named for its many-colored compounds, exists in the oxidation states of -2 to $+6$, inclusively. The existence of a particular oxidation state is dependent on many factors including pH, redox potentials, and kinetics. The $+3$ and $+6$ oxidation states are the most common ones found in aqueous solution. Change in oxidation state can change the affinity of an element in its chemical associations greatly in the surface environment.

Fig. 1.18 Examples of some elements and their ionic characteristics with the coordination characteristics with oxygen in the case of cations [data from Krauskopf (1967)]

Cation	Charge	Radius (Å)	Coordination
Na	1	0.97	6, 8
K	1	1.33	8, 12
Mg	2	0.66	6
Ca	2	0.99	6, 8
Sr	2	1.22	
Fe	2	0.77	6
Fe	3	0.63	
Mn	2	0.74	6
Mn	4	0.53	
Ti	4	0.68	6
Al	3	0.51	4, 6
Si	4	0.42	4
Anion	Charge	Radius (Å)	
S	2	1.85	
O	2	1.4	
OH	1	1.4	
F	1	1.36	

1.2.4 Cation Substitutions

The elements, which do not form strong covalent bonds form largely ionic bonds, tend to have a lack of an electron or more in their electronic orbital structure. Ionic bonds are less strong than covalent bonds. Li, Na, K, and Ca like cations which have a high ionic bonding tendency are very important to surface geochemistry in that they are easily displaced from a mineral under surface alteration conditions. Such of alteration is for the most part, concerning cation movement, initiated by the substitution of a hydrogen ion (H^+) for a cation in a structure. This ion exchange of the cation results in its migration toward the ambient aqueous fluid from which the hydrogen ion came. This ion exchange phenomenon is electro-neutral. The driving force is the low concentration of the cation in the aqueous solution relative to that in the solid phase (in this order). In order to attain an equilibrium concentration of cations in solution in the presence of a solid phase, hydrogen ions migrate into the solid and displace cations in the structure. This cation exchange is a vital initial starting point in attaining chemical equilibrium between unstable minerals, in rocks, in contact with aqueous solutions, in particular surface waters, which are unsaturated in cations due to their atmospheric origin (rain water).

An interesting example of relative bonding stability in a complex silicate material is shown in Fig. 1.19. The elemental concentrations of cations in a thirteenth-century cathedral window from Angers (France) have been affected by hydrogen substitution and cross diffusion in materials altered by rainwater for six

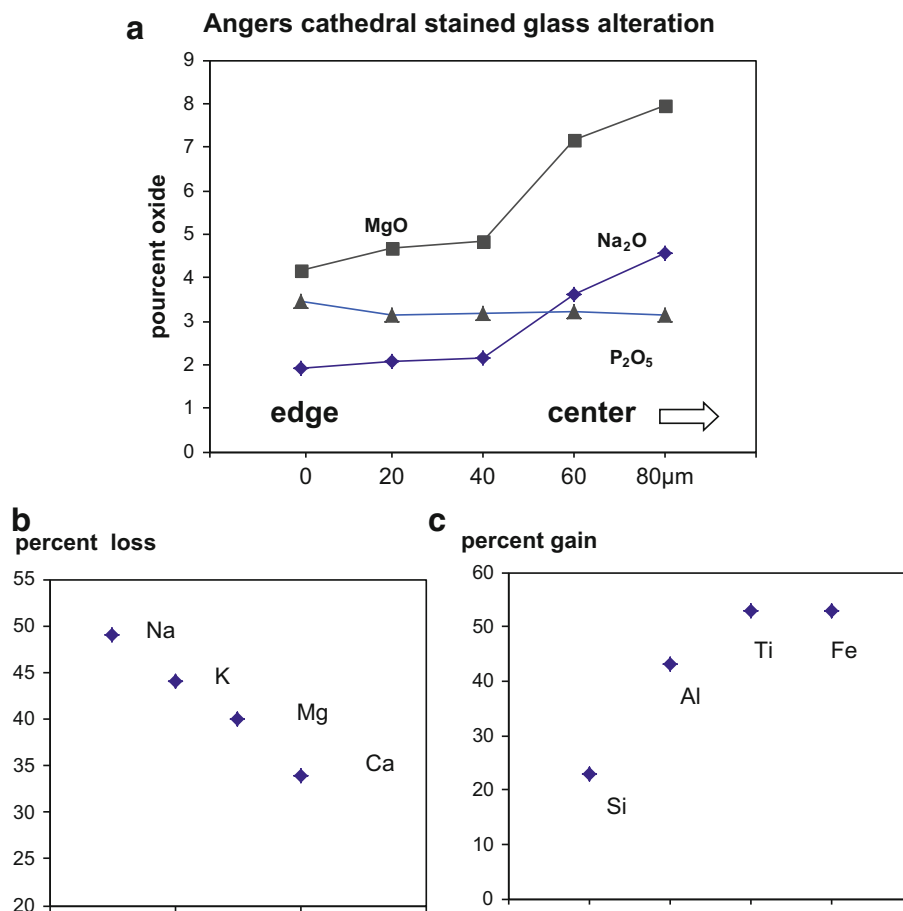


Fig. 1.19 Analyses of progressive stages of alteration through the surface layers to the unaltered glass on a thirteenth-century stained glass fragment from the Angers cathedral France (data from F Pivet). (a) Sequential analyses from the exterior to the un-altered portion of the glass in relative distance, approximately 20 μm between measurements. (b) Relative loss of Na, K, Mg, Ca. (c) Relative loss of Si, Al, Ti, Fe

centuries. The initial material is glass, an amorphous silicate formed at high temperature and highly unstable chemically under surface conditions. The chemical organization of the glass is essentially the oxyanion complex (Si–O, Al–O) compensated by more ionically bonded cations. In the glass there is a progressive loss of alkali and alkaline earth ions from the amorphous solid material (glass), which is reflected by a relative increase in silica content. Taking the most external point of the measurement zone, it is possible to classify the elements by relative percent loss compared to the initial glass material. The sequence $\text{Na} > \text{K} > \text{Mg} > \text{Ca}$ is quite clear. The most easily moved ion is sodium, while the most difficult to remove in the group is calcium. The difference in mobility is obviously due to the charge on sodium ions, 1+ while that of calcium is 2+ which produces a charge density twice that of sodium (Lide 2000). Less mobile ions such as Si, Al, or P change in relative abundance (Fig. 1.17c) indicating that even the less mobile, more covalently bonded ions can be removed during interaction of water with a silicate material. In the case of window glass, the removal of alkali and alkaline earth cations by

hydrogen cations does not result in a stable structure. The hydrogen ions react to form water molecules leaving a highly hydrated silica mass on the surface of the glass after the ionically bonded cations have been removed.

