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Principles and Dynamics of the Critical Zone

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Chapter 4

Regolith and Weathering (Rock Decay) in the Critical Zone

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4.1 INTRODUCTION

Weathering and the Critical Zone have been inextricably linked, as both nested process domains in Earth history, and as much more recent research priorities among environmental scientists. The United States National Research Council's (USNRC) (2001) report defined the Critical Zone as the "heterogeneous, near-surface environment in which complex interactions involving rock, soil, water, air and living organisms regulate the natural habitat and determine availability of life-sustaining resources." This is commonly identified as "the fragile skin of the planet defined from the outer extent of vegetation down to the lower limits of groundwater" (Brantley et al., 2007, p. 307). Shortly following the USNRC report, a collaborating body of Earth scientists initiated what was then called the Weathering Systems Science Consortium (WSSC) (Anderson et al., 2004), intent on studying "Earth's weathering engine" in the context of the Critical Zone. The WSSC evolved into a more-encompassing Critical Zone Exploration Network (CZEN) as the collaboration involved more ecologists, hydrologists, and pedologists less intent on examining the weathering engine. Still CZEN has been and is a significant locus of weathering research. Not to be ignored, however, is the longstanding pursuit of regolith science (Scott and Pain, 2008; Taylor and Eggleton, 2001; Cremeens et al., 1994; Ollier and Pain, 1996), more or less parallel to that of the Critical Zone although not named as such. Ollier and Pain (1996, p. vii) outlined in the preface of their book goals for "regolith studies" that are nearly exactly those espoused by CZEN for the same environment. In the effort to draw together disparate research approaches, this chapter on weathering systems will draw on a variety of sources and scientists who study weathering in the Critical Zone/regolith: geochemists, geomorphologists, soil scientists, hydrologists, petrologists, mineralogists, and others. Viles' (2013) discussion of weathering system synergies elucidates the environmental as well as disciplinary entanglements, pointing out disparities in questions

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asked and methodologies used, despite the convergence on a congruent topic of investigation.

Yatsu's (1988, p. 2) definition for "*weathering*" remains the simplest and most flexible: "Weathering is the alteration of rock or minerals *in situ*, at or near the surface of the earth and under the conditions which prevail there." Indeed, rocks and minerals do thermodynamically adjust within the active Critical Zone envelope. Yet, the term "weathering" implies a predominance of atmospheric control over processes, when in actuality the inherent properties of the rock and mineral may be foremost (Hall et al., 2012). Neither is the atmosphere itself the sole nor necessarily the dominant weathering agent. Hall et al. (2012) forwarded a replacement term, "*rock decay*." The same term was used by early geomorphologists (Merrill, 1906; Chalmers, 1898), and Ollier (1963) referred to chemical weathering as one of several types of "rock decay." Hutton (1788), in his famous paper, never used the term, "weathering," instead used "decay" (although the cause of which he generally ascribed to "sun and atmosphere"). The term, "decay," appears commonly in the stone conservation literature (e.g., Prikryl and Smith, 2007). A growing body of "weathering" scientists is following this example (cf. Dorn et al., 2013a).

Even so, "rock decay" is not quite sufficient to cover the realm of weathering of all earth surface materials. Materials need not be rock to decay. Unconsolidated sediments can decay *in situ*, in temporary surface storage prior to burial and cementation. Direct byproducts of surface weathering may also weather. For instance, neoformed duricrusts precipitated in the soil (Nash and McLaren, 2007) may undergo decay when environmental conditions modify, in which the precipitate is no longer stable in its present form. For illustration, Eren and Hatipoglu-Bagcit (2010) reported karst-like solution features in exposed hardpans of caliche in Turkey. Calcium carbonate precipitated in the soil in dry conditions, but the now-exhumed hardpan was exposed to solution from rainwater. Twidale (1987) explained karst-like sinkholes in laterized quartz and clay in tropical Australia that resulted from Holocene drying as well as biogenic decay agents.

Regolith is the "unconsolidated or secondarily cemented cover that overlies more coherent bedrock… formed by weathering, erosion, transport and/or deposition of older material. Everything from fresh rock to fresh air" (Scott and Pain, 2008, p. 427). Regolith therefore coincides with all of the Critical Zone apart from the subaerial vegetation, and happens to be the natural focus of rock and mineral decay. If the regolith develops from *in situ* bedrock, the term *saprolite* is sometimes used for decayed bedrock that retains the original rock structure and fabric. *Saprock* is the slightly weathered transitional form between saprolite and rock, whereas some authors use the term *saprolith* to cover the combination of saprolite and saprock (Scott and Pain, 2008). Finally, *soil* is the uppermost segment of the regolith generally (but not always) with incorporated decomposed biotic components as well as genetic horizon organization. Soil is at the direct interface of Earth materials at the atmosphere, surface water, and biosphere, and covered in this text by Dixon (Chapter 5). Figure 4.1 diagrams the profile of the regolith, otherwise known as the terrestrial portion of the Critical Zone, whereas Fig. 4.2 illustrates a real-world example, complete with its vegetative cover.

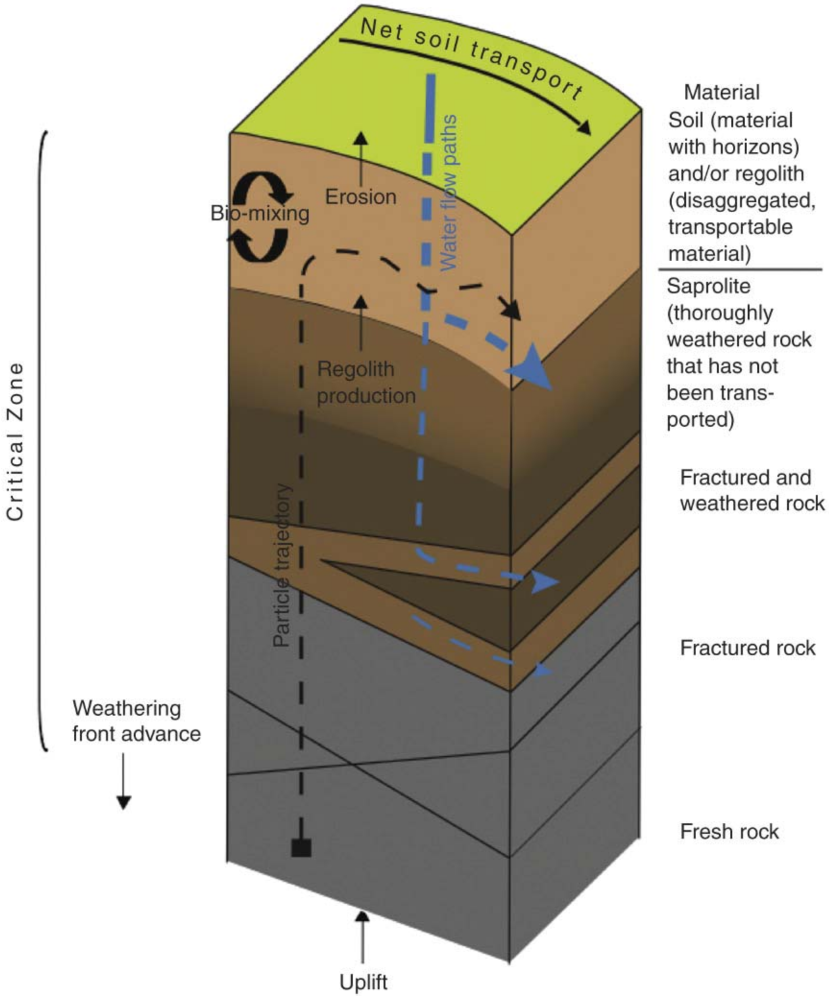

FIGURE 4.1 Profile of the terrestrial portion of the Critical Zone, or regolith, as conceptualized by Anderson et al. (2007). Penetration of the weathering front progresses from surface downward. Rock particles liberated by weathering have a net movement upward, then at the surface mixed and moved laterally and downslope. *(After Anderson et al. (2007).)*

4.2 WEATHERING RELEVANCE TO OTHER CRITICAL ZONE PROCESSES

Although a number of biological, atmospheric, and hydrologic processes operate and interact in the Critical Zone, the interfaces with the lithosphere illustrate the importance of weathering in the pedosphere and regolith, connected within the Critical Zone. The breakdown of rocks and minerals and the mobilization

FIGURE 4.2 A regolith profile, in decayed schist and gneiss, in a road cut near Evergreen, Colorado, USA. Relative scale is indicated by the nearby trees. Less resistant rock accounts for the concavities in the profile, while more resistant corestones and quartz veins stand out. Iron oxide staining is seen primarily along fracture zones and around corestones. The irregularity of the decay profile is evident, with highly decayed portions against less decayed portions incongruently, as identified by Phillips (2001b). *(Photo by author.)*

of elements are relevant to pedogenesis, water quality, atmosphere and climate, mineral resources, and life itself (Buss et al., 2013).

