

Andreas Bauer · Bruce D. Velde

Geochemistry at the Earth's Surface

Movement of Chemical Elements

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Introduction

Geochemistry is a frequently used term in geological studies that defines a discipline which has developed in importance over the past 40 years. The meaning of this term and the substance of the discipline is the relationship between the chemical properties of elements found in the geological sphere and their expression as minerals or other phases found in rocks. Essentially the elements that are the most common and abundant in surface materials are limited in number, such as Na, K, Mg, Ca, Al, Si, and Fe (called the major elements) with concentrations of elements such as Mn, P, S, C, Cl present in smaller amounts and considered as minor elements. The elements of industrial importance, such as the transition metals Cu, Cd, Co, Ni, Ti, and Au, among others, are of yet lesser abundance in rocks and most often occur as inclusions in phases dominated by major elements or as isolated concentrations due to special geological conditions. Other elements of low overall abundance in rocks such as As, Sb, and Sn are more difficult to classify in that their occurrence is limited to small and sporadic concentrations in rocks. In the classical geological chemical framework the elements found as gases in the atmosphere such as Ar, N, Ne, He, and others are little present. Some atmospheric elements such as C and O are present in both the realm of geological occurrence and the sphere of the surface atmosphere. Geochemistry is the study of the occurrence and reasons for these occurrences of different elements.

A further direction of investigation, used with great success to solve some specific problems, is the determination of the relative abundance of the isotopes of the elements present. Isotope geochemistry has proved to be a powerful tool in the determination of many geological processes of rock formation.

Our proposition in the present study is to use the available published information concerning elemental abundances at the surface of the earth, in the zone of atmosphere and rock interaction, to follow the selection and segregation of elements during the surface chemical processes which are dominated by the interaction of atmospheric and biologically determined chemical processes with rocks that have formed and attained chemical equilibrium under other conditions of temperature and pressure.

One fundamental point to remember is that rocks are composed roughly of half oxygen atoms and the atmosphere is still more oxygen rich. Water, the agent of change, is composed of oxygen and hydrogen atoms. Oxygen is the major element of the geological realm and especially that of surface geochemistry. Interactions of cations with oxygen are the dominant modes of chemical interaction. The geochemical actions initiated at the surface are essentially those of hydrogen exchange for cations in rock minerals which creates “hydrated” minerals such as the silicate clay minerals or hydroxy oxides of Fe or Al. Geochemistry at the earth’s surface is initiated by phase change through the interaction of water with rocks which sets the stage for geochemical exchange throughout the erosion, transportation, and deposition processes. The activity of oxygen and ensuing oxidation of metal elements are another fundamental constraint on surface geochemical reactions. Since most multi-oxidation state elements are in a more or less reduced state in rocks, oxidation disrupts the former chemical interactions in the minerals and this produces the destabilization of these phases and eventual formation of new minerals. However, biological activity at the interface of surface materials and the atmosphere creates variations in oxidation state of materials in many cases which reorganizes some of the material present and changes the chemical relations among ions and solids. Thus hydration and oxido-reduction are the key concepts to keep in mind when considering earth surface geochemistry. These are the chemical variables or active forces present.

This is the chemical framework. Then the first part of the term “geochemistry” must be considered. In many texts, treatises, and scientific papers, the concept of geological forces at play is not taken into account. Chemistry is essentially static, where the electronic configuration of the elements present is arranged as quickly as possible to create an assemblage of phases that are in chemical equilibrium. Geology by contrast is the realm of movement dynamics driven by the forces of tectonics (mountain building) and the forces of gravity which drive water movement, the major transport vector. The earth is a restless object, especially at its surface. Movement of matter in solid or dissolved form is the general rule.

Then the “geo” part of geochemistry is the study of the chemical accommodation to the dynamic forces of geological energy. However, the inherent instability generated by the earth processes is such that chemical equilibrium is often not attained and materials of contrasting chemistry are found together in the same environment. The work of the geochemist is then that of sorting out the nature of materials in a given sample and their origins in order to understand where they came from and what will happen to them as they approach a chemical equilibrium in a given setting. As a simple example, if one considers the sediments carried in a river and its load of dissolved elements, one must look at the relief and erosion rate of the drainage basin, its climatic variation, and geomorphologic characteristics in order to interpret the chemical variations of materials found in the river load and river water. These will be reflected in the sediment that is eventually deposited by the river along an inland lake or ocean shelf. Surface geochemistry is the interrelationship between chemistry and geology.

