Soils and weathering

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Weathering is the physical, chemical, and/or biochemical breakdown of rocks and minerals at the interface between the lithosphere and the atmosphere (Bridge and Demicco 2008). It is the starting point of pedogenesis because it produces regolith, which is defined as loose, unconsolidated deposits at the Earth's surface (Alexander 2013). Regolith originates from hard bedrock via weathering and biological processes. Regolith can have one of two origins: *residual regolith* (or *residuum*) which is formed in situ as bedrock weathers, or *transported regolith* which is transported to a site by wind, water, gravity, and so on (Schaetzl and Thompson 2014). The part of the regolith in which a soil develops is called its parent material. Rocks are weathered along fluid and gaseous pathways such as fractures, joints, faults, and so on. Weathered rocks are not necessarily covered by soil. Weathering is driven by the energy of the sun and involves exchanges between lithosphere, hydrosphere, atmosphere, and biosphere at low temperatures and under mainly subaerial conditions.

Weathering has traditionally been divided into *physical* (or *mechanical*) *weathering* and *chemical weathering*, but it is becoming increasingly apparent that biochemical weathering is also important (Velde and Meunier 2008). In reality, physical, chemical, and biochemical weathering processes work together. Alteration of the chemical or mineral composition of Earth materials does not occur during physical weathering, only a physical breakage of rocks into smaller pieces. Breakup of rocks and minerals create more surface area for chemical weathering, which operates mainly on the available surface area of minerals. Chemical and biochemical weathering both alter the chemical and mineralogical composition of rocks and regolith, producing new solid materials (e.g., clay minerals) and dissolved substances such as ions. Many of the dissolved solutes exit the soil system in groundwater or are biocycled by vegetation (Bridge and Demicco 2008).

During weathering, the fabric of the parent rock changes progressively from unaltered through to the most weathered zones (Figure 1). Weathered rock that retains much of its geologic fabric is called saprolite. Taylor and Eggleton (2001, 157–159) considered that regolith is composed of *saprock* and *saprolite,* where saprock is the altered coherent rock and saprolite is the altered soft rock. Together, saprock and saprolite form residual regolith, or residuum (Taylor and Eggleton 2001, 1–3), and above the saprolite, the altered soft rock is referred to as the *pedolith* (Figure 1).

Velde and Meunier (2008) proposed new definitions for altered rock facies based on physical properties that are easily observable in the field, that is, conservation or destruction of the primary rock structure and physical resistance (coherent, friable, soft, clay-enriched). Weathering profiles developed under temperate climate exhibit two altered rock types: coherent rock which may be sampled as self-sustained pieces that preserve the original rock texture and friable rock, which when sampled becomes gravel. According to these observations, one can distinguish three facies:
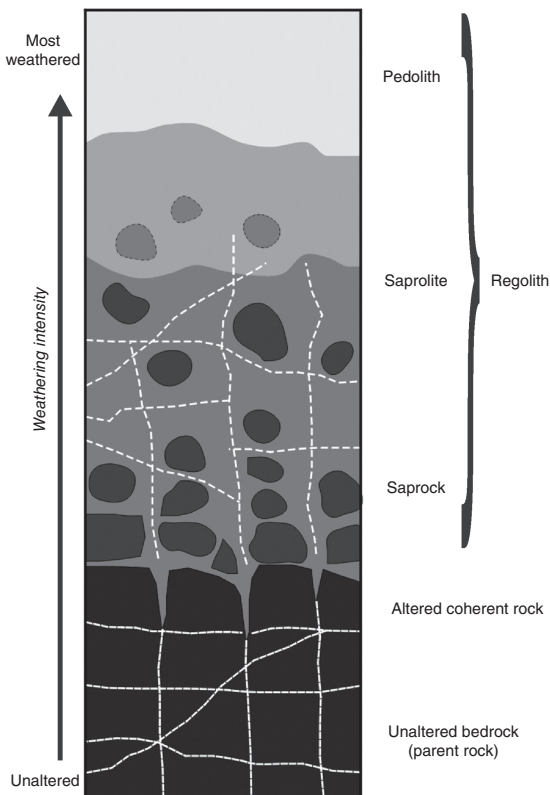
Figure 1 Classification of a typical weathering profile. Adapted from Migoń 2010. Reproduced by permission of The Geological Society.

