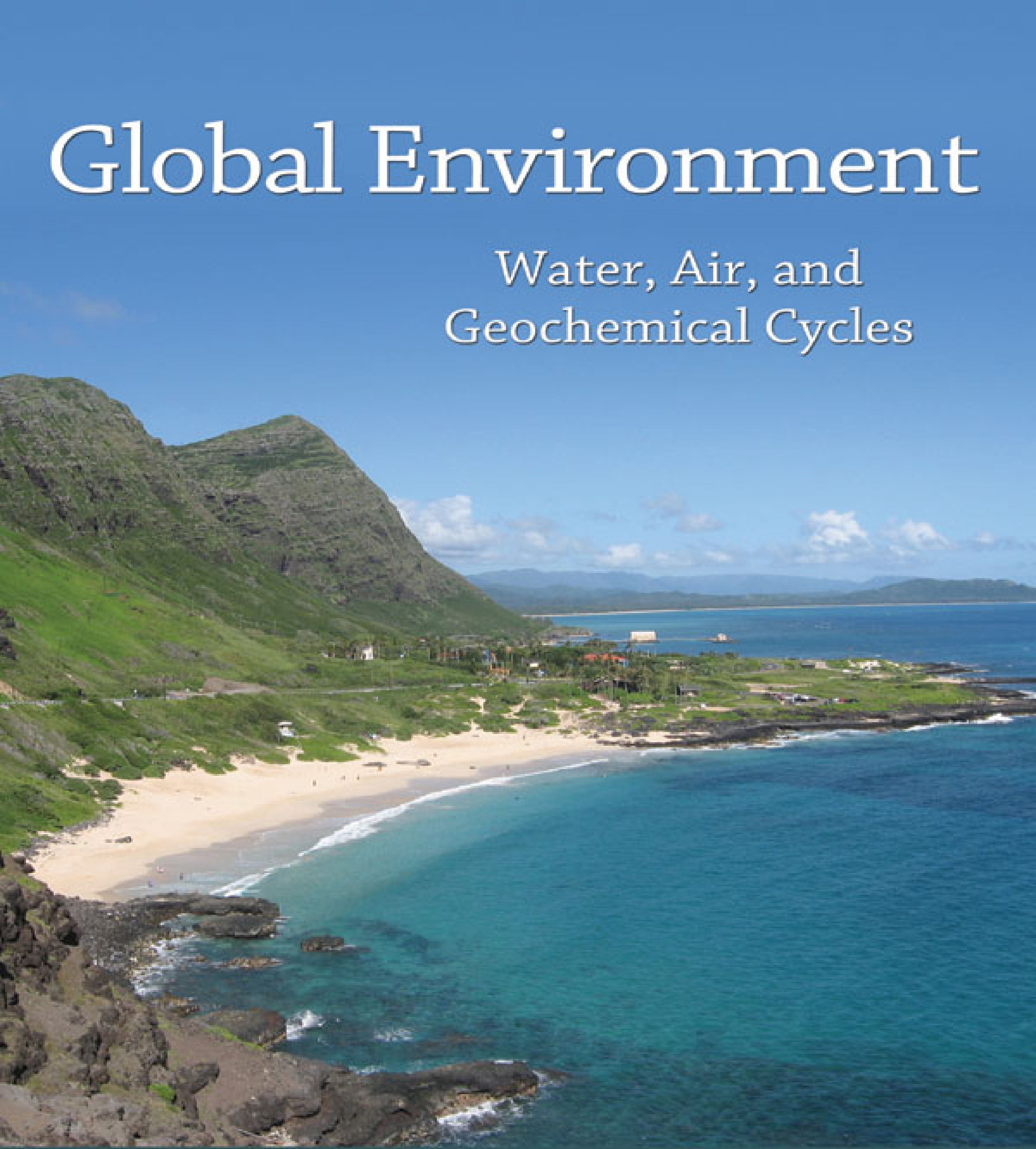

Global Environment

Water, Air, and Geochemical Cycles

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4

Chemical Weathering: Minerals, Plants, and Water Chemistry

Introduction

The process of chemical weathering brings together interaction between the lithosphere, the atmosphere, the hydrosphere, and the biosphere, all major components of the global environment. It exerts controls on the chemical composition of soil water, ground water, and river water; the nature and abundance of vegetation on land; and, over longer timescales, the CO_2 level of the atmosphere, the chemical composition and biology of the oceans, and the formation of different rock types. In this chapter we will examine how these interactions occur. Because of its fundamental importance, we focus first on water and the hydrological cycle.

An idea of the paths that rainwater may take once it strikes the ground, is shown diagrammatically in figure 4.1. Water that has been intercepted by vegetation and then drips off it is termed *throughfall*. Water infiltrating the soil is called *soil water*, and that passing directly into the nearest stream is referred to as *surface runoff*. Once in the soil, the water either passes downward or is taken up by plant and tree roots. In the latter case, the water is transported up through the tree and eventually evaporated from leaf surfaces. In this way the water is returned to the atmosphere, and the overall process is known as *transpiration*. Water trickling downward through the soil eventually encounters a level in the soil or underlying bedrock where all pore space is filled with water. At this point the water becomes *groundwater*, the rock or soil is said to be *saturated with water*, and the level where this occurs is known as the *water table* (fig. 4.1). (Above the water table, pore space is filled by a mixture of air and water to form the *unsaturated zone*.)

Groundwater flows underground until the water table intersects the land surface and the flowing water becomes surface water in the form of springs, rivers, swamps, and lakes. Surface water leaving its source is known as *runoff*. The continual contribution of groundwater to rivers, important between rainstorms, is known as *base flow*. Groundwater continues to flow due to a hydrostatic head built up by the recharge of new rainwater at the source. Because of diurnal, seasonal, and longer-term climatic changes, rainfall input and, consequently, the position of the water table can fluctuate, but the fluctuation and its timing can be considerably damped and delayed, depending upon the capacity of the subsurface rocks to store groundwater. (For further details on groundwater hydrology, consult Todd and Mays 2005).

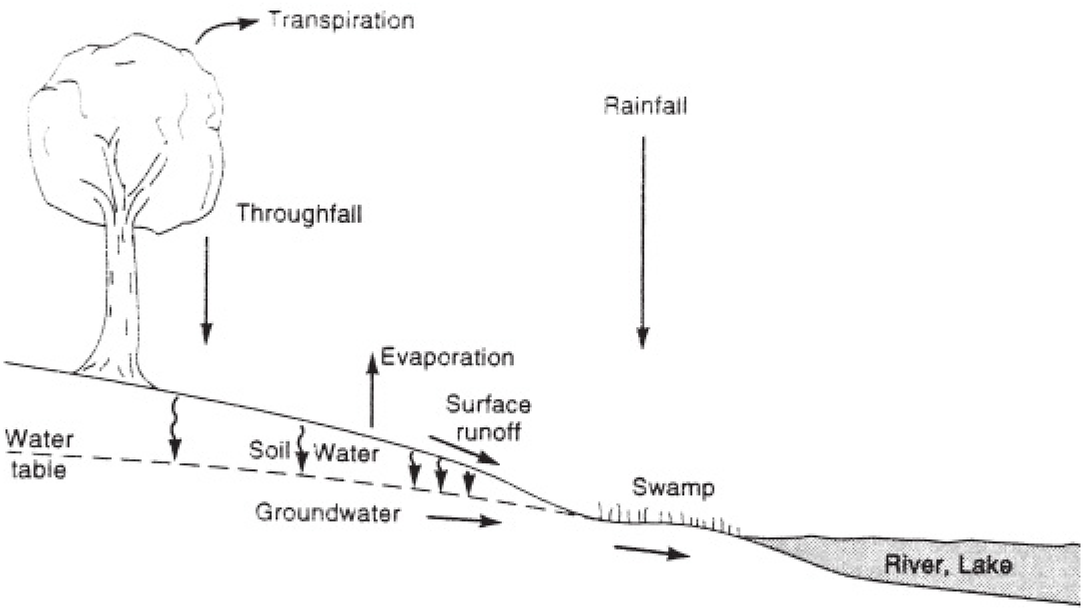


Figure 4.1 Pathways of water near the land surface.

Water coming into contact with rocks (and derived soils) reacts with primary minerals contained in them. The minerals dissolve to varying extents, and some of the dissolved constituents react with one another to form new, or secondary, minerals. Dissolution is brought about mainly by acids provided by plant activity and bacterial metabolism (and, in areas of pollution, by acid rain), and the overall process is called *chemical weathering*. Besides biological factors, chemical weathering is also aided by physical processes that act to break up rocks and expose additional mineral surface area to weathering solutions. This is known as *physical weathering*, and the dominant process is the fracturing of rocks by expansion accompanying the freezing of water in cracks. Thus, physical weathering is most important at higher latitudes and elevations. Together chemical, biological, and physical weathering result in the breakdown of rock and the formation of soil.

Rock-water interaction can continue, albeit much more slowly, to great depths, resulting in the formation of a thick, weathered residue called *saprolite*, which preserves the texture of the host rock. The water table and underlying groundwater may reside within saprolite as well as within the host rock. The word *soil* is strictly defined as the shallow zone where plant roots and macro-fauna destroy the host rock texture via a process known as *bioturbation*. The formal term for the combination of soil and saprolite is *regolith*, but common usage, as will be employed in this book, will designate regolith simply as soil.

Besides soil formation, chemical weathering also results in a radical change in the composition of soil water and groundwater. These changes reflect both the composition of the primary minerals and the degree of biological activity acting to bring about mineral dissolution. Although limited dissolution can occur by reactions of primary minerals with pure rainwater, it is safe to say that most weathering and consequent change in water composition is brought about, directly or indirectly, by biological activity, and it is this intimate interplay between rocks, water, and life that we shall discuss first in this chapter. In essence, this is a “tree’s eye” view of weathering.

Biogeochemical Cycling in Forests

In forested areas, natural water chemistry is influenced by the uptake, storage, and release of nutrients by the vegetation. (*Nutrients* are elements needed by living things.) A forest can be considered a reservoir of nutrient elements between their input and their release in streamwater runoff. Thus, biogeochemical cycles exist that illustrate interaction of the hydrologic (water) cycle with plant nutrient cycles. The degree of interaction varies, and, in some cases, the biological cycle may be in large part independent of the weathering process.

The major nutrient elements needed by plants are shown in table 4.1 in the order of concentrations required for growth.

Life cannot exist without water and carbon dioxide, which are the principal sources of carbon, hydrogen, and oxygen. In addition, essential life components, such as proteins, nucleic acids, and ATP, also require nitrogen, phosphorus, and sulfur. Together these elements combine to produce an overall average composition for land plants (on a mole basis) of $C_{1200}\ H_{1900}\ 0_{900}\ N_{35}\ P_{2}\ S_{1}$ (based on data of table 4.1). Other major elements include calcium, which is essential for plant cell-wall structure and strength; magnesium, which is an essential component in the chlorophyll used by plants for photosynthesis; and potassium, which is important for a variety of biochemical processes. The relative abundance of Ca and K varies between plants. (The data of table 4.1 are a rough global estimate). For example, the results of Rennie (1955) for European trees and Homann et al. (1992) on red alder and Douglas fir show two to three times more Ca than K in the trees.

Table 4.1 Elements essential for nutrition of plants

Element	Adequate concentration (% dry wt. of tissue)
Carbon	45

Oxygen	45
Hydrogen	6
Nitrogen	1.5
Potassium	1.0
Calcium	0.5
Phosphorus	0.2
Magnesium	0.2
Sulfur	0.1
Chlorine	0.01
Iron	0.01
Manganese	0.005
Zinc	0.002
Boron	0.002
Copper	0.0006
Molybdenum	0.00001

Source: Zinke 1977.