In this example the cations that are less strongly bonded (ionic bonding) are removed, being replaced by hydrogen ions which become water molecules. The remaining material represents more strongly bonded cations where the bonding type is largely covalent. One important way to characterize ions is by their ionic potential. Ionic potential is an ion's charge divided by its radius, and it is thus a measure of density of charge. Ionic potential gives a sense of how strongly or weakly the ion will be electrostatically attracted to ions of opposite charge, and to what extent the ion will repel other ions of like charge. There is a reasonable correlation between the observations in Fig. 1.19 and the data in Fig. 1.18.

1.2.5 Chemical Types of Atoms and Multi-element Units

1.2.5.1 Anions and Cations

The corresponding low bonding energy ions with negative charge (Cl, Br) are frequently associated with the cations mentioned above, forming salts, i.e., high solubility materials formed at the surface of the earth as a result of strong water loss and subsequent accumulation of dissolved elements into residual minerals upon evaporation.

These anion and cation elemental combinations are the most soluble elements found at the surface.

1.2.5.2 Cations and Oxygen Ions (Oxoanions)

An oxyanion or oxoanion is a chemical compound with the generic formula $A_xO_y^{z-}$ (where A represents a chemical element in a cationic form and O represents a negatively charged oxygen atom). Some elements are able to form more than one oxyanion, each containing a different number of oxygen atoms. For example, chlorine can combine with oxygen in four ways to form four different oxyanions: ClO_4^- , ClO_3^- , ClO_2^- , and ClO^- . Here the charge remains the same; only the number of oxygen atoms varies. Oxoanions are formed by a large majority of the chemical elements.

Associations of cations with oxygen through largely covalent bonds are a fundamental characteristic of surface geochemistry. The cation–oxygen units can form an anionic unit, which is completed by ionic bonds to cations when forming a solid phase. The most strongly bonded associations are in the order boron, carbon, silicon, aluminum, phosphorous, sulphur, arsenic, uranium, and oxygen. The configuration of these associations is that of an oxyanion complex that has an overall charge which is satisfied by another cation forming a solid phase. Thus the

covalently bonded cation is part of a tripartite structure where it satisfies part of the negative charge of the oxygen anion. The tendency is to form a strong, partly covalent bond, which determines the stability (solubility and resistance to cation exchange) of the phase. Usually the cations associated with a given oxyanion structure are multiple and can be exchanged under strong chemical potentials. The relative solubilities of these associations depend upon the cation forming the phase. The solubilities of oxyanion complexes can be considered as a measure of their stability under conditions of alteration. In general sulfates are the most soluble with K_{sp} (solubility products) of 10^{-5} – 10^{-10} (barium sulphate). Carbonates are less soluble with K_{sp} values ranging from 10^{-9} to 10^{-17} and the least soluble (most stable) oxyanion complexes are phosphates with K_{sp} values of 10^{-24} to 10^{-37} [data from Lide (2000)]. One can expect to see few sulfates in surface alteration environments, i.e., those where flowing water is the alteration agent, and phosphates should remain present.

1.2.6 Reduction of Oxoanions

Among these oxyanions some are chemically stable, at one specific oxidation state while others are susceptible to redox reactions. Sulfur and arsenic are typical elements of this type. This tendency to respond to changes in Eh is crucial to understanding surface geochemistry in that the environments of surface materials are often subject to changes in redox potentials generated by biologic activity.

Some oxoanions change oxidation state under surface conditions and are no longer associated with oxygen, such that they form cation–anion associations. Such is the case of sulfur and arsenic. Sulfur forms sulfide phases associating with cations. These states are highly dependent on specific Eh and pH conditions. The change in oxidation state and charge on the ion complex under surface environments is extremely important to an understanding of movement of materials under surface geochemical conditions.

Sulfur is a very important case with respect to redox sensitivity in that it is often used as an energy source in bacterial activity, either in the oxidation of sulfides or the reduction of sulfates. These changes can be very important for minor elements, which can be incorporated in one or the other of the sulfur phases. Under surface conditions it appears that the appearance of sulfides is largely due to biological action, especially bacteria where reduction of sulfate ions occurs (Pösfai and Dunin-Borkowsky 2006).

Sulfides are of highly variable solubility, but they are susceptible to oxidation and hence dissolution by surface chemical effects which leaves their presence dependent upon Eh factors more than water concentrations that promote dissolution.

1.2.6.1 Redox Cations (Transition Metals)

The transition elements are group of industrially important metals mainly due to their strong inter-atomic metallic bonding giving them generally high melting/boiling points and high tensile strength. The transition elements have low ionization energies. They exhibit a wide range of oxidation states or positively charged forms. The positive oxidation states allow transition elements to form many different ionic and partially ionic compounds. Some typical characteristics of transition elements are formation of colored compounds, and paramagnetism, variable oxidation states, and tendency to form complexes.

Redox reactions are reactions in which there is a simultaneous transfer of electrons from one chemical species to another. *Redox reactions* are really composed of two different reactions: *oxidation* (a loss of electrons) and *reduction* (a gain of electrons). A relatively large number of elements are generally associated with what are called metals. They can be reduced to the pure state by reduction of the electronic charge (copper is perhaps an example, Manceau et al. 2008). They are present in surface minerals or associated at their surfaces as cations. Some of these elements have the particular property of changing oxidation state under conditions of surface geochemistry. For example Plutonium can, for example, have four oxidation states (+3 to +6) under natural conditions. They also have a higher electronic affinity for other elements, especially oxygen. Transition metals may form oxides–cation or oxygen bonded units or they may enter into the oxyanion complexes. Very rarely they are present as a single phase due to strong reductive conditions. Normally elements in the metallic state become oxidized at the surface to form a metal oxide phase or hydroxy-oxide phase. The most common type of such elements in alterites is iron due to its high abundance, followed by manganese, and eventually other elements such as Ti, Cr, Ni, Co Cu, Zn, V which are considered in most geological contexts as trace elements due to their low abundance and incorporated into other phases as minor substitutions.