4.2.1 Pedogenesis

Soil is the literal foundation for terrestrial life, providing a physical platform, a water–air–nutrient reservoir, and a primary means to recycle both inorganic and organic elements for future use. Decay of organic material is beyond the focus of this chapter, although it is important to consider that almost all soil types have an organic component, and some byproducts of organic decay become rock/mineral decay agents. The processes of pedogenesis are well covered in Birkeland (1999), Schaetzl and Anderson (2005), and Phillips (1993, 2001a), and couched in the factorial controls on pedogenesis first expressed by Jenny (1941) and Simonson (1959). For the breakdown of rock and mineral, soil forming factors are essentially identical to those of weathering (Pope et al., 1995): the nature of the parent materials, influx of new material and efflux of byproducts, the atmospheric conditions over the timespan of the process (including temperature and moisture availability), the presence and type of biotic activity, the availability of abiotic and biotic weathering agents, and time. Pedogenesis in the Critical Zone is discussed in greater detail by Dixon (Chapter 5).

4.2.2 Water Quality

The transfer from atmospheric water to ground- and soil-water, and surface water takes place within the soil and regolith. Although diagenesis and hydrothermal processes below the Critical Zone impart dissolved solutes to groundwater, Critical Zone water also plays a role. With the assistance of water, rock-decay processes add dissolved solutes and suspended particulates deriving originally from rock. The net flow of water and solutes in the Critical Zone depends on the hydraulic gradient, downward under the influence of gravity (flushing components into the groundwater), or upward with strong vegetation uptake or evaporation (in which precipitates such as calcium and salts become part of the soil).

A segment of Critical Zone studies involves rock-decay processes and surface- and groundwaters interacting with polluted environments, such as exposed quarries, mine spoil, urban landfill, and agricultural soils. For instance, the problem of acid mine drainage involves water in contact with iron sulfide minerals in newly exposed rock (as mine spoil or as bare rock). One byproduct is sulfuric acid, itself a potent weathering agent, and a detrimental additive to aquatic life unaccustomed to low pH (Raymond and Oh, 2009; Bond et al., 2000). In the example of urban and industrial contaminants, biogeochemical surface reactions, essentially weathering processes although not necessarily identified as such in this body of research, are a key point in the analysis and remediation of polluted soils (cf. Trindade et al., 2005; Urum et al., 2004).

4.2.3 Supporting Life, Conditioning Ecosystems

Although ongoing research continues to identify a growing number of extremophiles (Rothschild and Mancinelli, 2001), the “normal” terrestrial ecosystem relies on a Critical Zone system that regulates and supports life, including recycling dead organisms, storing and making available nutrients and water, and physically supporting and sheltering organisms. Weathering processes help to provide nutrient elements out of decomposed minerals, and to produce soils that are acceptable to organism regeneration. The soil itself, as a product of weathering, strikes a balance of being porous enough to allow transfers of water, air, and nutrients, but also substantial enough to literally support the weight of vegetation or remain intact when tunneled by burrowing animals.

Members of the ecosystem present a feedback of weathering to the Critical Zone. Biotic agents contribute a significant, if not dominant, share of weathering work to the Critical Zone, involving multiple factors. First, root respiration is responsible for high concentrations of CO_2 in soil air, which in turn combines with water to form carbonic acid (Brook et al., 1983). Second, byproducts of organic decay directly contribute organic acids and chelates, discussed later. Third, penetration of roots and burrowing animals provide pathways for weathering agents and increased exposed surface area. Fourth, among the least understood, are the many symbiotic microorganismal, chemical reactions that exist in the pedosphere (cf. Leake et al., 2008; Chorover et al., 2007). Finally, there are newly discovered impacts of organisms beyond the classifications enumerated earlier. One such phenomenon is the verified enhancement of dissolution of Ca and Mg silicates associated with ant colonies (Dorn, 2014). Through mechanisms not yet understood, although perhaps involving geophagy of olivine and plagioclase, the process combines CO_2 to form pedospheric magnesium- and calcium carbonates, while acting as a terrestrial carbon sink.

4.2.4 Regulating the Environment and Climate

One of the most significant hypotheses put forth in weathering system science has been the role of weathering and the sequestration of carbon, and thus regulation of greenhouse gasses and climate. Originally developed by Raymo (1989), following a supposition by Chamberlin (1899), the hypothesis states that weathering of fresh silicate rocks (high on Reiche's (1950) weathering potential, see Figure 4.3) will draw down atmospheric carbon dioxide. Further, episodes of increased orogeny on a planetary scale (such as the Alpine orogeny) expose more fresh silicate rock, thereby allowing more weathering and more CO_2 drawdown, enough to precipitate global cooling. Indeed, the onset of large-scale orogeny does coincide with global cooling over late Cenozoic time, as well as earlier periods of coupled orogeny and climate change (Raymo and Ruddiman, 1992; Raymo, 1989). Originally beset by difficulties dating and quantifying the degree of weathering, the hypothesis has better support in recent work, by Raymo and her colleagues (cf. Raymo et al., 1997) as well as independent researchers (cf. Dupré et al., 2003; Kump et al., 2000; Liu et al., 2011). Still, some researchers find conflicting evidence. Dixon et al. (2012), working in the xeric climate of California, found evidence to suggest the opposite, tectonic/weathering forcing that increased orogeny beyond a certain threshold may retard chemical weathering. Nevertheless, the premise is strong justification for ongoing research, with age control, quantified rates and degrees of weathering, but over different climatic and tectonic settings.

4.2.5 Providing Natural Mineral Resources

The byproducts of weathering are occasionally useful as natural mineral resources, and their surface presence enhances their economic availability when compared to deeper strip mining, quarrying, or tunnel mining. Materials such as gravel and aggregates, glass sand, clay, and aluminum, magnesium, and iron ores may occur at the surface as end-products of weathering (Ollier and Pain,

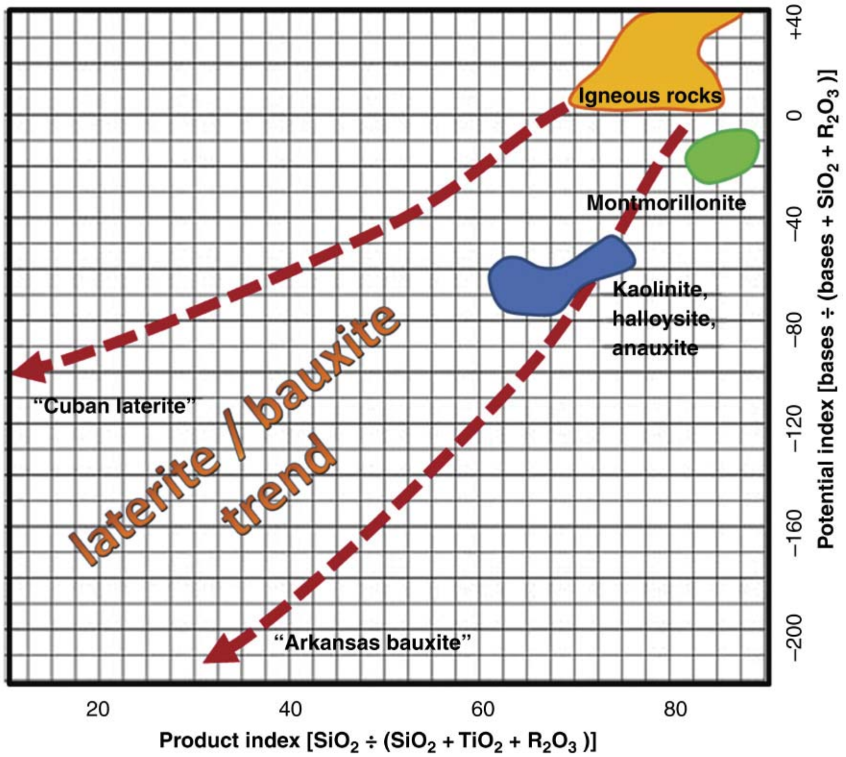

FIGURE 4.3 **Reiche's (1950) weathering product versus weathering potential indexes, showing the trend from igneous rocks to end-stage bauxite and laterite.** *(Reproduced from Pope (2013b).)*

