Part I
Biological Weathering

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Biological Weathering in the Terrestrial System: An Evolutionary Perspective

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ABSTRACT

Weathering is the process by which a solid breaks up into its building blocks when in thermodynamic disequilibrium with the surrounding environment. Weathering plays an important role in the formation of environments that can support life, including human life. It provides long-term control on nutrient availability in natural and agricultural ecosystems through release of lithogenic elements and formation of secondary minerals that allow storage of nutrients in soils. Life itself, however, has a profound effect on weathering processes. Absence of oxidants characterized the weathering environment on early Earth (4.6–2.4 Ga), when CO_2 released during volcanic activity was the principal driver of weathering processes. The advent of photosynthesis in the Archean and resulting biogenic flux of O_2 to the atmosphere, ultimately shifted weathering towards oxidation, influencing the mineral landscape and the cycles of nutrients that supported an evolving biosphere. Land colonization by vascular plants in the early Phanerozoic and evolution of mycorrhizal symbiosis enhanced weathering by selectively mining minerals and redistributing nutrients across plant and fungi in the ecosystem. Development of complex human societies and the ever-increasing influence people exert on the environment further impact weathering and nutrient cycling, both directly and indirectly.

1.1. INTRODUCTION

Modern-day silicate weathering is strongly influenced by abundant organic and inorganic forms of carbon linked to biological activity. Dissolution of the rock releases nutrients and creates ecological niches for microorganisms and plants, while microorganisms and plant roots in symbiosis with mycorrhizal fungi create hot spots where intense gradients in carbon and water affect mineral dissolution and chemical denudation, influencing soil formation, soil fertility, landscape evolution, and long-term productivity of terrestrial ecosystems. The fine balance between abiotic and biotic factors driving rock weathering is modulated by both planetary-scale forces (solar radiation, gravity, plate tectonics) and molecular-scale interactions, and is fundamental to the evolution of the terrestrial critical zone and its capacity for supporting life.

1.2. WEATHERING

Weathering is the process of physical and chemical breaking up of a solid, such as rock, into its elementary building blocks due to the thermodynamic disequilibrium with the surrounding environment (Figure 1.1). This simple but ubiquitous process in nature is a direct consequence of

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Biogeochemical Cycles: Ecological Drivers and Environmental Impact, Geophysical Monograph 251, First Edition.
Edited by Katerina Dontsova, Zsuzsanna Balogh-Brunstad and Gaël Le Roux.

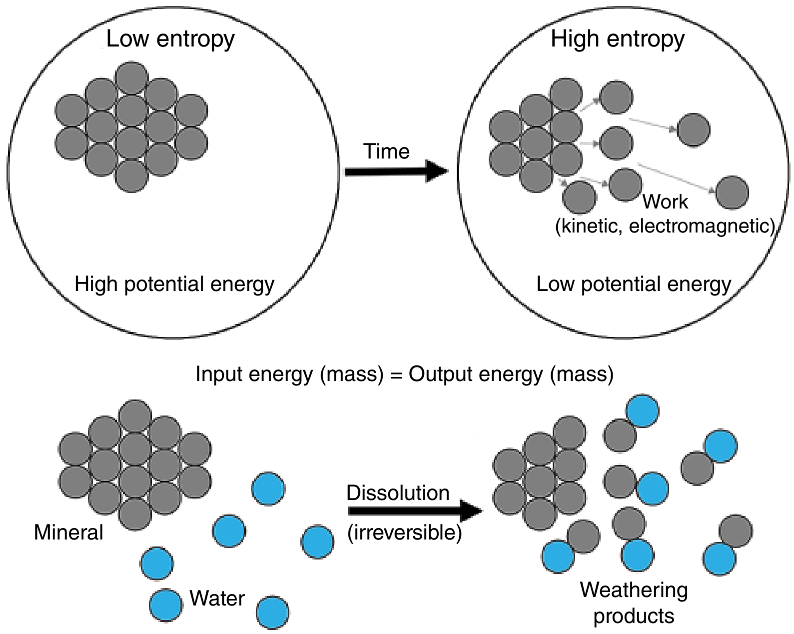

Figure 1.1 The principle of entropy in a theoretical, closed system, and how it applies to open-system natural processes, such as weathering. Initial conditions are characterized by low entropy (e.g., ordered mineral structures, water crystals) and high potential energy. As electromagnetic energy is applied over time, a portion of the initial potential energy irreversibly changes the system to a new, higher entropic state, e.g., breaking of mineral structures and binding of elements with liquid water molecules. Removal of destabilizing energy causes the system to move to a new configuration state, different from the initial one.