Redox cations are then found as oxides or in oxyanion complexes under surface chemical constraints. The possibility to change chemical association is very important in following the movement and fixation of these elements in surface environments. Scott and Pain (2008) indicate that in general a change in oxidation state to the more oxidized form reduces solubility in aqueous solution and hence a tendency to form an oxide or oxyhydroxide. In the reverse, a change in redox conditions to a more reduced state can move an ion from an oxide state into solution. This is a very important concept for the movement of materials at the surface under conditions of biological activity engendered by the plants. Biological action frequently affects the redox potential of surface environments and changes oxide materials into solutes.

1.2.6.2 Heavy Metal Elements

Over the past two decades, the term “heavy metals” has been widely used. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or eco-toxicity. There is no authoritative definition. Normally the term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations [for example mercury (Hg), cadmium (Cd), or thallium (Tl)]. Human activities have drastically altered the balance and biochemical and geochemical cycles of some heavy metals. Therefore, the concentration of heavy metals in soils has been an issue of great interest in the past few years not only to ecologists, biologists, and farmers but also environmentalists. Heavy metals are dangerous because they tend to bioaccumulate. In small quantities, certain heavy metals are nutritionally essential for a healthy life. Heavy metals are natural constituents of the Earth’s crust. They can be associated with sulfur, carbonate, or oxygen. Among the most prominent in surface materials (present in ppm or ppb quantities) are Sn, Sb, Cd, Pb, As, Bi, Hg.

A somewhat extraneous pair of elements, Ga and Ge, is chemically closely related to Al and Si, respectively, and can be seen to follow these major elements closely in relative abundance suggesting a constant substitution in mineral structures for the two major surface mineral-forming elements.

1.2.7 Metals

Some elements are most often found as metals such as gold, platinum, silver, and at times copper for example. Their abundance in ambient surface conditions is very low in general. However, they do form a pure mono-element phase.

1.2.7.1 Oxyhydroxide

The group of oxides, hydroxides, and oxyhydroxides comprises several cations such as Fe, Al, Mn, or Ti, where the anionic part is an oxygen ($-O$), a hydroxyl group ($-OH$), or an oxygen and a hydroxyl ($-OOH$). In alterites, oxides (hematite $\alpha\text{-Fe}_2\text{O}_3$, magnetite $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$, maghemite $\gamma\text{-Fe}_2\text{O}_3$, wuestite FeO , ilmenite FeTiO_3), and oxyhydroxides (goethite $\alpha\text{-FeOOH}$, lepidocrocite $\gamma\text{-FeOOH}$, ferrihydrite $\sim\text{FeOOH}$) do occur. This category of elemental combination is rather difficult to define since the material is rarely well crystallized and often of varying composition. The main cation components of these phases are iron or manganese. However, the surfaces of these materials attract many types of hydrous cations, which can be incorporated in the host mineral structure. In fact the attractive power of manganese oxides to incorporate transition metal and heavy metal elements is

many times greater than that of other phases in surface deposits (Manceau et al. 2000, 2007). Their attractive properties are perhaps due to their incomplete structures. At the edges of these minerals one finds many free or unsatisfied bonds. At these points, an unsatisfied Fe or O ion can attract ions to form a bond. The many uncompleted bonds at the edges of the grains create a capacity for fixing ions from aqueous solutions. In some instances, the alteration of vitreous volcanic rocks, one finds the same situation except that the cations are silicon and aluminum (Andosol materials, from Japanese *an* meaning dark and *do* soil), where the major elements of the un-crystallized silicate material form incomplete structures which fix and attract ions from solution that would be otherwise lost to the aqueous phase. In fact these poorly crystallized materials in soils are very reactive and can often determine the geochemical fate of trace elements in aqueous solution.

1.2.8 Special Elemental Groups

1.2.8.1 Rare Earth Elements (Lanthanides)

Rare earths are an interesting group of metals that have recently become quite useful in high tech, and today they are strategic materials in the world economy. Rare earth elements are most often treated as a group. They occur together either when present in concentrates or dispersed as trace elements in a silicate matrix. They have a general capacity to change oxidation state under surface conditions and can be selectively mobilized, at least in part, according to these electronic states. Most often they are associated with oxygen or oxyanions such as in zirconates or phosphates. There is some association with surface alteration minerals, probably silicates, but little is known about the crystallo-chemical attractions and incorporation. It appears that rare element transport predominantly occurs via preexisting high temperature minerals which are enriched in these elements (McLennan 1989).

1.2.8.2 Transuranic Radionuclides

Taking their name from being trans- or beyond uranium, transuranic radionuclides have atomic numbers greater than that of uranium, which is 92. All transuranic isotopes are radioactive. Transuranic radionuclides do not occur naturally in the environment. Very minor amounts can be present with some uranium ores. In Gabon, Africa, in a natural underground nuclear reactor sustained nuclear reactions estimated to have occurred about 1.9 billion years ago. Some transuranic radionuclides, including neptunium and plutonium, were produced. Like other radioactive isotopes such as those of naturally occurring uranium, radium, thorium the transuranic radionuclides undergo radioactive decay to create typically long chains of decay products.

Plutonium was dispersed worldwide from atmospheric testing of nuclear weapons conducted during the 1950s and 1960s. The fallout from these tests left very low concentrations of plutonium in soils around the world. Normally trans-uranic radionuclides are rare, but due to anthropogenic contaminations they might become important in the future in terms of surface geochemistry. The Fukushima Daiichi nuclear power plant (DNPP) accident caused massive releases of radioactivity into the environment. The released highly volatile fission products, such as ^{129m}Te , ^{131}I , ^{134}Cs , ^{136}Cs , and ^{137}Cs , were found to be widely distributed in Fukushima and its adjacent prefectures in eastern Japan. Zheng et al. (2012) reported the isotopic evidence for the release of Pu into the atmosphere and deposition on the ground in northwest and south of the Fukushima DNPP in the 20–30 km zones. These elements are typically more soluble in their reduced states, under certain conditions of redox potential, which change rapidly under surface conditions. Under other conditions they tend to form oxyhydroxide phases.