A generalized biogeochemical cycle of an element in a forested area is shown in figure 4.2. Trees pick up nutrients from both internal and external sources. Internal sources (Likens and Bormann 1995) result from biological processes. This includes the addition of nutrients to soil solutions by the microbial decomposition of foliage on the ground (*litter*), by nutrient-rich throughfall reaching the ground, and via exudations by roots. The primary external inputs are atmospheric gases, rainfall, trapped aerosol dust, and underlying rocks. Atmospheric gases and rain provide some of the sulfur, nitrogen, and phosphorus, whereas aerosols and rocks provide most of the potassium, magnesium, calcium, sodium, and silicon via chemical weathering. Losses from the forest take place via groundwater flow and streams.

An intermediate state of nutrient availability also exists as adsorbed ions and molecules on the surfaces of organic matter and secondary minerals such as clays. Adsorption represents a reservoir of nutrients that is in constant exchange equilibrium with the soil solution. Many factors, such as crystal chemistry, the presence of organic functional groups (e.g., -COOH), pH, temperature, etc., affect adsorption. (For a proper treatment of adsorption in soils, as well as a discussion of the allied process, ion exchange, consult Sparks (2003).

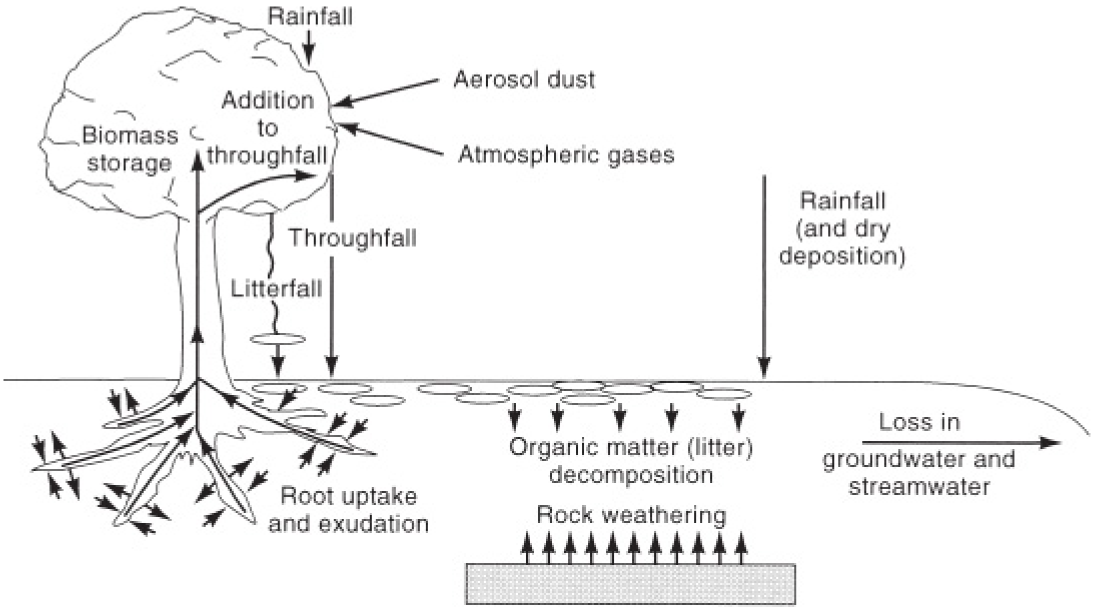


Figure 4.2 Biogeochemical cycling in forest.

If a forest is at steady state—i.e., if it isn't growing and storing nutrients— inputs equal outputs and the change in water composition, in passing from rainwater to streamwater, is due solely to the release of elements by rock weathering (and aerosol dust dissolution). For large forested regions, the assumption of steady state is probably valid but only in the absence of human deforestation (which has become a major global problem). For single, small watersheds, year-to-year variations in biological activity can have a major effect on runoff composition, and corrections for biomass storage (or release) should be made before any attempt is undertaken to estimate the degree of rock weathering from the composition of streamwaters or groundwaters.

Demonstration of the change in nutrient behavior as a result of change in the stage of development of a forest is shown by the work of Balogh-Brunsted et al. (2008), who followed the development over twenty years of a small experimental forest planted originally from seedlings. They found that during the earliest weathering-dominated phase, there was rapid uptake of the rock-derived nutrients Ca, Mg, and K by the trees with low loss in runoff. During an intermediate stage, as tree biomass per unit area became large, biocycling dominated and almost no nutrients were lost to runoff. Finally, after clear cutting and removal of the above-ground portions of the trees, a large release of nutrients, held in reserve by roots and soil exchange sites, was found.

An example of estimating rates of weathering by correcting for biomass storage is provided by the study of Taylor and Velbel (1991) of weathering in an area of the southern Appalachians (see also Velbel 1985). By constructing a series of mass balance expressions for the principal cations (Ca, Na, Mg, and K), they were able to combine streamwater and rainwater chemistry with determinations of mineralogy and the composition of biomass to calculate rates of weathering of the principal minerals in the rocks of this area. They found that by ignoring biomass storage they calculated mineral weathering rates that were too low by as much as a factor of 4.

The relative importance of the various inputs and outputs, and resulting storage or release of elements, varies both with the area considered and with the element. For example, Likens and Bormann (1995), in a forested New Hampshire area (Hubbard Brook Experimental Watershed), found that 80–90% of the streamwater output of calcium, magnesium, potassium, and sodium came from rock weathering, whereas nitrogen and sulfur were derived almost entirely from rain and atmospheric gases with little or none from weathering. (In this area, aerosol dust input was believed to be small because of the relatively humid climate.) Likens and Bormann also showed that the amount of total weathering, calculated after correction for biomass storage, was considerably greater than that indicated simply by concentrations in runoff minus those in rainfall.

Graustein and Armstrong (1983), working in a mountainous area in New Mexico surrounded by arid lowlands, found a much greater input from aerosols. Spruce and fir trees trapped considerable quantities of windblown dust, which was washed off by precipitation and became part of the throughfall (in addition to elements recycled by the tree and released from the foliage). Based partly on Sr isotope studies, they concluded that tree-trapped dust accounted for about two-thirds of the calcium added to throughfall as opposed to one-third from biologic recycling. Thus, calculations of rates of chemical weathering for Ca^{++} based on streamwater output minus precipitation input without considering tree-trapped dust input would have resulted in too large an estimate for the amount of bedrock weathering at this locality.

The source of nutrients can vary depending on slope and local relief. Porder et al. (2005) found that the proportion of nutrients derived from bedrock weathering on the Hawaiian islands was much greater on hill slopes, where much erosion occurs, than on uneroded uplands. Erosion helps to better expose bedrock to roots, whereas on flatter areas, especially under warm and wet climates as in Hawaii, large thicknesses of nutrient-poor clay can accumulate, shielding the bedrock from access by tree roots. In Hawaiian uneroded uplands, much of the nutrients for forests are derived from windblown dust and/or rainfall (Porder et al. 2007).

If one measures biological activity as the ratio of an element stored annually in living and dead vegetation to the annual loss from the area in streamflow, the elements in order of decreasing biological activity are

$$\mathrm{P > N > K > Ca > S > Mg > Na}$$

In general, the most biologically affected element is thus phosphorus, with nitrogen coming second. K and Ca are considerably affected by vegetation, while Na is little affected. Thus, in New Hampshire (Likens and Bormann, 1995) the annual increase in biomass storage for potassium was much greater than streamwater losses, while that for calcium was somewhat less than streamwater runoff. Further, the flux of potassium cycled internally by the vegetation was around twenty-five times the flux lost in streamflow, whereas that for Ca and Mg was about three to six times the loss via runoff.

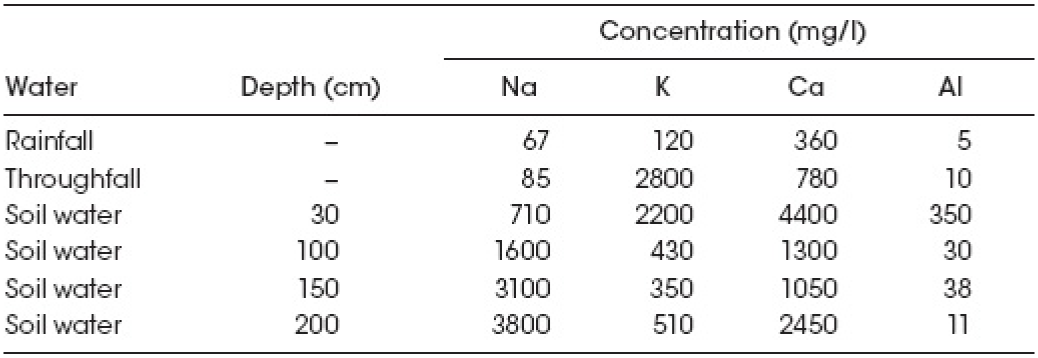
In temperate climates with deciduous forests, the biological control over elements such as potassium and nitrogen is strongly seasonal. During the forest growing season in summer, potassium input in precipitation is greater than potassium loss in runoff; apparently the vegetation takes up potassium from both the soil and from rainwater. Only during the dormant season, when leaves are on the ground, is the runoff output greater than the precipitation input. This is in contrast to Ca, Mg, Na, and Al, which show greater output than input regardless of the season.

Phosphorus input in precipitation in many forests is greater than output in streamflow because tremendous amounts of phosphate are stored in vegetation. Only in agricultural areas, where large amounts of waste and fertilizer phosphate enter the runoff, does stream runoff exceed precipitation input. Weathering is not as important a source for phosphate as it is for Ca, Mg, K, and Na.

Although the principal immediate source of nitrogen by far in forest biomass is nitrogen recycled from soil organic matter and soil solution (plus adsorbed NH_4^+ on clays), the ultimate source is almost entirely the atmosphere. Nitrogen is added from the atmosphere by way of nitrate and ammonium dissolved in rain and in certain plants (e.g., legumes) via the direct fixation of N_2 by symbiotic root microbes. An example of the addition of nitrogen by fixation is shown by the study on Hawaii by Vitousek (2005). (For a detailed discussion of the terrestrial cycle of nitrogen, see chapter 5). Almost no nitrogen is added from rock weathering.

The effect on soil water chemistry due to input from throughfall, the removal by plant roots, and vertical transport by downward percolating solutions, on concentrations of principal elements dissolved in soil water can vary from place to place and with depth in the soil. Some idea of depth variation, taken from the work of Graustein (1981) is shown in table 4.2. Note that K^+ and Ca^{++} added at the top of the soil by throughfall are depleted with depth, due to root uptake, but begin to build up at greater depths, due to rock weathering. By comparison, continual increase of sodium with depth is due only to weathering, because Na is not an essential nutrient for plants. High dissolved Al concentration in the shallow soil water is due to organic chelation (see the discussion in the next section on soil acids), and decrease in Al with depth is due to precipitation upon downward transport and chelate decomposition.

Table 4.2 Concentrations of Na, K, Ca, and Al in soil waters of a watershed forested with aspen trees, Sangre de Cristo Mountains, New Mexico, and in rainfall and throughfall in the same area



Water	Depth (cm)	Concentration (mg/l) Na	K	Ca	Al
Rainfall	–	67	120	360	5
Throughfall	–	85	2800	780	10
Soil water	30	710	2200	4400	350
Soil water	100	1600	430	1300	30
Soil water	150	3100	350	1050	38
Soil water	200	3800	510	2450	11

Source: Data from Graustein 1981.

