CHAPTER

4

The Lithosphere

INTRODUCTION

Since early geologic time, the atmosphere has interacted with the exposed crust of the Earth, causing rock weathering. Many of the volcanic gases in the Earth's earliest atmosphere dissolved in water to form acids that could react with surface minerals (Chapter 2). Later, as oxygen accumulated in the atmosphere, rock weathering occurred as a result of the oxidation of reduced minerals, such as pyrite, that were exposed at the Earth's surface. At least since the advent of land plants, rock minerals have also been exposed to high concentrations of carbon dioxide in the soil as a result of the metabolic activities of soil microbes and plant roots. Today, carbonic acid (H_2CO_3), derived by reaction of CO_2 with soil water, is a major cause of rock weathering in most ecosystems. In recent years, humans have added large quantities of NO_x and SO_2 to the atmosphere, causing acid rain (Chapter 3) and increasing the rate of rock weathering in many areas (Cronan 1980).

Siever (1974) proposed a basic equation to summarize the close linkage between the Earth's atmosphere and its crust:

$$\text{Igneous Rocks} + \text{Acid Volatiles} = \text{Sedimentary Rocks} + \text{Salty Oceans}. \qquad (4.1)$$

This formula recognizes that through geologic time the primary minerals of the Earth's crust have been exposed to reactive, acid-forming C, N, and S gases of the atmosphere. The products of the reaction are carried to the oceans, where they accumulate as dissolved salts or in ocean sediments (Li 1972). Large amounts of sedimentary rock have formed through geologic time; indeed, about two-thirds of the rocks now exposed on land are sedimentary rocks that have been uplifted by tectonic activity (Durr et al. 2005, Suchet et al. 2003, Wilkinson et al. 2010). With their uplift, these sedimentary rocks are subject to further weathering reactions with acid volatiles, in accord with Siever's basic equation. Eventually, geologic processes, known as subduction, carry sedimentary rocks to the deep Earth, where CO_2 is released and the solid constituents are converted back to primary minerals under great heat and pressure (Figure 1.3; see also Siever 1974).

This chapter reviews the basic types of rock weathering on land and the processes that drive these weathering reactions. Rock weathering is especially important to the bioavailability of elements that have no gaseous forms (e.g., Ca, K, Fe, and P; Table 4.1). Weathering is basic to soil fertility, biological diversity, and agricultural productivity (Huston 1993). Reactions between soil waters and the solid materials in soil determine the availability of essential elements to biota and the losses of these elements in runoff. Conversely, land plants and soil microbes affect rock weathering and soil development, potentially regulating global biogeochemistry and the Earth's climate. In this chapter, we examine soil development in the major ecosystems on Earth. Finally, we will estimate the global rate of rock weathering in an attempt to determine the annual new supply of biochemical elements on land and the total delivery of weathering products to rivers and the sea.

TABLE 4.1   Approximate Mean Composition of Earth's Continental Crust

Constituent	Percentage composition
Si	28.8
Al	7.96
Fe	4.32
Ca	3.85
Na	2.36
Mg	2.20
K	2.14
Ti	0.40
P	0.076
Mn	0.072
S	0.070

Source: Data from Wedepohl (1995).

I. PROCESSES AND REACTIONS

ROCK WEATHERING

Following geologic uplift and exposure at the Earth's surface, all rocks undergo weathering, a general term that encompasses a wide variety of processes that decompose rocks. Mechanical weathering is the fragmentation or loss of materials without a chemical reaction; in laboratory terminology it is equivalent to a physical change. Mechanical weathering is important in extreme and highly seasonal climates and in areas with much exposed rock. Wind abrasion is a form of mechanical weathering in arid environments, whereas the expansion of frozen water in rock crevices—often resulting in fractured rocks—is an important form of mechanical weathering in cold climates. Plant roots also fragment rock when they grow in crevices.
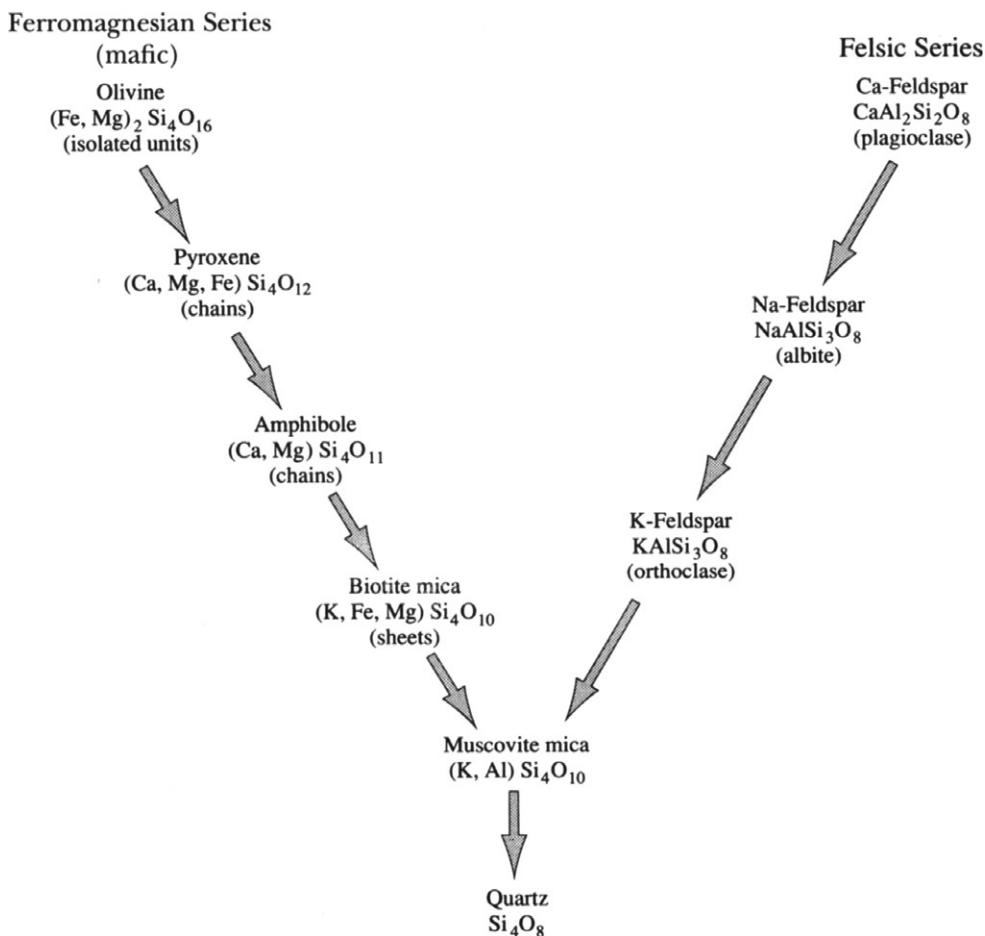
Where the products of mechanical weathering are not rapidly removed by erosion, thick soils develop, and the landscape is said to be "transport-limited." In other areas, finely divided rock and soil are removed by erosion—the loss of particulate solids from the ecosystem. The products of mechanical weathering may also be lost in catastrophic events such as landslides (Swanson et al. 1982). Indicative of the high rates of mechanical weathering and erosion at high elevations, rivers draining mountainous regions often carry exceptionally large sediment loads to the sea (Milliman and Syvitski 1992).

Chemical Weathering

Chemical weathering occurs when the minerals in rocks and soils react with acidic and oxidizing substances. Usually chemical weathering involves water, and various constituents are released as dissolved ions that are available for uptake by biota or that are lost in stream waters. In many cases, mechanical weathering is important in exposing the minerals in rocks to chemical attack (e.g., Miller and Drever 1977, Anbeek 1993, Nugent et al. 1998, Hilley et al. 2010). If the rate of mechanical weathering is slow, it may limit the rate of chemical weathering and lower the fertility of soils (Gabet and Mudd 2009).

The rate of chemical weathering depends on the mineral composition of rocks. Igneous and metamorphic rocks contain primary minerals (e.g., olivine and plagioclase) that were formed under conditions of high temperature and pressure deep in the Earth. These primary silicate minerals are crystalline in structure, and they are found in two classes—the ferromagnesian or *mafic* series and the plagioclase or *felsic* series—depending on the crystal structure and the presence of magnesium versus aluminum in the crystal lattice (Figure 4.1). Among these minerals, the rate of weathering tends to follow the reverse order of the sequence of mineral formation during the original cooling and crystallization of rock; that is, minerals that condensed first are the most susceptible to weathering reactions (Goldich 1938).

Minerals formed during rapid, early crystallization of magma at high temperatures contain few bonds that link the units of their crystalline structure. They also have frequent substitutions of various cations—for example, Ca, Na, K, Mg, and trace metals (Fe and Mn)—in their crystal lattice, distorting its shape and increasing its susceptibility to weathering. Thus, for example, olivine, which is formed under conditions of great heat and pressure deep within the Earth, is most likely to weather rapidly when exposed at the Earth's surface.

Ferromagnesian Series
(mafic)

Olivine
$(Fe, Mg)_2 Si_4O_{16}$
(isolated units)

Pyroxene
$(Ca, Mg, Fe) Si_4O_{12}$
(chains)

Amphibole
$(Ca, Mg) Si_4O_{11}$
(chains)

Biotite mica
$(K, Fe, Mg) Si_4O_{10}$
(sheets)

Felsic Series

Ca-Feldspar
$CaAl_2Si_2O_8$
(plagioclase)

Na-Feldspar
$NaAlSi_3O_8$
(albite)

K-Feldspar
$KAlSi_3O_8$
(orthoclase)

Muscovite mica
$(K, Al) Si_4O_{10}$

Quartz
Si_4O_8

FIGURE 4.1　Silicate minerals are divided into two classes, the ferromagnesian series and the felsic series, based on the presence of Mg or Al in the crystal structure. Among the ferromagnesian series, minerals that exist as isolated crystal units (e.g., olivine) are most susceptible to weathering, while those showing linkage of crystal units and a lower ratio of oxygen to silicon are more resistant. Among the felsic series, Ca-feldspar (plagioclase) is more suscep-tible to weathering than Na-feldspar (albite) and K-feldspar (orthoclase). Quartz is the most resistant of all. This weathering series is the reverse of the order in which these minerals are precipitated during the cooling of magma.

　　In rocks or soils of mixed composition, chemical weathering is concentrated on the relatively labile minerals, while other minerals may be unaffected (April et al. 1986, White et al. 1996, 2001). The dissolution and loss of some constituents may result in a reduction of the density of bedrock, with little collapse or loss of the initial rock volume—a process known as isovolumetric weath-ering. The product, "rotten" rock known as *saprolite*, comprises the lower soil profile of many regions, especially in the southeastern United States (Gardner et al. 1978, Velbel 1990, Stolt et al. 1992, Oh and Richter 2005). In other cases, the removal of some constituents is accompanied by the collapse of the soil profile and an apparent increase in the volumetric concentration of the elements that remain (e.g., Zr, Ti, and Fe; Brimhall et al. 1991).

Quartz is very resistant to chemical weathering and often remains when other minerals are lost (Figure 4.1). Quartz is a relatively simple silicate mineral consisting only of silicon and oxygen in tetrahedral crystals that are linked in three dimensions. In many cases, the sand fraction of soils is largely composed of quartz crystals that remain following the chemical weathering and loss of other constituents during soil development (Brimhall et al. 1991).

In addition to mineralogy, rock weathering also depends on climate (White and Blum 1995, Gislason et al. 2009). Chemical weathering involves chemical reactions, so it is not surprising that it occurs most rapidly under conditions of higher temperature and precipitation (White et al. 1998, West et al. 2005). Chemical weathering is more rapid in tropical forests than in temperate forests, and more rapid in most forests than in grasslands or deserts. Chemical weathering proceeds, albeit at low rates, in cold Antarctic environments (Hodson et al. 2010). White and Blum (1995) show that the loss of Si in stream water, which is often a good index of chemical weathering, is directly related to precipitation and temperature over much of the Earth's surface (Figure 4.2). With the ongoing global changes in climate, the likelihood of higher future temperatures and precipitation should increase the rate of chemical weathering worldwide.

The dominant form of chemical weathering is the carbonation reaction, driven by the formation of carbonic acid, H_2CO_3, in the soil solution:

$$H_2O + CO_2 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H_2CO_3. \qquad (4.2)$$
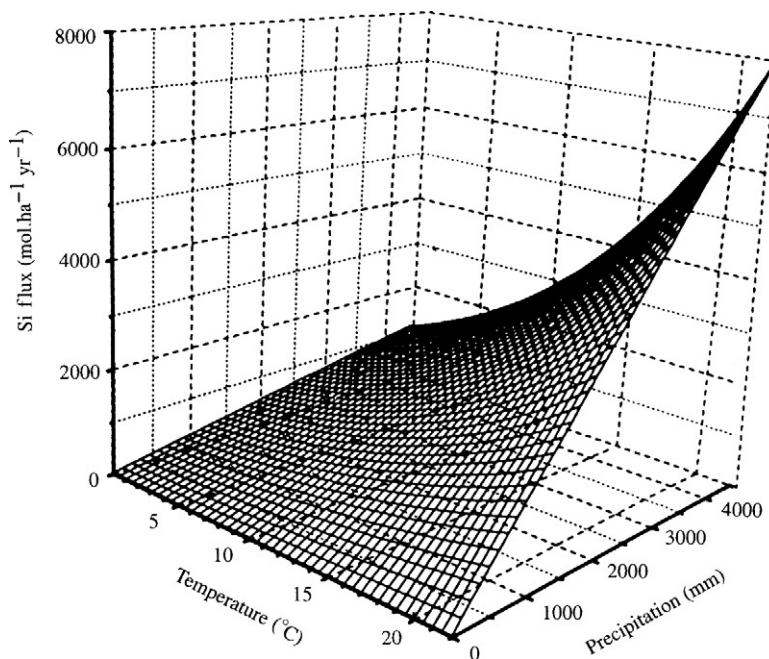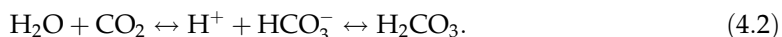

FIGURE 4.2 Loss of silicon (SiO_2) in runoff as a function of mean annual temperature and precipitation in various areas of the world. *Source: Modified from White and Blum (1995).*

Because plant roots and soil microbes release CO_2 to the soil, the concentration of H_2CO_3 in soil waters is often much greater than that in equilibrium with atmospheric CO_2 at 400 ppm (i.e., 0.04%) (Castelle and Galloway 1990, Amundson and Davidson 1990, Pinol et al. 1995). Buyanovsky and Wagner (1983) report seasonal CO_2 concentrations of greater than 7% in the soil beneath wheat fields in Missouri. Such high concentrations of CO_2 can extend to considerable depths in the soil profile, affecting the weathering of underlying rock (Sears and Langmuir 1982, Richter and Markewitz 1995). Wood and Petraitis (1984) found CO_2 concentrations of 1.0% at 36 m, which they link to the downward transport of organic materials that subsequently decompose at depth. Solomon and Cerling (1987) found that high concentrations of CO_2 accumulated in the soil under a mountain snowpack, potentially leading to significant weathering during the winter (see also Berner and Rao 1997).

Plant growth is greatest in warm and wet climates. As a result of root growth and activity, these areas maintain the highest levels of soil CO_2 and the greatest rates of carbonation weathering (Johnson et al. 1977). Examining data from a variety of ecosystems, Brook et al. (1983) found that the average concentration of soil CO_2 varies as a function of actual evapotranspiration, a composite measure of temperature and available soil moisture, at the site (Figure 4.3). However, rock weathering appears to be controlled by carbonation weathering even in arid regions (e.g., Routson et al. 1977). By maintaining high concentrations of CO_2 in the soil, plants and soil microbes control the process of rock weathering—a good example of *bio*geochemistry at the Earth's surface.