1996; Taylor and Eggleton, 2001). Likewise, precious and strategic metals such as nickel, gold, silver, and copper tend to concentrate in the upper reaches of well-weathered regolith, or may occur in placer deposits downstream of regolith source areas (Ollier and Pain, 1996; Taylor and Eggleton, 2001). Australia has been the focus of elaborate exploration of regolith resources, including geophysical methods and remote sensing to identify regolith structure as well as chemistry (Butt et al., 2008; Pain, 2008). Wilford (2011a) employed airborne gamma-ray spectrometry to assess the presence of potassium, thorium, and uranium, as part of a weathering intensity index, resulting in a continent-scale mapping of weathering intensity for Australia.

Soil is of course a vital natural resource and byproduct of weathering. The roots of the science of pedology are found in initial attempts to understand soil and manage it. Soil is subject to both natural and human impacts. Soil management and impacts are beyond the scope of this chapter, but Richter (2007) provided an overview of the history and future human interfaces with soil resources.

4.3 TYPES OF WEATHERING (ROCK DECAY)

The traditional view of rock weathering in textbooks separates mechanical and chemical weathering processes. The former involves breakdown of the rock or mineral into smaller pieces without changing its chemical composition, whereas the latter involves breakdown of the rock or mineral by means of changes to the chemical compositions (adding or subtracting atoms, ions, or molecules, at the smallest scale). Many authors consider biological weathering to be a separate third type of weathering. Indeed, biological agents are important and in many cases dominant, although ultimately chemical or mechanical in nature. At the nano-scale of the mineral surface (Dorn et al., 2013b), the creation of smaller particles – by mechanical or chemical means – is almost semantic. Depetris et al. (2014) state that mechanical weathering is first to occur as the opening or exposure of surface area to subsequent chemical processes. Opening surface area to chemical alteration is accurate, although it may also be argued that the mechanical flaws in the rock or mineral that represents a locus of failure may well have been initiated by chemical attack. In reality, chemical and mechanical processes of decay, including the biological types, are synergistic, occurring in parallel and often with positive feedback between processes. Blair (1975) summarizes the relationship well: "It is frequently difficult and unnecessary to separate physical weathering from chemical weathering, for the two usually work together." A summary of the processes is provided here.

4.3.1 Normal Stress

Stress exists where pressure or force exceeds the ductile capacity of the rock or mineral. Normal stresses include compressive and tensile forces. The simplest example of compressive stress is that of the mass of a heavier object resting on a rock, which may induce fracture. Tectonic forces of compression also impart fractures, even at the crystal level; these fractures are in turn avenues for weathering by other agents.

A common subject of study in the rock decay/weathering literature is the pressure exerted by substances expanding within confined spaces in the rock or mineral, such as in cracks or voids. Ice is a common example, where the volume of frozen water increases over its liquid state. In confined cracks, pressure exerted by the ice widens the crack; the process may be repeated as more liquid water is allowed in and also freezes. It is argued (Bland and Rolls, 1998), however, that confining pressures may not be as much as anticipated. First, ice is capable of compressing in a ductile fashion. Second, cracks are almost always actually planes of weakness within the rock, capable of spreading the stress laterally instead of against the walls of the crack. Water pressure in advance of ice crystal growth can be more important (Bland and Rolls, 1998). Alternately, thermal stress (given later) may in fact account for mechanical fracture observed in cold (Hall and Hall, 1991) and hot (Viles, 2005) condition.

Salt-crystal growth is similar in principle to ice-crystal growth, although with less controversy. Salts are common in dry regions but also present near ocean coasts, in urban areas, and as long-transport aerosols (Goudie and Viles, 1997; McDowell et al., 1990), so more prevalent than would be expected. A substantial body of research on salt-induced decay derives from stone conservation and cultural heritage studies. Salts enter the rock in water solution, and then precipitate out as growing crystals as the water evaporates, so some duration of drying is required. Repeated wetting and drying is capable of inducing cycles of salt-crystal stress on a rock, more capable of damage to the rock. Not only at the scale of visible fractures or crystal/detrital grain boundaries, salt-crystal stress is also observed at the micro- and nano-scale, rupturing mineral weaknesses and lattices (Pope et al., 1995). Calcite crystal growth from calcium carbonate deposition in dry areas would present similar mechanical stress in soft or decayed rock (Boettinger and Southard, 1990).

The growth of plant roots has long been associated with mechanical weathering (cf. Ollier and Pain, 1996; Yatsu, 1988), and recent studies attribute the importance of both large and fine roots to mechanical weathering in the soil (Gabet and Mudd, 2010; Richter et al., 2007). Many introductory textbooks feature illustrations of boulders pried apart by tree roots, an image that would seem obvious to accept. Bland and Rolls (1998, p. 159) argued that the pressure of plant roots is insufficient to fracture rocks except in very weak rock, given that the radial pressure is only exerted onto two rock planes in a crack. This posits that plant roots simply take advantage of existing fractures initiated by other mechanical processes; the appearance of physical stress is simply coincidental. Root stress may be one of many processes where field-observed phenomena have yet to be rationalized by laboratory or numerical modeling. Plant roots do play a role in disturbing the soil, including wind-thrown root masses that may rip up weakened regolith rock (Gabet and Mudd, 2010; Phillips and Marion, 2006). Researchers appear to agree that microscale root hyphae are capable of mechanical breakup of minerals, attributed to lichens, algae, and fine roots of vascular plants (Richter et al., 2007; Duane, 2006; Chen et al., 2000; Lee and Parsons, 1999; Hall and Otte, 1990). Mechanical processes include both compression stress by root hydration as well as the tensile "ripping up" of attached particles by roots or hyphae.

Degrees of mineral expansion and contraction are possible with wetting and drying. Mineral hydration can expand the crystal dimensions, exerting stress similar to that of salt. The process of hydration is a chemical one, in which hydroxide molecules are incorporated into the mineral, thereby changing its chemical composition. However, the process also resembles a mechanical stress at the molecular scale. Hydroxide ions disrupt the mineral lattice, rendering it weaker in some cases, as in silica hydration (cf. Aomine and Wada, 1962), or expanding and splitting the crystals, as in salt, clay, or mica hydration (Velde and Meunier, 2008; Doehne, 2002). Hydration can take place in any environment where at least hygroscopic water is present. Dehydration works in the opposite fashion, removing hydroxide ions from hydrated minerals, which has the potential to collapse the mineral structure.

Salts, iron minerals, calcite, clays, and even amorphous glass (e.g., in volcanic ash) can undergo hydration and expansion. The reported mechanical stress of "fissuresols" (Villa et al., 1995) probably derives from clay-mineral expansion and calcite crystal growth (Dorn, 2011). Clay hydration is a good example of a chemo-mechanical process: Water bonds to the phyllosilicate crystal lattice, this in turn causes the lattice to expand, exerting physical pressure.

Apart from the above-mentioned root-ripping, tensile stresses are relatively less relevant to rock decay. One important exception is the process of pressure unloading, also sometimes known as sheeting, dilation, and exfoliation.[1] Blackwelder (1925) is credited with the first comprehensive description of pressure unloading. Where large rock masses, formerly buried under tonnes of crust, regolith, or glacial ice, are exposed to the atmosphere, confining pressures are relaxed, and the rock expands. Where it exceeds the plastic expansion limits, the rock fractures parallel to the exposed surface. Perpendicular fractures also develop because rock is incapable of stretching to its new expanded volume. Domed rock structures as well as cliff faces experience unloading stress. Prior to separation and falling, the widening fractures can channel water into the rock, along with biotic and other external materials, contributing to further weathering. The released rock slabs fall and become components of the detrital geomorphic system (Pope, 2013a).