The rate of turnover of nutrients via the decomposition of litter varies with the type of vegetation, which in turn is a strong function of climate. Schlesinger (1997) lists the following mean residence times for forest litter:

boreal (high latitude) forest	353 yr
temperate coniferous forest	17 yr
temperate deciduous forest	4 yr
Mediterannean scrub	3.8 yr
tropical rain forest	0.4 yr

The overall effect here appears to be mean annual temperature as it affects the rate of decomposition of soil organic matter and the liberation of nutrients. Although litter on a global basis (55,000 Tg) is considerably less abundant than total soil organic matter (1,500,000 Tg) (Schlesinger 1991), it is more effective in nutrient regeneration because of its much faster turnover rate. (Total organic matter has a mean residence time on the scale of a few thousand years).

Besides nutrient cycling, trees exert an indirect control on water composition. This is brought about by transpiration. During transpiration pure water is lost via evaporation to the atmosphere from leaf surfaces. As a result the dissolved ions, such as Cl^-, not taken up by the tree become concentrated in soil water. Likens and Bormann 1995) have shown that at the New Hampshire location, where transpiration (plus evaporation) accounts for about 40% of the yearly water loss, the concentration of dissolved substances in runoff may be increased by as much as 60% over that which would have prevailed in the absence of this process.

Soil Water and Microorganisms: Acid Production

The chemical composition of soil water is affected by inputs from throughfall and rainfall, additions from rock weathering, and inputs and removals due to biological activity. In addition to the nutrient cycling discussed in the previous section, there are important biologically induced changes brought about by soil microorganisms, most notably the production of soil acids. These acids constitute the principal agents of rock weathering. Acids provide hydrogen ions, which replace cations on mineral surfaces, thus bringing about disintegration of the minerals. Also, some organic acids react with specific elements contained in minerals to form *chelates*, or soluble, multiply bonded metal-organic complexes. Acid production is accomplished by a variety of organisms, including bacteria, fungi, actinomycetes, and algae. (For a detailed discussion of soil microbiology, consult Paul 2007).

The principal acids produced by soil microorganisms are carbonic and sulfuric acids and a whole host of various organic acids. Carbonic acid (H_2CO_3) is produced by the oxidation of organic matter by microbes to CO_2. In other words, representing organic matter as CH_2O:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

This CO_2 then combines with water to form carbonic acid, which further partly dissociates (it is a weak acid) to H^+ and HCO_3:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Sulfuric acid (H_2SO_4) is produced by the bacterially catalyzed oxidation of sulfide minerals, and in soils developed on rocks with high sulfide mineral contents, high concentrations of this strong acid and, consequently, low pH values can result. This is especially true where mining has brought about enhanced oxidation of sulfides. (Further details on sulfuric acid weathering are provided later in this chapter.)

Organic acids are formed by a variety of processes. These include the production of H^+ on the surfaces of plant rootlets, the secretion of small molecular weight acids by microorganisms, and the partial breakdown of organic matter derived from dead plant debris. The latter process results in the formation of humic and fulvic acids (Schnitzer and Khan 1972; Sparks 2003). These are substances of high molecular weight that impart characteristic brown and yellow colors to soil solutions and chelate and solubilize several metallic elements (e.g., Fe, Al). Precipitation of the acids brings about the formation of humus.

Much of weathering is due to the secretion of organic acids of low molecular weight by a variety of organisms (E. K. Berner et al. 2004). For example, the symbotic fungi that live on tree roots (ectomycorrhizae) secrete oxalic acid ($H_2C_2O_4$), which provides H^+ and also reacts with iron and aluminum minerals to form iron and aluminum oxalate chelates (Drever and Vance 1994). Iron and aluminum, which are otherwise highly insoluble, are carried downward in the soil by oxalate until the oxalate itself is broken down to CO_2 and HCO_3^- by additional microorganisms. As a result, the iron and aluminum are precipitated in lower portions of the soil. The net effect of the oxalate is to move the iron and aluminum downward. This movement, which is also accomplished by humic, fulvic, and other soil acids, is one of the main processes that bring about the differentiation of soils into specific horizons (see the section below on soil formation).

Weathering by organic acids is demonstrated directly by the results of a study of volcanic ash in Wyoming by Antweiler and Drever (1983) (see also Drever and Vance 1994). They found an excellent positive correlation between dissolved Al (or Fe) and dissolved organic matter and a good negative correlation between pH and dissolved organic matter in soil solutions extracted using porous-cup lysimeters. This is just the result one would be expect if organic chelation of Al and Fe were important and if soil water pH was affected by organic acid dissociation.

Before leaving the topic of soil acids, it should be noted that human activities have resulted in the addition of excess acid to soil. This includes H_2SO_4 and HNO_3 from acid rain and H_2SO_4 from the mining of coal or metallic sulfides. Discussion of these anthropogenic sources is given in chapter 3 (rain) and chapter 5 (rivers).

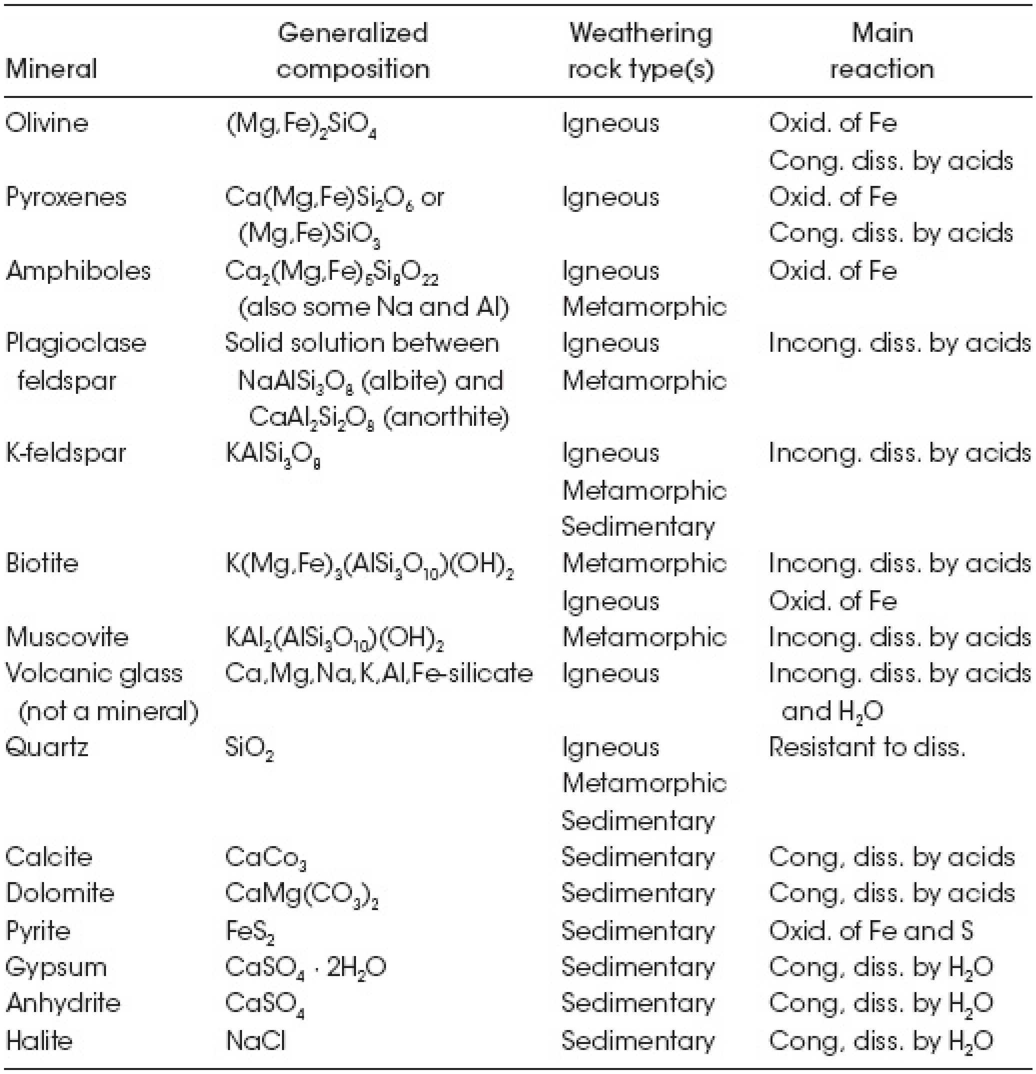
Chemical Weathering

Minerals Involved in Weathering

The chemical weathering of rocks and minerals has been alluded to throughout the previous discussion without detailing exactly what rocks and minerals are involved. As a guide we present in tables 4.3 and 4.4 lists of the most common minerals involved in weathering. Primary minerals (table 4.3) are those undergoing destruction by weathering, while secondary minerals (table 4.4) are those formed by weathering. (Technically speaking, all minerals can undergo destruction by weathering, but the secondary minerals are the most resistant.)

In interpreting table 4.3 those with no geological background may find it helpful to visualize rocks simply as aggregates of minerals. There are three basic types of rock: igneous, sedimentary, and metamorphic. *Igneous* rocks are formed by crystallization from a melt at high temperature and include the common rock types, granite (Na plagioclase feldspar, K-feldspar, quartz, biotite) and basalt (Ca-plagioclase feldspar, pyroxenes, olivine). *Sedimentary* rocks are deposited in water at the Earth's surface and include eroded debris from preexisting rocks (e.g., quartz and feldspar), as in sandstones; fine-grained secondary minerals formed by weathering (e.g., iron oxides and clays), as in shales; the skeletal remains of organisms (mainly $CaCO_3$), as in limestones; and precipitates from seawater (gypsum and halite), as in evaporites. *Metamorphic* rocks form by the recrystallization and alteration of sedimentary and igneous rocks at elevated temperatures and pressures (but without melting) and contain many different minerals, including amphiboles, muscovite, biotite, quartz, and feldspar.

Table 4.3 Common primary minerals that undergo weathering



Mineral	Generalized composition	Weathering rock type(s)	Main reaction
Olivine	$(Mg,Fe)_2SiO_4$	Igneous	Oxid. of Fe Cong. diss. by acids
Pyroxenes	$Ca(Mg,Fe)Si_2O_6$ or $(Mg,Fe)SiO_3$	Igneous	Oxid. of Fe Cong. diss. by acids
Amphiboles	$Ca_2(Mg,Fe)_5Si_8O_{22}$ (also some Na and Al)	Igneous Metamorphic	Oxid. of Fe
Plagioclase feldspar	Solid solution between $NaAlSi_3O_8$ (albite) and $CaAl_2Si_2O_8$ (anorthite)	Igneous Metamorphic	Incong. diss. by acids
K-feldspar	$KAlSi_3O_8$	Igneous Metamorphic Sedimentary	Incong. diss. by acids
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Metamorphic Igneous	Incong. diss. by acids Oxid. of Fe
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Metamorphic	Incong. diss. by acids
Volcanic glass (not a mineral)	Ca,Mg,Na,K,Al,Fe-silicate	Igneous	Incong. diss. by acids and H_2O
Quartz	SiO_2	Igneous Metamorphic Sedimentary	Resistant to diss.
Calcite	$CaCo_3$	Sedimentary	Cong. diss. by acids
Dolomite	$CaMg(CO_3)_2$	Sedimentary	Cong. diss. by acids
Pyrite	FeS_2	Sedimentary	Oxid. of Fe and S
Gypsum	$CaSO_4 \cdot 2H_2O$	Sedimentary	Cong. diss. by H_2O
Anhydrite	$CaSO_4$	Sedimentary	Cong. diss. by H_2O
Halite	NaCl	Sedimentary	Cong. diss. by H_2O

Note: cong. = congruent; incong. = incongruent; diss. = dissolution; oxid. = oxidation.