In the text that follows we have purposefully left out any reference to isotopic variations of the different chemical species in that there is not a great abundance of such information available and the changes and instability of surface materials render the interpretation of isotopic variation very difficult in many instances. If one studies the isotopic variation of an element in a given stable context, things can often be worked out to a satisfying degree, but such studies are not generally available and using them to interpret the overall variations of chemical isotopic abundance throughout a geological sequence is very difficult indeed. Hence we attempt to find the underlying relations between elements, of major and minor abundance depending upon the local chemical context and the dynamics of the geological setting.

It is clear in reading the following studies that there is much to be done yet in order to understand the many aspects of surface geochemistry; however, we hope to lay out some general principles and relationships that can be used as a basis for further work.

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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 built 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 altered 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

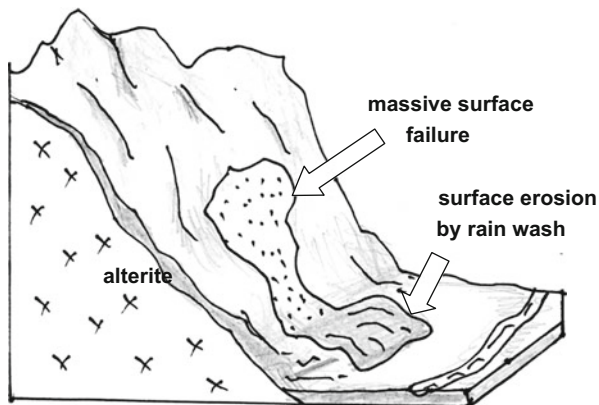
The basic paradigm of surface geochemistry is one where rocks formed at higher than surface temperatures are brought in contact with the atmosphere of the earth's surface and its chemical constraints. The reasons for this contact are the upward movement of rock masses by tectonic forces to form mountains. 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.

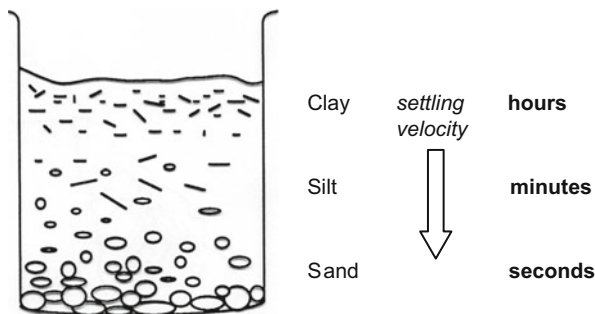


Fig. 1.3 Beaker experiment where heterogeneous alterite material is dispersed in water and allowed to settle. The largest grains are deposited first and the smallest last. Eventually the small grains can be held in suspension for very long periods of time if the water is moving and turbulent

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,

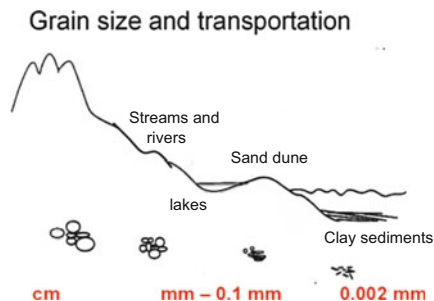


Fig. 1.4 Illustration of transport distance as a function of grains size in a landscape situation

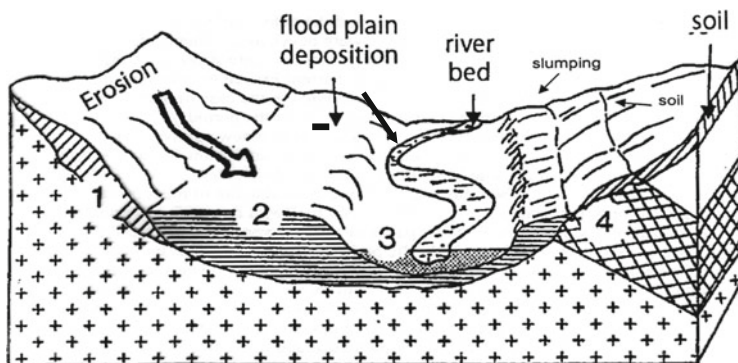


Fig. 1.5 Illustration of massive transport erosion and re-deposition along a river. 1 Surface erosion and slump movement of soil surface material, 2 temporary deposition of slump material which is eroded in its turn by rainfall erosion, 3 deposition of the overflow material from the stream when it reaches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