4.3.2 Thermal Shock and Fatigue

The role of thermal shock, of rapid temperature excursions within the rock, has been a longstanding debate in the study of mechanical rock decay. Early researchers such as Blackwelder (1933) and Reiche (1950) dismissed the importance of thermal shock in producing rock fragments. However, with field data indicating the extremes of temperature change that exist on rock faces, Hall and Hall (1991) demonstrated the potential for tensile contraction forces during temperature excursions in dry polar rock surfaces. Viles (2005) presented comparable data from a hot desert situation. In fact, Sumner et al. (2004) found similar ranges of temperature excursions in deserts of South Africa and Antarctica, capable of thermal shock weathering. Repeated thermal excursions could result in eventual material fatigue (Hall, 1999).

A subset of thermal shock could include explosive detachment, caused by rapid expansion due to extreme heat. Numerous researchers note spalling and granular separation after fires (Dorn, 2003; Ollier, 1983a; Blackwelder, 1927), and the explosive expansion of water vapor just below the rock surface is a likely cause. The prevalence of natural fires in a number of ecosystems

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[1] "Exfoliation" is also used by some authors to describe a thin-layer (~1 cm) diminishing of rocks, often with a combination of mechanical and chemical processes. On corestones, exfoliation is sometimes referred to as "spheroidal weathering." The processes are not identical and the terminology is potentially confusing.

(Belcher, 2013) suggests that fire weathering may be more important than previously suspected. Even more extreme than fire, Knight and Grab (2014) make a good argument for the occurrence of lightning weathering, certainly qualifying as explosive, on exposed mountain ridges. They suggest that in some locations, lightning-induced weathering is a better explanation for shattered rock previously attributed to ice weathering processes.

4.3.3 Solution and Dissolution

Solution and dissolution involve the ability of water, often fortified with acids, to remove ions. Solution is the most straightforward process, able to disrupt molecules in one step by creating a solute ion and an aqueous byproduct. Solution of calcium carbonate in the presence of acid precipitation or acidic groundwater produces calcium ions and bicarbonate:

$$\mathrm{CaCO_{3(s)} + H_2O + CO_{2(aq)} \rightarrow Ca^{2+}{}_{(aq)} + 2HCO_3{}^{-}{}_{(aq)}}$$

This process is relevant over a broad portion of the planet where carbonate rocks are present, and responsible in the extreme case for karst landscapes, but also for the common calcium load in surface waters.

Solution of silica, SiO_2, is also possible, although at much slower rates than solution of carbonate rocks. In the presence of water, silicate molecules dissociate into metastable monosilicic acid.

$$\mathrm{SiO_{2(s)}} + n\mathrm{H_2O} = \mathrm{Si(OH)_{4(aq)}}$$

Solution is the process by which quartz, among the most resistant of minerals, is capable of decay. In its most extreme form, silica solution is responsible for silica karst observed in sandstone and quartzite rocks (Wray, 2013). Such landscapes have been otherwise stable enough, in relative tectonic quiescence, to be exposed to the long-term effects of solution. At much smaller scales, silica solution is probably responsible for overgrowths and glazing observed on quartz sand particles (Krinsley and Doornkamp, 2011).

Dissolution is a more complex process, but important to the silicate minerals other than quartz. Acid is involved, such as carbonic acid by atmospheric precipitation or by combination of water with soil, air, organic acids near the soil, and around sulfide deposits (including mine waste). For example, the feldspar mineral albite decays in weak acid to the aluminosilicate clay, kaolinite, releasing also quartz (often as a precipitated silicate cement or amorphous coating) and sodium ions in solution:

$$\mathrm{2NaAlSi_3O_8 + 2H^{+} + H_2O = Al_2Si_2O_3(OH)_4 + 4SiO_2 + Na^{2+}}$$

Hydrolysis, sometimes also known as incongruent dissolution due to its multistep and parallel decomposition sequence, is also relevant to the decomposition of silicate minerals. It may take place with acids or with water. For aluminosilicate minerals, the process results in end-product clays with ions of potassium, sodium, calcium, and quartz precipitate (dissociating from an initial silicic acid byproduct), as in this example for an alkali feldspar:

$$2(K, Na)AlSi_3O_8 + 11H_2O = Al_2Si_2O_3(OH)_4 + 4H_4SiO_4 + K^+ + Na^+ + 2OH^-$$

Not all silicate decomposition results in the formation of clay, as in this example of olivine, but does produce iron and magnesium ions (which may precipitate out), as well as precipitated quartz (again dissociating from a silicic acid byproduct):

$$(Fe, Mg)_2SiO_4 + 4H_2O = H_4SiO_4 + Fe^{2+} + Mg^{2+} + 4OH^-$$

Dolomite decomposition is an example of hydrolysis outside of the silicate minerals, producing calcium and magnesium ions as well as carbonic acid as a byproduct, which in turn take part in further solution reactions:

$$CaMg(CO_3)_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 2OH^- + 2HCO_3{}^-$$

4.3.4 Rock and Mineral Decay by Organic Molecules

Organic chemicals that derive from living as well as decomposing dead organisms introduce unique and sometimes particularly intense decay agents into the near-surface regolith. The soil, particularly in the rhizosphere of root–soil interaction, is highly active chemically, including oxidation, solution, hydrolysis, and chelation reactions. Ollier and Pain (1996) pointed out the role of oxidation in plant uptake of iron and other nutrients, and the role of bacteria in silica depletion. Organic acids such as oxalic acid and humic acid can be effective in the decay of silicate minerals, such as this example of anorthite decomposition. (Scott and Pain, 2008, after Trencases, 1992):

$$\begin{aligned} CaAl_2Si_2O_8 + 8H^+ + [\text{organic ion}] = Ca^{2+} + 2(Al^{3+} + \\ \text{organic anion}) + 4H_2O + 2SiO_2 \end{aligned}$$

The reaction releases Al as an organic compound, as well as calcium ions and a quartz precipitate.

Chelation is the process by which metals such as aluminum and iron are preferentially extracted by acids and organic molecules (such as ligands) derived from decomposing vegetation. Lichens, as pioneer organisms at the lithosphere/biosphere interface, incorporate chelation and oxalic acid in initial rock decay (Wilson and Jones, 1983; Schatz, 1963). Masiello et al. (2004) attributed chelation processes for the translocation of iron and aluminum with carbon in grassland soils.

4.4 FACTORS RELEVANT TO ROCK DECAY

The degree and rate of rock decay is influenced by three arch-factors: (1) time, (2) availability of rock and mineral decay agents, and (3) efficacy of rock and mineral decay agents, indicated in Table 4.1. Rock decay tends to be a slow process, but decay increases with time up to the point of weathering-agent saturation or

TABLE 4.1 Cascading Factors of Rock and Mineral Decay

← More encompassing -More specific →

Time	Sources for decay agents	Environmental (exogenic) agents	Efficacy of decay agents	Vulnerability of the rock or mineral	Chemical composition	Molecular structure	Kinetic characteristics
					Access to the rock or mineral	Crystal or grain structure	Macroporosity
							Microporosity
							Surface area
						Depth	Surface erosion
							Rate of decay front
		Crustal (endogenic) agents		Power or energy of decay agent	Concentration and frequency		Recurrence factors
							Fatigue factors
							Dilution factors
					Environmental catalysts		Temperature
							Water
							Aeration
							Biosphere

The factors listed are encompassing and representative, although not necessarily exhaustive, as additional factors may be found.
Derived from multiple sources, including Viles (2013, 2001), Anderson et al. (2007), Phillips (2005), Pope et al. (1995), Simonson (1959), and Jenny (1941).

end-product stability. With enough time, extensive rock decay can take place, anywhere. Time is therefore the determinant factor for all others. The weathering system also requires available decay agents, and materials to decay (assumed, not indicated in Table 4.1). Exogenic decay agents derive from the environment, whereas endogenic decay agents derive from the crust itself (such as gravity, tectonic stress, geothermal heat). Decay agents are in turn rendered more or less effective by intrinsic properties of the rock or mineral, and by factors in the environment that catalyze or diminish the power of the decay agent. Additional sub-factors become relevant specific to the time and location. The environment is clearly important, but equally so is the nature of the rock and mineral.