1 Altered coherent rock, where the original structure of the rock is maintained, although some primary minerals show pockets of alteration in which their debris are mixed with newly formed clays.
2 Friable saprock, in which the original rock structure is conserved. The structure of the rock is maintained although its mechanical strength is much reduced. Porosity ranges from 10 to 20%.
3 Friable saprolite, in which the original structure is erased. It forms more or less continuous zones above and within the saprock.

Physical weathering

Bedrock on the surface may weather, or disintegrate, physically from the stresses of heating and cooling, wetting and drying, and/or freezing and thawing. Physical weathering (PW) is the term used to describe the disintegration of rocks and minerals into smaller pieces. The main physical and mechanical processes of weathering are the *abrasion* and *comminution* of rocks and minerals as a result of erosive, expansive, and compressive forces and hydration along grain boundaries (Retallack 2001). Abrasion is the rubbing of rocks against each other, whereas comminution refers to the physical breakup of rock by faulting as a result of tectonic movement. Abrasion and comminution can occur simultaneously. They involve rocks rubbing against one another, chipping and breaking off small pieces.

Rocks deep below the Earth's surface support the weight of the overlying column of rock. Lithostatic pressures can cause rocks to expand in the direction of least compressive stress, producing joints parallel to the principal stress direction (Bridge and Demicco 2008). As a result, all rocks contain fractures. This release of lithostatic pressure – often termed *unloading* – is most often due to the removal of overlying material by erosion.

Physical weathering acts on these joints to pry rocks apart and to break them into smaller pieces. Rocks can be physically weathered by *wedging* – prying them apart at cracks. The wedges can be formed by either ice or salt crystals. One of the main drivers of PW at the Earth's surface is the *freeze–thaw* cycle of water and the associated growth of ice crystals. Wedging occurs as the result of the expansion of water as it is converted to ice. Cracks filled with water are forced further apart when the temperature drops below freezing. The splitting process in freeze–thaw produces fresh, angular fragments of rock (see Figure 2). The growth of salt minerals

in fractures and pores exerts increased pressure, analogous to ice. Additionally, the hydration of anhydrous salts (such as anhydrite to gypsum) within rocks (Bridge and Demicco 2008) can cause wedging and break off angular slabs or blocks of rock. These mechanisms are commonly cited as the main PW processes in arid regions, where extremes of temperature and moisture occur, and where many soils contain salts.

Other mechanisms of PW include the breakdown of rocks due to differential *thermal expansion,* and the *contraction* of individual rock–forming minerals during diurnal temperature changes. Plants and animals also have physical effects during weathering. A large number of animals make tunnels through hard rock and under the ground. Surface rocks also get crushed when animals tread on them or dig into them. Even earthworms make tunnels in the ground which leads to the breakdown of stones and rocks over a period of time. Plant roots at times grow deep into the cracks present in rock. As the plant roots grow thicker and deeper, rocks may begin to break. Both pressure release and wedging break up rocks and minerals, creating more surface area for chemical weathering (see Figure 2).

Chemical weathering

Chemical weathering (CW) is the decomposition of rock materials by a series of chemical reactions. In most instances, the term biogeochemical weathering is more appropriate, as biota often interact chemically with the geological material to weather the minerals (Singer and Munns 2002). Chemical weathering generally occurs whenever water comes into contact with primary minerals (McBride 1994). The main processes of CW are solution, hydration, hydrolysis, oxidation, reduction, carbonation, and other reactions associated with inorganic and organic acids

(Osman 2013). All forms of chemical weathering tend to promote the decomposition of minerals in rocks to a less resistant and more stable form, commonly a clay mineral (see Figure 2).

All minerals have two formation categories: primary and secondary. *Primary minerals* are formed at high temperatures and pressures through geologic processes. Usually, they form as molten materials (lava, magma) cool and harden. Consequently, they are unstable under atmospheric conditions. The stability of primary minerals (resistance against weathering) generally follows the Bowen reaction series, as those formed under high pressure and temperature tend to be less stable under atmospheric conditions. *Secondary minerals* form under atmospheric conditions (such as those found in soils) but may be unstable if conditions change from those of their formation. Primary minerals tend to release their ionic constituents as they weather; this can lead to the "new" formation (i.e., precipitation or neoformation) of secondary minerals. Secondary minerals can also be formed from the solid–state transition of a primary mineral, for example, mica→vermiculite. Many forms of CW also release cations, anions, and salts to the soil or regolith system; these may later recombine to form other secondary minerals.