Uranium is a component of practically all rocks and therefore it is classified as a lithophilic element. Its relative abundance compares to silver, gold, and the light rare earths elements and it is more common than tin, mercury, and lead. It occurs in numerous minerals and is also found in lignite, monazite sands, phosphate rock, and phosphate fertilizers, in which the uranium concentration may reach as much as 200 mg kg^{-1} . Typical concentrations in phosphate fertilizer are 4 Bq (=0.32 mg) Uranium-238 and 1 Bq Radium-226 per g P_2O_5 . Uranium is usually present in minerals either as a major or as a minor component. Sometimes they are altered to form the bright-colored secondary uranium minerals (complex oxides, silicates, phosphates, vanadates). Also specific micas contain uranium in the form of sulfates, phosphates, carbonates, and arsenates, which are products of the weathering of original uranium ores. Uranium is found at an average concentration of $\sim 0.0003 \%$ in the Earth's crust.

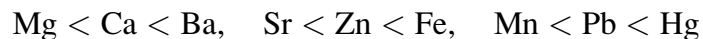
Rarely, both ions are oxygenated, having both an oxycation and an oxoanion. One of the better-known examples of this is uranyl nitrate $(\text{UO}_2)(\text{NO}_3)_2$. They form oxycation units in many cases (yl-ions, plutonyl for example). The uranyl ion is an oxycation of uranium in the oxidation state +6, with the chemical formula $[\text{UO}_2]^{2+}$.

1.2.9 Association of the Elements in Phases (Minerals) at the Surface

A very general classification of mineral phases can be made into a few groups, which dominate the minerals of the surface:

1. **Aluminosilicates** dominated by oxyanions with Si–O as the major component. These minerals have a large variety of cation substitutions as solid solutions in different crystal structures, with major elements, i.e., several percent of the element, or minor elements with less than 0.5 % of the element present substituting one for the other.

2. **Phosphates** are moderately stable structures involving the oxyanion P_4O^{3-} with low solubility at intermediate pH values but which are strongly affected by acid conditions. Usually Ca is the dominant cation present in common surface phosphate minerals, which are for the most part of biological origin. However, there are 391 different phosphate minerals listed in Huminicki and Hawthorne (2002), which suggest very complex substitutions and variations in crystal structures and chemistry in particular in the higher temperature phases.
3. **Oxides** where oxygen is the anion associated with various cations. These phases are usually composed of moderately covalent ions, which can change oxidation state relatively easily. Metals (i.e., cations of intermediate covalent tendency such as Fe, Ni, Cr, Mn) are oxidized from the divalent state prevalent in high temperature rocks and then they form stable oxide phases which are typically very insoluble. Metal cations which change oxidation state only in extreme cases (Cu, Ni, Zn, for example) tend to be dissolved into the aqueous solution but can be fixed temporarily on mineral surfaces (see Chap. 3) and are thus mobile but often follow minerals which are stable such as oxides of iron or manganese.
4. **Carbonates** where the oxyanion is CO_3^{2-} coupled to divalent cations (Ca, Mg, Fe for the major part). These minerals are special in the sense that the source of carbon is essentially atmospheric and hence the incorporation into a carbonate is through biological concentrations, either shell producing animals or through the decay of plant material by bacteria, which releases CO_2 in soils. This CO_2 can be combined with other elements present through further biological action. The solubility product constant (measure of relative stability under near-neutral pH conditions) indicates a wide range from 10^{-8} to 10^{-14} mol/l (Lide 2000, p. 174). The relative stability for several phases is



Basically the most common carbonates, calcite and magnesite, are less stable than the phases with higher degrees of covalent bonding character.

5. **Sulfates** where the oxoanion SO_4^{2-} is joined by divalent cations (Ca, Mg, etc.). Sodium, potassium, and magnesium sulfates are all soluble in water, whereas calcium and barium sulfates and the heavy metal sulfates are not. Dissolved sulfate may be reduced to sulfide, volatilized to the air as hydrogen sulfide, precipitated as an insoluble salt or incorporated in living organisms. Seawater contains about 2,700 mg sulfate per liter (Hitchcock 1975). Because sulfate is highly soluble and relatively stable in water, sulfate minerals are generally formed by concentration of surface waters or seawater in evaporitic basins. Atmospheric sulfur dioxide (SO_2), formed by the combustion of fossil fuels and by the metallurgical roasting process, may also contribute to the sulfate content of surface waters. It has frequently been observed that the levels of sulfate in surface water correlate with the levels of sulfur dioxide in emissions from anthropogenic sources.
6. **Halogenides** where the anions Cl, Br, I are associated with cations such as Na, K, Mg, Sr, among others. Again these minerals are evaporitic concentrates

of elements dissolved in surface water. The stability of these phases is low in the presence of water. They occur in situations where free water is scarce such as in evaporate deposits. The most soluble elements, the anions Cl, Br, I, will be removed from a solid rock most easily from an alteration site and moved over the longest flow paths.

7. **Alkali and alkaline earths.** Cations of low covalent tendency (Na, Ca, K for example) will initially be removed differentially into solution leaving less soluble cation–oxygen associations in the solid form, as silicates, oxides, and hydroxides. These elements can be associated with silicates in loosely held associations (K, Ca, and Mg), but they are in the long run removed from the alteration zone under conditions of strong water–solid interaction.

1.2.9.1 Oxoanions

Many different oxoanions are found in the soil environment, and the chemistry of these oxoanions is quite varied. Some oxoanions such as phosphate and sulfate are essential nutrients for plant growth and are found in relatively high concentrations in soils. Other oxoanions such as borate are micronutrients. They are essential for plant growth at low concentrations but become toxic at higher concentrations.

Another group of oxoanions, such as arsenate, arsenite, selenate, selenite, and chromate are frequently studied because they have little agronomic use and are instead detrimental to human health. These elements are both metals and metalloids and include antimony, arsenic, chromium, molybdenum, selenium, tungsten and vanadium. The oxyanions are all present in low concentrations in crustal rocks and can be concentrated in certain systems as a result of weathering reactions if geochemical conditions are favourable. Because most of the elements form anionic species at neutral to alkaline pH values, their adsorption behaviour onto oxide surfaces is different from that of trace metals such as Cd, Cu, Pb, Zn, Ni, Zn.