Reiche (1950) introduced a concept of “weathering potential,” useful to distinguish different materials with respect to eventual thermodynamic equilibrium, therefore a chemical weathering attribute. Materials with a high weathering potential consist of freshly exposed igneous rock, most out of balance with the ambient surface conditions of the Critical Zone. Materials with low weathering potential are near the end-stage of weathering, close to thermodynamically stable at the Critical Zone, such as bauxite and laterite. Reiche illustrated the weathering potential index (leachable bases compared to silica) graphed against a weathering product index (silica loss compared to more stable titanium and aluminum oxide), reproduced in Fig. 4.3.

It should not be surprising that different factors dominate in different settings; no single factor is capable of distinguishing or determining the degree of decay. This applies spatially, across regions and landscapes or at smaller scales such as slope elements, and vertically through the regolith profile. Climatic factors provide one example. Studies by Dixon et al. (2009) and Brady et al. (1999) show the importance of climatic variables such as rainfall, especially when combined with biotic weathering agents, in sampling transects over local to regional scales. However, Pope (2013b), Pope et al. (1995), Viles (2013), and Anderson et al. (2007) provide evidence for factors such as soil and regolith structure, overburden erosion rates, and differences in weathering agents over-ride presumed dominance of enhanced decay due to high temperatures and water availability in the tropics. Likewise, Dixon and Thorn (2005) reported the dominance of chemical processes in subarctic and alpine environments ordinarily presumed to have greatly dampened chemical activity. Decay agents and factors vary with depth as well. Anderson et al. (2007) illustrated the terrestrial Critical Zone profile (the regolith, reproduced in Fig. 4.1) with chemical or mechanical processes dominant nearest bedrock, and chemical processes dominant in the upper saprolite, whereas a mix of mechanical (including transport), chemical, and biological processes impact the soil. Anderson et al. pointed out that this is a generalization, where variation in these trends may be the result of weathering potential and weathering agent efficacy. Further, it is important to remember that weathering processes are, as mentioned earlier, synergistic, and not strictly only chemical or only mechanical. At the depths of the Critical Zone, the transition to the diagenesis-influenced crust, mechanical stresses help to break up the massive rock formed in the crust, yet chemical processes are not absent and may still take advantage of existing petrographic weaknesses, which may in turn fail under physical stress.

Scale is relevant to rock decay factors. Rock decay initiates with mineral decay, the smallest of building blocks within the rock (whether they be interlocking crystals or cemented detrital particles). Mineral decay ultimately rests on the nanoscale separation of molecules, either by chemical or mechanical means. Factors influencing the processes at the nanoscale “boundary layer” (Dorn et al., 2013b) may be quite different from those of ambient atmospheric conditions at the ground surface (Pope et al., 1995). Present “weather” and “climate” of the location may well be poor proxies for the actual nanoscale boundary layer. That said, the nanoscale boundary layer is not divorced from its environmental envelope. Nested environmental realms exert influence (Table 4.1), if not control, on successively smaller envelopes, from planetary and regional to local to site-specific and finally to the mineral surface environments.

Figure 4.4a and b illustrates the weathering/mineral system, including global factors but focusing on the weathering boundary layer. Note that both sides of

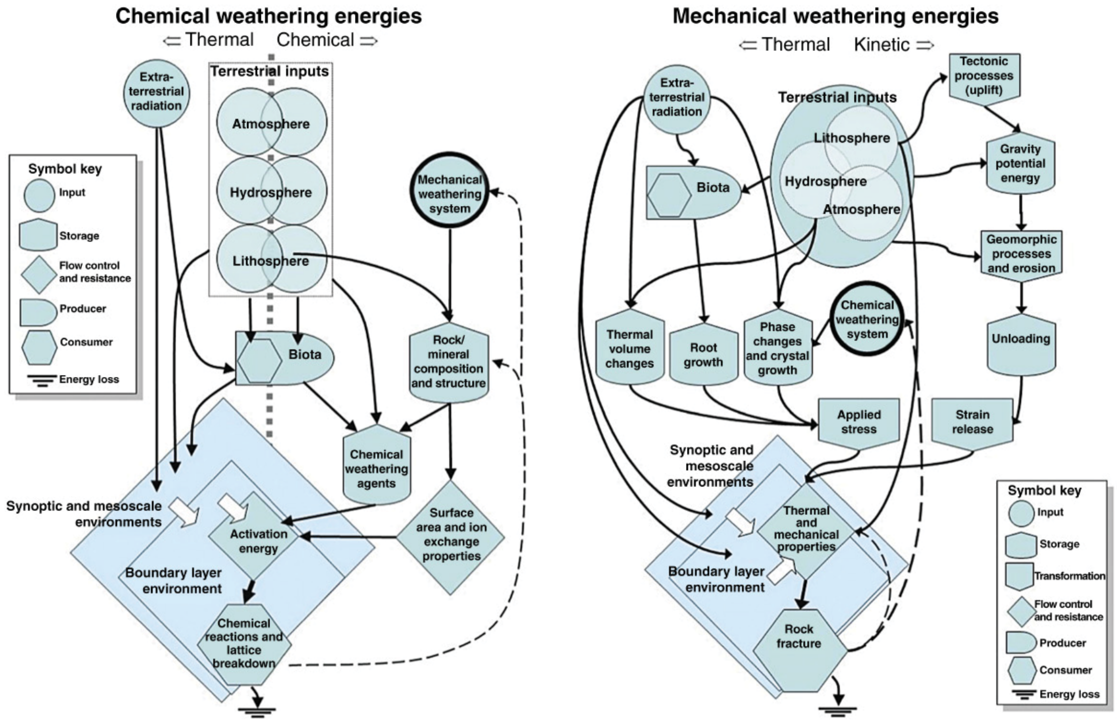

FIGURE 4.4 **The weathering (rock decay) system, expressed in terms of cascading energy.** Chemical (2a) and mechanical (2b) processes and factors are treated separately, but are connected by a feedback tunnel indicated in each diagram. Symbols follow the standard typology of systems.

the system, the mechanical and the chemical, are linked through a feedback "tunnel" indicated in each diagram. The system as illustrated is conceptual in energy contributed and used for weathering, borrowed in part from the ecosystem energetics of Odum (2000) and the factors illustrated in White et al. (1992). The combined lithosphere, hydrosphere, atmosphere, and biosphere (the terrestrial inputs) provide the chemical weathering agents, whereas the intensity and rates of these agents are modified by both external energy contributions and parent material properties (including mechanical processes). Likewise, mechanical weathering agents are sourced externally, and modified by external (such as geomorphic) and internal (rock/mineral) properties, as well as chemical weathering. As the process evolves, energy feedback (both positive and negative) moves into the system, as well as some net energy loss as the system progresses toward stability.

The concluding message is that it is possible to conceptually model decay agents and factors, but most researchers on the Critical Zone recognize that individual cases and locations are quite varied and often surprising. This is a reality that challenges our abilities to model the weathering system and to reconcile models with field observations (Dorn et al., 2013a).

4.5 ROCK DECAY IN THREE DIMENSIONS: THE "WEATHERING MANTLE"

Rock decay is readily apparent at the surface, with direct exposure to the elements, and at the near-surface, associated with pedogenesis. The Critical Zone is often much deeper (Fig. 4.1), and it is argued (Buss et al., 2013, for instance) that significant chemical decay is capable 10 m to more than 100 m below the surface. Terminology used in the weathering mantle varies; Table 4.2 illustrates the regolith zones and terminology used by several authors, suggesting congruence but some overlap. It should be noted that the terminology and classification is biased toward crystalline bedrock, and in humid-warm/hot environmental conditions (presently or presumed in the past). Figure 4.2 illustrates a typical regolith profile, in this case in weathered metamorphic rock.