The alteration processes that comprise CW occur between water (and its constituent dissolved substances, particularly acids) and minerals, operating at the mineral surface. Physical weathering, therefore, sets the stage for CW by increasing the surface area of minerals. Minerals are not ordinarily soluble in water, but in soils and regolith, acids, bases, and dissolved organic substances enhance their solubility. Most minerals in igneous and metamorphic rocks formed at around $1000°C$ and at many thousands of kilopascal pressure, under chemically reducing conditions. However, where they are exposed at the Earth's surface at approximately $15–25°C$, at
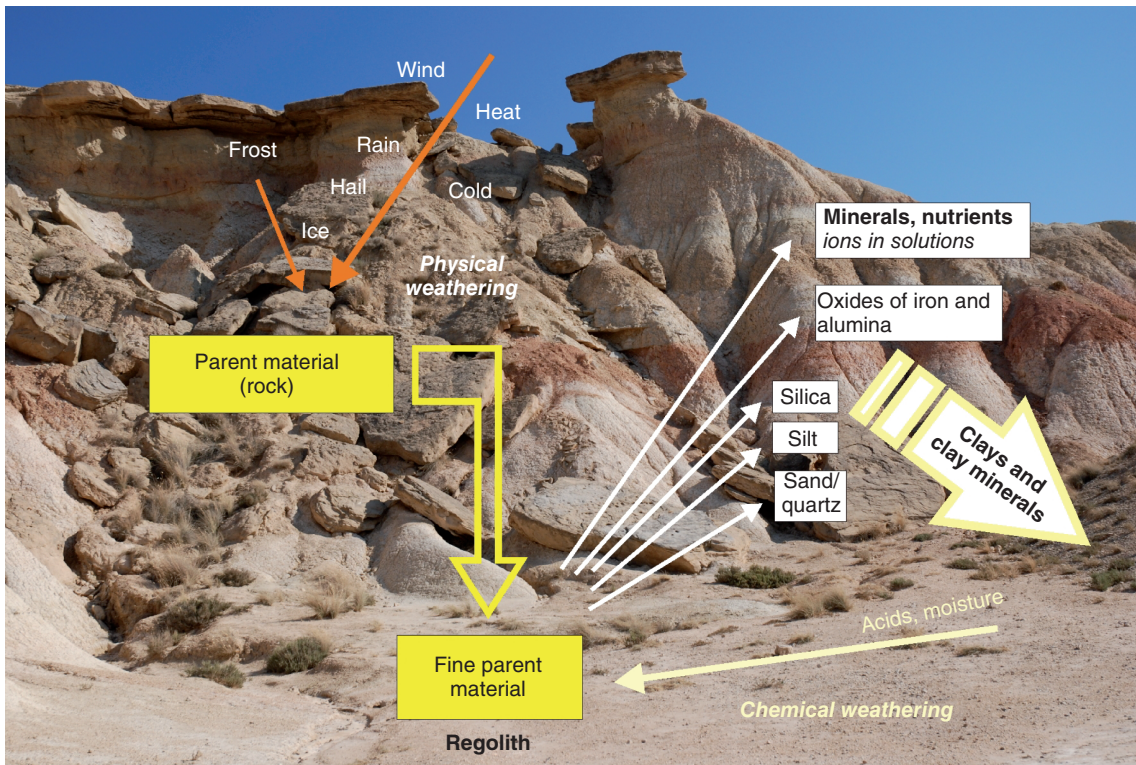
Figure 2 An exposure of bedrock, showing the effects of physical and chemical weathering.

Table 1 Solubility of ions depends on their ionic potential.

Ionic potential[a]	Examples	Solubility/mobility
≤3.0	K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}	Soluble, mobile
3.0–9.5	Fe^{3+}, Al^{3+}	Soluble under acidic conditions, mobility depends on pH
≥9.5	$H_3SiO_3^-$	Forms oxi–anion complexes, solubility depends on pH, soluble around pH 7

[a]Ionic potential is defined as charge/ionic radius.

100 kPa pressure, and with abundant free oxygen dissolved in meteoric surface waters, primary minerals readily break down chemically (Bridge and Demicco 2008).