the universal Second Law of Thermodynamics, which connects energy and work (e.g., heat, chemical, mechanical) along the dimension of time. The law postulates that in an isolated physical system, entropy (a thermodynamic measure of unavailable energy) increases irreversibly over time (e.g., energy dissipates) when the system is out of equilibrium, or it remains constant when the system is at equilibrium (Bailyn, 1994). Open, out of equilibrium systems, such as natural environments, spontaneously evolve to reach a thermodynamic equilibrium with the outside environment, dissipating the available free energy to maintain existing gradients, unless electromagnetic radiation, kinetic/chemical, and gravitational sources of external energy are introduced. As a result, comets disintegrate over time, oceans mix, and exposed rock weathers irreversibly.

Thermodynamics is a unifying principle in Earth sciences, and can predict energy and mass transfer processes among Earth's various solid, fluid, and gaseous reservoirs, from weather, to crustal renewal and weathering. These processes can be quantified in terms of mass and energy balance between input and output components. For instance, in the present-day terrestrial environment, rock weathering can be expressed as the sum of its products (equation 1.1) (Zaharescu et al., 2017):

$$\text{Weathering} = \Sigma \text{ secondary solids, dissolved solutes, volatiles, biota} \quad (1.1)$$

1.3. THE EARLY ANOXIC EARTH

Earth is subject to one of the largest thermodynamic disequilibria in the inner solar system, with large fractions of matter and energy mixing in surface and subsurface portions of global cycles (Kleidon, 2010a). Despite a considerable decrease in the available energy from its formation, but with an evolving biosphere, Earth surface processes have maintained strong environmental gradients counteracting entropy. One important gradient is the surface redox state. The planetary surface has experienced a drastic change in its redox environment, from greatly reducing in the Hadean and Archean geological eons (4.6–2.4 Ga; Holland, 1984; Sverjensky & Lee, 2010), to one characterized by a sharp disequilibrium gradient between an oxygen-rich atmosphere–hydrosphere system and a reduced crust (2.4 Ga to present). The capacity of life to independently produce chemical-free energy (generally by using the energy transfer at the redox boundary), which counteracts entropy, further enhances this gradient and largely explains the cycles of matter we see today (Kleidon, 2010b).

During the first half of Earth's history (4.6–2.4 Ga), a lack of free oxidants such as O_2 at Earth's surface, but abundant CO_2 due to volcanic outgassing (Brimblecombe, 2013), governed mineral dissolution,