In the deepest regolith, the influences of the surface (meteoric water, ambient surface temperatures) transition to those of the crust (geothermal heat, diagenetic processes), although in most cases, the Critical Zone derives minimal direct deep earth influence. Temperature ranges reach near-equilibrium at depths of 1 m or less (Anderson, 1998). The boundary between diagenetic and weathering processes is ill defined, and perhaps semantic. Ollier and Pain (1996, p. 72) rightly point out that decay occurs in both water-saturated (e.g., below the water table) and water-unsaturated zones; this entire thickness is encompassed in the defined "Critical Zone." Precipitated elements that would derive from hydrothermal interactions help distinguish hydrothermal alteration from surface-derived weathering (cf. Thuro and Scholz, 2003; May, 1994). Even so, the results are not straightforward, and sometimes controversial (Ollier, 1983b; Young and Dixon, 1983).

TABLE 4.2 Segments of the Regolith or Weathering Mantle as Described by Different Authors

Authors	Pavich et al. (1989)	Ackworth (1987)	Jones (1985)	Eggleton (2001) and Migoń (2013)	Anderson et al. (2007), see Fig. 4.1
Regions	*Appalachian Piedmont*	*Humid tropics*	*Humid tropics*	*"Idealized regolith"*	*Vertical Critical Zone*
←Increasing depth	Soil	A horizon	Quartz-rich soil	Pedolith	Soil and/or regolith
	Massive subsoil	B oxic horizon	Duricrust		
	Saprolite	Upper saprolite: sandy-clay/ clayey-sand	Completely decomposed rock	Saprolite	Saprolite
		Mid-saprolite: massive secondary clays	Decomposed rock, original structure		
		Lower saprolite: altered rock	Weathered rock, some pseudomorphs	Saprock	
	Weathered rock	Transition bedrock, fractured	Slightly weathered rock		Fractured + weathered rock
					Fractured rock
			Weathering front	Weathering front	Weathering front
	Fresh rock	Fresh rock		Bedrock	Fresh rock

Deep regolith profiles are noted in tropical and subtropical locations, indeed one of the Critical Zone Observatories is established in the deeply weathered terrain of Luquillo, Puerto Rico, for the purposes of observing deep decay processes. Although conditions favoring intense and effective decay are present in tropical environments – abundant water, organic compounds, and high temperatures – time and stability are also relevant to developing deep profiles. Deep regolith profiles do occur outside the tropics, and although some argue that these can be relict of past tropical times over the long durations of regolith formation (by climate change or tectonic drift), deep weathering need not be tropical in origin (Pope, 2013b). Blair (1975), for instance, described deep grus in some places more than 50 m thick in Pikes Peak granite of the Colorado (USA) Front Range. In prestressed rock fabric, groundwater was responsible for chemical deterioration of biotite, lending to expansion and disaggregation. Although Chapin and Kelley (1997) presumed deep chemical weathering in the Pikes Peak granite to a warmer, wetter climate on the Eocene-aged erosion surface, Blair (1975) found the profile devoid of clay mineral formation characteristic of feldspar decay seen in the tropics. Bazilevskaya et al. (2013) summarized 27 studies in both temperate and tropical climates and found that although granitic terrain regoliths of similar age were slightly thicker, they were not statistically so, and regoliths of similar age on rocks of basaltic composition were thinner in tropical climates. (These results parallel the relative lack of variation in chemical denudation rates across climatic regions, noted by Saunders and Young (1983), and summarized and discussed in Pope et al. (1995).) Dosseto et al. (2011) showed that soil production rates (regolith in general) in granitic parent materials are "relatively insensitive to climate."

Regolith thickness can be thought of as a balance between regolith production by weathering at the saprolite/rock interface (the weathering front), and loss of material by erosional stripping at the surface. Ahnert (1987) modeled the production of regolith thickness determined by weathering rate and differentiation between chemical and mechanical weathering efficacy (Fig. 4.5), and precedes a similar conclusion by Gabet and Mudd (2009) by more than 20 years. In effect, regolith thickness influences the rate of weathering. The model predicts a "critical thickness" (C_c) at which rates of weathering peak, when there is at least some chemical weathering in the system (e.g., almost always). In systems of purely mechanical weathering (rare), weathering rates decrease continuously as disaggregation relieves the stress on solid rock, and further mechanical weathering is unlikely to have continuing impact. For systems with combined mechanical and chemical weathering (almost all) or only chemical

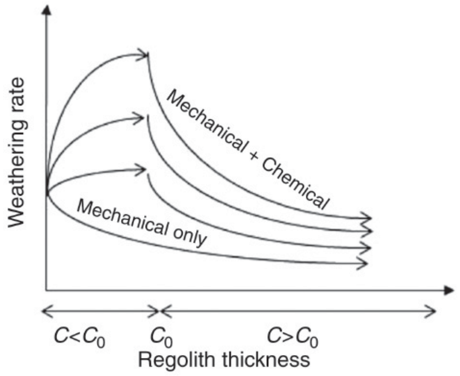

FIGURE 4.5 Ahnert's (1987) concept of regolith thickness as a function of weathering rate and type of weathering.

weathering (also rare), weathering rates increase from initial exposure up to the critical thickness point, owing to increasing porosity in the regolith and ability to maintain water. In a previous study, Ahnert (1976) described a zone of "optimal chemical weathering" somewhat below the surface which decreased as overburden cover increased (also observed in recent studies, such as Brantley and Lebedeva, 2011, and Bazilevskaya et al., 2013). The modeled relationship (see also Fig. 4.5) is as follows, for degree of weathering per unit time, W (an overall weathering rate), from the onset of weathering until the critical thickness has reached ($C < C_0$):

$$\text{for } C < C_c, \quad W = W_c\left(1.0 + k\frac{C}{C_c} - \frac{C^2}{C_c^2}\right)$$

where W_c is the chemical weathering rate, k is a coefficient, C is the regolith thickness, and C_c is the specific critical regolith thickness. Smaller values of regolith thickness C compared to the critical thickness C_c equate to lower unit weathering. Beyond (thicker than) the critical thickness ($C > C_0$), weathering rates decrease with progressively increasing regolith thickness:

$$\text{for } C > C_c, \quad W = W_c \; k \; e^{-k(C - C_c)}$$

This is a negative exponential function, in which the unit-weathering rate decreases with increasing regolith thickness. Beyond the critical thickness, it becomes more likely that weathering agents lose efficacy (for instance, become saturated) and also more likely that the regolith components approach thermodynamic equilibrium.

The regolith thickness model of Ahnert (1987), as well as Phillips' (2014) concept of convergent weathering intensity and weathering rate, could be applied to explain the "unexpected" regolith thickness differences observed by Bazilevskaya et al. (2013). In their study in the Virginia (USA) piedmont, granitic profiles were much thicker than those on diabase, which is the opposite of what was expected, based on mineralogical composition. Although potentially weathering is slower due to higher silica content, the granitic rock was deeply permeated through the loss of biotite, and was able to develop a critical depth thicker than that of nominally faster-weathering diabase. Migoń (2013) summarized a number of factors that are conducive to deep weathering mantles, reproduced in Table 4.3.

With long term decay of the regolith comes mass loss. Although Ahnert's (1987) model confines itself simply to weathering production, the impacts of surface material loss also determine regolith thickness. The concept of "weathering-limited" versus "transport-limited" landscapes comes into play. Transport-limited landscapes are those in which erosion processes are slower than weathering production. Tropical conditions of high moisture and temperature are commonly used to illustrate transport limitation. Weathering-limited is applied to locations where erosion exceeds weathering production. Textbooks cite

TABLE 4.3 Migoń's (2013) **Summary of Factors of Enhancement or Limitation to Deep Weathering Mantles**

Rock property factors	**Enhanced deep weathering**	**Limited deep weathering**
Mineralogy and rock chemistry	• Rocks with a large proportion of easily weatherable minerals • Rock with less Si, but more Fe, Ca, Na, and Mg	• Quartz-rich rocks • Rocks higher in Si, or rich in feldspars
Fabric	• Weak fabric, susceptible to granular disintegration • High primary or secondary porosity	• Interlocking crystal structure • Low primary porosity
Discontinuities	• High fracture density • Discontinuous, irregular joint network which slows water movement	• Massive rocks with widely spaced fractures • Wide and continuous joints, rapid through-flow
Geomorphic factors	**Enhanced deep weathering**	**Limited deep weathering**
Local relief	Mid- and foot- slope, water more available	Upper slopes and hilltops, less water
Regional relief	Low relief, limited surface erosion, retains weathered mantle	Higher relief, more erosion, lower residence time of mantle
Climatic factors	**Enhanced deep weathering**	**Limited deep weathering**
Precipitation	Higher precipitation, faster weathering	Less precipitation, slower weathering
Temperature	Higher temperature, faster chemical reactions	Lower temperature, slower chemical reactions; ground freezing shuts down deep weathering

deserts and polar areas as lacking sufficient weathering to keep pace with erosion. Pope (2013b) and Pope et al. (1995) pointed out that weathering efficacy is not the sole factor in weathering/erosion limitation. Factors that retard erosion, such as dense vegetation, lower slopes, and higher infiltration rates tend to be associated with many presumed "high weathering" climates. Conversely, slopes lacking vegetation and with higher rates of surface runoff would result in high erosion, regardless of weathering intensity.