Dissolution occurs when rocks and/or minerals are dissolved by water. Dissolution of the most common ions of the Earth's crust is largely determined by the pH of the soil solution (Figure 3). The dissolved material, typically as ions, is transported away in water or biocycled, leaving a void in the rock. Commonly, this kind of loss is what makes saprolite weaker than its parent rock, but because some minerals remain unweathered, the saprolite retains the structure of the parent rock. The readiness of a given ion for dissolution primarily depends on the ratio of its charge and radius (ionic potential, Table 1).
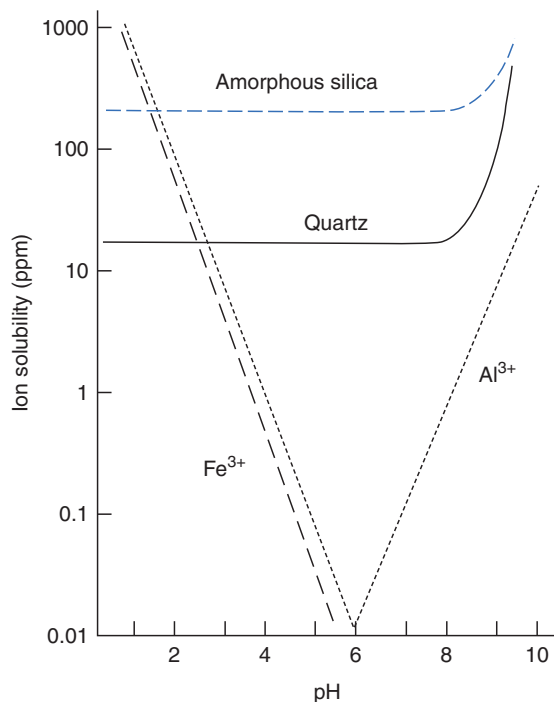
Figure 3 Solubility of quartz and the most common ions of the Earth's crust as a function of solution pH. Adapted from Buol *et al*. 2011.

Hydration refers to the association of water molecules with minerals (Buol *et al*. 2011). During the hydration process, water molecules form a hydration shell around the ions of dissociated salts. Hydration primarily affects the mineral surfaces and (broken) edges of minerals, but in some cases it may dissolve the entire mineral (congruent dissolution).

Carbonation is a very active and common CW process, involving carbonic acid, and affecting mainly carbonate types of rocks (e.g., limestone, dolostone). Carbonic acid is naturally produced by dissolution of CO_2 in water. Carbon dioxide is available from the atmosphere and exists at high levels in regolith, because it is added as a product of microbial and root respiration. Thus, most carbonation processes are biochemical in nature. Carbonic acid is capable of dissolving

many different types of minerals, bringing them into solution. The reaction for the dissolution of $CaCO_3$ is:

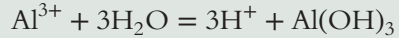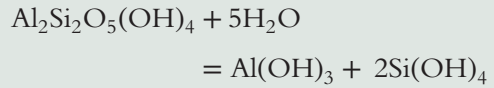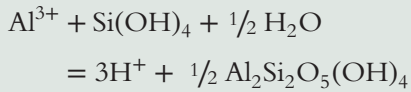$$CaCO_3 + 2H_2CO_3 = 2HCO_3^- + Ca^{2+}$$
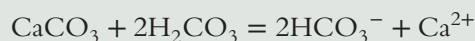
Carbonation can have an etching effect upon some rocks, especially limestone. The removal of cement that holds sand particles together leads to this disintegration.

Hydrolysis (splitting of the water molecules) is probably the most effective chemical weathering process. Hydrolysis occurs when primary minerals react with water, in the form of H^+ and OH^- ions, to form other products. Hydrolysis is the reaction of acid (H^+) with a cation-rich mineral grain to produce a clay mineral and various kinds of free cations. As a result, clay minerals accumulate in the soil and the cations are released, to later be leached or taken up by plants in solution (Retallack 2001). In hydrolysis, hydrogen ions (H^+) in the water molecules replace other ions in the minerals. Due to this replacement, the mineral becomes susceptible to decomposition by further hydrolysis or other chemical reactions. Feldspars, the most common minerals in most rocks, are particularly prone to hydrolysis, reacting with water and free hydrogen ions to form secondary minerals. Hydrolysis is more rapid in silicate minerals characterized by well-developed cleavage (e.g., feldspars, pyroxenes) and is less effective in quartz. An example for hydrolysis (under acidic conditions) is shown by the following equation that describes the weathering of albite:

$$NaAlSi_3O_8 + 4H_2O + 4H^+$$
$$= 3Si(OH)_4 + Na^+ + Al^{3+}$$
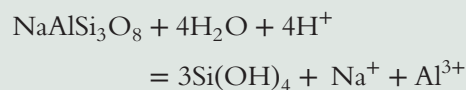
Under less acidic conditions (pH 7) and long weathering, kaolinite may be formed, most typically in Ultisols:

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$$Al^{3+} + Si(OH)_4 + \tfrac{1}{2} H_2O$$
$$= 3H^+ + \tfrac{1}{2} Al_2Si_2O_5(OH)_4$$

$$Al_2Si_2O_5(OH)_4 + 5H_2O$$
$$= Al(OH)_3 + 2Si(OH)_4$$

When weathering further proceeds and $Si(OH)_4$ is progressively removed from the upper soil horizons, kaolinite disintegrates and loses silica (desilication), forming gibbsite (Figure 4). In this manner, reddish Oxisols with high gibb–site content develop. Al^{3+} may also directly react with water, forming gibbsite. This process would be typical for soils of udic and perudic soil moisture regimes under tropical climates.

$$Al^{3+} + 3H_2O = 3H^+ + Al(OH)_3$$

Commonly, the silicic acid that is released by hydrolysis precipitates to form amorphous clay minerals like allophane and imogolite, and other, more structured secondary phyllosilicates (e.g., smectites; Figure 4). Short-range order amor–phous silicates are often the first weathering
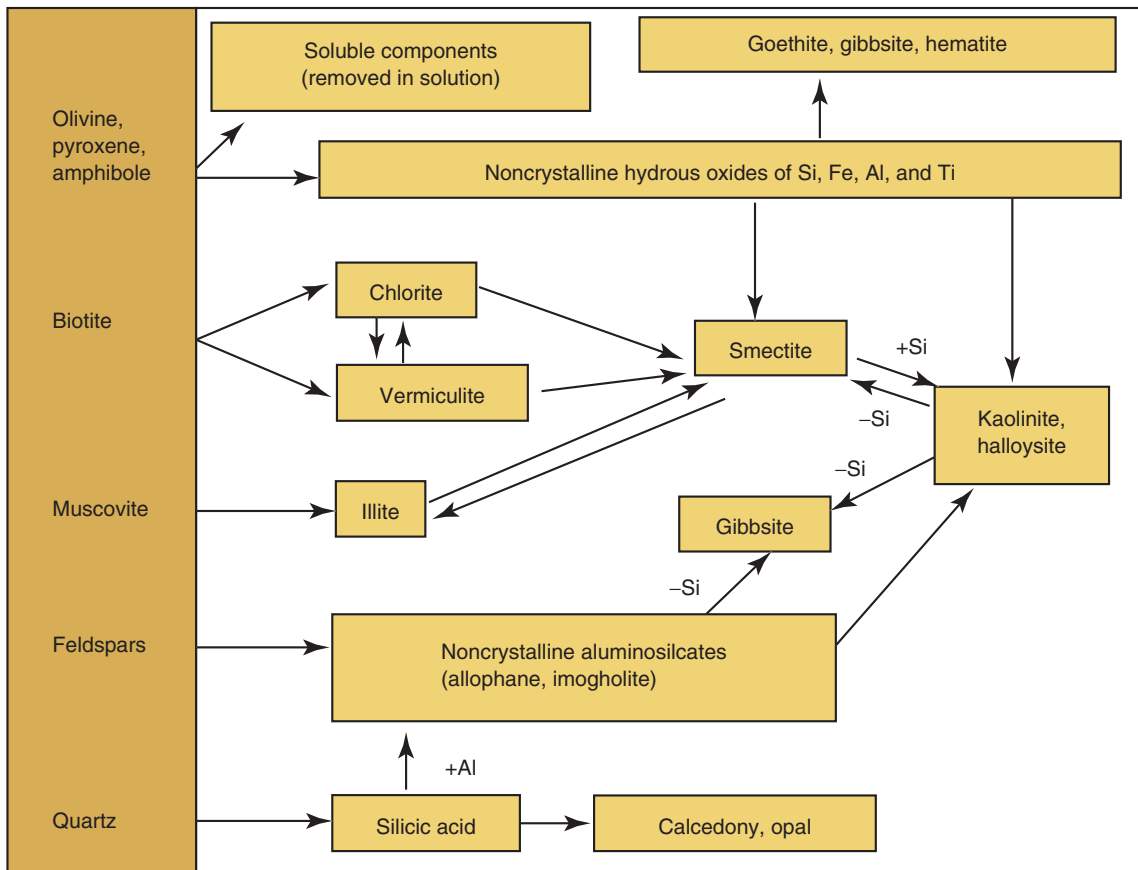

Figure 4 Weathering pathways for the common rock-forming minerals of the Earth's crust. Adapted from Mason 1966.