Carbonic acid attacks silicate rocks. For example, weathering of the Na-feldspar, albite, proceeds as

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow$$
$$2Na^+ + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4. \tag{4.3}$$
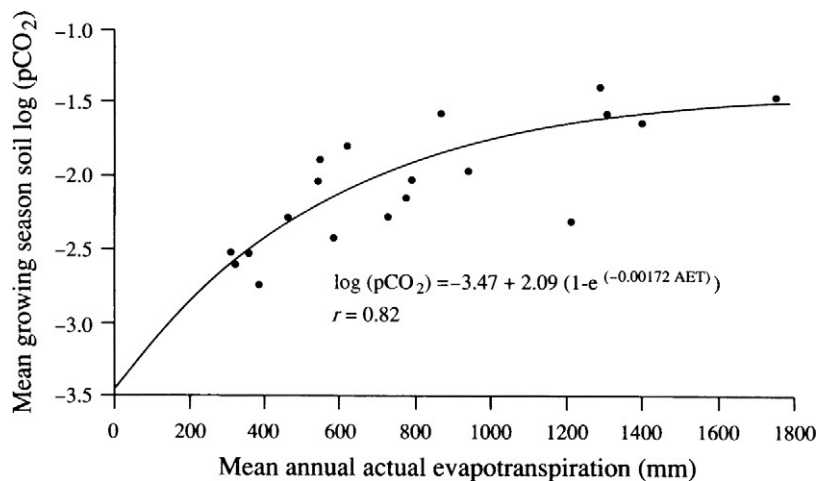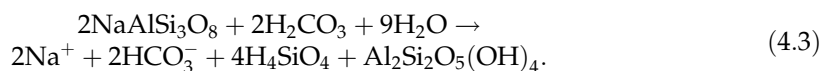
FIGURE 4.3   The relationship between the mean concentration of CO_2 in the soil pore space and the actual evapotranspiration of the site for various ecosystems of the world. *Source: From Brook et al. (1983).*

During this process, a primary mineral is converted to a secondary mineral, kaolinite, by the removal of Na^+ and soluble silica. A sign that carbonation weathering has occurred is the observation that HCO_3^- is the dominant anion in runoff waters (Ohte and Tokuchi 1999). Formation of kaolinite involves hydration with H^+ and water. The secondary mineral has a lower ratio of Si to Al as a result of the loss of some Si to stream waters. Because only some of the constituents of the primary mineral are released, this type of weathering reaction is known as an *incongruent dissolution*. Under conditions of high rainfall, as in the humid tropics, kaolinite may undergo a second incongruent dissolution to form another secondary mineral, gibbsite:

$$Al_2Si_2O_5(OH)_4 + 5H_2O \rightarrow 2H_4SiO_4 + Al_2O_3 \cdot 3H_2O. \tag{4.4}$$
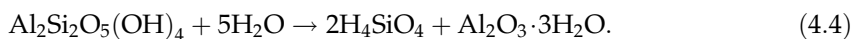
Some weathering reactions involve congruent dissolutions. In moist climates, limestone undergoes a relatively rapid congruent dissolution during carbonation weathering:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-. \tag{4.5}$$

Olivine ($FeMgSiO_4$) also undergoes congruent dissolution in water, releasing Fe, Mg, and Si (Grandstaff 1986). The magnesium and silicon are lost in runoff waters, but usually the Fe reacts with oxygen, resulting in the precipitation of Fe_2O_3 in the soil profile. Similarly, pyrite (FeS_2) undergoes a congruent reaction during its oxidation:

$$4FeS_2 + 8H_2O + 15O_2 \rightarrow 2Fe_2O_3 + 16H^+ + 8SO_4^{2-}. \tag{4.6}$$
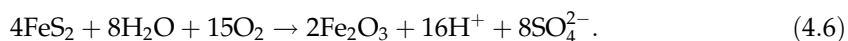
The H^+ produced in this reaction accounts for the acidity of runoff from many mining operations. As with the weathering of olivine, the Fe from weathered pyrite is subsequently precipitated as Fe_2O_3 in the soil profile or streambed (Bloomfield 1972, Johnson et al. 1992). Often this reaction is mediated by the chemoautotrophic bacterium *Thiobacillus ferrooxidans* (Eq. 2.16; Temple and Colmer 1951, Ralph 1979, Schrenk et al. 1998).

In addition to carbonic acid, organisms release a variety of organic acids to the soil solution that can be involved in the weathering of silicate minerals (Ugolini and Sletten 1991). Many simple organic compounds, including acetic and citric acids, are released from plant roots (Smith 1976, Tyler and Ström 1995, Jones 1998). Phenolic acids (i.e., tannins) are released during the decomposition of plant litter, and soil microbes produce fulvic and humic acids during decomposition of plant remains (Chapter 5). Many fungi release oxalic acid that results in chemical weathering (Cromack et al. 1979, Lapeyrie et al. 1987, Welch and Ullman 1993, Cama and Ganor 2006). Organic acids from plant roots and microbes can weather biotite mica, releasing K (Boyle and Voigt 1973, April and Keller 1990). Soil microbes appear to preferentially colonize and weather the surface of minerals that contain elements, such as phosphorus, that are otherwise in short supply for their growth and reproduction (Rogers et al. 1998, Banfield et al. 1999).

In addition to their contributions to total acidity, organic acids speed weathering reactions in the soil by combining with some weathering products, in a process called *chelation*.[1] When Fe and Al combine with fulvic acid, they are mobile and move to the lower soil profile in percolating water (Dahlgren and Walker 1993, Lundström 1993). When these elements are involved in chelation, their inorganic concentration in the soil solution remains low, the

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[1] Derived from the Greek word for claw, chelation applies when an organic molecule forms two or more separate covalent bonds with an ion, usually a metal, that keeps it in solution.

equilibrium between dissolved products and mineral forms is not achieved, and chemical weathering may continue unabated (Berggren and Mulder 1995, Zhang and Bloom 1999). Grandstaff (1986) found that additions of small concentrations of EDTA (an organic chelation agent) to weathering solutions increased the dissolution of olivine by 110 times over inorganic conditions. Fulvic and humic acids increase the weathering of a variety of silicate minerals, including quartz, particularly when the soil solution is neutral or slightly acid (Tan 1980, Bennett et al. 1988, Wogelius and Walther 1991, Welch and Ullman 1993).

Organic acids often dominate the acidity of the upper soil profile, while carbonic acid is important below (Ugolini et al. 1977). In general, organic acids dominate the weathering processes in cool temperate forests where decomposition processes are slow and incomplete, whereas carbonic acid drives the chemical weathering in tropical forests where lower concentrations of fulvic acids remain after the decomposition of plant debris (Johnson et al. 1977, Ohte and Tokuchi 1999).

There is much debate about changes in the rate of chemical weathering through geologic time, especially as a result of the evolution of vascular land plants (Berner and Kothavala 2001, Drever 1994). Greater rock weathering, beginning with the initial colonization of land by plants, is likely to have been responsible for a decline in atmospheric CO_2 300 to 400 million years ago, owing to the consumption of CO_2 in carbonation weathering (Knoll and James 1987, Berner 1997, Mora et al. 1996). Various workers have found evidence for higher rates of rock weathering under areas of vegetation (Moulton et al. 2000), suggesting that higher plants add large amounts of CO_2 to the soil from root metabolism and from the decomposition of plant debris by microbes (Kelly et al. 1998). This view holds that the process of photosynthesis acts to speed the transfer of an acid volatile, CO_2, from the atmosphere to the soil profile. Even before the advent of vascular land plants, the Earth's surface may have been covered with algae and lichens, producing relatively high levels of CO_2 in the soil (Keller and Wood 1993, Retallack 1997).

Other workers disagree, suggesting that tectonic uplift and erosion—processes that stimulate mechanical weathering—are the most important determinants of the rate of chemical weathering (Hilley and Porder 2008, Gabet and Mudd 2009, Riebe et al. 2003, Dixon et al. 2012). Still others argue that temperature and precipitation are the dominant factors controlling chemical weathering, with plants playing a lesser role (Gislason et al. 2009, Ohte and Tokuchi 1999, Kump et al. 2000). In sum, a variety of factors—tectonics, mineralogy, climate plants, and soil microbes—play important roles in determining the rate of rock weathering, and it may be impossible to attribute a predominant role to any one of them (Gaillardet et al. 1999, Gabet and Mudd 2009, Anderson et al. 2002).

Because carbonation weathering consumes atmospheric CO_2, the rate of rock weathering on Earth has a major long-term effect on global climate. Schwartzman and Volk (1989) suggest that without CO_2-enhanced chemical weathering, the temperature of the Earth would be too hot for all but the most primitive microbes. As atmospheric CO_2 increases, we can expect rates of rock weathering to increase. This weathering will be mediated directly by increasing soil CO_2 concentrations and indirectly by rising global temperatures (compare Figure 4.2). Several experiments show that the amount of CO_2 in the soil profile increases when plants are grown at high CO_2 (Andrews and Schlesinger 2001, Bernhardt et al. 2006, Williams et al. 2003, Karberg et al. 2005; Figure 4.4). And in soil-warming experiments, greater microbial activity leads to higher concentrations of CO_2 in the soil pore space, and presumably greater carbonation weathering (Figure 4.5).
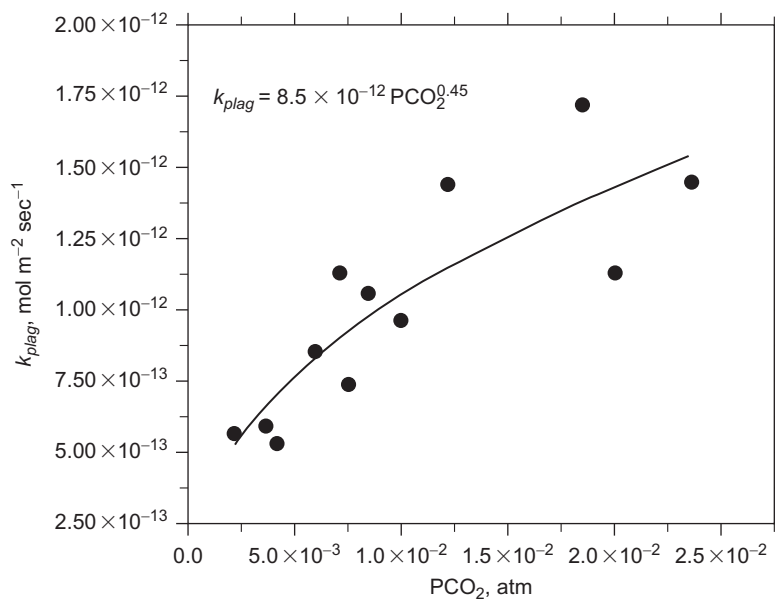
FIGURE 4.4 Dissolution of Ca-feldspar (plagioclase) as a function of soil CO_2 concentrations in watersheds of the Sierra Nevada (California), subject to differential hydrothermal activity. *Source: From Navarre-Sitchler and Thyne (2007).*
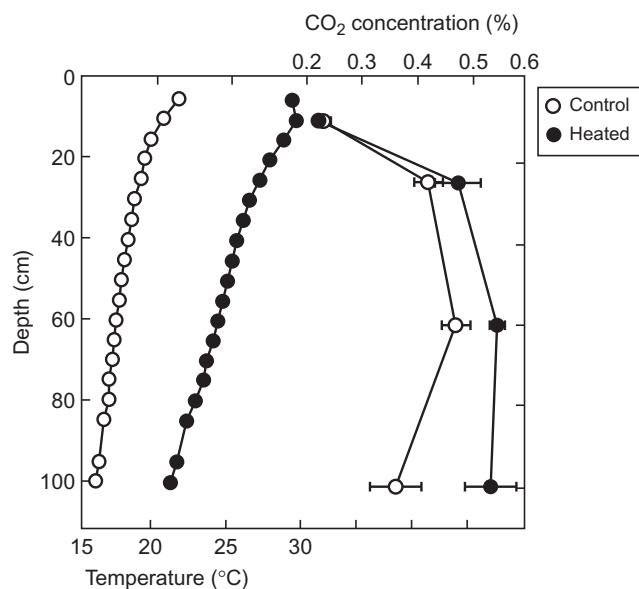
FIGURE 4.5 Soil temperature and pore-space CO_2 concentration (mean $\pm$S.E.) as a function of depth in control and experimentally heated ($+ 5^{\circ}$C) plots in a hardwood forest in Massachusetts. *Source: From unpublished work of Megonigal.*

I. PROCESSES AND REACTIONS

Secondary Minerals

Secondary minerals are formed as byproducts of weathering at the Earth's surface. Usually the formation of secondary minerals begins near the site where primary minerals are being attacked, perhaps even originating as coatings on the crystal surfaces (Casey et al. 1993, Nugent et al. 1998). Although weathering leads to the loss of Si as a dissolved constituent in stream water (Figure 4.2), some Si is often retained in the formation of secondary minerals (see Eq. 4.3).

Many types of secondary minerals can form in soils during chemical weathering. The secondary minerals in temperate forest soils are often dominated by layered silicate or "clay" minerals. These exist as small (< 0.002-mm) particles that control the structural and chemical properties of soils. In general, two types of layers characterize the crystalline structure of secondary, aluminosilicate clay minerals—Si layers and layers dominated by Al, Fe, and Mg. These layers are held together by shared oxygen atoms. Clay minerals and the size of their crystal units are recognized by the number, order, and ratio of these layers (Birkeland 1984). Moderately weathered soils are often dominated by secondary minerals such as montmorillonite and illite, which have a 2:1 ratio of Si- to Al-dominated layers. More strongly weathered soils, such as in the southeastern United States, are dominated by kaolinite clays with a 1:1 ratio of layers, reflecting a greater loss of Si.

Because secondary minerals may incorporate elements important to biochemistry, one cannot assume that the release of those elements from primary minerals leads to an immediate increase in the pool of ions available for uptake by plants. Magnesium is often fixed in the crystal lattice of montmorillonite, whereas illite contains K (Martin and Sparks 1985, Harris et al. 1988). These are common secondary minerals in temperate soils. Similarly, although little nitrogen is contained in primary minerals, some 2:1 clay minerals incorporate N as ammonium (NH_4) in their crystal lattice (Holloway and Dahlgren 2002). Ammonium contained in clay minerals can represent more than 10% of the total N in some soils (Stevenson 1982, Smith et al. 1994, Johnson et al. 2012). The weathering of sedimentary rocks containing ancient clay minerals with "fixed" ammonium can release large quantities of nitrogen to stream waters (Holloway et al. 1998). Recognizing the widespread nitrogen limitation on land (Chapter 6), the release of nitrogen from rock weathering may play an important role in determining the availability of N for plant growth (Mengel and Scherer 1981, Baethgen and Alley 1987, Green et al. 1994, Morford et al. 2011).

In contrast to the loss of Si and other cations (e.g., Ca and Na) to runoff waters, Al and Fe are relatively insoluble in soils unless they are involved in chelation relations with organic matter (Huang 1988, Alvarez et al. 1992, Allan and Roulet 1994, Ross and Bartlett 1996). In the absence of chelation reactions, these elements tend to accumulate in the soil as oxides. Initially, free Fe accumulates in amorphous and poorly crystallized forms, known as ferrihydrite, which are often quantified by extraction in a weak oxalate solution (Shoji et al. 1993, Birkeland 1984). With increasing time, most Fe is found in crystalline oxides and hydroxides, which are traditionally extracted using a reducing solution of citrate-dithionate (Chorover et al. 2004). Some of these mineral transformations involve bacteria and thus are biogeochemical in nature (Fassbinder et al. 1990).