Lastly, chemical denudation requires mention in regolith thickness. Weathering removes material by dissolved ions in ground- and soil-water. Volume is not necessarily lost: deeply decayed saprolite can be thought of as a "skeletal" remnant of former rock, with as much as one-third of the mass missing in the form of removed ions and translocated fines (Schaetzl and Anderson, 2005, p. 172). In other cases, mass loss results in a compaction of the surface, and sometimes lowering. Pavich (1989) attributed the undulating geomorphic surface of the Appalachian Piedmont to long-term decay and then settling of the resulting saprolite, as opposed to an old erosion surface (peneplain). This process may account for other deeply decayed and geomorphically old surfaces elsewhere (Phillips, 2002).

4.6 ROCK DECAY IN THE FOURTH DIMENSION: TIME AND RATES IN THE CRITICAL ZONE

Weathering rates have been studied from the scale of mineral lattices to soil profiles to entire landmasses. Although weathering varies by three-dimensional space, across geographic area and into the surface thickness, it also varies over time. Observing weathering over time introduces the fourth dimension, and the ability to classify rates of change done by weathering. Figure 4.6, based on the work of Wilford (2011b), illustrates the idealized evolution of regolith, with the concomitant losses of cations (useful for calculating weathering ratios), as well as changes in properties of the regolith such as permeability and water holding capacity, fertility, and biological activity.

In chemical decay processes, the relationship between reaction rate and temperature is demonstrated by the Arrhenius equation:

$$\ln k = \ln A - \ln\left(\frac{E_\mathrm{a}}{RT}\right)$$

where k is the rate constant, A is the molecular collision factor, E_a is the activation energy of the substance, R is the gas constant, and T is the temperature. In low temperature geochemical reactions such as rock decay, the nature of the rock composition factors into the activation energy, the efficacy of weathering agents would be reflected in the molecular collision factor, and temperature would become an important variable, the relation of rock decay to climate. Thus, rates would increase when ambient temperatures increase and/or decay agents increase. The equation can be solved for activation energy E_a when differing decay outcomes (such as mass loss, ΔM) can be compared at different temperatures (such as between locations, or the same location at different times):

$$E_\mathrm{a} = \frac{R\left(\ln(\Delta M_1/\Delta M_2)\right)}{T_1^{-1} - T_2^{-1}}$$

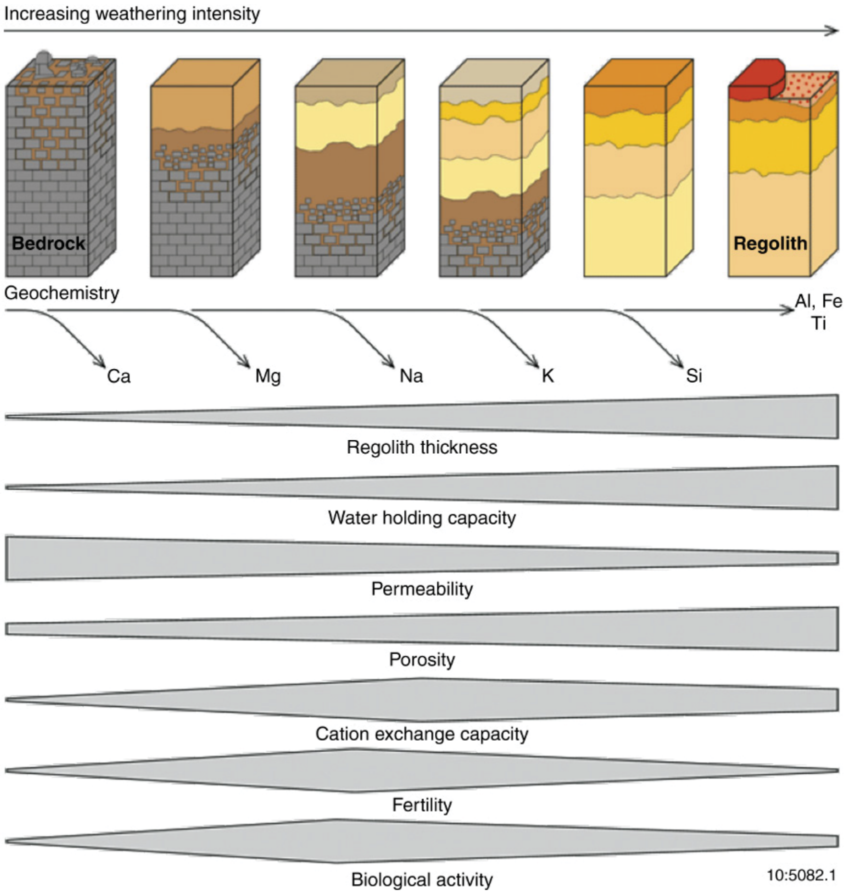

FIGURE 4.6 Evolution of an idealized regolith profile. *(From Wilford (2011b), weathering intensity map of the Australian continent. AusGeo News 101, March 2011.)*

In this case, it can be seen how the activation energy, the minimal energy needed for the reaction to take place, is lower when ambient temperatures are higher.

Contact time with water is important to chemical reactions in the regolith. The Critical Zone encompasses the vadose profile, in which the matrix is water-unsaturated except for specific saturation events or seasons. The amount of water in contact with soil or regolith particles ranges from adsorbed films on particles (“hygroscopic” water) to water filling small pores (“capillary” water) to saturated conditions in which pores are completely full, and varies considerably based on texture/particle size and composition (Schaetzl and Anderson, 2005). Saturated water is influenced by positive gravitational potential, whereas pore and adsorbed water would have negative potential (osmotic or matric, respectively), thus greater attraction to the particle (Brady and Weil, 2008). Adsorbed water is theoretically capable of chemical decay processes on mineral surfaces (Zilberbrand, 1999). However, without re-supply these thin film solutions acquire more negative potential, and would quickly saturate and lose effectiveness. Studies of mineral decay associated with adsorbed or hygroscopic films are mostly limited to the stone conservation literature (Camuffo, 1995; Larsen and Nielsen, 1990), with relatively little attention to natural environments, although the status of nanoscale observation is well developed (MacInnis and Brantley, 1993; Brantley et al., 1993; Dorn et al., 2013b).

In general, the residence time (t_R) of water in the soil and regolith is a function of both volume (V) and flow rate (Q) (Langmuir, 1997):

$$t_{\mathrm{R}} = \frac{V}{Q}$$

Residence time for water in the soil increases with increasing depth in the soil and regolith. Within the soil profile, depending on texture and permeability, residence times of water are on the order of <1–4 months, whereas deeper into the regolith, residence times are measured in years to decades (Bleam, 2012; Matsutani et al., 1993; Langmuir, 1997; Stewart and McDonnell, 1991). Some mineral-water reactions take place nearly instantly, but reactions such as hydrolysis and recrystallization may evolve over many thousands of years (Langmuir, 1997). Thus, longer exposure to water results in greater potential for decay, up to the point of solute saturation in the water. As an illustration of contact time correlation to chemical activity, lake alkalinity has been shown to increase with time as the groundwater residence time increases in the soil and regolith (Wolock et al., 1989). Although chemical reaction rates would theoretically slow as solutions become saturated or decay products reach end-stage equilibrium, it appears that long-resident (25 years) regolith water does not show a rate decrease (Wolock et al., 1989).