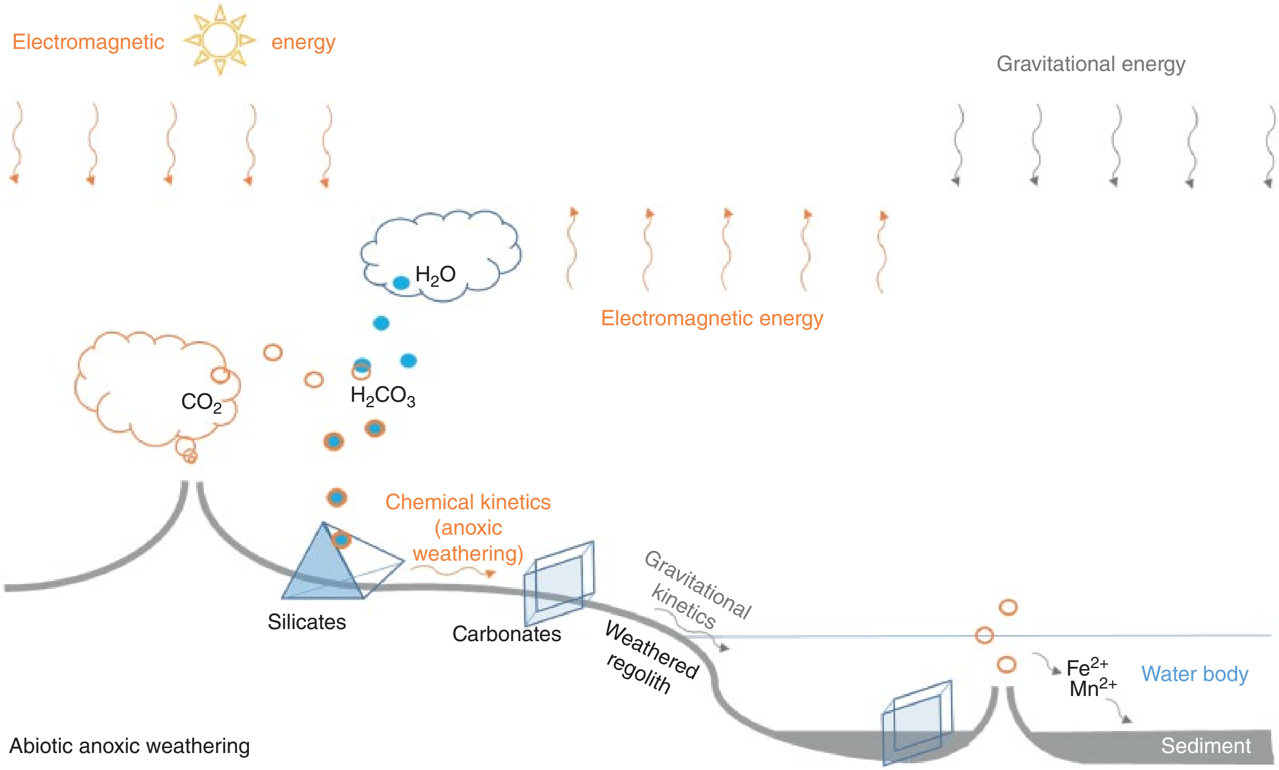

Figure 1.2 Simplified schematic of carbon and energy flows during the Archean Eon (3.5 Ga). Volcanic degassing releases CO_2 (together with other gases and aerosols) to the atmosphere, which reacts with water vapor to produce carbonic acid. In an anoxic atmosphere, silicate rocks exposed through tectonic forces or volcanism react with carbonic acid from precipitation and release chemical elements as dissolved ions. If supersaturating conditions prevail, carbonates of different reduced ions (e.g., Fe^{2+}, Mn^{2+}) form. Gravitational forces transport and deposit weathered products to lakes, rivers, or marine sediments, where they are solidified over geologic time through diagenesis. Sedimentary rocks resulting from diagenesis can thus record the initial conditions of the weathering environment (e.g., redox variability in Proterozoic Banded Iron Formations).

the formation of secondary minerals (Hazen, 2013), and niche and habitat development on the vacant land (when first life emerged), ultimately shaping the distributions of protoecosystems in the landscape (Figure 1.2). It is still not entirely clear when life on Earth first emerged (4.2–3.8Ga; Bell et al., 2015; Battistuzzi et al., 2004). In a late Hadean to early Archean environment, however, with an abundance of carbon, both highly oxidized (CO_2, carbonates, bicarbonates) and highly reduced (CH_4 and various hydrocarbon complexes; Arndt, 2013; Zerkle et al., 2012), biota–mineral interactions would have been very modest (Hazen, 2013; Hazen et al., 2008). Such interactions were likely chemolithotrophic, limited to epilithic and endolithic surfaces under a highly erosive environment (Sleep, 2010). The carbon cycle, while perhaps not strongly mediated by life on earliest Earth, was a significant driver of silicate rock weathering through the acid-generating capacity of rainwater-dissolved CO_2 (Ushikubo et al., 2008). Carbon release (crustal CO_2 outgassing) and capture (aqueous carbonate formation during H_2CO_3 –mineral reactions) is temperature dependent; and this would have created a primordial planetary thermostat, stabilizing the early climate and pH of surface waters (Berner, 2004; Walker et al., 1981). Ocean-floor volcanism and weathering provided complementary carbon feedbacks to terrestrial weathering, but their relative contributions are not entirely understood (Coogan & Dosso, 2015).

Various planetary models have highlighted the critical importance of the early carbon cycle for silicate weathering budgets and the global climate. The most recent estimates suggest that the young anoxic Earth featured a temperate climate and a circumneutral ocean pH around 6.6 (compared to 8.2 in modern times) due to stabilizing feedbacks from both terrestrial and ocean floor weathering (Krissansen-Totton et al., 2018). Methane should also be expected for an anoxic Archean atmosphere (3.8–2.4 Ga), derived from serpentinization—the anaerobic oxidation and hydrolysis of hot, low-silica ferromagnesian minerals (Kasting, 2014; Preiner et al., 2018)—and methanogenesis, when it evolved in Archean microbes (Catling & Kasting, 2017).