Crystalline oxides and hydrous oxides of Fe (e.g., goethite and hematite) and Al (e.g., gibbsite and boehmite) are common in many tropical soils, where high temperatures and rainfall
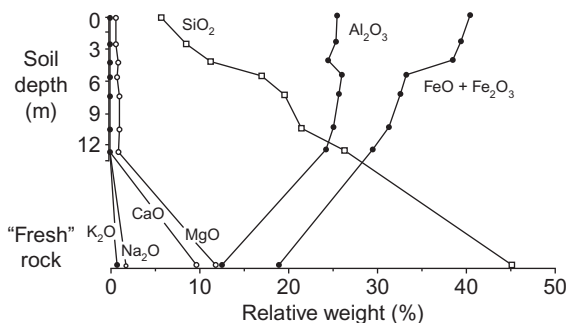
FIGURE 4.6 Content of different rock-forming minerals (% mass) above basalt bedrock in Kauai, Hawaii. *Source: From Bluth and Kump (1994).*

cause relatively rapid decomposition of plant debris and few organic acids remain to chelate and mobilize Fe and Al. Under these climatic conditions, the secondary clay minerals typical of temperate zone soils are subject to weathering, with the near-complete removal of Si, Ca, K, and other basic cations in stream water (Figure 4.6). However, in an interesting example of the importance of biota in soil development, Lucas et al. (1993) show that kaolinite may persist in the upper horizons of some rainforest soils due to the plant uptake of Si from the lower soil profile and the return of Si to the soil surface in plant debris (see also, Alexandre et al. 1997, Markewitz and Richter 1998, Gerard et al. 2008, Conley 2002). Similar plant "pumping" also maintains higher levels of K at the surface of many soils (Jobbagy and Jackson 2004, Barre et al. 2009).

SOIL CHEMICAL REACTIONS

Following their release by weathering, the availability of essential biochemical elements to biota is controlled by a number of reactions that determine the equilibrium between concentrations in the soil solution and contents that are associated with soil minerals or organic materials. In contrast to the kinetics of weathering reactions, soil exchange reactions occur relatively rapidly (Furrer et al. 1989, Maher 2010). The specific soil reactions differ depending on how soil development has progressed under the influence of climate, time, biota, topographic position, and the parent material of the site (Jenny 1980).

Cation Exchange Capacity

The layered silicate clay minerals that dominate temperate zone soils possess a net negative charge that attracts and holds cations dissolved in the soil solution. This negative charge has several origins; most of it arises from ionic substitutions within silicate clays, especially in 2:1 clays. For example, when Mg^{2+} substitutes for Al^{3+} in montmorillonite, there is an unsatisfied negative charge in the internal crystal lattice. This negative charge is permanent in the sense that it arises inside the crystal structure and cannot be neutralized by covalent bonding of cations from the soil solution. Permanent charge is expressed as a zone or "halo" of negative charge surrounding the surface of clay particles in the soil.

A second source of negative charge is found at the edges of clay particles, where hydroxide (−OH) groups are often exposed to the soil solution. Depending on the pH of the solution, the H^+ ion may be more or less strongly bound to this group. In most cases, a considerable number of the H^+ are dissociated, leaving negative charges ($-O^-$) that can attract and bind cations (e.g., Ca^{2+}, K^+, and NH_4^+). This cation exchange capacity is known as *pH-dependent charge*. The binding is reversible and exists in equilibrium with ionic concentrations in the soil solution.

In many temperate soils, a large amount of cation exchange capacity is also contributed by soil organic matter (Yuan et al. 1967). These are pH-dependent charges originating from the phenolic (−OH) and organic acid (−COOH) groups of soil humic materials. In some sandy soils, as in central Florida, and in many highly weathered soils, nearly all cation exchange is the result of soil organic matter (e.g., Daniels et al. 1987, Richter et al. 1994). Organic matter is also the major source of cation exchange in desert soils that contain relatively small amounts of secondary clay minerals as a result of limited chemical weathering.

The total negative charge in a soil is expressed as mEq/100 g or cmol(+)/kg of soil, which constitutes the cation exchange capacity (CEC). Exchange of cations occurs as a function of chemical mass balance with the soil solution. Elaborate models of ion exchange have been developed by soil chemists (Sposito 1989). In general, cations are held on the exchange sites and displace one another in the sequence

$$Al^{3+} > H^+ > Sr^{2+} > Ca^{2+} > Mg^{2+} > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+ \qquad (4.7)$$

(Sparks 2004, Sahai 2000). This sequence assumes equal molar concentrations in the initial soil solution and can be altered by the presence of large quantities of the more weakly held ions. Agricultural liming, for example, is an attempt to displace Al^{3+} ions from the exchange sites by "swamping" the soil solution with excess Ca^{2+}. In most cases, few cation exchange sites are actually occupied by H^+, which quickly weathers soil minerals, releasing Al and other cations.

Cations other than Al and H are informally known as base cations, since they tend to form bases—for example, $Ca(OH)_2$—when they are released to the soil solution (Birkeland 1984, p. 23). The percentage of the total cation exchange capacity occupied by base cations is termed *base saturation*. Both cation exchange capacity and base saturation increase during initial soil development on newly exposed parent materials. However, as the weathering of soil minerals continues, cation exchange capacity and base saturation decline (Bockheim 1980). Temperate forest soils dominated by 2:1 clay minerals have greater cation exchange capacity than those dominated by 1:1 clay minerals such as kaolinite. Highly weathered soils in the humid tropics are dominated by aluminum hydroxide minerals, which offer essentially no cation exchange capacity in the mineral fraction at their natural soil pH.
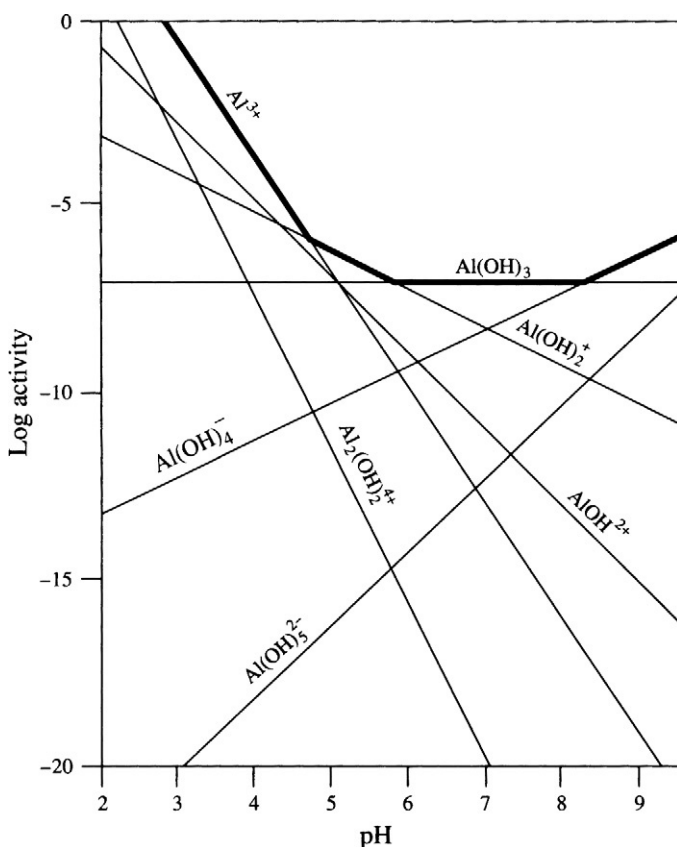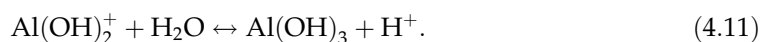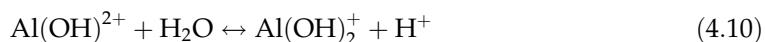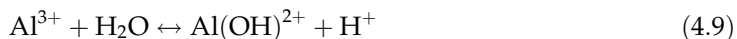
Soil Buffering

Cation exchange capacity acts to buffer the acidity of many temperate soils. When H^+ is added to the soil solution, it exchanges for cations, especially Ca, on clay minerals and organic matter (Bache 1984, James and Riha 1986). Over a wide range of pH, temperate soils maintain a constant value (k) for the expression

$$pH - 1/2(pCa) = k, \qquad (4.8)$$

which is known as the lime potential. This expression suggests that when H^+ is added to the soil solution (lower pH), the concentration of Ca^{2+} increases in the soil solution (lower pCa), so that k remains constant. The 1/2 reflects the valence of Ca^{2+} versus H^+. As long as there is sufficient base saturation (e.g., >15%), buffering by CEC explains why the pH of many temperate soils may show relatively little change when they are exposed to acid rain (Federer and Hornbeck 1985, David et al. 1991, Johnson et al. 1994, Likens et al. 1996).

In strongly acid soils, as in the humid tropics, there is little CEC to buffer the soil solution. These soils are buffered by various geochemical reactions involving aluminum (Figure 4.7). Aluminum is not a base cation inasmuch as its release to the soil solution leads to the formation of H^+ when Al^{3+} is precipitated as aluminum hydroxide:

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+ \tag{4.9}$$

$$Al(OH)^{2+} + H_2O \leftrightarrow Al(OH)_2^+ + H^+ \tag{4.10}$$

$$Al(OH)_2^+ + H_2O \leftrightarrow Al(OH)_3 + H^+. \tag{4.11}$$

FIGURE 4.7   The solubility of aluminum as a function of pH. For pH in the neutral range, gibbsite [$Al(OH)_3$] controls aluminum solubility, and there is little Al^{+3} in solution. Al^{+3} becomes more soluble at pH < 4.7. *Source: From Lindsay (1979).*

These reactions account for the acidity of many soils in the humid tropics (Sanchez et al. 1982a). Note that the reactions are reversible, so that the soil solution is also buffered against additions of H^+ by the dissolution of aluminum hydroxide. The acid rain received by the northeastern United States appears to dissolve gibbsite [$Al(OH)_3$] from many forest soils, leading to high concentrations of Al^{3+} that are toxic to fish in lakes and streams at high elevations. As stream waters flow to lower elevations, H^+ is consumed in weathering reactions with various silicate minerals, stream water pH increases, and aluminum hydroxides are precipitated (Johnson et al. 1981a). In other regions, dissolution of Al-organic complexes (rather than gibbsite) appears to control the concentration of dissolved Al^{3+} in the soil solution (Mulder and Stein 1994, Allan and Roulet 1994).

Anion Adsorption Capacity

In contrast to the permanent, negative charge in soils of the temperate zone, tropical soils dominated by oxides and hydrous oxides of iron and aluminum show variable charge, depending on soil pH (Uehara and Gillman 1981, Sollins et al. 1988, Arai and Sparks 2007). Under acid conditions these soils possess positive charge, as a result of the association of H^+ with the surface hydroxide groups (Figure 4.8). With an experimental increase in pH, a soil sample is observed to pass through a zero point of charge (ZPC), where the number of cation and anion exchange sites is equal. These soils develop cation exchange capacity at high pH. For gibbsite, the ZPC occurs around pH 9.0, so significant anion adsorption capacity (AAC) is present in acid tropical soils in most field situations.

It is important to recognize that these reactions occur on soil constituents everywhere, but the ZPC of layered silicate minerals or soil organic matter occurs at pH < 2.0, so they offer little anion adsorption capacity in most conditions (Sposito 1989, Polubesova et al. 1995). The ZPC of a bulk soil sample will depend on the relative mix of various minerals and organic matter (Chorover and Sposito 1995). Tropical soils in Costa Rica show a ZPC at a pH of about 4.0, as a result of their mixture of soil organic matter and gibbsite (Sollins et al. 1988). Some anion adsorption capacity is found in temperate soils when iron and aluminum oxides and hydroxides occur in the lower soil profile (Johnson et al. 1981a, 1986a).

Anion adsorption capacity is typically greater on poorly crystalline forms of Fe and Al (oxalate-extractable), which have greater surface area than crystalline forms (dithionate-extractable) (Parfitt and Smart 1978, Johnson et al. 1986a, Chorover et al. 2004). Potential adsorption of various anions, including sulfate from acid rain, is positively correlated to the oxalate-extractable Al in a variety of soils (Harrison et al. 1989, Courchesne and Hendershot 1989, MacDonald and Hart 1990, Walbridge et al. 1991).

Anion adsorption follows the sequence

$$PO_4^{3-} > SO_4^{2-} > Cl^- > NO_3^-, \tag{4.12}$$
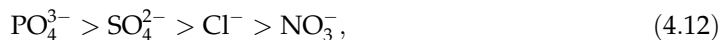
which accounts for the low availability of phosphorus in many tropical soils (Strahm and Harrison 2007). Frequently anion exchange is described using a Langmuir model, in which the content of anions held on exchange sites is expressed as a function of the concentration in the solution (Travis and Etnier 1981, Reuss and Johnson 1986, Autry and Fitzgerald 1993). Phosphorus, sulfate, and selenate (SeO_4^{2-}) are so strongly held that the binding is known

Low pH
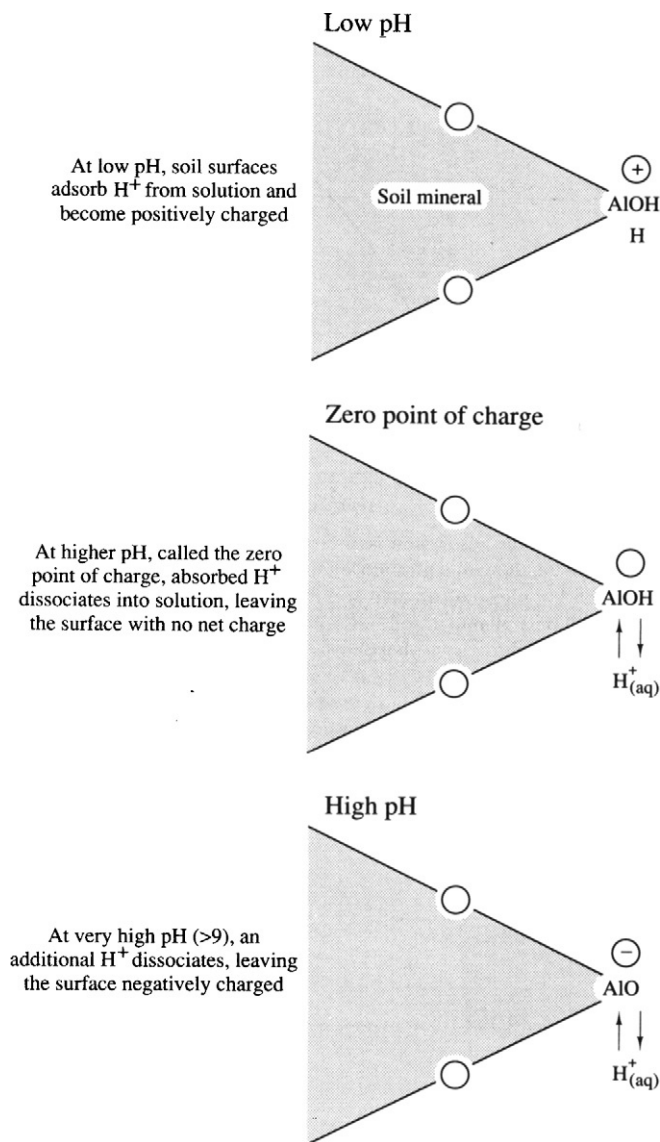
FIGURE 4.8 Variation in surface charge on iron and aluminum hydroxides as a function of pH of the soil solution. *Source: From Johnson and Cole (1980).*

At low pH, soil surfaces adsorb H^+ from solution and become positively charged

Soil mineral

$(+)$
AlOH
H

Zero point of charge

At higher pH, called the zero point of charge, absorbed H^+ dissociates into solution, leaving the surface with no net charge

AlOH

$H^+_{(aq)}$

High pH

At very high pH (>9), an additional H^+ dissociates, leaving the surface negatively charged

$\ominus$
AlO

$H^+_{(aq)}$

as *specific adsorption* or ligand exchange, which is thought to replace $-OH$ groups on the surface of the minerals (Figure 4.9; Hingston et al. 1967, Guadalix and Pardo 1991, Bhatti et al. 1998). Here, the adsorption of SO_4^{2-} from acid rain is associated with an increase in soil pH, a decline in apparent ZPC, and higher cation exchange capacity (e.g., Marcano-Martinez and McBride 1989, David et al. 1991). All these anions are also involved in nonspecific adsorption, which is more readily reversible with changes in their concentration in the soil solution.