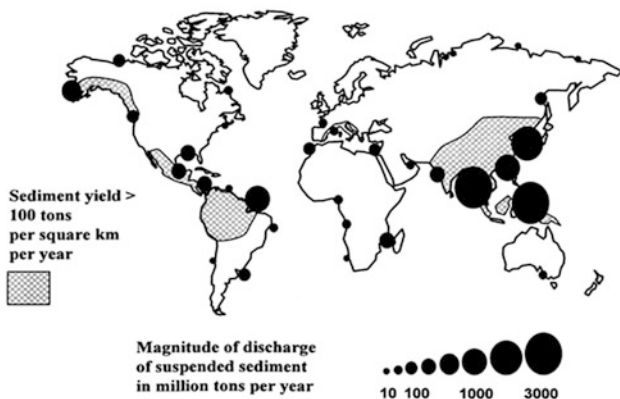


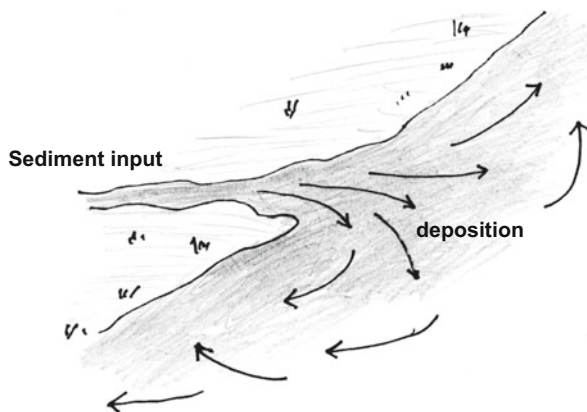
Fig. 1.6 Sediment yield map for major geographic areas [adapted from Hillier (1995)]. The Western Pacific Islands are combined. Highest yield occurs in areas of high relief and/or high rainfall

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



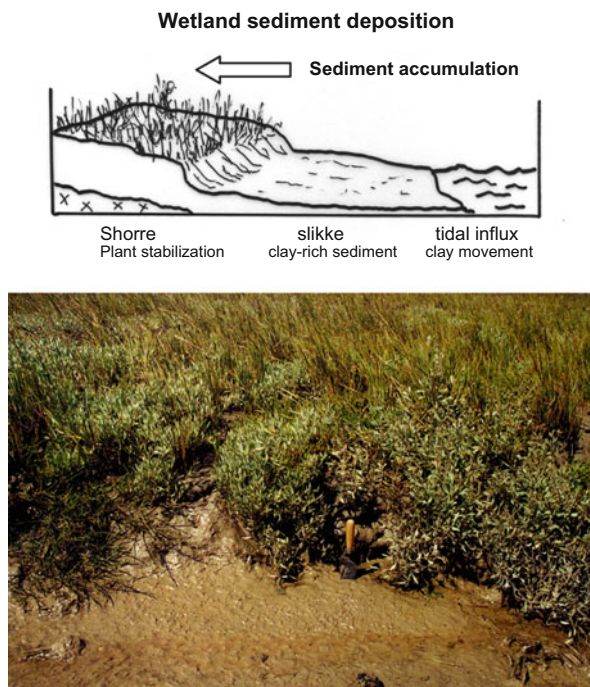
environment (essentially quartz) and the newly formed materials that have been the result of water–rock interaction (clays and mud). In any event most clays are detrital, probably more than 90 %. They are supplied to the sedimentary systems from two main sources. One source is rocks, and the other is 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