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product on volcanic parent materials, and are primarily found in Andisols. Halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) may also appear as a weathering product of volcanic ash (as the end product of the allophane-imogolite-halloysite sequence; Figure 4).

At higher pH and Mg concentrations, montmorillonite may be formed by the resilication of kaolinite (Jenny 1980) due to the process called *neoformation,* which involves the dissolution of kaolinite and its subsequent reprecipitation in the form of montmorillonite (Figure 4).

Oxidation reactions are those in which an element suffers electron loss when forming a compound (Retallack 2001). Oxidation is the process of addition of oxygen to minerals. The absorption is usually from O_2 dissolved in groundwater and that present in atmosphere. Oxidation is more active in the presence of moisture, resulting in hydrated oxides (e.g., minerals containing Fe and Mg). Oxidation in minerals occurs when oxygen reacts with iron-bearing minerals to form iron oxide minerals (iron rusting), for example, goethite.

$$FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$$

The latter minerals give rocks red or orange colorations, indicative of oxidation and aerated conditions.

The environment in which soils form may also be reducing, usually when waterlogged conditions exist. *Reduction* is important to weathering in such soils, because many cations are more soluble when reduced than when oxidized (Singer and Munns 2002). A common process in soils is the vertical fluctuation of the groundwater table which changes the location of the boundary between the phreatic (saturated) and vadose (aerated) zones. The location of the groundwater table and the level of water saturation control the pH and Eh (redox potential) conditions of the subsoil and determine the oxidation forms

of several ions, including iron, manganese, and arsenic. The changes between reducing and oxidizing conditions will result in the electron transfer reactions between ions like Fe^{2+} and Fe^{3+}, Mn^{2+} and Mn^{4+}, and As^{3+} and As^{5+}.

Ion exchange refers to two different processes in the crystal lattice of clay minerals. The first process is called the isomorphic substitution and results in the appearance of permanent charges in the clay minerals due to the replacement of Si^{4+} by Al^{3+} or Al^{3+} by Fe^{2+}. The second type of ion exchange occurs in the interlayer of the 2:1 clay minerals, primarily in micas. This type of chemical weathering process is typical under acidic conditions where a large concentration of H^+ is available for ion exchange. With the removal of more than 50% of the interlayer K^+ (and replaced by H^+), the sheet alignment in micas is lost and distortion of the lattice may happen; the mineral eventually collapses and weathers. With the complete removal of the interlayer K^+, vermiculite and smectite-type layered silicates are formed.

Organic acids also play important roles in weathering. These acids can either be released directly from the organism or be derived as byproducts of organic decomposition. *Chelation* is a process in which metal ions are usually bonded to an organic compound (ligand). These organic complexes usually have aromatic (ring-like) structures which incorporate the metal ion. Once formed, this structure is stable and may persist in the soil (Buol *et al.* 2011). Because of chelation, otherwise insoluble metal ions become soluble and may subsequently be removed from the soil. This process is typical in Spodosols, where metal oxides (sesquioxides, such as Al_2O_3 and Fe_2O_3) are removed from the A-horizon in percolating water, forming A_2 or E-horizons (Schaetzl and Thompson 2014). These substances then accumulate in the deeper Bs or Bsh horizons. In other cases, however,

organic ligands are stabilized by the metal ion, resulting in the relative accumulation of the organic-metal complexes in the upper soil horizons. An example of the ring-like structure of a chelate would be a complex between an oxalate anion and a metal ion:

$$M(H_2O)_6{}^{n+} + {}^-OOC - COO^-$$
$$= ((H_2O)_4M - (OOC)_2)^{(n-2)+} + 2H_2O$$
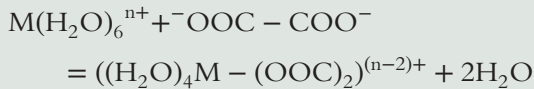
Any one rock or mineral, however, weathers at different rates in different climatic conditions. Chemical weathering is slow in cold and dry areas. In the humid tropics, not only is the rate of weathering rapid (especially chemical weathering), but also the weathering products are lost quickly. In nature, physical and chemical weathering operate individually, or concurrently. In most cases, one accelerates the other.

SEE ALSO: Lithologic discontinuities in soils; Paleosols; Soil biology and organisms; Soil and clay mineralogy; Weathering processes and landforms

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