I. PROCESSES AND REACTIONS
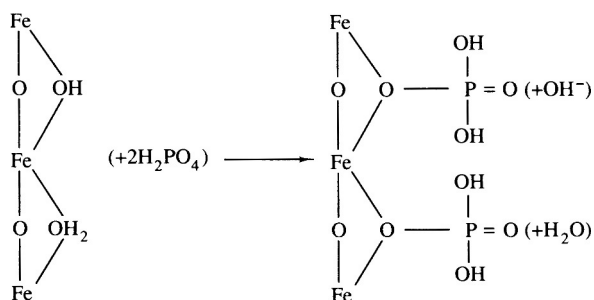
FIGURE 4.9 The specific adsorption of phosphate by iron sesquioxides may release OH or H_2O to the soil solution. *Source: From Binkley (1986).*

Anion adsorption capacity is inhibited by soil organic matter, especially organic anions, which tend to bind to the reactive surfaces of Fe and Al minerals (Johnson and Todd 1983, Hue 1991, Karltun and Gustafsson 1993, Gu et al. 1995). Soils or soil layers that are rich in organic matter are less efficient in anion adsorption than those dominated solely by Fe and Al oxide and hydroxide minerals. Percolating waters often carry SO_4^{2-} from the upper, organic layers of the soil to lower depths, where it is captured by Fe and Al minerals (Dethier et al. 1988, Vance and David 1991). Thus, anion adsorption capacity is determined by the effects of soil organic matter on a variety of soil properties: increasing AAC by inhibiting the crystallization of Fe and Al minerals, but reducing AAC by binding to the anion exchange sites (Johnson et al. 1986a, Kaiser and Zech 1998).

Phosphorus Minerals

Phosphorus (P) deserves special attention, since it is often in limited supply for plants. The only primary mineral with significant phosphorus content is apatite, which can undergo carbonation weathering in a congruent reaction, releasing P:

$$Ca_5(PO_4)_3OH + 4H_2CO_3 \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4HCO_3^- + H_2O. \tag{4.13}$$
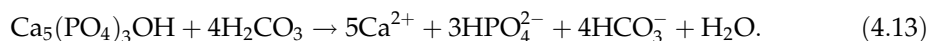
Although this phosphorus may be accumulated by biota (organic-P), a large proportion of the available P is involved in reactions with other soil minerals, leading to its precipitation in unavailable forms.

As seen in Figure 4.10, the maximum level of available phosphorus in the soil solution is found at a pH of about 7.0. In acid soils, P availability is controlled by direct precipitation with iron and aluminum (Lindsay and Moreno 1960, Arai and Sparks 2007), whereas in alkaline soils phosphorus is often precipitated with calcium minerals (Cole and Olsen 1959, Lajtha and Bloomer 1988), and therefore may be deficient for optimal plant growth (Tyler 1994). Binding to iron and aluminum oxides accounts for the low availability of phosphorus in many tropical soils (Sanchez et al. 1982b, Smeck 1985, Agbenin 2003). When phosphorus is captured in the interior of crystalline Fe and Al oxides, it is known as occluded P, which is essentially unavailable to biota.

Walker and Syers (1976) diagram the general evolution of phosphorus availability during the weathering of rocks containing apatite (Figure 4.11). Apatite weathers rapidly, giving rise to phosphorus contained in various other forms and to a decline of total phosphorus in the system due to losses in runoff (Singleton and Lavkulich 1987a, Schlesinger et al. 1998,
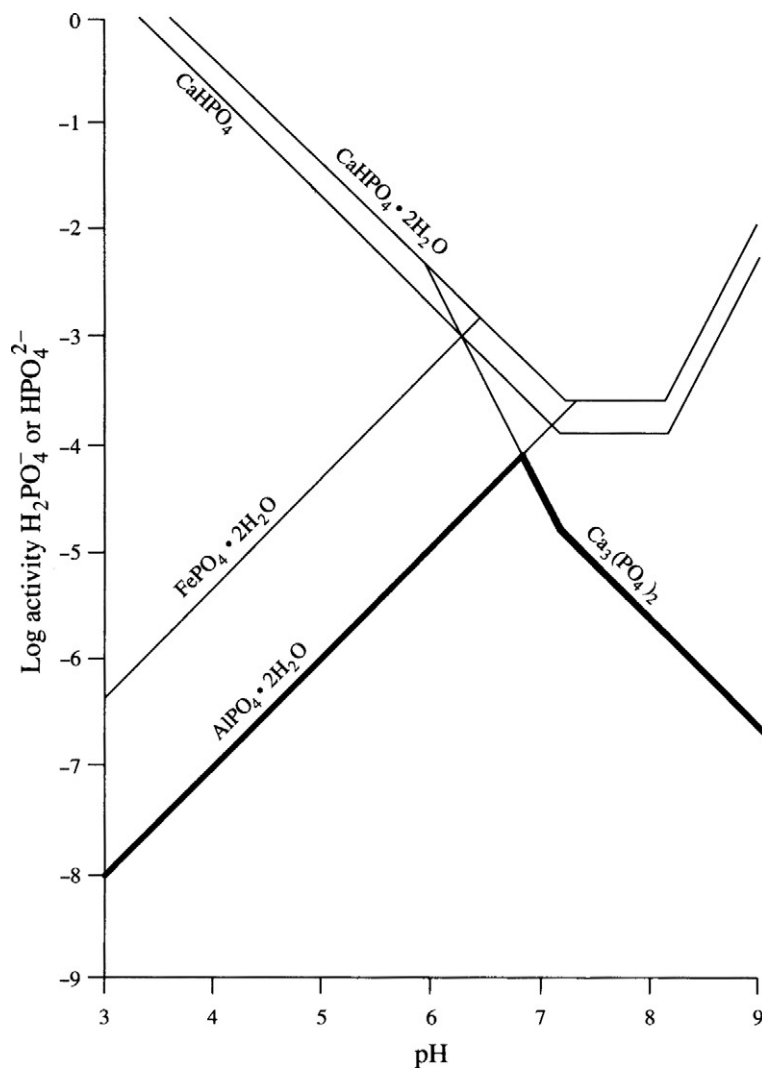
FIGURE 4.10 The solubility of phosphorus in the soil solution as a function of pH. Precipitation with Al sets the upper limit on dissolved phosphate at low pH (bold line); precipitation with Ca sets a similar limit at high pH. Phosphorus is most available at a pH of about 7.0. *Modified from Lindsay and Vlek (1977).*

Filippelli and Souch 1999, Selmants and Hart 2010). Nonoccluded phosphorus includes forms that are held on the surface of soil minerals by a variety of reactions, including anion adsorption. With time, crystalline oxide minerals accumulate, and phosphorus accumulates in occluded forms. At the later stages of weathering and soil development, occluded and organic P dominate the forms of P remaining in the system (Cross and Schlesinger 1995, Crews et al. 1995, Richardson et al. 2004, Yang and Post 2011). At this stage, almost all available phosphorus may be found in organic forms in the upper soil profile, while phosphorus
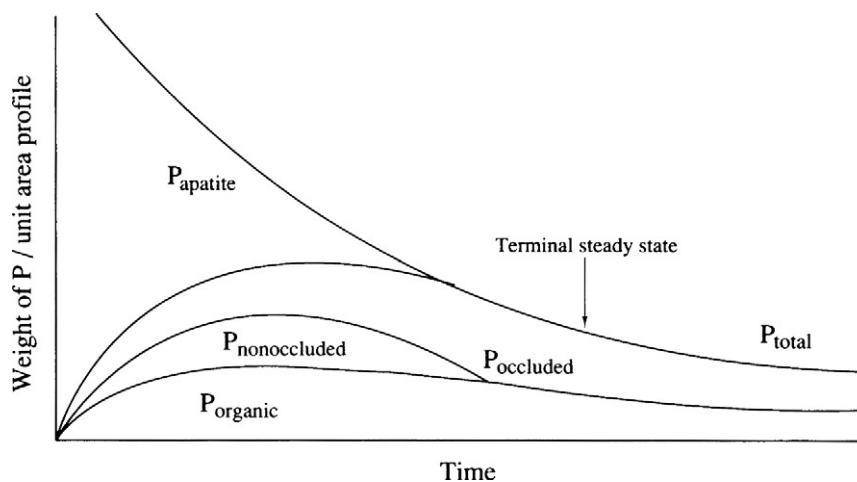
FIGURE 4.11   Changes in the forms of phosphorus found during soil development on sand dunes in New Zealand. *Source: Modified from Walker and Syers (1976).*

found at lower depths is largely bound with secondary minerals (Yanai 1992). Plant growth may depend almost entirely on the release of phosphorus from dead organic matter, defining a biogeochemical cycle of phosphorus in the upper soil horizons (Wood et al. 1984).

As seen for the weathering of silicate minerals, organic acids can influence the release of phosphorus during rock weathering. Jurinak et al. (1986) show how the production of oxalic acid (CH_2O_4) by plant roots can lead to the weathering of P from apatite. Oxalate production is directly related to soil phosphorus availability in sandy soils of Florida (Figure 4.12).
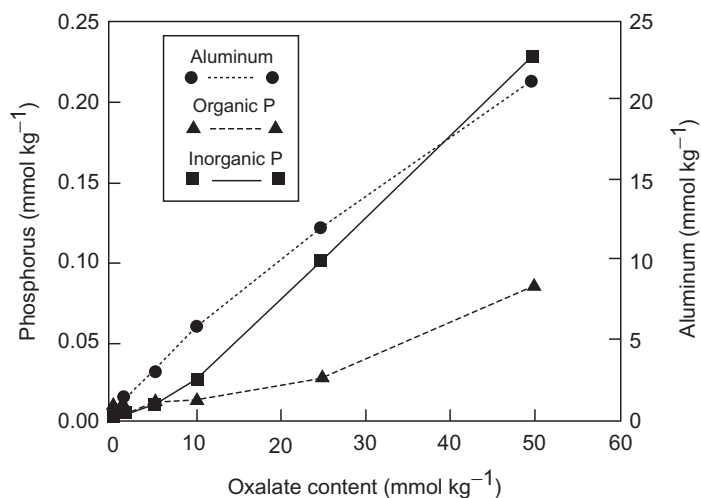
FIGURE 4.12   Release of inorganic P, organic P, and Al from a spodic horizon of a pine forest in Florida, following a single oxalate addition at different levels. *Source: From Fox and Commerford (1992a). Used with permission of American Society of Agronomy.*

Organic acids can inhibit the crystallization of Al and Fe oxides, reducing the rate of phosphorus occlusion (Schwertmann 1966, Kodama and Schnitzer 1977, 1980), and allowing non-crystalline (amorphous) forms to dominate the P-adsorption capacity of the soil (Walbridge et al. 1991, Yuan and Lavkulich 1994).

In addition, phosphorus may be more available in the presence of organic acids, such as oxalate, which remove Fe and Ca from the soil solution by chelation and precipitation (Graustein et al. 1977, Welch et al. 2002, Wang et al. 2008). The production and release of oxalic acid by mycorrhizal fungi (Chapter 6) explains their importance to the phosphorus nutrition of higher plants (Bolan et al. 1984, Cromack et al. 1979) and the greater availability of phosphorus under fungal mats (Fisher 1972, 1977). Some workers believe that the mobilization of phosphorus by symbiotic fungi was a precursor to the successful establishment of plants on land (Chapter 2).

SOIL DEVELOPMENT

Soils usually consist of a number of layers, or horizons, that collectively constitute the complete soil profile, or *pedon*. Rock weathering, water movement, and organic decomposition all influence the development of a soil profile under varying climatic conditions. Indeed, Jenny (1941, 1980) suggested that soil profile development could only be understood in the context of the interactions of climate, biota, topography, parent material, and time. Today, humans are one of the organisms that have dramatic effects on soil development in many regions (Amundson and Jenny 1991, Richter 2007). Recognition of the processes that occur in the different layers of soil is an essential part of understanding biogeochemical cycles on land. Chemical weathering occurs in the upper soil profile as well as in the underlying layers of fractured rock. In this section, we consider soil development in forests, grasslands, and deserts.

Forests

In forests it is often easy to separate an organic layer, the forest floor or "O-horizon," from the underlying layers of mineral soil. The thickness and presence of the forest floor varies throughout the year, especially in regions where plant litterfall is strongly seasonal. In some tropical forests decomposition of fresh litter is so rapid that there is little surface litter (Olson 1963, Vogt et al. 1986). On the other hand, slow decomposition in coniferous forests, especially in the boreal zone, results in the accumulation of a thick forest floor, known as a *mor*, that is sharply differentiated from the underlying soil (Romell 1935). Much of the arctic zone is characterized by waterlogged soils, in which the entire rooting zone is composed of organic materials. Such peatland soils are known as *Histosols*. We will treat the special properties of waterlogged organic soils in Chapter 7.

The upper mineral soil is designated as the A-horizon. Soil water percolating through the forest floor often contains a variety of organic acids derived from the microbial decomposition of litter (Vance and David 1991, Strobel 2001). These organic acids dominate the weathering of soil minerals in the A-horizon. Solutions collected beneath the A-horizon carry cations and

TABLE 4.2   Chemical Composition of Precipitation, Soil Solutions, and Groundwater
in a 175-year-old *Abies amabilis* Stand in Northern Washington

| Solution	pH	Total cations (mEq/liter)	Soluble ions (mg/liter)			Total (mg/liter)	
			Fe	Si	Al	N	P
Precipitation							
Above canopy	5.8	0.03	<0.01	0.09	0.03	0.60	0.01
Below canopy	5.0	0.10	0.02	0.09	0.06	0.40	0.05
Forest floor	4.7	0.14	0.04	3.50	0.79	0.54	0.04
Soil							
15 cm E	4.6	0.12	0.04	3.55	0.50	0.41	0.02
30 cm B_s	5.0	0.08	0.01	3.87	0.27	0.20	0.02
60 cm B3	5.6	0.25	0.02	2.90	0.58	0.37	0.03
Groundwater	6.2	0.26	0.01	4.29	0.02	0.14	0.01

*Source: Data from Ugolini et al. (1977), Soil Science **124**: 291–302. Copyright (1977) Williams and Wilkins.*

silicate, derived from weathering reactions (Table 4.2). Iron and Al are removed from the A-horizon by chelation with fulvic acid and low-molecular-weight (LMW) organic acids that percolate downward from the forest floor (Antweiler and Drever 1983, Driscoll et al. 1985, Zysset et al. 1999, Fuss et al. 2011). The removal of mineral components from the A-horizon is known as *eluviation*, while the downward transport of Fe and Al in conjunction with organic acids is known as *podzolization* (Chesworth and Macias-Vasquez 1985, Lundström et al. 2000a).