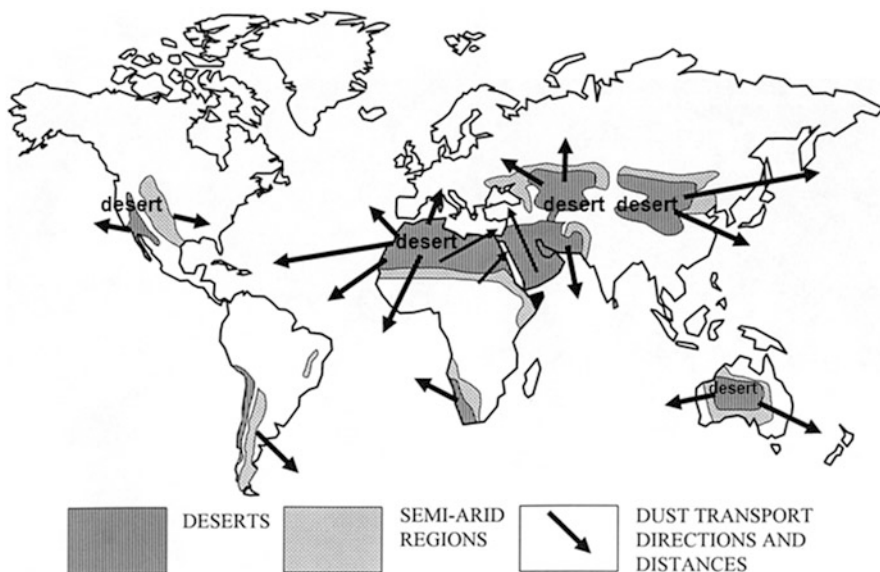


Fig. 1.9 Illustration of major movement patterns and transport distances of dust material and loess. Loess (dust borne by wind currents) originates in desertic areas on either side of the tropical zones of high rainfall. Long-distance transport involves particles with grain sizes of $<20\ \mu\text{m}$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

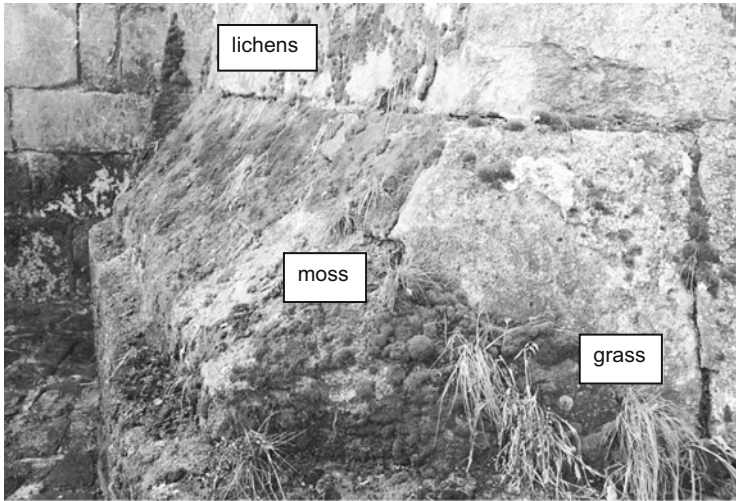


Fig. 1.10 Thirteenth-century church wall (Ile de France) made of limestone where lichens, moss, and eventually grasses fix clays and begin the development of soil formation

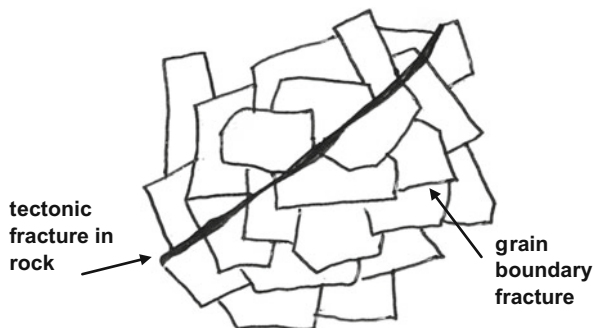
In some instances these contacts produce new silicate minerals (Adamo and Violante 2000), but most often they show a layer of calcium oxalate without the production of new silicate minerals. (Arocena, Univ. North BC personal communication). At water–rock interfaces, within the rock itself, alteration 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].