At the mineral boundary layer, surface area and solution concentration are relevant to the decay rate. Lasaga (1994) modeled these relationships as follows, with a given mineral θ influenced by a solution i:

$$r = \frac{\mathrm{d}c_i}{\mathrm{d}t}\Big|_{\mathrm{diss}} = \frac{A_\theta}{V}\beta_{i\theta}k_\theta$$

where $\mathrm{d}c_i/\mathrm{d}t$ is the change in solution concentration as the dissolution reaction progresses, A_θ is the exposed area of the mineral, V is the volume of fluid in contact, $\beta_{i\theta}$ is the stoichiometric constant, and k_θ is the rate constant. Bricker et al. (2005) indicate that difficulties in estimating exposed surface area or "wetted surface area" (which also includes internal microfractures) would be cause for discrepancies in modeled versus field-observed dissolution rates. However, Pope (1995) demonstrated a means to quantify internal weathering, by image processing of backscatter electron micrographs that would be applicable to the model.

Individual minerals have different susceptibility to decay, so would have different rates of decay. A given rock (composed of several minerals) would decay initially as fast as its most susceptible minerals, although its remnants would comprise its least susceptible minerals. Lasaga et al. (1994) calculated the persistence of various minerals subjected to decay:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = -k_i \overline{V}_i$$

where for a specific mineral grain i the change in the mineral grain radius over time is a product of the dissolution rate k and the molar volume $\overline{V}$ of the mineral grain. The results mirror those assumed by Goldich's (1938) sequence of mineral weathering. A single 1-mm crystal of quartz would persist 34 million years at a log rate of $-13.39\,\mathrm{mol/m^2s}$. Rock decay end-product kaolinite would persist six million years at a log decay rate of $-13.28\,\mathrm{mol/m^2s}$. At the other end of the spectrum, a 1-mm crystal of anorthite (calcium feldspar) would last just 112 years at a log decay rate of $-8.55\,\mathrm{mol/m^2s}$, and the pyroxene wollastonite (calcium silicate) persists 79 years at a log decay rate of $-8.00\,\mathrm{mol/m^2s}$. The minerals with low-residence-time and high-decay-susceptibility also corresponds high "weathering potential" (Reiche, 1950). It should be noted that these trends are not absolute. Exceptions are possible if minerals have different susceptibilities to decay agents, as in the case where olivine persists anomalously in microenvironments devoid of organic decay agents (Wasklewicz, 1994). For the most part, mineral persistence explains the prevalence of quartz in the terrestrial surface environment, and provides a means of measuring the maturity of sediments (Folk, 1951) and the relative age of soils by mineral depletion (Birkeland, 1999). Rates of weathering of individual minerals are covered well in earlier edited works such as Colman and Dethier (1986) and White and Brantley (1995).

Calculating the persistence of a rock, composed of many minerals, becomes more complicated, and the persistence of soils and regolith profiles much more complicated. Further generalizations are required. Although most researchers recognize the primacy of the nanoscale boundary layer as the first occurrence of decay, getting from there to rock, pedon, and regolith scale is not straightforward, with a "gray box" understanding of up-scale connections and factors. All the while, the holistic nature of combined processes and combined factors needs to be recognized. Decay outcomes of soil and regolith production (matched against negative feedbacks of erosion), and contribution to runoff solute loads, provide a sense of the combined processes. Recent studies calculated generalized regolith production rates from an assemblage of individual mineral or rock weathering rates. Ferrier et al. (2010) attempted this method at Rio Icacos, Puerto Rico, arriving at rates of <200 to >3000 moles/hectare/year. Cation and silica depletion across an assemblage of rock types was used by Hartmann and Moosdorf (2011) to estimate chemical flux across multiple watersheds in Japan, potentially extrapolated to global scales.

Rates of soil and regolith formation and residence time have been a perennial topic of research, but with limited ability to pin down definitively, until recently. Researchers relied on relative and semiquantitative dating techniques (such as soil development indexes, weathering rinds on cobbles, depletion of certain minerals, accumulation of caliche, cf. Chapter 8 in Birkeland, 1999). Paleosols and buried soils could sometimes be dated with radiocarbon, luminescence, or isotope decay in volcanic deposits on bracketing strata. However, the understanding of cosmogenic isotope pathways in the Critical Zone (Graly et al., 2010 for a recent study) led to revolutionary advances in discerning soil and regolith evolution. Pavich et al. pioneered the use of Be-10 to estimate ages of soil and regolith profiles, first in the Virginia piedmont, and later elsewhere in the Appalachian Mountains (Markewich et al., 1994; Pavich, 1989; Pavich et al., 1989, 1985), arriving at a regolith residence time approximating one million years. The methods have since been applied to many locales (cf. Heimsath et al., 1997; Riebe et al., 2003; Hewawasa et al., 2013). The residence time of a particular regolith particle increases as it progresses upward to the surface (see Fig. 4.1). Dosseto et al. (2011), using uranium-series isotopes, found soil residence times less than 10 ka at the lowest reaches of a regolith profile (~16 m), but exceeding 80 ka at the surface.

In the simplest sense, the advance of the rock decay front into fresh bedrock over time can be conceptualized as a crude linear rate, for instance, × meters per million years, presuming a profile of measurable depth and an exposure surface age. Hewawasa et al. (2013) conclude a weathering front advance rate of 6–14 mm/ka in slowly weathering crystalline rock in Sri Lanka, based on a regolith base ~10-m deep and ages constrained by cosmogenic nuclide accumulation in the soil as well as river dissolved loads. Rates in reality are most certainly not linear, instead are perhaps more nonequilibrium to a point, but most likely complex and chaotic (Phillips, 2001b), not unlike other geomorphic systems (Phillips, 2005, 2014).

4.7 CONCLUSIONS

Rock decay processes are at the center of the Critical Zone, the weathering engine that modifies the Earth's crust to adjust to surface atmospheric, hydrologic, and biotic conditions. It is for this reason that weathering research has reached tremendous output, not only to explain surface processes, but also to contribute toward better understanding of surface and near-surface hydrology, ecology, climate regulation, and applications in natural resources.

Weathering is a synergistic mechano-chemical process; individual processes such as stress release, pressure, and water and acid reactions provide positive feedback to each other, and in general work together. Weathering processes focus on a nanoscale boundary layer of mineral destruction, although nested environments, at increasing scales, are the sources of weathering agents and process modifying factors. But, although weathering takes place at a point location, the integration of weathering throughout the thickness of the regolith provides the key benefit of the Critical Zone concept: a holistic, three-dimensional porous body, leaky to the interior of the surface crust by groundwater, and to the subaerial exterior via organisms and the atmosphere. The formation of this regolith zone is found to be thousands if not millions of years of development. The rates of formation, and of depletion, provide a critical focus of ongoing studies across geographic areas.

4.7.1 A Note on Critical Zone Interdisciplinarity and Weathering System Science

The Weathering System Science Consortium, one of the first scientific collaborations inspired by the NRC's Critical Zone charge, is an ideal concept of converging ideas from different disciplines – geomorphology, hydrology, pedology, mineralogy, petrology, geochemistry – tackling a common research goal. It has been successful enough that the consortium broadened its name, and the CZEN now spreads into other sciences such as ecology and geohydrology. Yet, the Critical Zone movement has not reached all in the broad scope of weathering system science, nor has CZEN been able to recognize parallel (and in some cases long-term) efforts toward the same goals. Case in point, there are still "schools" of research that continue to talk past each other without much cross fertilization. This lack of cross-fertilization is best recognized in the keystone texts and seminal research papers. Powerful sources that they are, the works of Drever (2005) and Anderson and Anderson (2010), of Taylor and Eggleton (2001) and Scott and Pain (2008), and of Turkington et al. (2005), and of the contemporary researchers contributing or cited therein, seldom cite each other, although often working in the same types of environments. Partially this derives from approaching from different disciplinary cultures, attending only a comfortable availability of conferences and symposia, and some from differing research goals, such as resource development, environmental quality, or landscape evolution. CZEN attempts to bridge those gaps, and has gained the following, although some by happenstance and less by direct recruiting outside the immediate scholarly connections.

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