We may compare the solubility of minerals in the same groups, i.e., carbonates, sulphates, phosphates by their solubility products (Lide 2000), which indicate the effects of different ionic substitution on mineral stability. In general sulphates are the most soluble (and hence least stable under conditions of surface alteration) having a K_{sp} (solubility product constant) $< 10^{-10}$ for the elements Ca, Ba, Hg, Pb, Cd, Sr, while carbonates (Ca, Ba, Fe, Mg, Mn, Hg, Zn, Pb, Cd, Sr) are less soluble with K_{sp} values of 10^{-14} – 10^{-17} and phosphates are even less soluble with K_{sp} constants of $< 10^{-24}$. The stability sequence would then be, in general, sulfate $<$ carbonate $<$ phosphate. Using Ca compounds as an example, the sequence is sulfate (10^{-5}), carbonate (10^{-9}), and phosphate (10^{-33}).

1.2.10 Elements in Surface Phases

Geochemistry is the study of the distribution and stability of elements in the environment that we live in. Surface geochemistry is especially concerned with the distribution of elements in solids, on solids, and in aqueous phases. Solids tend to move slowly and liquids move more rapidly. However, solids can be moved in liquids, in suspension, if they have a sufficient size. Aqueous phases provide readily available elements for biological activity, for the better or the worse. The distribution of elements dissolved in aqueous solution is more or less straightforward concerning their chemical activity, which follows concentration and the chemical parameters of interaction with the water molecules that surround them (see Chap. 2). The distribution of elements in solids is more complicated.

In the formation of phases, there is the necessity of having sufficient amounts of the proper components present to provoke the formation of a phase: one reaches the saturation limit of its presence in the medium of transport. However, in each phase, there is the possibility of substituting one element (atom by atom) by another within the structure. Also there is the possibility of attracting elements from solution, as hydrated ions, to the surface of a solid. Thus, several possibilities are possible for different elements to be present within or on a mineral phase.

Generally speaking the elements of major abundance form phases that correspond to their relative abundance in the chemical–geological system in which they form (not necessarily corresponding to their solubility product). This results in a limited number of species for a given chemical environment, usually three or four. Minor elements have lower elemental abundance and are not sufficiently chemically active to form a specific phase. Hence, they either find a space in a major element phase, in substitution at low concentration levels, or they can be attracted to mineral surfaces. If none of this is possible, the element remains in aqueous solution and is transported out of the system. Of course this situation pertains for some major elements, which are moved out of the system of solid phases in solutions. Sodium is a classical example.

1.2.10.1 Atomic Substitutions within Crystals

Solid phases are for the most part composed of what can be called major elements, major in the sense that their concentrations are sufficiently large to form a specific mineral phase. Mono-elemental phases are extremely rare in nature, gold being one. Consequently, the distribution of major elements is interdependent upon the presence of other elements. The most abundant element in surface minerals is oxygen, making up around half of the atoms present in the phases. There is no restriction to its presence, since it is available in the atmosphere and it is dissolved in surface waters. Thus surface minerals are essentially oxygen-rich. Other elements are combined with oxygen forming minerals depending upon the type of ions that are involved with the oxygen and its relative ionic concentration.

1.2.11 *Silicates*

The most common minerals at the surface are called silicates, where the silicon–oxygen covalent structure dominates the chemistry and structure of the minerals. Silicates can be defined as compounds containing $[\text{SiO}_4]^{4-}$ anions. The main structural unit of silicates is a tetrahedral cluster containing one silicon atom and four oxygen atoms. This means that silicon is a dominant cation numerically and that the highly covalent Si–O bond determines the mineral chemistry. Frequently aluminum is associated with the silicon–oxygen bonding structures, as a substituting ion. These covalent ion structures need more cationic compensation to form a complete structure, except in the case of the pure mineral SiO_2 quartz. This mineral is special in that there is no substitution of other cations in the structure. It is a pure phase, a rare occurrence in surface mineralogy. Curiously it has a very great stability under surface conditions, often persisting beyond its thermodynamic limits to remain present when other minerals have been dissolved or transformed. This is why white beaches over the globe are most often formed of quartz grains, which are metastably present but very evident.

The tetrahedral clusters can be polymerized, i.e., linked to each other through the bridging oxygen atoms. They are able to form polymers by means of linkage with one, two, three, or four neighboring tetrahedra, forming siloxane Si–O–Si bonds. Other ions can be located in the silicate lattices. Usually these ions are “major elements” Na, Ca, K, Fe, Mg. Hence most silicates are composed of several of the ten major elements with minor proportions of other elements in the minerals.

One feature of great importance in silicate minerals is the sharing of electrons by oxygens with more than one cation. In fact a strongly attached network, in two or three dimensions, is formed through this inter-linkage and electron sharing. The dominant feature of silicates is the arrangement of oxygen ions around silicon cations; for the most part four oxygen ions are linked to a silicon ion forming a tetrahedral structure. These same silicon linked oxygen ions can be linked with other cations forming yet other geometric structures around the other cations, such as an octahedron when six oxygen ions are linked to the cation. Ionic substitutions are regulated by charge and more importantly relative ionic diameter since the oxygen polyhedra have a given space within the polyhedral structure that they form. Substitutions of one cation for another in silicates are to a large extent a function of charge and ionic size.

Elements of minor abundance substitute for major elements in crystal structures following the same chemical criteria. In general alkali elements substitute for other alkalis, transition metals for transition metals, and so forth. However there are some surprises, which will be discussed in further chapters. One is lead and another is potassium, lead being a large and heavy divalent ion, while potassium is smaller and monovalent. Nothing could be more dissimilar at first glance than this ion pair. Yet lead is often found to substitute in high temperature silicate mineral structures for potassium (Taylor and Eggleton 2001, p. 142). It is probable that this relationship continues at the surface, if one considers the data for elemental distribution in

materials where mineral structures are such that lead could substitute for potassium (micas and smectites). Minor element substitutions do not follow the rules in all cases.