Also included in table 4.3 are the principal weathering reactions that each primary mineral undergoes. Weathering reactions are classified here according to the nature of the attacking substance and whether the primary mineral simply dissolves or whether a portion of it reprecipitates to form a secondary mineral or minerals. Simple dissolution is referred to as *congruent dissolution*, and dissolution with reprecipitation of some of the components of the mineral is called *incongruent dissolution*. Attacking substances are separated into soil acids, dissolved oxygen, and water itself. Dissolved oxygen only attacks those minerals that contain reduced forms of elements, principally iron and sulfur, and that undergo oxidation to form new minerals. Although most minerals are attacked mainly by soil acids, a few very soluble ones simply dissolve in water. This is shown in table 4.3. In addition, these soluble minerals may also re-precipitate under arid conditions. This is why gypsum appears in the tables both as a primary and secondary mineral.

Table 4.4 Common secondary minerals formed by weathering in soils

Mineral	Composition
Hematite	Fe_2O_3
Goethite	$HFeO_2$
Gibbsite	$Al(OH)_3$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Smectite	(½ Ca, Na) $Al_3MgSi_8O_{20}\ (OH)_4 \cdot nH_2O$ (average composition)
Vermiculite	Basically biotite or muscovite composition with K^+ replacedc by hydrated cations
Calcite	$CaCO_3$
Opaline silica (not a mineral)	$SiO_2 \cdot nH_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$

Table 4.5 Mineral weatherability based on field observations

Halite
Gypsum, anhydrite
Pyrite
Calcite
Dolomite
Volcanic glass

Olivine
Ca-plagioclase
Pyroxenes
Ca-Na plagioclase
Amphiboles
Na-plagioclase
Biotite
K-feldspar
Muscovite
Smectite
Quartz
Kaolinite
Gibbsite, hematite, goethite

Note: Weatherability decreases from top to bottom. Exact positions can change one or two places due to effects of grain size, climate, etc. See also Goldich 1938 and Loughnan 1969.

Minerals can be listed in order of their degree of resistance to weathering. In other words, if two minerals are present in the same soil and attacked by the same acids for the same length of time, one will be destroyed faster than the other. On the basis of observations of partly weathered rocks and soils and of responses to different climatic conditions, a table has been prepared (table 4.5) of minerals listed in order of increasing resistance to weathering. This table is similar to those prepared by others (e.g., Goldich 1938; Loughnan 1969; and is based largely on this older work. Although some reordering can occur in different soils, overall the order shown is considered to be well established. Goldich (1938) noted that the order shown for igneous silicate minerals parallels their temperature of formation from molten magma. In other words, the silicate minerals that weather fastest (e.g., olivine) are those which originally formed at the highest temperatures. The reason for this correlation is not clear, but a common explanation (e.g., Goldich 1938) is that minerals formed under conditions more distantly removed from those at the Earth's surface are less stable there and thus weather faster. This explanation agrees with the position of the common secondary minerals at the bottom of the list but does not account for the high weatherability of nonsilicates, such as halite, gypsum, calcite, and pyrite, which also form under Earth surface conditions.

Table 4.6 Mean lifetimes of silicate minerals of one mm diameter at pH 5 based on laboratory experiments

Mineral	**Mean lifetime (1 mm; pH = 5) yr**
Olivine (forsterite)	2,000
Amphibole (tremolite)	10,000
Pyroxene (enstatite)	16,000
Ca-plagioclase (anorthite)	80,000
Pyroxene (diposide)	140,000
Na-plagioclase (albite)	500,000
Muscovite	720,000
K-feldspar	740,000
Quartz	34,000,000

Source: Lasaga 1984; Brantley 2004.

In general agreement with the data of table 4.5 are the rates of dissolution of specific silicate minerals, as measured in laboratory experiments. A compilation derived from Lasaga (1984) and Brantley (2004) is shown in table 4.6. A quantitative idea of the differences in rates of weathering is shown by the residence times for a 1 mm diameter crystal at pH 5. However, these times should not be taken literally because of the many complications affecting weathering rates in the field (and the fact that minerals dissolve much faster in the laboratory than in the field—see the section below on rate of weathering).

Silicate Weathering Reactions: Secondary Mineral Formation

Because silicate minerals constitute the fundamental components of most major rock types, it is important to inquire in detail into how they weather and to what they weather. As noted in table 4.3, some weathering reactions involve simple congruent dissolution by water or acids. In the case of silicate minerals, congruent dissolution is rare and confined only to olivine, amphiboles, and pyroxenes that are relatively free of iron. (Congruent quartz dissolution is also rare.) In this case we have the following reactions, assuming that attack is by carbonic acid:

$$Mg_2SiO_4 + 4H_2CO_3 \rightarrow 2Mg^{++} + 4HCO_3^- + H_4SiO_4 \qquad (4.1)$$

$$2H_2O + CaMgSi_2O_6 + 4H_2CO_3 \rightarrow Ca^{++} + Mg^{++} + 4HCO_3^- + 2H_4SiO_4 \qquad (4.2)$$

(Note that dissolved silica is represented here as H_4SiO_4, which closely represents the actual form found in solution. It is sometimes also represented by the alternative formula $Si(OH)_4$. We shall not represent silica in solution by SiO_2, as is commonly done, because it can be confused with quartz.)

Most other silicate minerals, especially those containing aluminum, dissolve incongruently, with the consequent formation of iron oxides and/or clay minerals. (*Clay minerals* is a common term applied to fine-grained aluminosilicates and includes kaolinite, smectite, and vermiculite as well as other minerals, such as chlorite, not discussed here). The most abundant silicate mineral in the Earth's crust, which also readily undergoes weathering, is plagioclase feldspar. On this basis we begin our discussion of weathering reactions using Na-plagioclase, or albite.

Let us suppose that albite, $NaAlSi_3O_8$, is attacked by an organic acid, here represented as oxalic acid, $H_2C_2O_4$. First of all, the oxalic acid dissociates to form H^+ ions:

$$H_2C_2O_4 \rightarrow 2H^+ + C_2O_4^{--} \qquad (4.3)$$

These H^+ ions then attack albite, liberating its constituent elements to solution:

$$4H^+ + 4H_2O + NaAlSi_3O_8 \rightarrow Al^{+++} + Na^+ + 3H_4SiO_4 \qquad (4.4)$$

Since oxalate ion $C_20_4^{--}$ readily reacts with Al^{+++} to form a chelate (Drever and Vance 1994), we also have

$$Al^{+++} + C_2O_4^{--} \rightarrow Al(C_20_4)^+ \qquad (4.5)$$

If we combine reactions 4.3–4.5 so as to cancel H^+ ion, we obtain

$$2H_2C_2O_4 + 4H_2O + NaAlSi_3O_8 \rightarrow Al(C_2O_4)^+ + Na^+ + C_2O_4^{--} + 3H_4SiO_4 \qquad (4.6)$$

This is a dissolution reaction characteristic of the uppermost, highly acid portion of most temperate soils.

Aluminum oxalate and oxalate ion in solution are not stable, however, due to bacterial decomposition. On passing downward in migrating soil water, the oxalate is oxidized by bacteria, and the liberated Al^{+++}, which is unstable in solution at most pH values found in soils, precipitates to form $Al(OH)_3$ or clay minerals. Let us assume here that the common clay mineral kaolinite, $A1_2Si_2O_5(OH)_4$, is formed. The reactions are

$$2C_2O_4^{--} + O_2 + 2H_2O \rightarrow 4HCO_3^- \qquad (4.7)$$

$$2Al(C_2O_4)^+ + O_2 + 2H_4SiO_4 \rightarrow Al_2Si_2O_5(OH)_4 + 4CO_2 + H_2O + 2H^+ \qquad (4.8)$$

Multiplying reaction 4.6 by 2, and adding to reactions 4.7 and 4.8, we obtain the overall reaction:

$$4H_2C_2O_4 + 2O_2 + 9H_2O + 2NaAlSi_3O_8 \rightarrow$$
$$Al_2Si_2O_5(OH)_4 + 2Na^+ + 4HCO_3^- + 2H^+ + 4CO_2 + 4H_4SiO_4 \qquad (4.9)$$

As written, this reaction is not quite complete. Since H^+ and HCO_3^- rapidly react with one another, we must take into account:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \qquad (4.10)$$

Doubling reaction 4.10 and adding to 4.9, we obtain the final overall reaction for the weathering by oxalic acid of albite to kaolinite:

$$4H_2C_2O_4 + 2O_2 + 7H_2O + 2NaAlSi_3O_8 \rightarrow$$
$$Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4 + 6CO_2 \qquad (4.11)$$

Note that reaction 4.11, even though the attacking acid is oxalic acid, ends up with the production of only Na^+, HCO_3^-, and H_4SiO_4 in solution. (The CO_2 is readily lost as a gas from the soil.) These are the dissolved species that would be found if the water were to pass out of the soil zone to become groundwater and eventually stream and river water. There is no memory of the oxalate, and it is as though the albite had actually reacted with carbonic acid:

$$2H_2CO_3 + 9H_2O + 2NaAlSi_3O_8 \rightarrow$$
$$Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4 \qquad (4.12)$$

In fact, recalling that H_2CO_3 forms by the reaction

$$H_2O + CO_2 \rightarrow H_2CO_3$$

the only difference between reactions 4.11 and 4.12 is

$$4H_2C_2O_4 + 2O_2 \rightarrow 8CO_2 + 4H_2O \qquad (4.13)$$

which is the reaction for the oxidative decomposition of oxalic acid.

What has been said above for oxalic acid and albite is true of any organic acid and silicate (and carbonate) mineral. Thus, even though the actual acid attacking a mineral is organic, the overall reaction, as far as most groundwater and river-water composition is concerned, can be represented as though the only attacking acid were H_2CO_3. In other words, we find HCO_3^- and not $C_2O_4^{--}$ in most ground and river waters. (In some rivers draining swampy areas of heavy organic matter production, organic acids and their anions can resist bacterial oxidation and survive to become carried some distance in the rivers; see chapter 5). The simplification provided by this reasoning enables the prediction of the origin of ions in groundwaters without concern for the type of organic acid actually attacking the primary minerals. Thus, the assumption that silicate weathering consists solely of attack by carbonic (and sulfuric) acids is justified even though, when looked at in detail, it is not correct. The organic acids really do much of the attacking, but they disappear. From now on in our discussion of weathering we shall adopt the convention of writing reactions in terms only of H_2CO_3, but it should be remembered that this is only a convention and a shorthand way of representing a series of chemical weathering reactions that are far more complex.

Whether weathering is accomplished by carbonic acid or organic acids, the net effect, shown by the above reactions, is to convert biologically derived carbon to dissolved bicarbonate. Since the ultimate source of the biological carbon (as carbonic or organic acids) is the fixation of atmospheric CO_2 by photosynthesis, this means that during silicate weathering CO_2 is removed from the atmosphere and lost to form the bicarbonate dissolved in natural waters. If the bicarbonate is carried to the ocean by rivers (chapter 8) it can be removed there as calcium carbonate and the atmospheric CO_2 permanently lost from the stmosphere to the geologic record. This is a major process affecting the concentration of atmospheric CO_2 over geologic time (see chapter 2).

In the above example, we assumed that all aluminum liberated by feldspar dissolution was precipitated to form a secondary mineral (in this case, kaolinite). This is a reasonable assumption for most soils (e.g., Loughnan 1969). Except for localized redistribution accompanying chelate transport, aluminum does not migrate any appreciable distance in solution and normally accumulates in soils as weathering proceeds. In fact the change in the ratio of other elements to aluminum in soils is often used as a measure of the degree of removal by weathering (e.g., Goldich 1938). Iron, because of its insolubility in the presence of dissolved O_2, also accumulates in soils, as ferric oxides. Because of their lack of removal in solution, we shall continue in all overall weathering reactions, as is the custom, to assign Al and Fe only to secondary minerals and allow none to appear in solution.