Although it occurs throughout the world, podzolization is particularly intense in subarctic (boreal) and cool temperate forests (e.g., Ugolini et al. 1987, De Kimpe and Martel 1976, Langley-Turnbaugh and Bockheim 1998). Many of these areas are characterized by coniferous forests that produce litterfall that is rich in phenolic compounds and organic acids (Cronan and Aiken 1985, Strobel 2001). In these ecosystems, decomposition is slow and incomplete, and large quantities of organic acids are available to percolate from the forest floor into the underlying A-horizon. The pH of the soil solution is often as low as 4.0 (Dethier et al. 1988, Vance and David 1991).

When the removal of Fe, Al, and organic matter is very strong, a whitish layer is easily recognized beneath the forest floor (Figure 4.13). This horizon is sometimes designated as an A_e- or E- (eluvial) horizon, which may consist entirely of quartz grains that are resistant to weathering and relatively insoluble under acid conditions (Pedro et al. 1978). These eluvial horizons reflect the importance of biota in soil development; in the absence of organic chelation, one would expect Fe and Al to accumulate as weathering products and for Si to dominate the losses from the upper soil profile.

During soil development, substances leached from the A- and E-horizons are deposited in the underlying B-horizons (Jersak et al. 1995, Langley-Turnbaugh and Bockheim 1998). These are defined as the zone of deposition or the *illuvial* horizons, where secondary clay minerals
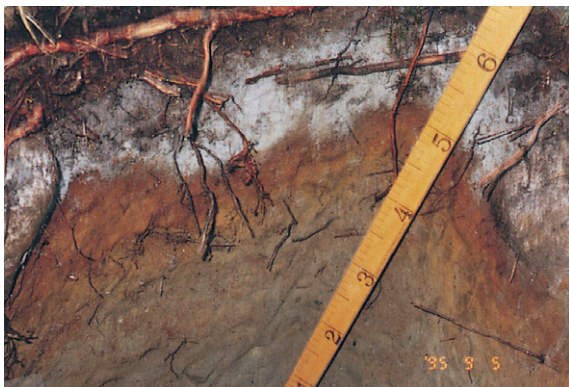
FIGURE 4.13 Soil profile, Nyanget, Svartberget Forest Research Station, north Sweden, showing the E- (whitish) and B-horizons. The scale is in decimeters. The role of biology in the process of podzolization is exemplified by the removal of Al and Fe minerals from the E-horizon in complexes with organic acids and their precipitation as oxides in the B-horizon. *Source: From Lundström et al. (2000b).*

accumulate. Clay minerals arrest the downward movement of dissolved organic compounds that are carrying Fe and Al (Greenland 1971, Chesworth and Macias-Vasquez 1985, Cronan and Aiken 1985, Schulthess and Huang 1991, Jansen et al. 2005). Typically, Fe oxides and hydrous-oxides precipitate first, and Al moves lower in the profile (Adams et al. 1980, Olsson and Melkerud 1989, Law et al. 1991a), but the mechanisms underlying this difference are not entirely clear (Lundström et al. 2000a).

Strongly podzolized soils, *Spodosols*, are characterized by a dark *spodic* horizon-designated B_{hs} that is rich in Fe and organic matter. On fresh parent materials, a spodic horizon can develop in 350 to 1000 years (Singleton and Lavkulich 1987b; Protz et al. 1984, 1988; Barrett and Schaetzl 1992). In New England forests, the accumulation of organic matter in the spodic horizon appears to limit the loss of dissolved organic carbon in streams (McDowell and Wood 1984). Most of the Fe and Al in the B-horizon is found in crystalline oxides (e.g., Fe_2O_3), but near root channels and pockets of buried organic matter, Fe^{3+} may be reduced to Fe^{2+} and leached away (Fimmen et al. 2008, Dubinsky et al. 2010, Fuss et al. 2011). Phosphorus can be mobilized from these areas of the B-horizon, which often appear grayish in the field (Chacon et al. 2006).

In warmer climates, decomposition is more rapid, smaller quantities of fulvic acids remain to percolate through the A-horizon, podzolization is less intense, and there is no sharply defined E-horizon (Pedro et al. 1978). In most areas of the tropics, decomposition is so complete that there is almost no soluble organic acid percolating through the soil profile (Johnson et al. 1977). In the absence of podzolization, Fe and Al are not removed from the upper soil profile by chelation; rather, they are precipitated as oxides and hydroxides that accumulate in the zone of active weathering. Unless they cycle through vegetation, cations and Si are lost to runoff. Podzolization is found in only a few tropical soils, usually those that develop on sandy parent materials (Bravard and Righi 1989).

Soils in tropical forests may be many meters in depth, because in many areas they have developed over millions of years without disturbances such as glaciation (Birkeland 1984). In the absence of clear zones of eluviation and illuviation, the distinction of A- and B-horizons is difficult. Long periods of intense weathering have removed cations and silicon from the entire soil profile. The climate of most tropical regions includes high precipitation, and the solubility of Si increases with increasing temperature (Figure 4.2). Many tropical soils

are classified as *Oxisols*, on the basis of high contents of Fe and Al oxides throughout the soil profile (Richter and Babbar 1991). Over large portions of lowland tropical rainforests, soils are acid (with Al buffering), low in base cations, and infertile with P deficiency (Sanchez et al. 1982b). Under extreme conditions, these soils are known informally as *laterite*.

A comparative index of soil formation and the degree of podzolization is seen in the ratio of Si to sesquioxides (Fe and Al) in the soil profile (Table 4.3). In boreal forest soils, Si is relatively immobile and Fe and Al are removed, which results in high values for this ratio in the A-horizon. The accumulation of secondary minerals such as montmorillonite in the moderately weathered soils of the glaciated portion of the United States yields Si/sesquioxide ratios of two to four as a result of the ratio of Si to Al in the crystal lattice. Silicon/sesquioxide ratios are lower in more highly weathered soils. During soil development in the southeastern United States, low ratios characterize older soils in which kaolinite (a 1:1 mineral) has accumulated as a secondary mineral (Figure 4.14). Tropical Oxisols and Ultisols have very low values for this ratio in all horizons because they are dominated by kaolinite and iron and aluminum minerals.

Below the B-horizons, the C-horizon consists of coarsely fragmented soil material with little organic content. Carbonation weathering tends to predominate in the C-horizon, which may consist of a thick saprolite (Ugolini et al. 1977). Weathering can extend to a depth of hundreds of meters in the soil profile (Richter and Markewitz 1995), and it controls the chemistry of groundwater. For a rainforest in Puerto Rico, nearly all of the Al was released by weathering in the upper soil profile, but 50% of the Si in stream water was derived from weathering in the C-horizon (Riebe et al. 2003). When the soil has developed from local materials, the C-horizon shows mineralogical similarity to the underlying parent rock. In contrast, when the parent materials have been deposited by transport, there may be little correspondence between the C-horizon and the underlying bedrock. Some of the world's richest agricultural soils are found on transported materials, such as glacial till, floodplain deposits, and volcanic ash.

The distribution of soils forms a continuous gradient over broad geographic regions. For example, the degree of podzolization varies beneath deciduous and coniferous forests in the same geographic region (Stanley and Ciolkosz 1981, De Kimpe and Martel 1976). Soil profile

TABLE 4.3 Silicon/Sesquioxide ($Al_2O_3 + Fe_2O_3$) Ratios for the A- and B-Horizons of Some Soils in Different Climatic Regions

Region	Number of sites	Mean Si/sesquioxide ratio		References
		A-horizon	B-horizon	
Boreal	1	12.0	8.1	Wright et al. (1959)
Boreal	1	9.3	6.7	Leahey (1947)
Cool-temperate	4	4.07	2.28	Mackney (1961)
Warm-temperate	6	3.77	3.15	Tan and Troth (1982)
Tropical	5	1.47	1.61	Tan and Troth (1982)

Note that the removal of Al and Fe results in high values in boreal and cool temperate soils, especially in the A-horizon. Lower values characterize tropical soils, where there is little differentiation between horizons as a result of the removal of Si from the entire profile in long periods of weathering.
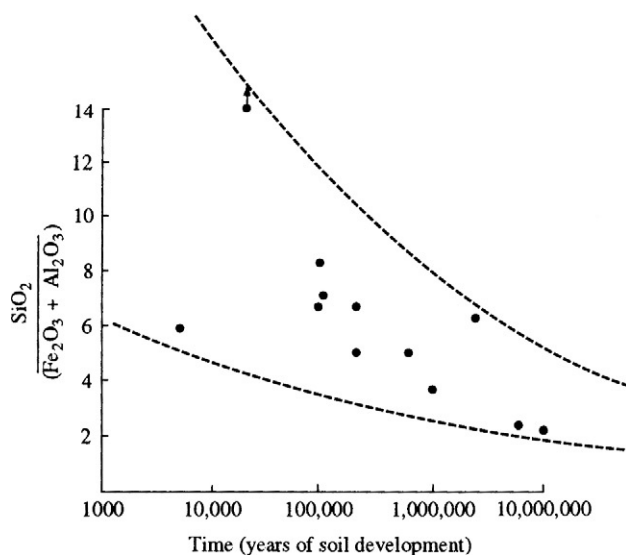
FIGURE 4.14 Changes in Si-to-sesquioxide ratio during the long-term development of soils in the southeastern United States (Markewitz and Pavich 1991). The data are recalculated from Markewitz et al. (1989)

development on steep slopes is often incomplete as a result of landslides and other mechanical weathering events. Soils in floodplain areas and those that have received deposits of volcanic ash may have "buried" horizons (Dahlgren et al. 1999). In areas of recent disturbance, soils with little or no profile development are known as *Inceptisols* and *Entisols*, respectively. In all cases one must remember that soil profile development is slow compared to changes in vegetation.

Soil profile development is also affected by human activities. In the Piedmont region of the southeastern United States, the forest floor often resides directly on top of the B-horizon. Here, the A-horizon was lost by erosion during past agricultural use. In the northeastern United States, forest Spodosols are now exposed to acid rain. At high elevations, the acidity of the solution percolating through the forest floor and A-horizon is not dominated by organic or carbonic acids, but by "strong" acids such as H_2SO_4 (see Chapter 13). At normal levels of acidity, aluminum is mobile only as an organic chelate, and it is precipitated in the B-horizon. Under the present conditions of higher acidity, Al is mobile as Al^{3+}, a potentially toxic form that is carried through the lower profile to stream waters, with SO_4^{2-} as a balancing anion (Figure 4.7; Johnson et al. 1972, Cronan 1980, Reuss et al. 1987). The overall rate of chemical weathering has increased (Cronan 1980, April et al. 1986). Fortunately, with the implementation of the Clean Air Act in the early 1990s, the deposition of acidity and SO_4^{2-} and the stream water losses of Al^{3+} are beginning to decline (Palmer and Driscoll 2002, Clow and Mast 2002, Likens et al. 2002).

Grasslands

In contrast to soil development in forests, where precipitation greatly exceeds evapotranspiration and excess water is available for soil leaching and runoff, soil development in grasslands proceeds under conditions of relative drought. The products of chemical weathering
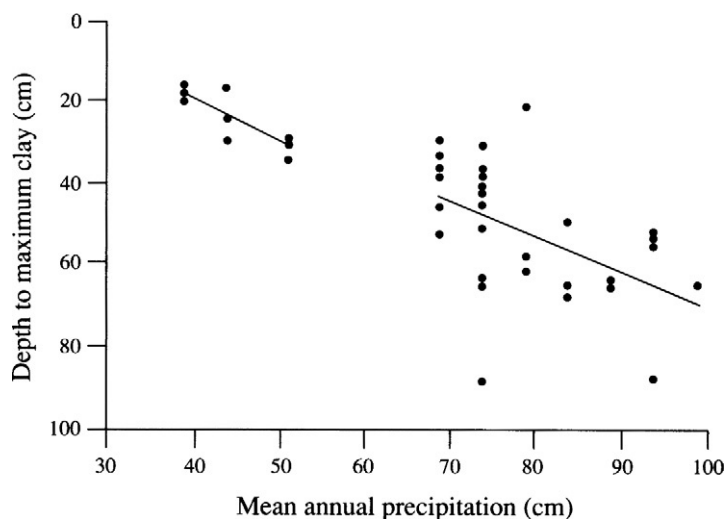
FIGURE 4.15   Depth-to-peak content of clay in the soil profile, an index of weathering and soil development, decreases from east to west across the Great Plains of the United States as a function of the decrease in mean annual precipitation. *Source: From Honeycutt et al. (1990). Used with permission of American Society of Agronomy.*

are not rapidly leached from the soil profile, so soils remain near neutral pH with high base saturation. High contents of Ca and other cations tend to flocculate[2] clay minerals and fulvic acids in the upper profile (Oades 1988), limiting podzolization and the downward movement of weathering products. Often there is little development of a clay-rich or B_t-horizon in grassland soils until the upper profile has been leached free of Ca. Overall, the intensity of chemical weathering and podzolization in grassland soils is much less than in forests (Madsen and Nornberg 1995).

Trends in the development of grassland soils are best seen by examining a transect across the midportion of the United States. Mean annual precipitation decreases westward from the tallgrass prairie near the Mississippi River valley to the shortgrass prairie at the base of the Rocky Mountains. Honeycutt et al. (1990) show that the thickness of the soil profile—measured by the depth to the peak content of clay—decreases from east to west along this gradient (Figure 4.15). Along the same gradient, base saturation, pH, and the content of calcium increase (Ruhe 1984, Gunal and Ransom 2006). Similar trends are seen along a gradient of decreasing precipitation in tropical grasslands of eastern Africa (Scott 1962). In the western Great Plains, the leaching of the soil profile is so limited that Ca precipitates as $CaCO_3$, which accumulates in the lower profile in calcic horizons, designated B_k and informally known as *caliche*.

The climatic regime of grasslands results in lower levels of plant growth than in forests, and smaller quantities of plant residues are added to the soil each year. Nevertheless, grassland soils contain large stores of organic matter because the limited availability of water also results in slower rates of decomposition (Chapter 5). Most grassland soils in the temperate zone are classified as *Mollisols*, on the basis of a high content of organic carbon and high base saturation in the surface layers.

[2] Flocculation occurs when materials that are moving in water as colloids form insoluble aggregates, usually by the neutralization of hydrophyllic surface charges.

As seen for forest ecosystems, soil properties in grasslands vary locally as a result of differences in underlying parent materials and hillslope positions. Schimel et al. (1985) showed how the downslope movement of materials results in thin soils on hillslopes and accumulations of organic matter and nitrogen in local depressions. Similarly, Aguilar and Heil (1988) found that grassland soils derived from sandstone have lower contents of organic carbon, nitrogen, and total P than soils derived from fine-textured materials, such as shale, which have a higher content of clay minerals. The proportion of P contained in organic forms is greater for soils derived from sandstone. These differences in soil properties can strongly affect the local productivity of grasslands.

Deserts

The trends in soil development that are seen with increasing aridity in grasslands reach their extreme expression in deserts. Desert soils often contain clay minerals and horizons of clay accumulations derived from eolian dust, giving the appearance that substantial weathering has occurred (Singer 1989, Reheis and Kihl 1995). In fact, soil development in deserts occurs slowly because of limited weathering and leaching of the soil profile. In the face of limited weathering and runoff, many desert soils show a net gain of materials from atmospheric deposition (Ewing et al. 2006, Michalski et al. 2004a, Schlesinger et al. 2000).