1.2.12 Oxides and Hydroxides

A second possibility is the formation of what are called oxides and hydroxides, i.e., minerals with oxygen but not containing silicon. The oxides and hydroxides present in soils reflect the environmental conditions of soil formation. They are variable in structure, composition, and degree of crystallinity. The formation of different types of oxides and hydroxides is controlled by temperature, moisture, organic material, pH, and Eh control. The oxides are most commonly dominated by Fe or Mn cations. The oxides may also occur in a more complex manner as oxyhydroxides. Oxyhydroxides are chemical compounds that commonly form in aqueous environments with different content in cations (e.g., Fe^{2+} and Fe^{3+}), oxygen, hydroxyl, water, and some amounts of SO_4^{2-} , CO_3^{2-} , and Cl^- .

1.2.13 Carbonates

Other surface minerals, frequently encountered, are carbonates. Carbonate minerals are the most stable minerals of carbonic acid. Most of them are simple salts (e.g., Calcite CaCO_3), others contain additional anions (e.g., malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$). Carbonic acid is relatively weak and prefers to bond with elements of low ionic potentials (sodium, potassium, strontium, calcium). Cations with high ionic potentials such as Cu^{2+} or rare earth elements form only if F^- , OH^- groups or O^{2-} are present to weaken the CO_3^{2-} complex. An example is azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. About 170 different carbonate minerals are known. In nature carbonates are mainly composed of calcium carbonate as calcite and rarely as aragonite, of magnesian calcite, of dolomite, and occasionally of iron-rich carbonate such as ferroan calcite, siderite and ankerite.

1.2.14 Phosphates

Phosphate is a salt of phosphoric acid. The fundamental building block is the PO_4^{3-} tetrahedron. Soils generally contain 500–1,000 parts per million (ppm) of total phosphorus (inorganic and organic), but most of this is in a “fixed” form that is unavailable for plant use.

The two main categories of phosphorus (P) in soils are organic and inorganic. Organic forms of P are found in humus and other organic material. A mineralization

process involving soil organisms releases phosphorus in organic materials. Inorganic phosphorus is negatively charged in most soils. Because of its particular chemistry, phosphorus reacts readily with positively charged iron (Fe), aluminum (Al), and calcium (Ca) ions to form relatively insoluble substances. The solubility of the various inorganic phosphorus compounds directly affects the availability of phosphorus for plant growth. The solubility is influenced by the soil pH. Soil phosphorus is most available for plant use at pH values of 6–7. When pH is less than 6, plant available phosphorus becomes increasingly tied up in aluminum phosphates. As soils become more acidic (pH below 5), phosphorus is fixed in iron phosphates.

Apatite is the most common phosphate mineral. The bones and teeth of most animals, including humans, are composed of calcium phosphate, which is the same material as Apatite. Apatite is named from the Greek word *apate* (in Greek mythology, Apatite was the personification of deceit and was one of the evil spirits released from Pandora's box) since Apatite has a similar appearance to so many minerals.

For the most part the formation of phosphate sedimentary material is due to precipitation from aqueous solution. Many freshwater deposits of fish remains become phosphate repositories.

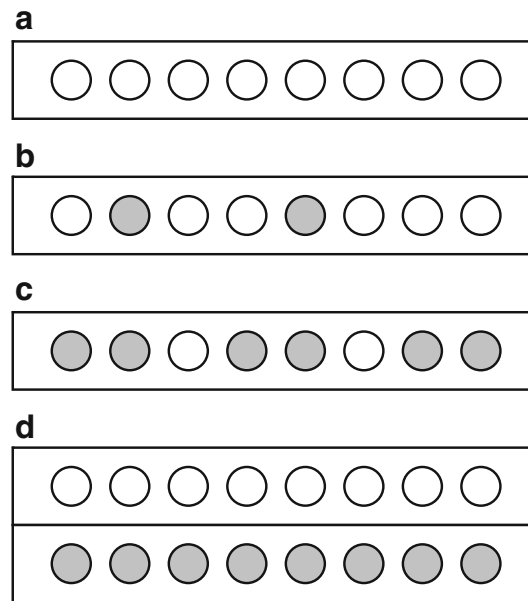
1.2.15 Sulfates

Sulfates are salts of sulfuric acid, containing the group SO_4 . Sulfates occur naturally in numerous minerals, including barite (BaSO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Sodium, potassium, and magnesium sulfates are all highly soluble in water, whereas calcium and barium sulfates and many heavy metal sulfates are less soluble. Atmospheric sulfur dioxide, formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulfate content of surface waters.

Sulfate occurs naturally in the aquatic environment or it can have an anthropogenic origin. When sulfate naturally occurs in aquatic environments, it can be the result of the decomposition of leaves, atmospheric deposition, or the weathering of certain geologic formations including pyrite (iron disulfide) and gypsum (calcium sulfate).

1.2.16 Substitutions of Ions in Mineral Structures

The major phases, composed of major elements, are rarely pure in the sense that only one or two cations are present. However in some minerals the cations can be of several types. The mixture of major elements in the same mineral in varying proportions is called solid solution (the minerals being in the solid state as opposed to liquids). Depending upon the mineral and the temperature at which it has formed,



Types of chemical substitutions in
a mineral structure

Fig. 1.20 Substitutions of ions within a fixed crystal structure. This can occur in a random manner, or in a more ordered and regular manner in specific crystallographic sites. The phyllosilicate structure is based on a network of polymerised SiO_4^- ions extending essentially in a two-dimensional structure, represented by rectangular forms in the diagram. The substitutions are in identical crystallographic sites where elements of the same ionic charge are distributed in different manners. **(a)** No substitution in a given crystallographic site. **(b)** Random substitution in a given crystallographic site. **(c)** Regular substitutions in a given site. **(d)** Segregation of ion types layer by layer in a given crystallographic site

minerals can accommodate more or less substitution of one element for another. Surface minerals tend to show a range of substitution for some minerals and no substitution for others. Figure 1.20 shows several types of substitutions found in surface minerals.

One may have a pure phase (case A), a substitution in a random manner, i.e., no regular succession of elements in substitution sites (case B), regular substitution (case C), or segregated substitutions (case D). If the segregated substitutions form large segments of the crystal structure, one will distinguish two phases by X-ray diffraction identification methods and even though they form one contiguous crystal, one may consider them as two phase systems. The segregated substitutions can be in a random order within the crystal, or with a regular repetition case as shown in example D in Fig. 1.20.