Although all Al is reprecipitated to form a secondary mineral, it need not always be kaolinite. Two other common aluminous weathering products are gibbsite, $Al(OH)_3$, and smectite, a complex cation Al-silicate (see table 4.4). (Vermiculite forms by the loss of K^+ from biotite and muscovite and constitutes a special case of structural inheritance that will not be discussed here.) Conditions under which each of these minerals would be expected to form can be deduced on the basis of some rather simple reasoning: Weathering of primary aluminosilicates to gibbsite, kaolinite, or smectite should occur under different conditions because of fundamental differences in the composition of the three phases. Smectite contains Al, Si, and various cations; kaolinite contains only Al and Si; and gibbsite, only Al (see table 4.4). In addition, the ratio of Si/Al is higher in smectite than it is in kaolinite. Thus, we would expect that increase of H_4SiO_4 in solution would favor the formation of kaolinite over gibbsite and, at higher values, smectite over kaolinite. In addition, increase in cations— e.g., Na^+—should favor smectite. Quantitative representation of these ideas is shown in figure 4.3.

Here a plot of log $[Na^+]/[H^+]$ versus log $[H_4SiO_4]$, where brackets represent molar concentrations in solution, shows the regions of stability for the various secondary minerals as well as that of albite in aqueous solution. If a natural water has concentrations of $[Na^+]$, $[H^+]$, and $[H_4SiO_4]$, that fall in, let us say, the field for kaolinite, we would expect to find kaolinite forming from this water, and so forth for the other minerals. Note that as both $[H_4SiO_4]$ and $[Na^+]$ are increased (for constant pH), kaolinite and smectite, respectively, become the favored phases. By use of this diagram the compositional evolution of a water reacting with albite can be predicted (for details consult Helgeson et al. 1969).

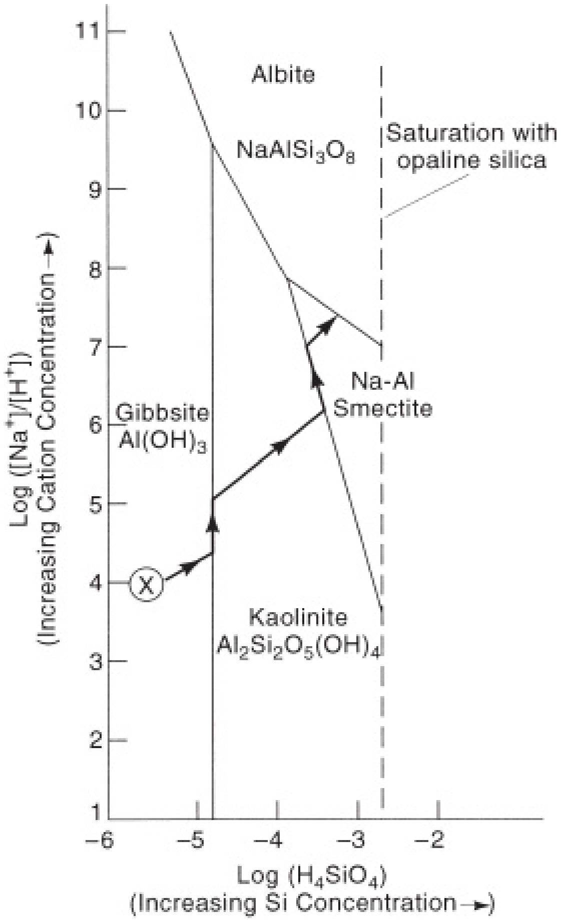


Figure 4.3 Stability fields of gibbsite, kaolinite, smectite, and albite as a function of log $[Na^+]/[K^+]$ and log $[H_4SiO_4]$ in solution. Brackets denote concentrations in moles per liter. Smectite is represented by by its pure Na-Al end member, and analcite and other zeolite

formation is ignored. A typical weathering reaction path taken for a closed system is shown by the heavy line with arrows.

Modified and recalculated from Bricker and Garrels 1965 and Helgeson et al. 1969.

With reference to figure 4.3, following the reasoning of Helgeson et al. (1969), imagine the sequence of events as albite (again used to represent a typical primary aluminosilicate) undergoes dissolution during weathering at constant pH. If we start with a very dilute solution (low Na^+; low H_4SiO_4) its composition will fall in the field of stability of gibbsite (marked *X* on figure 4.3). The weathering reaction in this case is

$$7H_2O + H_2CO_3 + NaAlSi_3O_8 \rightarrow Al(OH)_3 + Na^+ + HCO_3^- + 3H_4SiO_4 \quad (4.14)$$

If the water does not leave the rock, concentrations of Na^+, HCO_3^-, and H_4SiO_4 will build up and the solution composition will move to the northeast on the diagram following the arrow-marked path. When the boundary between gibbsite and kaolinite is reached, gibbsite begins to convert to kaolinite by the addition of silica:

$$2H_4SiO_4 + 2Al(OH)_3 \rightarrow Al_2Si_2O_5(OH)_4 + 5H_2O \qquad (4.15)$$

During this reaction all silica released by albite dissolution is used to convert gibbsite to kaolinite, and this is why the solution path on the diagram turns abruptly northward. After all gibbsite is converted to kaolinite, we proceed again along a northeasterly trend until the boundary between kaolinite and smectite is reached. Again we follow the kaolinite-smectite boundary until all kaolinite is converted to smectite by the addition of silica and sodium. We then proceed again to the northeast as smectite forms from albite until we reach the albite-smectite boundary. At this point, the solution is saturated with albite; it cannot continue to dissolve, and therefore weathering ceases.

The scenario described above is what would be expected if the water always stayed in contact with the albite (and there were no kinetic problems with the precipitation of secondary minerals). In other words, this is analogous to adding water and albite to a beaker and letting them react until albite solubility is reached. It is a closed system. Soils, on the other hand, are open to flow of water through them. Thus, concentrations will build up during contact of the water with albite (or other primary minerals), but further buildup will cease when the water leaves the rocks. The faster the rock is flushed with water, the shorter the time of contact with the primary minerals and the lower the dissolved concentrations in the exiting waters. A steady state is attained between rate of addition by dissolution and rate of water flow, so that the water composition for any given soil containing albite may fall anywhere along the reaction path of figure 4.3, depending on the relative magnitude of these two rates. Gibbsite formation should represent a high degree of flushing with removal of both cations and silica; kaolinite should represent less rapid flushing where less silica is removed; and smectite should represent rather stagnant conditions of water flow so that appreciable buildup of both silica and cations can occur. Also, for a given rate of flushing, more rapidly reacting minerals providing more silica and cations to solution should favor the formation of smectite or kaolinite over gibbsite.

These predictions are borne out when actual soils are examined. In general, gibbsite forms only in areas where there is very rapid flushing due to a combination of high rainfall and good drainage due to high relief. An example is the island of Jamaica, where valuable deposits of bauxite (an ore of aluminum consisting largely of gibbsitelike minerals) are formed as a result of intense weathering accompanying high rainfall in a mountainous terrain. Less strong flushing, but still enough to remove all cations, is found in most tropical and subtropical soils, and here, as predicted, the characteristic secondary mineral is kaolinite.

Smectite is the characteristic mineral of soils of semiarid regions and where volcanic glass is the primary material undergoing weathering. In semiarid regions, rainfall is low and water adheres to soil grains for long periods before being replaced by new water. Volcanic glass is the most reactive silicate known and is weathered very rapidly. Again, both observations are in agreement with our predictions.

A nice demonstration of the effects of flushing by water on the weathering of a single rock type is shown by the studies of Sherman (1952) and Mohr and van Baren (1954). Sherman found that clay mineralogy of the soils developed on the basalt of the island of Hawaii are correlated very well with mean annual rainfall. (Rainfall varies considerably on Hawaii because of the effects of rain shadowing by mountains.) Mohr and van Baren found that for the same rock type and same rainfall, soils on islands of Indonesia showed different clay minerals, depending on the degree of drainage. Upland soils, where drainage was good, consisted of kaolinite, whereas those in poorly drained or swampy depressions consisted of smectite. This is again what would be expected from our predictions.

Further illustration of the importance of flushing is shown by the study of Velbel (1985). On hill slopes of the southern Appalachian Mountains of the United States, Velbel found that differences in water-flow path resulted in the formation of different clay minerals from the same plagioclase-rich rock subjected to the same climate and same relief. Gibbsite formed in surficial zones where the water residence time was short because of a small flow path. At depth both gibbsite and kaolinite were found where the water travel distance was much greater. The entrapment of water in the slightly weathered and deeply buried underlying rock resulted in long residence times and the formation of smectite.

Mechanism of Silicate Dissolution

Of all mineral groups, silicates have received the most attention in weathering studies because they make up the most abundant rock types. How primary silicates dissolve during weathering, however, is not well agreed upon. One theory is that silicate dissolution occurs by means of the formation of a protective surface layer of altered composition on each mineral grain (e.g., Luce, Bartlett, and Parks 1972; Paces 1973; Busenberg and Clemency 1976; Chou and Wollast 1984; and many subsequent authors). This layer is assumed to be so tight that it severely inhibits the migration of dissolved species to and from the surface of the primary mineral, and in this way it is protective. The layer forms from components of the underlying primary mineral, and as weathering proceeds, it increases in thickness. It was invoked originally to explain the results of laboratory dissolution experiments (simulating weathering) where rates of dissolution were seen to decrease with time due presumably to the thickening of a protective surface layer of altered composition.

When applied to most mineral grains taken from actual soils (e.g., Berner and Holdren 1977, 1979; Berner and Schott 1982; Blum et al. 1991) or to the surfaces of mineral grains from laboratory experiments at neutral pH (Schott et al. 1981), attempts to prove the existence of a protective surface layer with altered composition and appreciable thickness, using both electron microscopic and surface chemical techniques, have proven to be negative. At pH values representative of soils (e.g., pH = 6), Schott et al. concluded that any altered composition layer on magnesian pyroxenes must be at most a few atomic layers thick. By contrast, more recent experimental and theoretical work (see Brantley 2004 for a review) has emphasized surface formation of an appreciably thick altered layer, but it is based almost entirely on results for low pH experiments outside the normal pH range found in most soils.

The recent work of Hellmann et al. (2003), using state of the art high-resolution and energy-filtered transmission electron microscopy, found that even at low pH (1.0) plagioclase dissolution resulted in the formation of a reprecipitated silica-rich layer with no crystallochemical continuity with the host feldspar and unlikely protection against dissolution of the host mineral. This is in agreement with the findings of Schott et al. (1981), who got similar results for the laboratory dissolution of enstatite and diopside at low pH.

In the absence of direct biological contact (see below), what really appears to happen during weathering of most silicate minerals (at least for feldspars, pyroxenes, and amphiboles) is that soil solutions penetrate through permeable (nonprotective) clay layers right to the bare surfaces of the primary mineral grains and there react with them. Dissolution does not occur at all places on the surface so as to produce general rounding of the grains, as predicted by the protective surface layer theory, but instead affects only those portions of the surface where there is excess energy, such as at outcrops of dislocations. (*Dislocations* are rows of atoms in a crystal that are slightly out of place and therefore more energetic.) As a result of selective etching, distinct crystallographically controlled etch pits form on the mineral surface and upon growth and coalescence form interesting features. Some examples taken from our studies of soil feldspars and pyroxenes are shown in figure 4.4.

These etch pits reflect the crystal structure of the underlying mineral and therefore are regular in shape and aligned in certain directions. (For a general discussion of the microscopic study of soil minerals, consult Nahon 1991).