Despite the limited chemical weathering in deserts, the small amount of water percolating through these soils transports substances both vertically in the profile and horizontally across the landscape. As water is removed by plant uptake, soluble substances precipitate. Typically, well-developed desert soils contain $CaCO_3$ horizons that show progressive development and cementation through time (Gile et al. 1966). When desert soils contain distinct horizons, they are classified as *Aridisols* (Dregne 1976).

Because $CaCO_3$ precipitates in desert soils in equilibrium with CO_2 derived from plant root respiration,

$$2CO_2 + 2H_2O \rightarrow 2H^+ + 2HCO_3^- \tag{4.14}$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + H_2O + CO_2, \tag{4.15}$$
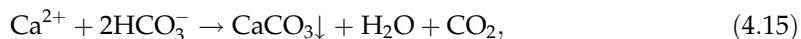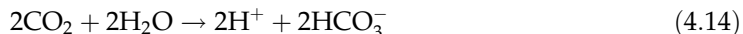
the carbonate carries a carbon isotopic signature that can be traced to photosynthesis (Chapter 5) and used as an index of past climate and vegetation (Quade et al. 1989a). Seasonal variations in the activity of plant roots (Schlesinger 1985) and soil microbes (Monger et al. 1991) affect $CaCO_3$ deposition and other aspects of soil development in deserts, despite the outward appearance that abiotic processes should be dominant. For instance, beneath desert shrubs, the deposition of $CaCO_3$ is inhibited by the presence of dissolved organic materials in the soil solution (Inskeep and Bloom 1986, Reddy et al. 1990, Suarez et al. 1992), and calcic horizons are found deeper in the soil profile.

Depth to the $CaCO_3$ horizon in deserts shows a direct relation to mean annual rainfall and wetting of the soil profile (Arkley 1963). Beneath the $CaCO_3$, one may find horizons in which $CaSO_4 \cdot 2H_2O$ (gypsum) or NaCl are dominant, reflecting the greater solubility and downward movement of these salts (Yaalon 1965, Marion et al. 2008). Similar patterns are seen across the landscape, where Na, Cl, and SO_4 are carried to intermittent lakes in basin lows,

while Ca remains in the upland soils of the adjacent piedmont (Drever and Smith 1978, Eghbal et al. 1989, Amundson et al. 1989a).

Despite sparse plant cover, much of the nutrient cycling in desert ecosystems is controlled by biota. With widespread root systems, desert shrubs accumulate nutrients from a large area and concentrate dead organic matter in the local area beneath their canopy. Most of the annual turnover of N, P, and other elements is controlled by biogeochemical processes in these "islands of fertility" (Schlesinger et al. 1996, Titus et al. 2002).

Models of Soil Development

The processes underlying soil profile development are conducive to simulation modeling. Models of soil chemistry include the weathering reactions described earlier in this chapter and equilibrium constants for the exchange of cations and anions between the soil solution and the mineral phases (Furrer et al. 1989). Depending on the time scale of the simulation, a model of soil chemistry usually routes daily or annual precipitation sequentially through the soil profile, where the solution achieves an equilibrium with the soil minerals in each horizon. Removal of water from the soil profile is calculated from estimates of evaporation from the soil surface, plant uptake, and runoff to streams. Simulation models of soil processes have been constructed to predict soil profile development and to calculate losses of dissolved constituents in forested regions subject to acid rain (Reuss 1980; Cosby et al. 1985, 1986; David et al. 1988).

The long-term development of soils in arid regions is simulated in a model, CALDEP, developed by Marion et al. (1985), in which daily precipitation achieves equilibrium with carbonate biogeochemistry as it percolates through the soil profile. Plant root respiration is explicitly included in the calculation, and it varies seasonally and with depth in the profile. Plants also control the loss of water from the soil surface by evapotranspiration. The model suggests that the $CaCO_3$ horizon will be deeper in a soil profile developed from coarse-textured parent materials, which allow greater percolation of water, and when plant root respiration varies seasonally, showing high values of soil CO_2 during the growing season.

Using current climatic conditions to parameterize precipitation and evaporation, the model was run to simulate 500 years of soil profile development (Figure 4.16). The model predicted mean depths to the $CaCO_3$ that were much shallower than observed in a sample of 16 desert soils from Arizona. When the model was reparameterized using the cool, wet conditions that are thought to have been widespread in this region during the latest Pleistocene glaciation, the predicted depth of $CaCO_3$ closely matched that found in the field.

These conditions produced greater percolation of soil moisture and lower rates of evaporation from the soil surface. Such models are only as good as the data used in the simulations, and rarely can models establish the importance of processes unequivocally. Nevertheless, models are useful for hypothesis development and for organizing research priorities. CALDEP suggests that most $CaCO_3$ horizons were formed during the Pleistocene, when deserts received more precipitation than today—consistent with the age of many desert soil carbonates (Schlesinger 1985). In the southwestern United States, most calcic horizons are >10,000 years old, and the $CaCO_3$ has accumulated at rates of 1.0 to 5.0 g m^{-2} yr^{-1} from the downward transport of Ca-rich minerals deposited from the atmosphere (Schlesinger 1985, Capo and Chadwick 1999, Van der Hoven and Quade 2002).
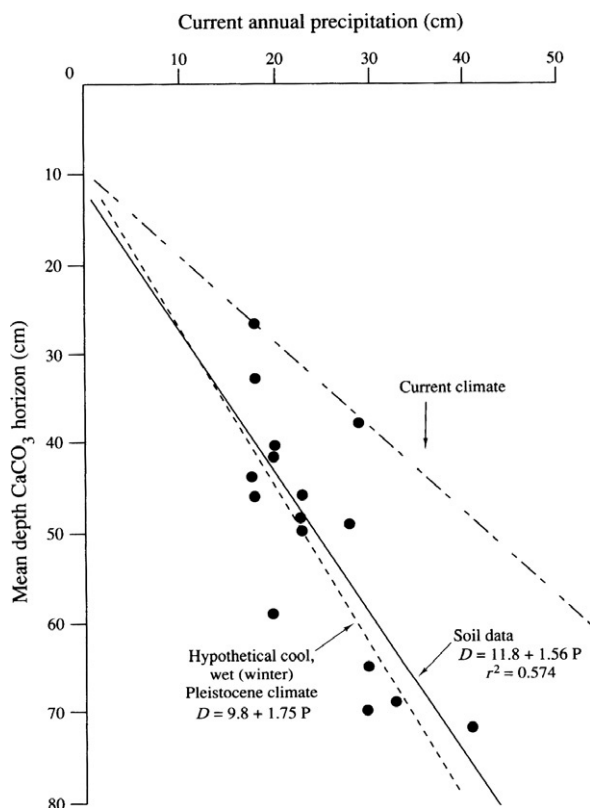
FIGURE 4.16 Depth to $CaCO_3$ in desert soils of Arizona, as a function of mean annual precipitation. The dashed line shows the prediction from the CALDEP model using current precipitation regimes. The solid line shows the best fit to actual data reported from the field. The dotted line shows the predictions when the model is run with postulated climatic data from the latest Pleistocene pluvial period. *Source: Modified from Marion et al. (1985).*

Labels in figure:
- Current annual precipitation (cm)
- Mean depth $CaCO_3$ horizon (cm)
- Current climate
- Soil data $D = 11.8 + 1.56\ P$ $r^2 = 0.574$
- Hypothetical cool, wet (winter) Pleistocene climate $D = 9.8 + 1.75\ P$

WEATHERING RATES

Rock weathering and soil development are difficult to study because the processes occur slowly and the soil profile is nearly impossible to sample without disturbing many of the chemical reactions of interest. Nevertheless, estimates of weathering are needed to understand the biogeochemistry of local watersheds, where essential elements for biota are derived from the underlying rock (Chapter 6). Often we must infer weathering rates from what remains in the soil profile and what is lost to stream water. Estimates of the dissolved and suspended load of rivers allow us to calculate a global rate of chemical weathering, which supplies nutrient elements to land and marine biota.

Chemical Weathering Rates

Variations in the concentration of dissolved ions in streams can be related to the rate of discharge, the origin of their waters, and chemical weathering (Johnson et al. 1969, Maher 2011). In a simple geochemical system, we might expect that stream water concentrations would be highest at periods of low flow, because most of the water would be derived from drainage of the soil profile where it would be in equilibrium with various rock weathering

and ion-exchange reactions. As stream flow increases, we might expect concentrations to de-cline as an increasing proportion of the flow is derived from precipitation and surface runoff, with little or no equilibration with the soil mineral phases. This simple geochemical model often explains the behavior of major ions in stream water (Ca, Mg, Na, Si, Cl, SO_4, and HCO_3), which are readily soluble in water and available in excess of biotic demand (Meyer et al. 1988).

During rainfall or seasonal flooding, the concentrations of dissolved ions in stream waters are often higher as the waters are rising than during the equivalent flows during the receding period (Whitfield and Schreier 1981, McDiffett et al. 1989). The effect, known as *hysteresis*, is thought to result from an initial flushing of the highly concentrated waters that accumulate in the soil pores during periods of low flow. Not all ions show consistent hysteresis patterns, so to calculate the total annual loss of dissolved ions from a watershed, the stream flow discharge for each day must be multiplied by the concentration measured at that discharge and the products summed for all 365 days.

Even for elements that show lower concentrations at greater discharge, the total removal from the landscape is greatest during years of high stream flow (Figure 4.17)—that is, the in-crease in flow predominates over the expected dilution of dissolved materials. In compari-sons made over large geographic regions, concentrations are greatest in rivers that drain areas with limited runoff, but total transport is greater in rivers with greater discharge (e.g., Figure 4.18; Bluth and Kump 1994, Gaillardet et al. 1999).

Jennings (1983) shows a dilution of Ca and Mg with increasing discharge in areas of lime-stone in New Zealand, but the slope of the relationship changes slightly from summer to win-ter, reflecting a greater weathering of limestone by the more active respiration of roots during the summer (see also, Laudelout and Robert 1994). Plants also exert control on stream water chemistry by the uptake of essential nutrient elements. In most areas, the concentrations of plant-essential nutrients, such as potassium and nitrate, show little relation to stream water
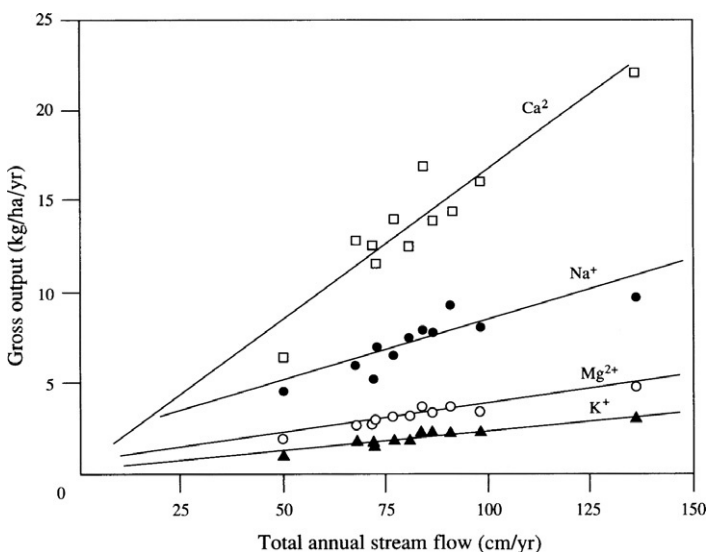
FIGURE 4.17   Annual stream water loss of major cations as a function of the stream discharge in different years in the Hubbard Brook Experimental For-est in New Hampshire. *Source: From Likens and Bormann 1995a).*
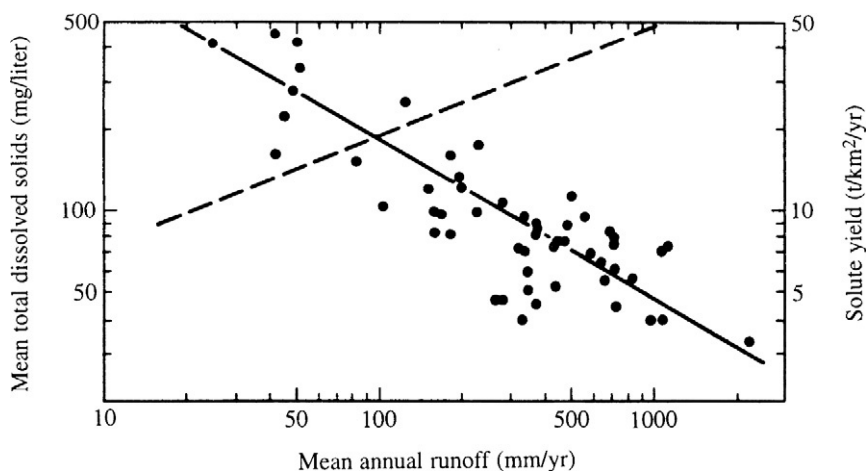
FIGURE 4.18   Variation in the concentration of total dissolved solids (*solid line*) and the total annual transport of dissolved substances (*dashed line*, shown without data) for various streams in Kenya as a function of mean annual runoff. *Source: From Dunne and Leopold (1978). Used with permission of Springer-Verlag.*

discharge because they are regulated by microbial activity and root uptake (Lewis and Grant 1979, Feller and Kimmins 1979, McDowell and Asbury 1994). In a deciduous forest in New Hampshire, the lowest potassium and nitrate concentrations in stream water are found during the low-flow periods of summer, when biotic demands are greatest (Johnson et al. 1969, Likens et al. 1994).

Plant uptake of essential elements and the retention of cations on soil minerals complicate the use of stream water concentrations to calculate the rate of chemical weathering over short periods of time (Taylor and Velbel 1991, Gardner 1990). However the eventual loss of cations to riverflow explains the decline in base saturation and pH during soil development (Bockheim 1980). Losses of dissolved constituents from terrestrial ecosystems represent the products of chemical weathering and constitute *chemical denudation* of the landscape.

One of the best-known attempts to calculate the rate of chemical weathering began in 1963, when Gene Likens, Herbert Bormann, and Noye Johnson quantified the chemical budgets for the Hubbard Brook forest in New Hampshire (Likens and Bormann 1995a). Here, a number of comparable watersheds are underlain by impermeable bedrock with no apparent subsurface drainage to groundwater. These workers reasoned that if the atmospheric inputs of chemical elements are subtracted from the stream water losses, the difference should reflect the annual release from rock weathering. They estimated the rate of rock weathering using the equation

$$\text{Weathering} = \frac{(\text{Ca lost in stream water}) - (\text{Ca received in precipitation})}{(\text{Ca in parent material}) - (\text{Ca in residual material in soil})} \qquad (4.16)$$

The solution of this equation shows rather different amounts of weathering when the calculations are performed using other rock-forming elements (Table 4.4). The observed losses of calcium and sodium in stream water imply higher rates of weathering than what is calculated using potassium and magnesium in the same equation. Johnson et al. (1968) suggest that the latter elements are accumulating in secondary minerals (illite and vermiculite) in the soil.

TABLE 4.4   Calculation of the Rate of Primary Mineral Weathering, Using the Stream Water Losses and Mineral Concentrations of Cationic Elements

Element	Annual net loss (kg ha^{-1} yr^{-1})	Concentration in rock (kg/kg of rock)	Concentration in soil (kg/kg of soil)	Calculated rock weathering (kg ha^{-1} yr^{-1})
Ca	8.0	0.014	0.004	800
Na	4.6	0.016	0.010	770
K	0.1	0.029	0.024	20
Mg	1.8	0.011	0.001	180

Source: Data from Johnson et al. (1968).

In addition, trees may take up and store essential elements in long-lived tissues (e.g., wood growth), temporarily reducing the loss of some elements in stream water (Taylor and Velbel 1991; see also Chapter 6).