Elements of minor abundance (<0.1 wt%) can be found in various types of substitutions, but are rarely identified as such. Usually one assumes random substitution in a crystal for elements of minor abundance. These minor element substitutions within the crystal are stable, i.e., the elements will not be released unless the crystal becomes unstable and is transformed into another or dissolved. The

amount of substitution of different ions in a crystal is to a certain extent controlled by temperature. It is well known that at high temperature (approaching the temperature of melting), more elements can be substituted in a given structure for a silicate mineral. However one finds also that substitutions are found in phases formed at very low temperatures. Surface minerals often contain significant amounts of various elements in substitution in mineral structures when formed under surface environments. This phenomenon can be explained as follows: as temperature is high, thermal agitation loosens the mineral structure allowing different elements to enter a structure even though they have slightly differing ionic sizes. At lower temperatures these elements diffuse out of the structure to form a specific phase of their own. At very low temperatures the thermal energy is very low. Here there is a disorder in elemental occupancy of crystallographic sites as minerals are formed because there is not enough energy to allow misplaced ions to diffuse out of the structure to form another specific phase. Disorder occurs for lack of thermal agitation energy at low temperature whereas disorder is created at high temperatures because there is too much energy present. This is illustrated in Fig. 1.21 where element Y is substituted in phase A in varying amounts according to temperature conditions.

Ionic substitutions follow, generally, a pattern of constraints based upon ionic charge and ionic size. In Fig. 1.22 several elements are shown as a function of ionic charge and ionic diameter.

The elements grouped in this space can often be found in different proportions in the same mineral type. Those found at some distance tend not to be associated. This is especially true for ions of high charge. However in more complex situations one may find multiple substitutions where an ion of higher charge substitutes for an ion via a coupled substitution of an element of lower charge substituting in another site. One example is



This occurs in the same crystal but different crystallographic sites. In one site the ionic charge is increased and in the other it is reduced by the substitution keeping overall electronic balance, which is necessary for mineral stability. Multiple site substitutions are especially common in silicate minerals, especially those of the clay mineral group.

Substitutions of elements, one for another in a mineral structure, can then be rather complex. The simple case is exchange of ions of the same valence, for example, Na for K. Here the limiting factor is the size of the ion within the mineral structure. The greater the difference in size, the less substitution will occur in the same mineral. However, in a crystal which has a large number of oxygen ions present, the positions of cations is largely determined by the arrangement of oxygen ions. If there are four contiguous with a cation the space is smaller than if there are six coordinated to the ion. Data in Steinberg et al. (1979, p. 316) indicate that the space left for an atom in fourfold coordination is roughly 20–30 % less than when in sixfold coordination. Oxidation state of an ion changes its volume and hence

Fig. 1.21 Illustration of the effect of temperature on the substitution of element Y in phase A. More Y is substituted at low and high temperatures

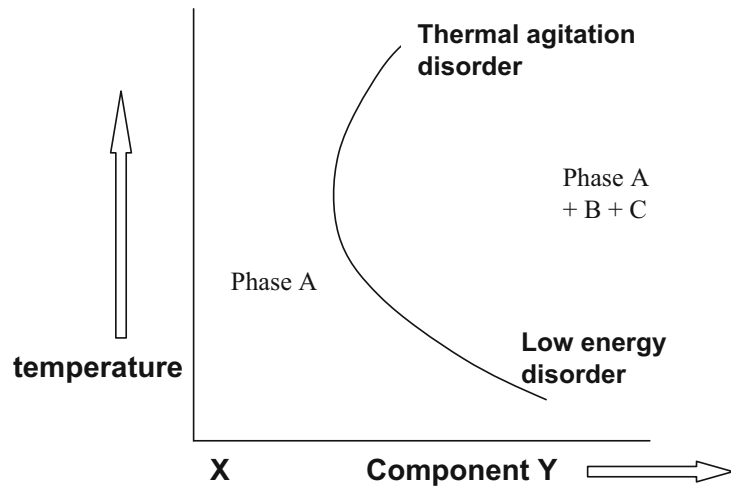
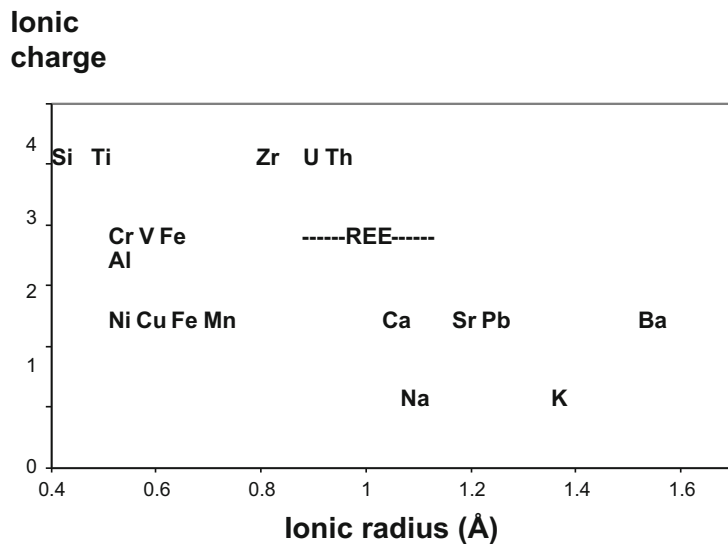


Fig. 1.22 Charge–ionic size relations after Brookins (1989)



influences its acceptance in a crystal structure (see Fig. 1.18). Hence the oxidation state of an ion plays a role in substitutions where it must follow charge balance criteria as well as ionic dimension characteristics which can determine its presence in a given mineral structure.

If we consider the alkali feldspars, for example, there is a high degree of substitution in the structure at high, magmatic temperatures, which reduces as the ambient temperature of the rock or crystallization of new minerals occurs. From an almost complete solid solution in high temperature magmas the limit decreases with temperature until at near surface conditions one finds only almost pure Na or K minerals forming low albite and adularia. One would expect then almost pure mineral compositions in surface minerals, however this is far from being the case. In fact it appears that those minerals formed at surface conditions have a greater capacity for solid solution (elemental substitution) than those minerals formed at

slightly higher temperature, 120 °C, or so under diagenetic mineral conditions of formation.