For some minerals, principally the garnets, a protective surface layer dissolution mechanism may be operative. Velbel (1993) has shown that the ratio of the molar volume of secondary weathering products to the molar volume of the primary mineral undergoing dissolution is a key factor in whether dissolution via a protective layer is possible. For most primary minerals all reasonable weathering products (e.g., clay minerals and hydrous aluminum and iron oxides) have insufficient volume, during mole-for-mole weathering, to cover the primary mineral surfaces and thus provide a protective layer. Only the garnets, among common minerals, seem to fulfill the necessary criterion for total covering of the surface. In agreement with this prediction is the finding by Velbel of a lack of etch pitting and a tight covering of gibbsite and goethite on the surfaces of almandine garnet grains in soils from the southern Appalachian Mountains.

Dissolution of primary minerals by soil solutions, therefore, occurs mainly via etch pit formation and growth of the pits. If the pits are located primarily at outcrops of dislocations, then a fundamental controlling factor on dissolution of a given mineral during weathering is the density of dislocations. (Dissolution of different minerals is still controlled by differences in chemical composition.) This can help to explain different rates of dissolution of minerals of similar composition under the same soil conditions. For example, the work of Holdren and Berner (1979) has shown that adularia, $KAlSi_3O_8$, reacts in the laboratory with hydrofluoric acid (as a simulator of soil acids) much more slowly than does microcline, which has essentially the same chemical composition, $KAlSi_3O_8$. The major difference between the two minerals is the presence of numerous twinning dislocations in microcline and very few in adularia. In addition, electron microscope studies (Berner and Schott 1982) show that coexisting hypersthene and augite (two pyroxene minerals in the same soil) weather at different rates mainly because of differences in dislocation density. This is illustrated in figure 4.4c. The reason that augite has more etch pits and weathers faster is that there is a structural misfit at the boundaries between exsolution layers of different composition perpendicular to the c axis of the mineral.

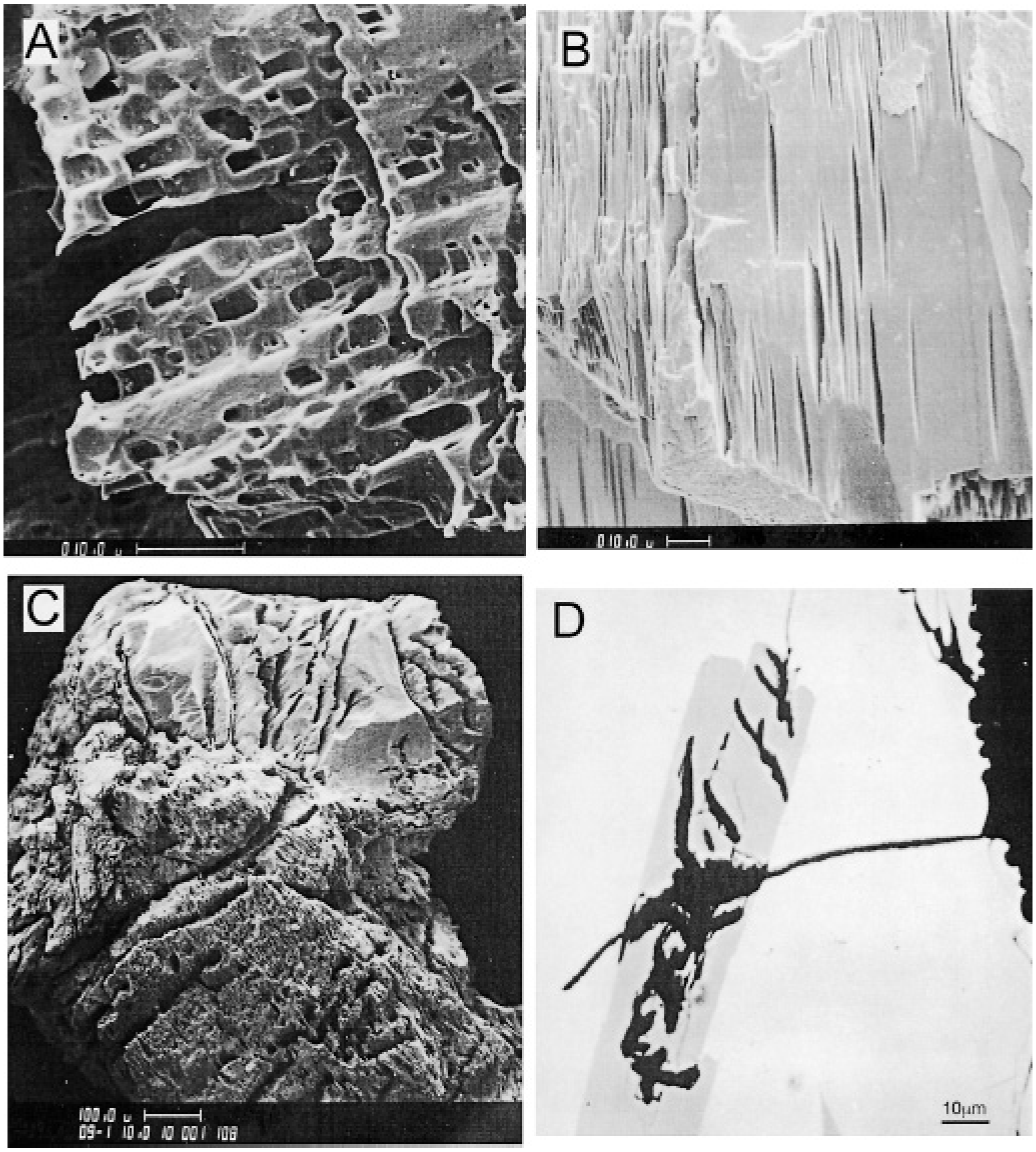


Figure 4.4 Scanning electron photomicrographs of partly weathered mineral grains from soils (fine soil particles removed by ultrasonic cleaning). (A) Square-shaped (prismatic) etch pits developed on dislocations of plagioclase feldspar (X3000); (B) lens-shaped etch pits developed on dislocations in hornblende (amphibole) (X1000); (C) two pyroxene grains joined together—note that the lower (augite) grain is more heavily etched than the upper (hypersthene) grain, due to a greater density of dislocations in augite (X50); (D) the selective etching of an elongated calcium plagioclase crystal, enclosed in glassy basalt, presumably by a mycorrhizal hypha emanating from a plant root (now missing in upper right dark space) (X500).

Berner and Holdren 1977, 1979; Berner and Schott 1982; Berner and Cochran 1998.

Much weathering does not occur simply by reaction between soil solutions and mineral surfaces. Certain microflora, such as the mycorrhizae associated with tree roots, can produce micropores in minerals by directly boring into them using secreted chelating acids. The amazing behavior of these microorganisms is that they preferentially seek out nutrient elements within the host rock. Jongmans et al. (1997) cite mycorrhizal invasion of a granitic rock with selective dissolution of minor apatite in order to obtain phosphorus. Similar biosensing and selective attack of apatite by ectomycorrizae in an experimental mineral mixture was found by Leake et al. (2008). In figure 4.4d is shown the invasion of a glassy basaltic rock by a mycorrhizal hyphae and selective attack of a calcium-rich phenocryst. This type of weathering, documented for basalt on the island of Hawaii (Berner and Cochran 1998) may be important in the earliest stages of weathering of bare rock but is confined to within the zone of plant rootlets (known as the *rhizosphere*).

Rate of Silicate Weathering

There has been much interest in determining the rate of chemical weathering of regions ranging in size from small watersheds to continents in order to calculate rates of chemical lowering of the regions, to explain natural water chemistry, and to calculate the rate of uptake of atmospheric CO_2 by weathering (for the latter see, e.g., Suchet et al. 2003). Continental and global weathering rates are covered in the present book in chapter 5, where the chemistry of large rivers is discussed. The purpose here is to cover the topic of weathering rates on the small watershed scale and how they are obtained. Further information on weathering rates can be found in White and Brantley (1995) and White (2004).

The most straightforward method for determining rates of weathering is to measure the chemical composition of the host rock, compare it to its weathered counterpart, and use some independent method for determining the age of the weathered material. For age dating in mountainous areas one can estimate the duration of weathering as equivalent to the time, since the underlying rock was scraped clean via earlier glacial activity. Another approach is to date, via isotopic methods, the ages of marine or riverine terraces that have been subjected to tectonic uplift (e.g., White et al. 2005). Weathering of isotopically dated basalt flows has also been done (Porder et al. 2007).

A new method for determining rates of weathering, developed over the past two decades, uses the radiogenic nuclides produced in minerals subjected to bombardment by cosmic rays (Lal 1991). The most common mineral used is quartz, which upon bombardment produces ^{10}Be. The mean free path in soils of cosmic rays and ^{10}Be formation is only a few centimeters. Thus, the degree of buildup of ^{10}Be in the soil is a measure of the time of exposure to the atmosphere. A steady state is assumed between surface exposure to cosmic rays, erosion, and radioactive decay, and this allows calculation of the rate of erosion (Brown et al. 1995). (For most rates of erosion the correction for radioactive decay is small.) Determining the content of a given element in the host rock and in the derived soil, and normalizing for an inert element like zirconium, allows rates of chemical weathering to be calculated from rates of total denudation, which is equal to the sum of physical and chemical weathering (Riebe et al. 2003).

Another procedure for measuring rates of weathering on the watershed scale is to compute an input-output budget from mean annual flow and chemical composition of the water at the stream outlet of the watershed, combined with input fluxes from rain and snow and corrections for biologic storage or release. The difference between stream output and rainfall input plus biological release is assumed to represent mineral dissolution. An example of this type of study is that of Velbel (1985) of an area in the southern Appalachian Mountains of the United States. By constructing a series of mass balance expressions for the principal cations (Ca, Na, Mg, and K), Velbel was able to combine stream and rainwater chemistry with determinations of mineralogy and the composition of biomass to calculate rates of weathering of the principal minerals in the rocks of this area.

In addition to field studies, there have been theoretical models constructed to calculate rates and mechanisms of weathering (e.g., Sverdrup and Warfvinge1995; Soler and Lasaga 1996; Fletcher et al. 2006; Lebedeva et al. 2007; Maher et al. 2008). Such rates are calculated from laboratory kinetic rate data and thermodynamic equilibria, from which are derived functional relations to important variables such as pH, temperature, degree of undersaturation, and concentrations of dissolved reacting species, including organic acids. These are combined with properties of rocks and soils/saprolites, either measured or predicted from other soil studies. This includes such things as erosion rate, permeability, and interstitial water flow rate, aqueous and gaseous diffusion. pH and chemical composition of soil waters, temperature, and surface areas of each of the dissolving minerals. In these studies, results are then compared with observations of weathering regimes observed in the field. In some studies, such as that of Maher et al. (2008), good agreement has been found between theoretical predictions and field measurements.

Laboratory mineral dissolution rates by themselves are always much slower than field rates for the same minerals (White and Brantley 1995). Disagreement is due to such things as the coating of mineral surface by clays that inhibits water/mineral contact. Soil hydrology is very important and can explain a lot of the difference between lab and field results (Velbel 1993). In soils variable flow paths and the wetting and drying of mineral surfaces is very different from laboratory studies, where exposure of suspended particles to highly undersaturated stirred solution is continuous. A solution trapped in small soil pores between rainfalls can come to equlibrium with the minerals undergoing dissolution, so that dissolution essentially ceases. New rainfall can then flush out these pores. Furthermore, flow paths in soils are complicated by inhomogeneities such as pedogenic clay horizons, worm and rodent burrows, root molds, dessication cracks, and primary layering. This, combined with spatial and temporal variations in soil moisture due to variations in rainfall intensity, makes it difficult to estimate the degree and duration of wetting of mineral surfaces in order to use laboratory dissolution data to accurately predict rates of weathering in the field.