Recent studies of modern biological soil crusts (with N_2 fixation qualities linking to primordial element cycles) advance the idea that in the pre-oxygenic world, early land-colonizing diazotrophic microbes were the first to endow the biosphere with the capacity to capture free nitrogen gas (N_2) from the atmosphere into usable forms (e.g., NH_3; Thomazo et al., 2018). By developing the nitrogenase enzymatic system, an oxygen-sensitive Fe–Mo protein, these communities would have been able to transform N_2 into bioavailable forms, either using hydrogen to reduce it to ammonia, or using oxygen to oxidize it to nitrites and nitrate in soil and water (Thomazo et al., 2018). Most of the biosphere would have relied on incipient N_2 fixation. The Archean signatures of such transformations have been recently dated to more than 3.2 Ga in South Africa fluvial deposits (Homann et al., 2018). By linking rock-derived nutrients with nitrogen from the atmosphere, these microbes, together with sulfur reducers that appeared earlier (3.47 Ga; Shen & Buick, 2004), are thought to have established the first nutrient links among the biosphere, atmosphere, geosphere, and hydrosphere, or the earliest biogeochemical cycles. This also would have helped fertilize the early oceans and connect marine and continental biogeochemical cycles before the Great Oxidation Event (GOE; Thomazo et al., 2018).

The mineral diversity of the upper continental crust likely increased modestly during the emergence of a young biosphere, most likely in localized carbonate and sulfate hot spots (e.g., biogenic pyrite) with little effect on the depositionary (soil and sediment) environment (Hazen et al., 2008; Shen & Buick, 2004).

Remnants of early Earth biogeochemical cycles can be found in modern anoxic analogs such as the deep biosphere—several kilometers under terrestrial and marine floors (Ijiri et al., 2018; Lever et al., 2013), where endolithic cyanobacteria were recently discovered (Puente-Sánchez et al., 2018)—some marine and lacustrine sediments (Bowles et al., 2014; Wallmann et al., 2008), and pelagic areas of anoxic lakes and seas, e.g. Lake Matano (SE Asia), Black Sea (eastern Europe), and Cariaco Basin (NE South America; Crowe, 2008; Reinhard et al., 2014; Wright et al., 2012).

1.4. THE GREAT OXIDATION EVENT

The revolutionary "invention" of photosynthesis and nitrogen fixation by Cyanobacteria at some point in the Archean (Olson, 2006; Schirrmeister et al., 2015; Shih, 2015) triggered a cascade of events in the weathering environment, the mineral landscape, and the cycles of nutrients that supported an evolving and more complex biosphere. Oxygen enrichment by photosynthetic biota slowly consumed the available pool of redox-sensitive elements (e.g., Fe, Mn, Cu, Mo, Cr) from surface environments in the late Archean, followed by their depletion in the deep oceans at the end of Proterozoic (Scott et al., 2008). This shifted the redox balance of most of Earth's surface towards an oxidative state, increasing the surface thermodynamic disequilibrium gradient, and providing a major biological conduit for nutrient flows between continental crust, atmosphere, and hydrosphere (Figure 1.3). Microbial methane production likely further increased Earth's oxygen reservoir, and its role in surface chemistry, by facilitating hydrogen (from water) to escape from the atmosphere to space by methane photolysis (Catling et al., 2001; Fixen et al., 2016).

Oxidation of terrestrial landscapes was not a one-time event (Figure 1.3). Episodic (few million years span) increases in continental oxidative weathering prior to the GOE have been indicated by Se spikes in rock formations of Western Australia, resulting from oxidation of sulfide minerals on land about 2.66 Ga (Koehler et al., 2018). Other traces of oxidative weathering "oases" (likely due to stromatolithic photosynthesis) have been dated using sulphur isotopes in Archean sedimentary pyrites as far back as 3 and 2.97 Ga in the Pangola Supergroup, South Africa (Crowe et al., 2013; Eickmann et al., 2018), and using radiogenic Os to 2.5 Ga (late Archean) in Mount McRae Shale, Western Australia (Kendall et al., 2015; Reinhard et al., 2009; Stüeken et al., 2012). Possible pathways for the first biological oxidative weathering and biological organic matter stabilization in soil/sediment by cyanobacteria–archaea–fungi consortia therefore may have occurred in soil and aquatic ecosystems on land during early Archean times (Lalonde & Konhauser, 2015), as well as in cryptoendolithic ecosystems in silicate rock crust as found in present day East Antarctica (Mergelov et al., 2018). Hints for the existence of such endolithic ecosystems, likely aquatic, have been preserved in both Archean and Proterozoic mineral deposits (Golubic & Seong-Joo, 1999; McLoughlin et al., 2007).