In Fig. 1.21 the substitution of element X for element Y is seen to occur at high temperature due to thermal agitation as well as at low temperatures where there is not enough energy to form a well-ordered mineral with the constituent elements in chemical equilibrium. An example of this sort of initial wide range of substitution is given by Velde et al. (1991) where diagenetic chlorites, formed in sedimentary rocks at temperatures between 50 and 120 °C, have a relatively wide range of composition from one grain to another in the same sample at lower temperatures which decreases to a small range of compositional variation in rocks formed at higher temperatures.

The surface minerals with the highest degree of solid solution or elemental substitution are the clay minerals. These minerals have high degrees of substitutions in certain parts of their structure while in others there is relatively little substitution. This particularity has led to a great amount of mineral nomenclature and perhaps confusion as to what the true functions and range of compositions are in these minerals.

1.2.17 Mineral Surface Reactions

Some elements can be attracted to mineral surfaces due to charge imbalances on crystal faces in particular edge faces where the crystal ionic linkages are not compensated, such as the oxygen–cation compensations, and either cations or anions are present without a compensating ion to equilibrate electronic charge on the ion. To these locations charged elements in solution can be attracted by the electrostatic imbalance and fixed, temporarily on the crystal surface. The ions in solution are always hydrated and have some water molecules associated with them.

Since they are not integrated into the overall structural electronic compensation structure, their presence is ephemeral, and another ion can replace the surface ions due to a higher activity in solution and/or higher activity for the surface. This phenomenon, cation exchange, is extremely important for the movement of minor elements at the surface of the earth. Since they are not present in high enough concentration to form a phase or mineral corresponding to their chemistry, they are attached in very small quantities to sites on other crystals. Surface mineral phase can carry these minor elements, but their presence is determined by the chemical activity or their concentration in the aqueous solution of their environment. This action is quite important when it comes to understanding the pathways of minor elements at the surface of the earth. The phenomenon of surface attachment is treated in detail in Chap. 2.

A second site of temporary ion retention is within the clay structure when a charge imbalance due to ionic substitution occurs in the silicate structure. Temporary ionic substitution occurs between the charged clay layers. These are called “interlayer” substitutions, where the presence of an ion is due to its relative

concentration in solution and the affinity the mineral has for it as a function of its charge and ionic dimensions. Again this phenomenon, extremely important for surface geochemistry is treated in detail in Chap. 2.

The surface attraction phenomenon is driven by the surface availability, or the amount of surface compared to the volume of the minerals. The smaller the crystal, the greater the surface area and hence the greater will be the possibility of attracting elements from the aqueous solutions onto the mineral surfaces for a given mass of solid. Since the underlying principle of surface phase transformation of rocks into alterite and eventually soil materials is the formation of small crystals [see Chap. 4 in Velde and Meunier (2008)] the materials formed at the surface become very “surface reactive” with substantial crystal surface area being present. This property is very important when one wishes to follow the fate of elements at the surface of the earth. An enormous amount of transportation and displacement of minor elements, i.e., those not involved in the formation of mineral phases, is accomplished on mineral grain surfaces.

1.2.18 Summary

The major chemical influences on surface chemistry are water and oxidation. In aqueous solutions pH is a major factor for dissolution of minerals. The stability of a mineral can be measured relatively in terms of its solubility as a function of pH. Low pH increases the dissolution of carbonate and silicate minerals. Intermediate pH values, those of soils in the range pH 4 to pH 8, tend to favor mineral stability. Carbonates are the least stable (most soluble) followed by minerals from basic magmatic rocks (olivine, pyroxene) and then by minerals from acid eruptive rocks (feldspars, muscovite). Minerals with the lowest solubility are those formed at the surface of the earth such as iron oxides, clays, and eventually the least soluble, quartz.

The effect of pH can be correlated with rainfall, the more rain the lower the pH. This control is largely one of biome types, which follow rainfall abundance. In fact evergreen forests, either in the tropics or at altitude in mountain areas (conifer forests), produce acidic soils whereas deciduous forest and prairies produce soils of higher pH. The biome effect can change pH by three units in well-drained soils. The biological factor for pH control is very important to the stability of surface minerals, especially those with cations susceptible to changes in oxidation state. Not only does biology control pH it also controls Eh conditions. Thus iron minerals and manganese minerals will be susceptible to the biocontrols of Eh and their dissolution or precipitation can be induced by biologic action.

The same occurs exists for sulfur-bearing minerals. The more reduced form of sulfur (S^{2-}) where sulfur is an anion as in pyrite, FeS , can be changed into an oxyanion upon oxidation. The reverse can be true, when bacterial action reduces the sulfur oxyanion to form the sulfur anion. This example would occur in a reversible reaction of weathering, oxidation, and dissolution of a sulfur-bearing mineral which

is re-generated due to biological action. Sulfur is an element of minor abundance in surface environments, but it is extremely important. In forming an iron sulfide, for example, it will incorporate a large range of trace elements in the structure in stable form as long as the redox conditions persist. Thus the immobilization or release of a range of trace elements depends upon the action of bacteria, which use the change in oxidation state of sulfur as a source of energy. In doing so they can change the balance of bioavailable elements in a surface environment.

In the literature and our text, one speaks of soluble elements and insoluble elements. This of course indicates the propensity of an element to be found in ionic form in aqueous solution. Cations (such as Na, K, Ca, and Mg) are easily dissolved as are anions (such as Cl, F, Br). The elements that are bound to oxygen, such as Si and Al, are less likely to be found in solution and are called insoluble elements. This means in fact that the solubility of the oxides is low compared to that of an ionic species. The type of chemical bonding of an element relative to oxygen is primordial to its behavior at the surface of the earth.

1.3 Useful Source Books

- Gill R (1989) Chemical fundamentals of geology. Chapman & Hall, London, p. 290
Goldschmidt V (1954) Geochemistry. Clarendon Press, Oxford, p. 730
Holland H, Turkian K (eds) (2004) Treatise on geochemistry, vol. 5. Elsevier, Amsterdam
Krauskopf K (1967) Introduction to geochemistry. McGraw Hill, New York, p. 721
Mason B (1958) Principles of geochemistry. Wiley, New York, 329 pp
McQueen K (2008) Regolith geochemistry, Ch 5. In: Scott K, Pain C (eds) Regolith Science. Springer, Heidelberg, p. 461
Wedephol H (1969) Handbook of geochemistry, vol. I. Springer, Heidelberg