Many important factors affect the rate of chemical weathering. This includes: (1) climate as represented by temperature and rainfall; (2) physical erosion resulting in increased relief and stripping and exposure of fresh rock to weathering; (3) lithology, which expresses the different rates of dissolution of different minerals; and (4) vegetation as it accelerates mineral dissolution. To investigate the effects of each of these processes, it is necessary to hold constant the others, which under most conditions is difficult. Once this is done, it allows study of weathering via a multidimensional approach that considers several factors affecting weathering rates (West et al. 2005).

From simple chemical reasoning, an increase in temperature is to be expected to bring about faster mineral dissolution. This is demonstrated by laboratory experiments (for a summary, see White 2004) and field studies. A classic field study of the role of temperature in weathering is that of Jenny (1941). He isolated the effect of temperature from rainfall and lithology, by measuring the percentage of clay in soils developed on mafic igneous rocks under similar rainfalls along a north-south transect of the eastern United States, and found a clear positive correlation of clay development with temperature. White and Blum (1995) studied the rates of weathering of granitic rocks from a variety of worldwide localities and were able to separate out the effects of rainfall from temperature. Their results are shown in figure 4.5. An analogous study by Dessert et al. (2001) on basaltic rocks also showed increased weathering rate with increased temperature and increased rainfall.

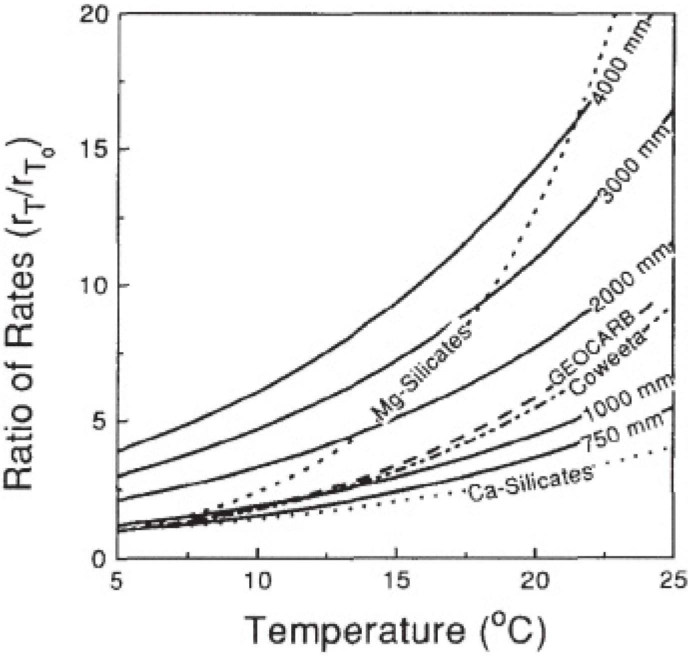


Figure 4.5 Ratio of rates of release of silica during weathering of granitic rocks as a function of mean annual temperature and rainfall. The standard state is a temperature (rTo) of 5°C. and rainfall of 1000 mm. For comparison, dashed and dotted lines show the results of other studies (temperature only) based on the experimental dissolution of Ca and Mg silicates, a field study in Coweeta, N.C., and predictions via a theoretical model (GEOCARB).

After White and Blum 1995.

A problem with studies of the effect of temperature on weathering rate is that the effect of temperature is not studied in total isolation from other factors affecting weathering rate, because data by necessity are obtained from different geographic localities. Better isolation of the temperature effect has been accomplished by a recent study (Gislason et al. 2008) that obtained data on water chemistry, discharge, and mean annual air temperature for several Icelandic streams collected over a span of time (forty-four years), during which each stream underwent warming. By studying each single river over time, variations in lithology and relief were avoided. They demonstrate a 4–14% rise in weathering flux with a one-degree rise in temperature for each locality.

A classic and rather unique study of the effect of rainfall on weathering rate for constant temperature, lithology, and relief was done by Jenny (1941). Jenny avoided varying temperature and lithology by analyzing soils developed on windblown dust (loess) along an east-west transect through the west-central United States, following an isotherm for mean annual temperature. His results are shown in figure 4.6. The effect of increased rainfall on weathering rate is clear.

The study of Stallard (1995) emphasizes the role of physical erosion in controlling the rate of chemical weathering. Stallard distinguished two endmember situations. They are *weathering limited erosion* and *transport limited erosion*. Where slopes are steep and rainfall is sufficient, as in humid mountainous areas, rapid erosion may strip off almost all soil and expose bedrock to further weathering. This is the weathering-limited end member. The opposite situation occurs in lowlands, where weathering products continue to pile up until the soil (plus saprolite) becomes so thick that water has trouble in reaching the bedrock. This is transport limited erosion and weathering. No additional weathering can take place until the soil overburden is removed by erosion. An outstanding example of this is the Amazon River lowlands. In many localities an intermediate situation is reached whereby there is a constant thickness of soil over the bedrock and the production of soil by weathering is balanced by its removal by erosion. This is known as *steady-state weathering*. The steady state assumption is necessary to the use of cosmogenic nuclides to date weathering rate.

To our knowledge, only one definitive study has been done of the rates of weathering of granitic vs basaltic rocks subjected to essentially the *same* climate, vegetation, and relief. The field study of Taylor (2000) in Idaho (USA) of waters draining soils developed on nearby forested granites and basalts showed that the fluxes of cations and silica were about two to three times greater for streams draining basalt than those draining granite. Similar results were obtained by the analysis of soil profiles.

Only a few studies have been conducted on the effect of higher plants on chemical weathering with constant climate and constant lithology. A review of plants and weathering is provided in E. K. Berner et al. (2004). Drever and Zobrist (1992) studied weathering rates, via stream analyses, in the southern Swiss Alps, where they found the flux of bicarbonate from silicate weathering to be twenty times higher under deciduous forest at lower elevations than under lichen-encrusted rocks above tree line. Because mean annual temperature decreases with elevation, they had to make a correction for the effect of changing temperature on weathering rate and concluded that trees accelerated silicate weathering, over the rather barren rocks above tree line, by a factor of about 8.

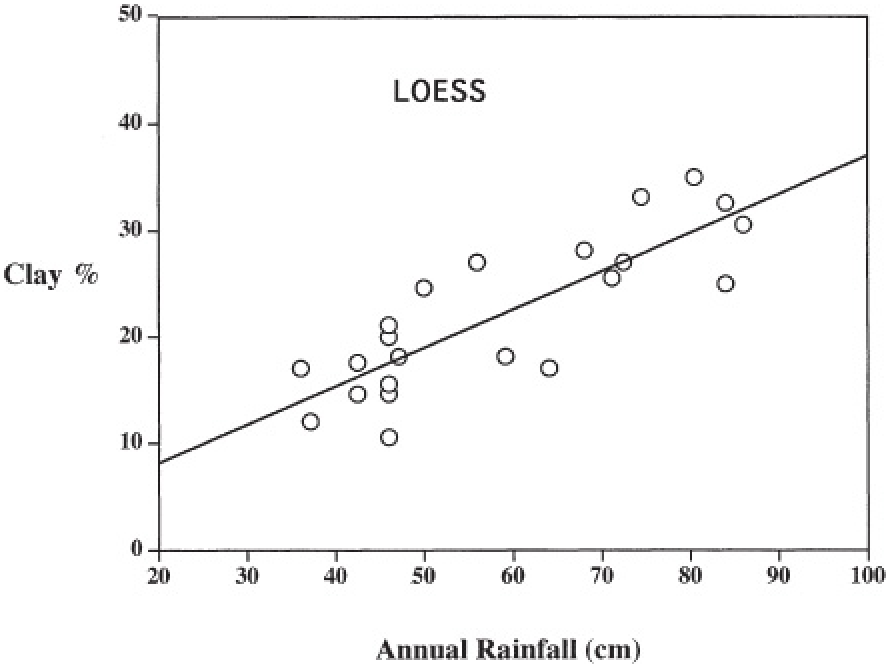


Figure 4.6 Rate of weathering as a function of mean annual rainfall. Results are based on the percentage of clay in soils developed on glacial loess across an isotherm running east-west through the central U.S. *Data from Jenny 1941.*

A more detailed study of the effect of vegetation on weathering was conducted by Moulton et al. (2000) in western Iceland. Here weathering rate was determined by analyses of streamwaters draining the same basaltic rock populated in nearby locations by (1) small birch trees, (2) conifers, and (3) scattered mosses and lichens. Relief, rainfall, and lithology for the three locations was essentially identical. After minor corrections for input dissolved in rainfall and uptake by vegetation and storage in soil clays, the stream fluxes of dissolved Ca and Mg were found to be about the same for the birch and conifer trees and three to four times higher than that for the moss and lichen-covered location. This gives additional credence to the idea that trees greatly accelerate the release of ions by weathering.

The reason why trees accelerate weathering, compared to barren ground or that occupied by mosses and lichens, is severalfold (see Berner et al. 2004):

> (1) Tree roots, especially when accompanied by mycorrhizal fungi, secrete organic acids that are effective in dissolving and chelating minerals (see fig. 4.4d). The large, fine-root mass of trees exposes a very much larger interface between plants and minerals than do the hyphae of mosses and lichens. Also, the rate of nutrient uptake by large, fast-growing plants, with nutrients supplied by rock weathering, is orders of magnitude greater than that for lichens and mosses.
>
> (2) The vast collection of tree roots stabilizes soils against erosion, allowing retention of moisture for further weathering.
>
> (3) Trees undergo extensive transpiration, which leads to enhanced air moisture and locally enhanced rainfall in forests. This supplies fresh, dilute waters for further weathering.
>
> (4) Under trees, abundant soil organic matter ages to humic substances that are acidic and that may also attack primary minerals.

Silicate Weathering: Soil Formation

Soil can be defined as “a complex system of air, water, decomposing organic matter, living plants and animals, in addition to the residues of rock weathering, organized into definite structural patterns as dictated by the environmental conditions” (Loughnan 1969, p. 115). The dominant control, on a worldwide basis, of soil formation is climate. In fact, most classifications of soils (zonal soils) are based primarily on climatic differences. A common classification is that shown in table 4.7.

(For a more detailed discussion of soil classification, consult Retallack 2001 and Eswaran et al. 2002). In addition to the role of rainfall as it affects flushing of the rock (as discussed above), climate exerts an important influence on weathering via its control on vegetation and the organic content of soils. High rainfall, which enhances plant growth, and low temperature, which retards bacterial destruction, both favor the accumulation of organic matter in soils. Organic matter is important, as mentioned earlier, in that it is the source of carbonic and organic acids and chelating compounds that react with silicate minerals. It is because of the accumulation of organic matter that the most acid soils in table 4.7 are those formed under cool, humid conditions—in other words, the spodisols. (Histosols are even richer in organic matter, but due to lack of water circulation, little weathering takes place in them.) By contrast, less organic matter accumulates in the warm climate oxysols (latosols and laterites) due to almost complete destruction of organic matter by microorganisms, and in desert and semiarid soils (aridosols) due to a lack of appreciable plant growth.

Since our concern is mainly with weathering and the global environment, we needn't go into great detail about various soil types and classifications. However, a few additional comments concerning some of the soils of table 4.7 are in order. The characteristic soils of humid temperate regions are the spodisols and alfisols. Spodisols (formerly podzols) are characterized by a strong vertical zonation, an example of which is shown in figure 4.7.

The top of the soil (O horizon) consists of leaf litter, which becomes decayed to structureless humus upon burial (A horizon). The downward flow of water, which becomes highly acidic upon passing through the organic layers, results in intense leaching and removal of the immediately underlying material, resulting in a residue consisting mainly of resistant quartz (E horizon). Cations, silica, organic matter, and even Al and Fe are removed. The Al and Fe, however, as well as some silica and dissolved organic matter (humic and fulvic acids), do not leave tbe rock and are precipitated at depth in the so-called B horizon. Underlying the B horizon is the C horizon (fig. 4.7), or the zone where the rock is only slightly weathered and little affected by biological activity.