In calculating weathering rates, it is often useful to examine the watershed budgets for Cl and Si. In nearly all cases, the atmospheric inputs of Si are trivial, so Si in stream water is an index of net chemical weathering, which is its only source (e.g., Figure 4.2). In contrast, the Cl content of rocks is normally very low. Nearly all Cl$^-$ in stream water is derived from the atmosphere, passing through the system relatively unimpeded by biotic activity or geochemical reactions (but see Lovett et al. 2005, Oberg et al. 2005). A balanced budget for Cl is often indicative of an accurate hydrologic budget for the watershed (Juang and Johnson 1967, Svensson et al. 2012).

Release from rock weathering is the dominant source of Ca, Mg, K, Fe, and P in stream waters draining the Hubbard Brook Experimental Forest, whereas deposition from the atmosphere is the dominant input for Cl, S, and N, which have a small content in rocks (Table 4.5).

TABLE 4.5   Inputs and Outputs of Elements from Hubbard Brook Experimental Forest

	Inputs (%)		Output as percent of input
	Atmosphere	Weathering	
Ca	9	91	59
Mg	15	85	78
K	11	89	24
Fe	0	100	25
P	1	99	1
S	96	4	90
N	100	0	19
Na	22	78	98
Cl	100	0	74

Source: Data from Likens et al. (1981).

In forests not subject to regional inputs of acid rain, the proportion of sulfur that is derived from the atmosphere is often somewhat lower than that at Hubbard Brook (e.g., Mitchell et al. 1986). A large number of watershed studies have been conducted, allowing similar calculations of weathering rates for a variety of ecosystems (Table 4.6; Likens and Bormann 1995b, Henderson et al. 1978, Feller and Kimmins 1979, Velbel 1992).

A relative index of chemical weathering is calculated by summing the annual losses of various elements in stream water. In comparisons of ecosystems of the world, chemical denudation is found to increase with increasing runoff (Figure 4.2). Total dissolved transport ranges from 47.6 to 372.7 kg ha^{-1} yr^{-1} among the watersheds in Table 4.6, and Alexander (1988) found that chemical denudation ranged from 20 to 200 kg ha^{-1} yr^{-1} among 18 undisturbed ecosystems in a variety of climatic regimes. Often there is much regional variability in calculated weathering rates (Nezat et al. 2004, Schaller et al. 2010), but globally, rivers transport about 4×10^{15} g of dissolved substances to the oceans each year—an average of about 267 kg ha^{-1} yr^{-1} for the Earth's land surface (refer to Table 4.8 later in chapter).

In most areas underlain by silicate rocks, the loss of elements in stream water relative to their concentration in bedrock follows the order

$$Ca > Na > Mg > K > Si > Fe > Al, \tag{4.17}$$

but the order is affected by the specific composition of bedrock and the secondary minerals that are formed in the soil profile (Holland 1978, Harden 1988, Hudson 1995). This general order reflects the tendency for Ca- and Na-silicates to weather easily and for the

TABLE 4.6 Net Transport (export minus atmospheric deposition) of Major Ions, Soluble Silica, and Suspended Solids from Various Watersheds of Forested Ecosystems

Watershed characteristics	Caura River, Venezuela	Gambia River, West Africa	Catoctin Mtns., Maryland	Hubbard Brook, New Hampshire
Size (km^2)	47,500	42,000	5.5	2
Precipitation (cm)	450	94	112	130
Vegetation	Tropical	Savanna	Temperate	Temperate
Net dissolved transport (kg ha^{-1} yr^{-1})				
Na	19.4	3.9	7.3	5.9
K	13.6	1.4	14.1	1.5
Ca	14.2	4.0	11.9	11.7
Mg	5.7	2.0	15.6	2.7
HCO$_3^-$	124.0	20.3	78.1	7.7
Cl$^-$	−1.4	0.6	16.6	−1.6
SO$_4^{2-}$	1.5	0.4	21.2	14.8
SiO$_2$	195.7	15.0	56.1	37.7
Total transport (kg ha^{-1} yr^{-1})	372.7	47.6	220.9	80.4

Source: Modified from Lewis et al. (1987). Used with permission of Springer.

limited incorporation of Ca and Na in secondary minerals. The composition of individual streams may differ strongly from these patterns depending on local conditions. For instance, streams draining areas of carbonate terrain are dominated by Ca and HCO_3 (e.g., Laudelout and Robert 1994), and stream waters may contain high concentrations of Na, Cl, and SO_4 where evaporite minerals are exposed (e.g., Stallard and Edmond 1983). In most cases, Fe and Al are retained in the lower soil profile as oxides and hydroxides, which are essentially immobile (Chesworth et al. 1981, Olsson and Melkerud 2000, Lichter 1998).

Because temperate forest soils are dominated by clay minerals with permanent negative charge, the loss of cations is determined by the availability of anions that "carry" cations through the soil profile to stream waters (Gorham et al. 1979, Johnson and Cole 1980, Terman 1977, Christ et al. 1999). In most cases, the dominant anion in soil water is bicarbonate (HCO_3^-); thus, the activities of plant roots and soil biota control chemical weathering and the composition of stream water. The high stream water concentration of HCO_3^- in the rainforest of Venezuela (Table 4.6) reflects the importance of carbonation weathering in tropical ecosystems (refer to Figures 4.3 and 4.4). The total mobilization of cations and silicon in the Venezuelan study is also high, consistent with our expectations of rapid chemical weathering in tropical climates (Figure 4.2). In Chapter 6, we will see how an increase in the availability of NO_3^-—a mobile anion—increases the loss of cations following disturbances, such as forest cutting (Figure 6.12).

In both the northeastern United States and much of Europe, losses of base cations appear to have increased in recent years because of the large amounts of H^+ and SO_4^{2-} delivered to the soil by acid rain (Tamm and Hällbäcken 1986, Sjöström and Qvarfort 1992, Wright et al. 1994, Fernandez et al. 2003, Lapenis et al. 2004, Blake et al. 1999, Warby et al. 2009). Some of the cations are lost from the cation exchange capacity, while others are derived from increased rates of chemical weathering under the influence of strong acids (Miller et al. 1993, Likens et al. 1996). The cations move through the soil to stream water, with SO_4^{2-} acting as a balancing anion. In contrast, in the more highly weathered soils of the southeastern United States, increased losses of cations from acid rain have been less dramatic because the soils in this region have greater anion adsorption capacity, so SO_4^{2-} is retained on soil minerals and cannot act as a mobile anion (Reuss and Johnson 1986, Harrison et al. 1989, Cronan et al. 1990). As a historical index of anion adsorption in Tennessee, Johnson et al. (1981a) found a lower content of SO_4^{2-} in the soils beneath a house built in 1890 (67 mg/kg) compared to that in adjacent field soils (195 mg/kg) that have been exposed to acid rain throughout the twentieth century.

In soils of the humid tropics, dominated by variable-charge minerals, one might expect that the abundance of mobile *cations* might determine the loss of anions from adsorption sites. Indeed, the loss of nitrate is retarded as water passes through experimental columns of tropical and volcanic soils (Wong et al. 1990, Bellini et al. 1996, Maeda et al. 2008, Strahm and Harrison 2006), and the loss of NO_3^- from forests in Costa Rica is reduced by a high soil anion adsorption capacity (Matson et al. 1987, Reynolds-Vargas et al. 1994, Ryan et al. 2001). In many cases, the adsorption of SO_4^{2-} in tropical soils reduces its importance as a mobile anion in the stream waters and groundwaters draining these regions (Szikszay et al. 1990; Table 4.6).

The organic compounds in river water, especially the fulvic acids, are important in the dissolved transport of Fe and Al. Because, these metals form complexes with organic acids, they are carried at concentrations well in excess of the solubility of Fe and Al hydroxides in river water (Perdue et al. 1976). The importance of dissolved organic acids in the transport of metals to the sea is a good example of the influence of terrestrial biota over simple geochemical processes that might otherwise determine the movement of materials on the surface of the Earth.

The composition of "average" river water was calculated by Livingstone (1963a) from measurements on a large number of rivers (Table 4.7; see also Table 9.1). Livingstone's estimate of total dissolved transport, 3.76×10^{15} g/yr, is largely confirmed by more recent work (e.g., Meybeck 1979; see also Table 4.8). Nearly all the Ca, Mg, and K in river water is derived from rock weathering (Table 4.9). Weathering of carbonates is the dominant source for Ca, while silicates are the dominant source for Mg and K (Holland 1978). Primary minerals in igneous rocks account for 30% of the dissolved constituents from chemical weathering delivered to the ocean—slightly less than the proportional exposure of igneous rocks at the Earth's surface (Durr et al. 2005). The chemical weathering of sedimentary rocks, especially carbonates, accounts for the remainder (Li 1972, Blatt and Jones 1975, Suchet et al. 2003).

Not all of the constituents in rivers are derived from rock weathering. Reflecting the importance of carbonation weathering, about two-thirds of the HCO_3^- in rivers is derived from the atmosphere, either directly from CO_2 or indirectly via organic decomposition and root respiration that contribute CO_2 to the soil profile (Holland 1978, Meybeck 1987, Moosdorf et al. 2011). Because chemical weathering involves the reaction between atmospheric constituents and rock minerals, weathering of 100 kg of igneous rock results in 113 kg of sediments that are deposited in the ocean and about 2.5 kg of salts that are added to seawater (Li 1972). Thus, a significant fraction of the transport of total dissolved substances in rivers is derived from the atmosphere and does not represent true chemical denudation of the continents (Berner and Berner 1987).

TABLE 4.7   Mean Composition of Dissolved Ions in River Waters of the World

Continent	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe	SiO_2	Sum
North America	68	20	8	1	21	5	9	1.4	0.16	9	142
South America	31	4.8	4.9	0.7	7.2	1.5	4	2	1.4	11.9	69
Europe	95	24	6.9	3.7	31.1	5.6	5.4	1.7	0.8	7.5	182
Asia	79	8.4	8.7	0.7	18.4	5.6	9.3		0.01	11.7	142
Africa	43	13.5	12.1	0.8	12.5	3.8	11		1.3	23.2	121
Australia	31.6	2.6	10	0.05	3.9	2.7	2.9	1.4	0.3	3.9	59
World	58.4	11.2	7.8	1	15	4.1	6.3	2.3	0.67	13.1	120
Anions[a]	0.958	0.233	0.220	0.017							1.428
Cations[a]					0.750	0.342	0.274	0.059			1.425

[a] Millequivalents of strongly ionized components.
Source: Livingstone (1963b); concentrations in mg/liter.

TABLE 4.8   Chemical and Mechanical Denudation of the Continents

Continent	Chemical denudation[a]		Mechanical denudation[b]		Ratio mechanical/ chemical
	Total (10^{14} g/yr)	Per unit area (kg ha^{-1} yr^{-1})	Total (10^{14} g/yr)	Per unit area (kg ha^{-1} yr^{-1})	
N. America	7.0	330	14.6	840	2.1
S. America	5.5	280	17.9	1000	3.3
Asia	14.9	320	94.3	3040	6.3
Africa	7.1	240	5.3	350	0.7
Europe	4.6	420	2.3	500	0.5
Australia	0.2	20	0.6	280	3.0
Total	39.3	267	135.0	918	3.4

[a] Source: From Garrels and MacKenzie (1971).
[b] Source: From Milliman and Meade (1982).

TABLE 4.9   Sources of Major Elements in World River Waters (in percent of actual concentrations)

Element	Atmospheric cyclic salt	Weathering			Pollution
		Carbonates	Silicates	Evaporites	
Ca^{2+}	0.1	65	18	8	9
HCO_3^-	$\ll 1$	61	37	0	2
Na^+	8	0	22	42	28
Cl^-	13	0	0	57	30
SO_4^{2-a}	2	0	0	22	43
Mg^{2+}	2	36	54	$\ll 1$	8
K^+	1	0	87	5	7
H_4SiO_4	$\ll 1$	0	99+	0	0

[a] SO_4^{2-} is also derived from the weathering of pyrite.
Source: From Berner and Berner (1987). Used with permission of Prentice Hall.

A significant fraction of the Na, Cl, and SO$_4$ in riverflow is also derived from the atmosphere—from marine aerosols ("cyclic salts"; Chapter 3) that are deposited on land,[3] but at least some Na is also derived from weathering, since its content in river water is in excess of the molar equivalent of Cl, which would be expected if seasalt were the sole source.

[3] The amount of Cl in rivers that is derived from the atmosphere is the subject of some controversy (Berner and Berner 1987). Some budgets (e.g., Table 4.9) suggest that only a small amount of Cl is "cyclic," based on the observations by Stallard and Edmond (1981, 1983) in the Amazon Basin. Other workers have assumed that a larger fraction of the Cl in global riverflow is derived from the sea, with values ranging from 85% (Dobrovolsky 1994, p. 83) to nearly 100% (Möller 1990; compare Figure 3.16).

The river transport of some dissolved ions has been increased by human activities, such as mining, which accelerate the natural rate of crustal exposure and rock weathering on Earth (Bertine and Goldberg 1971, Martin and Meybeck 1979). And the widespread use of roadsalt as a de-icer has dramatically increased the concentration of Cl in runoff waters (Kaushal et al. 2005). Humans have enhanced the atmospheric deposition of NO_3 and SO_4, accounting for the relatively high concentrations of these ions in the runoff from industrialized continents (refer to Tables 4.7 and 4.9). The flux of HCO_3^- in the Mississippi River appears to have increased significantly during the past century as a result of a variety of human activities such as agricultural liming and rising CO_2 in Earth's atmosphere (Raymond et al. 2008).

Gibbs (1970) used the concentrations of ions in major world rivers to examine the origins of the dissolved constituents in their waters. Rivers dominated by precipitation show low concentrations of dissolved substances, and a high ratio of Cl to the total of $Cl + HCO_3^-$, reflecting the importance of Cl from rainfall (Zone A in Figure 4.19). Rivers in which the dissolved load is largely derived from chemical weathering show higher concentrations of dissolved substances, and HCO_3^- is the dominant anion (Zone B), reflecting the importance of carbonation weathering in most soils. Rivers that pass through arid regions lose a significant amount of water to evaporation before reaching the ocean. These rivers (Zone C) show the greatest concentrations of dissolved ions and high ratios of $Cl/(Cl + HCO_3^-)$, because HCO_3^- has been removed by the chemical precipitation of minerals such as $CaCO_3$ on the streambed (Holland 1978). In this scheme, seawater represents the endpoint of the evaporative concentration of river waters. These relationships are also seen when Na and Ca are used to scale the x axis in Figure 4.19, with the relative concentration of Na as an index of rainfall and Ca as an index of chemical weathering (Gaillardet et al. 1999).

Mechanical Weathering

In addition to chemical denudation, a large amount of material derived from mechanical weathering is eroded from land and carried in rivers as the particulate or suspended load. These materials have received less attention from biogeochemists because their elemental contents are not immediately available to biota.

The concentration of suspended sediment often shows a curvilinear relationship with stream flow, increasing exponentially at high flows (Parker and Troutman 1989; Figure 4.20). At low flows, suspended sediments are dominated by organic materials, but the proportion of organic matter declines as the amount of suspended sediment increases during high flows, when soil erosion is greatest (Meybeck 1982, Ittekkot and Arain 1986, Paolini 1995). Long-term records show that the sediment transport during occasional extreme events often exceeds the total transport during long periods of more normal conditions (Van Sickle 1981, Swanson et al. 1982). Large concentrations of suspended sediments are found during flash floods in deserts (Baker 1977, Fisher and Minckley 1978, Laronne and Reid 1993).