The GOE, a planetary scale photosynthesis-driven shift in the redox state of Earth's surface occurring in the late Archean (Catling, 2013; Kump, 2008; Lyons et al., 2014), irreversibly set the reduced crust on an oxidative weathering path that has remained stable up to the present. Abundant "biological oxygen" amounted to major changes in the interaction of geosphere, atmosphere, hydrosphere, and biosphere. One of the consequences was a diversification boost in the mineral world, with the incorporation of a large number of novel life-promoted oxide species, particularly minerals of different (oxidized) species of As, Co, Cu, Fe, Mn, Ni, S, U, and Zn, and other trace elements (Hazen, Sverjensky, et al., 2013;

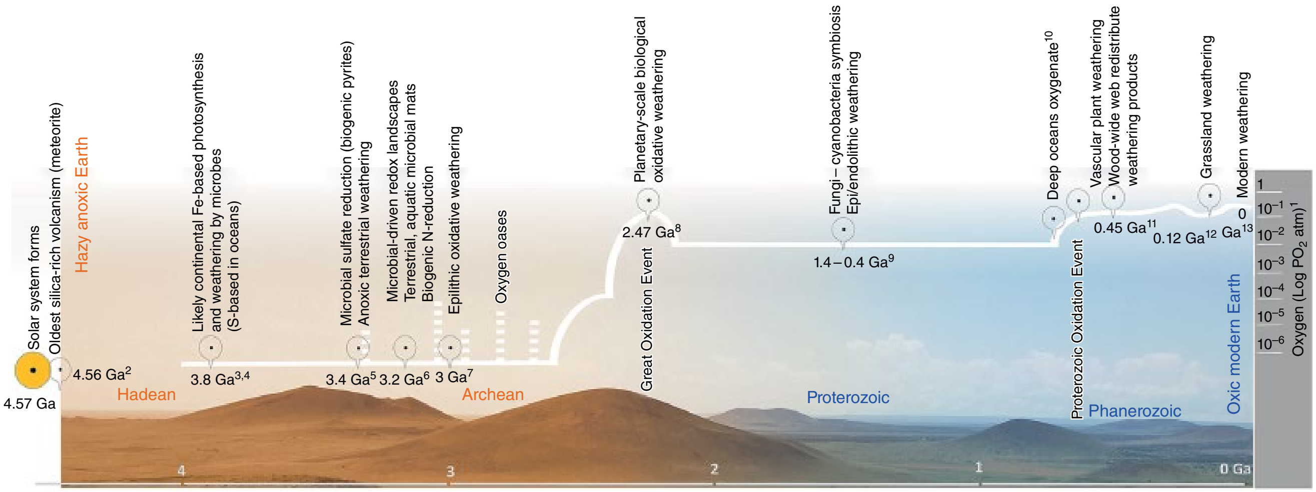

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Figure 1.3 Timeline of major events in the geosphere–atmosphere–biosphere interactions and how they shaped Earth system evolution, including a fundamental shift in its surface thermodynamic disequilibrium attained during The Great Oxidation Event.

Sverjensky & Lee, 2010), phosphates, and new carbon-based biominerals such as organic biominerals and bio-carbonates (Hazen, Downs, et al., 2013). It is estimated that about 4000 of the total of about 5500 minerals found on Earth today emerged during this major environmental redox shift (Hazen & Ferry, 2010; Pasero, 2018). Biogenic atmospheric oxygenation also freed an unprecedented amount of potential energy at the redox boundary, which stimulated the emergence of oxygen-breathing eukaryotic life. This, in turn, would have further stabilized the planetary surface to a new biogeochemical state (Lenton et al., 2018; Lovelock, 1995).