Table 4.7 Soil classification

ENTISOL	Negligible degree of soil formation or zonation, due to short time available or located on slopes subject to constant removal by erosion.
INCEPTISOL	Intermediate stage of development between entisols

	and other soil types. Immature soils.
HISTOSOL	Organic-rich soils with thick, peaty horizons. Formed in low-lying, permanently water-logged areas.
VERTISOL	Uniform, thick clay-rich profiles with deep cracks and hummocky topography produced by intense seasonal drying of expandable clay minerals such as smectites. High exchangeable cations (base-rich).
MOLLISOL	Well-developed, base-rich surface horizon of mixed clay and organic matter plus a subsurface clayey, calcareous, or gypsiferous horizon. Found under grassland vegetation in subhumid to semiarid climates.
ARIDOSOL	Soils of arid regions with shallow calcareous. gypsiferous, or saline horizons. Often contain wind-blown dust.
SPODISOL	Strong zonation showing a base-poor and amorphous Al-and Fe-rich B horizon normally overlaid by a quartz-rich, strongly leached E horizon in turn overlaid by a highly acidic surface organic layer.(Formerly called *podzol*.) Typically under coniferous forests in temperate climates.
ALFISOL	Forest soils with a base-rich (smectitic) clayey subsurface layer B horizon overlaid by a well-defined, light-colored surface horizon A. High content of primary weatherable minerals (e.g., feldspars).
ULTISOL	Forest soils (mainly deciduous) with base-poor (e.g., kaolinitic) clayey subsurface B horizon and low content of primary minerals due to extensive weathering in warm, humid climates.
OXYSOL	Deeply weathered reddish, kaolinitic clay-rich and iron-rich soils of tropical humid climates (formerly called *laterite*). Almost no remaining primary minerals.

Source: Adapted after Retallack 2001.

In other soil types one also encounters vertical zonation, but often different from that exhibited by spodisols. For example, in mollisols, the characteristic soils of subhumid temperate grasslands, as well as in aridosols, one often finds the precipitation of $CaCO_3$ at depth within the B horizon due to the dominance, during dry periods, of evaporation over downward percolation and leaching.

In tropical and subtropical soils there is little burial of organic matter, but still there is intense leaching of cations and silica, due to heavy rainfall, resulting in the buildup of residual iron and aluminum within the B horizon (ultisols and oxysols). In desert soils (aridosols), or in soils that have been subjected to weathering for only short periods (entisols), vertical zonation is often poorly developed due to a relative lack of weathering. Examples of the latter soils are those developed on young glacial deposits or on relatively recent volcanic flows.

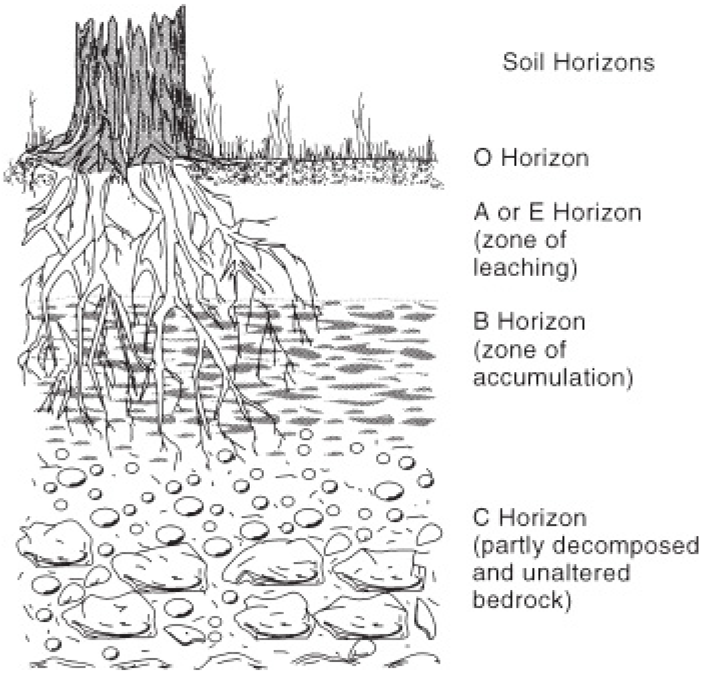


Figure 4.7 Cross-section of a typical spodisol developed in a temperate humid climate. *After Drever 1992.*

Carbonate Weathering

Compared to silicates, carbonate minerals weather far more simply. Dissolution is normally congruent, and the overall reaction, accomplished by carbonic acid (H_2CO_3) attack (or organic acid attack, which can be represented as H_2CO_3; see above) is for calcite:

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{++} + 2HCO_3^- \qquad (4.16)$$

and for dolomite:

$$2H_2CO_3 + CaMg(CO_3)_2 \rightarrow Ca^{++} + Mg^{++} + 4HCO_3^- \qquad (4.17)$$

Carbonate minerals are not as abundant as silicate minerals, but they exert a dominant influence on groundwater and river-water composition. Most of the dissolved Ca^{++} and HCO_3^- in river water, on a worldwide basis, arises from carbonate dissolution via reactions 4.16 and 4.17 (see chapter 5).

Many rocks mapped as silicates contain traces of carbonates, which can greatly affect water composition derived from weathering. Even granites can contain traces of calcite that dominate initial weathering and resulting water composition (White et al. 1999). Initial weathering of largely granitic terrain in the Himalayas was found to be dominated by carbonate dissolution, even though carbonates constitute only about 1% of the bedrock (Jacobson et al. 2002).

Calcium carbonate dissolution, under certain circumstances, can be followed by reprecipitation. In soil water and groundwater where carbonic (and organic) acid concentrations are high, the resulting concentrations of Ca^{++} and HCO_3^- can build up to high values. If the waters then encounter conditions where degassing of dissolved CO_2 occurs, the waters may become supersaturated with respect to $CaCO_3$. Carbonic acid constantly maintains equilibrium with dissolved CO_2: and if CO_2 is lost from solution, reaction 4.18 shifts to the right, using up H_2CO_3, and consequently reaction 4.16 shifts to the left to replace the H_2CO_3. If Ca^{++} and HCO_3^- are present in high enough concentrations, $CaCO_3$ precipitation may then take place.

$$H_2CO_3 \leftrightarrow H_2O + CO_2 \tag{4.18}$$

An outstanding example of the reprecipitation of $CaCO_3$ occurs in limestone caves. Limestone is a rock consisting largely of calcite. It undergoes congruent dissolution during weathering along joints, cracks, and other avenues of water flow by carbonic acid derived from the overlying soils. The Ca^{++} and HCO_3^- are normally removed from the rock, and as a result enlargement of cracks and ultimately the formation of caves takes place. If a cave is sufficiently connected, via cracks, to the atmosphere, a low atmospheric value of CO_2 gas is maintained in the cave air. In this case, water emerging in the cave from above and containing high levels of H_2CO_3, CO_2, and HCO_3^- can lose CO_2 to the cave atmosphere. As a result, supersaturation with $CaCO_3$ is attained and calcite is precipitated to form stalactites, stalagmites, and other cave deposits. Cave deposits also form in dolostones (dolomite rocks), but in this case dolomite is not reprecipitated. There are severe problems in precipitating dolomite so that, in solutions supersaturated with respect to dolomite and calcite, calcite is invariably the precipitate with Mg lost to solution. Thus, in dolostones we find caves that contain deposits of calcite, not dolomite (see, e.g., Holland et al. 1964).

Calcite can also precipitate in soils. (The Ca^{++} and HCO_3^- may come from the weathering of silicates rather than carbonates.) This comes about by a similar process of degassing, but the precipitation occurs much closer to the ground surface. In arid climates, downward percolating soil waters undergo degassing and loss of CO_2 at a depth of only a few tens of centimeters in the soil. (The CO_2 is picked up from organic decay at even shallower depths.) As a result, calcite precipitation takes place, and the resulting deposit is referred to as *caliche* (for a discussion of soil carbonate, see Retallack 2001).

Sulfide Weathering

Sulfide minerals occur in minor quantities in many different rock types and locally in major quantities in ore deposits. The most abundant mineral, by far, is pyrite (FeS_2), which is found mainly in organic-rich, fine-grained sedimentary rocks known as *black shales* and in coal. Upon exposure to dissolved oxygen during weathering, pyrite (and other sulfides) are chemically unstable and rapidly undergo oxidative decomposition. This decomposition is important in that it results in the production of sulfuric acid, which can be used, in turn, to bring about further weathering of silicate and carbonate minerals. Sulfuric acid forms as follows: (Various other reactions can be written involving Fe^{++} or Fe^{+++} in solution, etc., but in all cases there is a distinct lowering of pH due to the formation of H_2SO_4.) Almost always the oxidation is catalyzed by bacteria (Stumm and Morgan 1996). The acidity of water draining rocks where sulfide oxidation is taking place depends on the content of sulfides and the presence of other minerals, especially carbonates, which can readily neutralize acid. During coal mining, large expanses of pyrite-bearing coal are suddenly exposed to oxygenated water, and because associated rocks generally contain little carbonate, the waters draining coal-mining localities are very acid. Values of pH of less than 3, resulting from bacterial catalysis of pyrite oxidation, are common for such mine-drainage waters (Stumm and Morgan 1996).

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4 \qquad (4.19)$$

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{--} \qquad (4.20)$$

By contrast, calcareous rocks that also contain pyrite do not weather to produce highly acid water. Instead the sulfuric acid is neutralized by $CaCO_3$. Reactions are

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 16H^+ + 8SO_4^{--} \qquad (4.21)$$

$$16H^+ + 16CaCO_3 \rightarrow 16Ca^{++} + 16HCO_3^- \qquad (4.22)$$

which, added together, give

$$\begin{aligned}&4FeS_2 + 15O_2 + 8H_2O + 16CaCO_3 \rightarrow \\ &2Fe_2O_3 + 16Ca^{++} + 8SO_4^{--} + 16HCO_3^- \qquad (4.23)\end{aligned}$$

In this way Ca^{++}-SO_4^{--}-HCO_3^- groundwaters and streamwaters can arise. In arid and semiarid regions where evaporative concentration of soil waters is common, the Ca^{++} and SO_4^{--} concentrations often reach the point where the precipitation of gypsum, $CaSO_4 \cdot 2H_2O$ takes place. The common occurrence of gypsum crystals in weathered outcrops of calcareous black shales in the western interior of the United States is an example of this process.

Sulfuric acid is also partially neutralized by silicate minerals. It is this neutralization, in fact, that constitute one of the more important weathering reactions for silicates—e.g., for albite:

$$\begin{aligned}&H_2SO_4 + 9H_2O + 2NaAlSi_3O_8 \rightarrow \\ &Al_2Si_2O_5(OH)_4 + 2Na^+ + SO_4^{--} + 4H_4SiO_4 \qquad (4.24)\end{aligned}$$

Sometimes, if there is sufficient pyrite (or other sulfides), acidity can be so high that common secondary minerals, such as kaolinite and iron oxides, become unstable and dissolve:

$$6H^+ + Al_2Si_2O_5(OH)_4 \rightarrow 2Al^{+++} + 2H_4SiO_4 + H_2O \qquad (4.25)$$

$$6H^+ + Fe_2O_3 \rightarrow 2Fe^{+++} + 3H_2O \qquad (4.26)$$

In this case, sulfate minerals such as alunite, $KAl_3(SO_4)_2(OH)_6$, or jarosite, $KFe_3(SO_4)_2(OH)_6$, may form. Finding these minerals in soils is a good indication that the soils are highly acidic (van Breeman 1976).