Transport of suspended sediments in world rivers is affected by many factors, including elevation, topographic relief, and runoff from the watershed (Gaillardet et al. 1999). Although the rivers draining arid regions show high concentrations of suspended sediments, their total flow is limited, so the loss of soil materials per unit of landscape is rather low (Milliman and
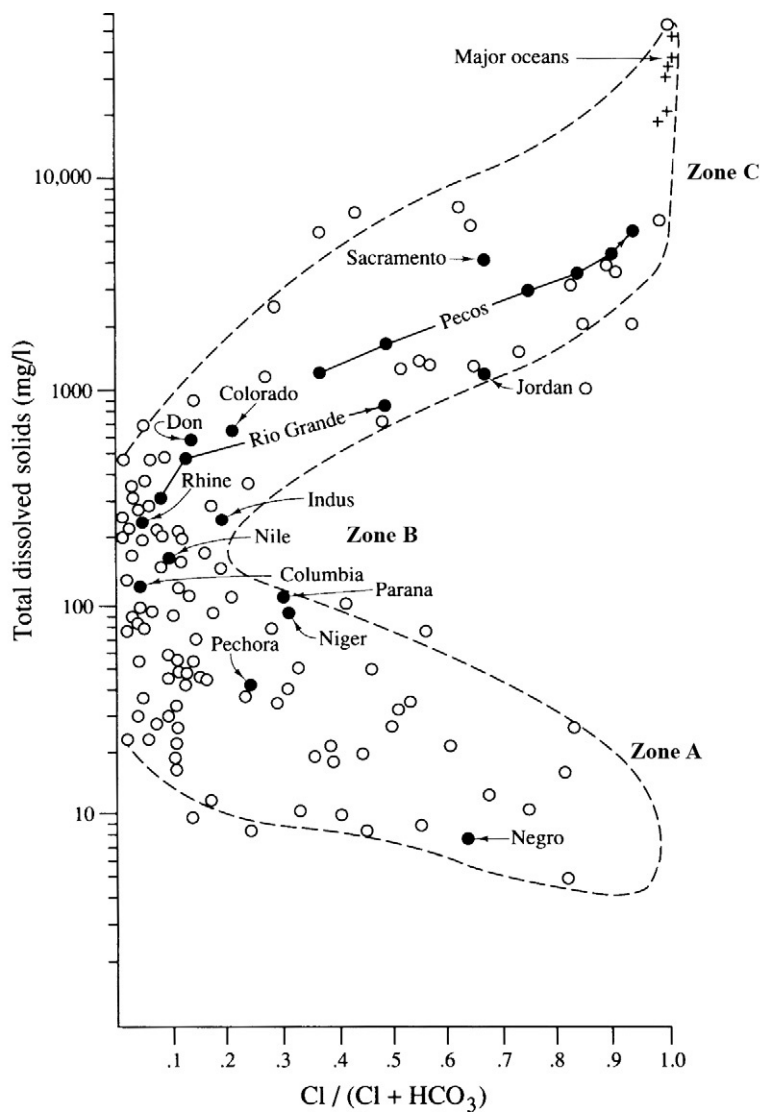
FIGURE 4.19   Variations in the total dissolved solids in rivers and lakes as a function of the ratio of Cl/ (Cl + HCO₃) in their waters. *Source: From Gibbs (1970). Used with permission of the American Association for the Advancement of Science.*
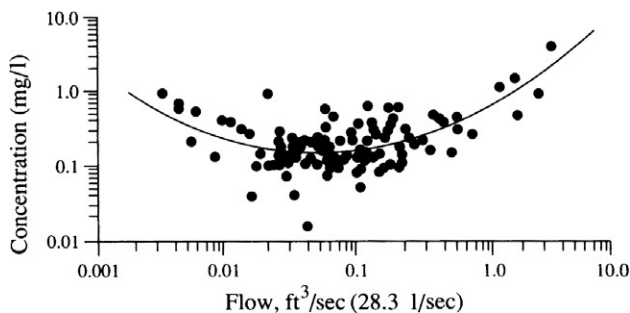
FIGURE 4.20   Concentration of particulate matter as a function of stream flow in the Hubbard Brook Experimental Forest of New Hampshire (U.S.A.). *Source: From Bormann et al. (1974). Used with permission of the Ecological Society of America.*

Meade 1983). Rivers draining southern Asia carry 70% of the global transport of suspended sediments, 13.5×10^{15} g/yr (refer to Table 4.8). Large sediment loads in the rivers of China are derived from the erosion of massive deposits of wind-derived soils, loess, in their drainage basin. In contrast, despite carrying 20% of the world's riverflow, the Amazon River carries only about 600 to 900×10^{12} g of suspended sediment each year, about 5% of the world's total (Mikhailov 2010, Wittmann et al. 2011). Most of the Amazon Basin is situated at low elevations with limited topographic relief, which accounts for its relatively low yield of suspended sediments (Meybeck 1977).

Much of the sediment removed from uplands is deposited in stream channels and flood-plains in the lower reaches of rivers (Trimble 1977, Longmore et al. 1983, Gurtz et al. 1988). Thus, the sediment yield per unit area of watershed declines with increasing watershed area (Milliman and Meade 1983). Despite large seasonal variations in volume, the daily sediment transport of the Amazon is rather constant as a result of storage of sediment in the floodplain during periods of rising waters and remobilization during falling waters (Meade et al. 1985).

Erosion increases when vegetation is removed (Bormann et al. 1974), and global land cleared by humans for agriculture, mining, and construction has dramatically increased the transport of suspended sediments in many parts of the world (Wilkinson and McElroy 2007, Hooke et al. 2000). For instance, in the eastern United States, coal mining now vastly exceeds all natural processes that mobilize materials from the Earth's crust (Figure 4.21). Worldwide, human activities have simultaneously nearly doubled the transport of suspended materials in rivers, but reduced the amount of the mobilized material reaching the oceans owing to the construction of dams and reservoirs (Syvitski et al. 2005). Large amounts of suspended sediment are captured in lakes and floodplains and behind dams and other human structures (Dynesius and Nilsson 1994, Vorosmarty et al. 2003, Walling and Fang 2003).

Total Denudation Rates

The total denudation of land is dominated by the products of mechanical weathering, which exceeds chemical weathering by three to four times, worldwide (Table 4.8). The mean rate of total continental denudation is about 1000 kg ha^{-1} yr^{-1}, with approximately 75% carried in the suspended sediments in rivers (Alexander 1988, Tamrazyan 1989, Wakatsuki and Rasyidin 1992, Gaillardet et al. 1999). The importance of mechanical weathering increases with elevation (e.g., Reiners et al. 2003, Gaillardet et al. 1999); differences in mean elevation among the continents explain much of the variation in mechanical weathering in Table 4.8.

Recent estimates of the total transport of suspended materials in all rivers of the world range from 12.6 to 13.5×10^{15} g/yr (Milliman and Meade 1983, Syvitski et al. 2005). Assuming that the specific gravity of suspended sediment is 2.5 g/cm^3, these estimates are 4 to 5 times higher than estimates (1.27 km^3/yr) of the volume of deep ocean sediments derived from land (Howell and Murray 1986) and the current volume of sedimentary materials being subducted into the mantle (0.73 km^3/yr; Plank and Langmuir 1998). Presumably, most sediment is deposited near the shore, in continental shelf deposits (Chapter 9). Gregor (1970) suggests that the global rate of sediment transport, an overall measure of mechanical weathering, may have been about four times greater before the land surface was colonized by plants (compare Wilkinson and McElroy 2007). Indeed, today, especially high concentrations of
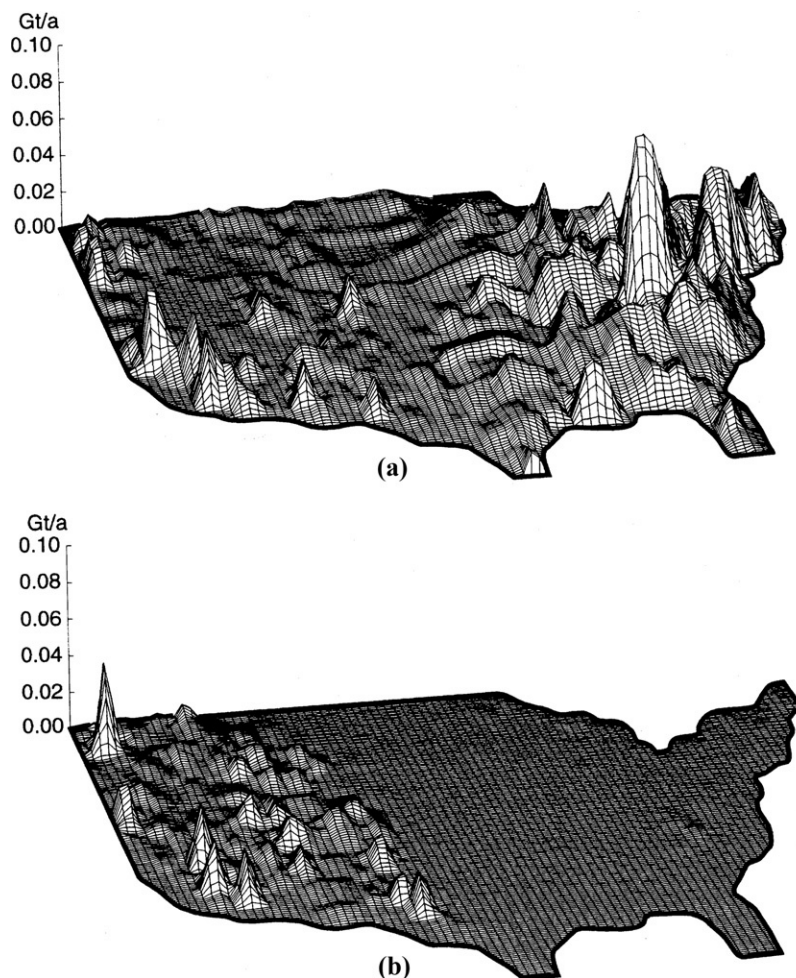
FIGURE 4.21   Rate at which surficial materials are mobilized from the Earth's crust (Gt/yr $= 10^{15}$ g/yr) in grid cells measuring $1 \times 1°$ latitude and longitude by humans (A) and rivers (B). The massive mobilization of crustal materials in the eastern United States is largely the result of surface mining for coal (Hooke 1999).

suspended sediment are seen in rivers draining arid and semi-arid regions where vegetation is sparse (Milliman and Meade 1983).

Because Fe, Al, and Mn are only slightly soluble in water, particulate and suspended sediments account for most of the removal of these elements from terrestrial ecosystems (Table 4.10; Benoit and Rozan 1999). The numbers shown in the table are estimated by comparisons of the concentrations in bedrock to those in weathered residues (river particulates); both are normalized to Al. Suspended sediments are also enriched in phosphorus, owing to chemical reactions between dissolved P and various soil minerals (Avnimelech and McHenry 1984, Sharpley 1985). As a result of a variety of human activities, the river transport of many metals (e.g., Cu, Pb, and Zn) is now greater than the transport under preindustrial

TABLE 4.10   Loss or Gain of Major Elements during Chemical Weathering

Element	Surficial rock	Weathered river particulate	% lost or gained
		wt%	
Al	6.93	10.6	0
Fe	3.59	5.75	0
Mn	0.072	0.25	+230
Na	1.42	0.27	−88
Ca	4.5	0.63	−91
Mg	1.64	0.63	−75
K	2.44	2.25	−40
Si	27.5	27.0	−36

Note: The changes in concentration are normalized to Al.
Source: From Canfield (1997).

TABLE 4.11   Estimates of Some Elemental Fluxes to the Oceans in Rivers (10^{12} g yr^{-1})

	Ca	Na	Mg	Si	Fe	Cu	Pb	Zn
River particulate load	345	110	209	4430	733	1.55	2.3	5.4
River dissolved load	495	131	129	203	1.5	0.37	0.04	1.1
Total river load	840	241	338	4630	734	1.9	2.3	6.5
Theoretical load[a]	946	298	345	5780	754	0.67	0.33	2.6
Discrepancy	N.S.	N.S.	N.S.	N.S.	N.S.	+1.2	+2.0	+3.9
World mining production	—	—	—	—	—	4.4	3.0	3.9

[a] *Based on weathering of average rock.*
Source: From Martin and Meybeck (1979). N.S., not significant.

conditions (Table 4.11), but it is interesting to note that the concentration of Pb in rivers has declined recently, presumably as a result of the decreased use of leaded gasoline in automobiles (Smith et al. 1987, Trefry et al. 1985).

SUMMARY

In this chapter we have seen that the rates of weathering and soil development are strongly affected by biota, particularly through carbonation weathering and the production of organic acids in the soil profile (Kelly et al. 1998). It is tempting to speculate that the rate of carbonation weathering was lower before the advent of land plants, when it depended solely on the

downward diffusion of atmospheric CO_2 through the soil profile. However, at periods in Earth's early history, the concentration of atmospheric CO_2 was most certainly higher than today, presumably yielding high rates of carbonation weathering. Weathering is also driven by the availability of water. The high concentration of CO_2 on Venus (Table 2.6) is ineffective in weathering because the surface of the planet is dry (Nozette and Lewis 1982).

By mining minerals from its crust and extracting buried fossil fuels from the Earth, humans have increased the global rates of chemical and mechanical weathering and added significant quantities of dissolved materials to global riverflow. Currently, the removal of fossil fuels from the Earth's crust mobilizes and oxidizes carbon at a rate (9×10^{15} g/yr), which exceeds the total of all natural chemical weathering (Table 4.8). Human exposure and erosion of soils in agricultural use have increased the global denudation due to mechanical weathering by a factor of about 2 (Syvitski et al. 2005), leading to increases in the rate of sediment accumulation in estuaries and river deltas (Chapter 8).

Chemical weathering is a source of essential elements for the biochemistry of life, but stream water runoff removes these elements from the land surface. Chemical reactions among soil constituents and uptake by biota determine the rate of loss, but the inevitable removal of cations results in lower soil pH and base saturation through time (Bockheim 1980). Phosphorus is particularly critical as a soil nutrient because it is not abundant in crustal rocks and is easily precipitated in unavailable forms in the soil. Old soils in highly weathered landscapes are composed of resistant, residual Fe and Al oxide minerals. In these soils, P is often deficient and even the small atmospheric inputs of P are important for plant growth (Chadwick et al. 1999; Chapter 6).

Recommended Readings

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PROBLEMS

4.1. Consider a forested watershed in which evapotranspiration removes about 50% of the annual rainfall and there are no losses of water to groundwater. A scientist makes the following observations:

Precipitation:
- Amount: 100 cm/year
- Mg concentration: 0.05 mg/l

Stream water:
- Volume 1.5×10^8 l/year
- Mg concentration: 0.40 mg/l

Bedrock:
- Al concentration: 10 g/kg
- Weathering rate: 800 kg/ha/year
- Al/Mg ratio: 5

Diagram the Mg cycle in this system, expressing the inputs and outputs in terms of kilograms per hectare (10,000 m^2) per year. Assuming all these measurements are accurate, how might you explain the small discrepancy this scientist encounters in the budget for Mg?

4.2. Using the rates of chemical and mechanical denudation in Table 4.8, and assuming that the Earth's continental crust is in steady state, estimate the mean rate of uplift of the continental crust in cm per year.

4.3. Calculate the transport of major ions to the sea, using the data of Table 9.1 and a global riverflux of 4×10^{16} l/yr. Using the data given in Table 4.9 what is the fraction of the annual flux of HCO$_3$ in rivers that is derived from the atmosphere? How much should the global rate of chemical denudation (Table 4.8) be reduced to account for the HCO$_3$ that is derived from the atmosphere?

4.4. What is the relative transport of crustal materials from land to sea in soil dust versus in rivers?