Land colonization by vascular plants in the early Phanerozoic (Middle to Late Ordovician, 0.45 Ga), and the almost concomitant evolution of glomeromycota symbiosis, to which arbuscular mycorrhiza belongs (Morris et al., 2018; Strullu-Derrien et al., 2018), would have introduced the first network of plant roots and fungal mycelia we now recognize as the "Wood Wide Web" (Simard et al., 1997). They enhanced weathering by selectively mining minerals and redistributing nutrients and information across plant and fungi individuals and species in the ecosystem (Klein et al., 2016). This increased ecosystem resilience allowed the emergence of a more complex terrestrial biosphere, including diverse forests and grassland ecosystems, which further captured and fixed C and N from the atmosphere into biomass and stabilized the global cycles of rock-derived nutrients. Biosphere diversification also shifted biomass distribution from predominantly a subsurface biosphere in a microbial world, to above-ground ecosystems after photosynthetic plants colonized the land (McMahon & Parnell, 2018). It is estimated that as much as 80% of current planetary biomass is hosted in land plants (Bar-On et al., 2018). The emergence of organic and clay-rich soils following the rise of the terrestrial biosphere in the Phanerozoic also meant that plant roots, mycorrhizal fungi, and the rhizosphere microbiome became the main drivers of continental weathering and biogeochemical cycles (Hazen, Sverjensky, et al., 2013).

The following sections will provide a comprehensive update on the role of different ecosystem components in modern weathering and the carbon cycle, including the inevitable anthropogenic effect.

1.5. MODERN-DAY OXIDATIVE WEATHERING

Vast nutrient and energy transfers between Earth's solid, fluid, and gaseous reservoirs support the development of modern terrestrial ecosystems. Under the oxygen-rich atmosphere, this planetary-scale bioreaction continuously consumes exposed rock minerals, oxygen, and CO_2 to drive the cycling of C, N and rock-derived elements through oxidative weathering. Bedrock weathering prepares the terrestrial surface for developing ecosystems by physically and chemically altering rocks, releasing major and micronutrients to pore water, transporting them to rivers, lakes, and seas, integrating them into secondary minerals and organic–mineral aggregates, and delivering them in accessible forms to various biota. There is a very tight coupling between the exposed upper crust and the biosphere, which results in a slow but continuous physical fracturing and chemical alteration of bedrock to secondary minerals in a continuous flow or "river" of clay minerals which progresses upwards, then follows gravity gradients to constantly replenish the biosphere's nutrient-rich substrates (Holbrook et al., 2019; Richter, 2017). The intensity of these processes as well as the nutrient and mineral make-up of bedrock dictates the functioning of the overlaying ecosystems, and their feedbacks to the wider hydrosphere and atmosphere (Kaspari & Powers, 2016; Zaharescu, Hooda, Burghelea, & Palanca-Soler, 2016).

The transfer of chemical elements between rock and living systems during weathering unfolds over a wide range of scales, from molecules to the entire biosphere, and these transfers have been the focus of a plethora of studies. Particularly noteworthy is the comprehensive effort to understand matter and energy fluxes in the shallow and porous crust harboring life in the interdisciplinary framework of Critical Zone science (Richter & Billings, 2015). Recent advances in isotope geochemistry, hydrology, ecology, and remote sensing have made it possible to better constrain the interactions between different components of atmosphere, geosphere, and biosphere at various scales and better understand how they shape the surface of Earth and transform parent rock to soil and sediments that sustain life (Chorover et al., 2011; Zaharescu, Palanca-Soler, Hooda, et al., 2016).

Incipient stages of mineral weathering, when the first microbes, fungi, and plant roots explore freshly exposed mineral surfaces, are among the most active (Zaharescu et al., 2017), and they trigger the flow of energy and nutrients feeding the major biogeochemical cycles. Mass-balance approaches are often used to follow the flow of chemical elements from minerals thorough different ecosystem components during weathering in both natural and experimental settings (Anderson et al., 2002; Burghelea et al., 2018; Yousefifard et al., 2012). The modern-day silicate-weathering environment is characterized by abundant carbon in oxidized (CO_2) and reduced (organic acids, siderophores, and biopolymers) forms, mostly released by the biosphere through respiration, decomposition, and other metabolic activities. Human activity adds an important and increasing fraction of carbon through the fossil-fuel extractive industry (Figure 1.4). Interactions among abiotic and biotic components of the biosphere modulate modern-day weathering

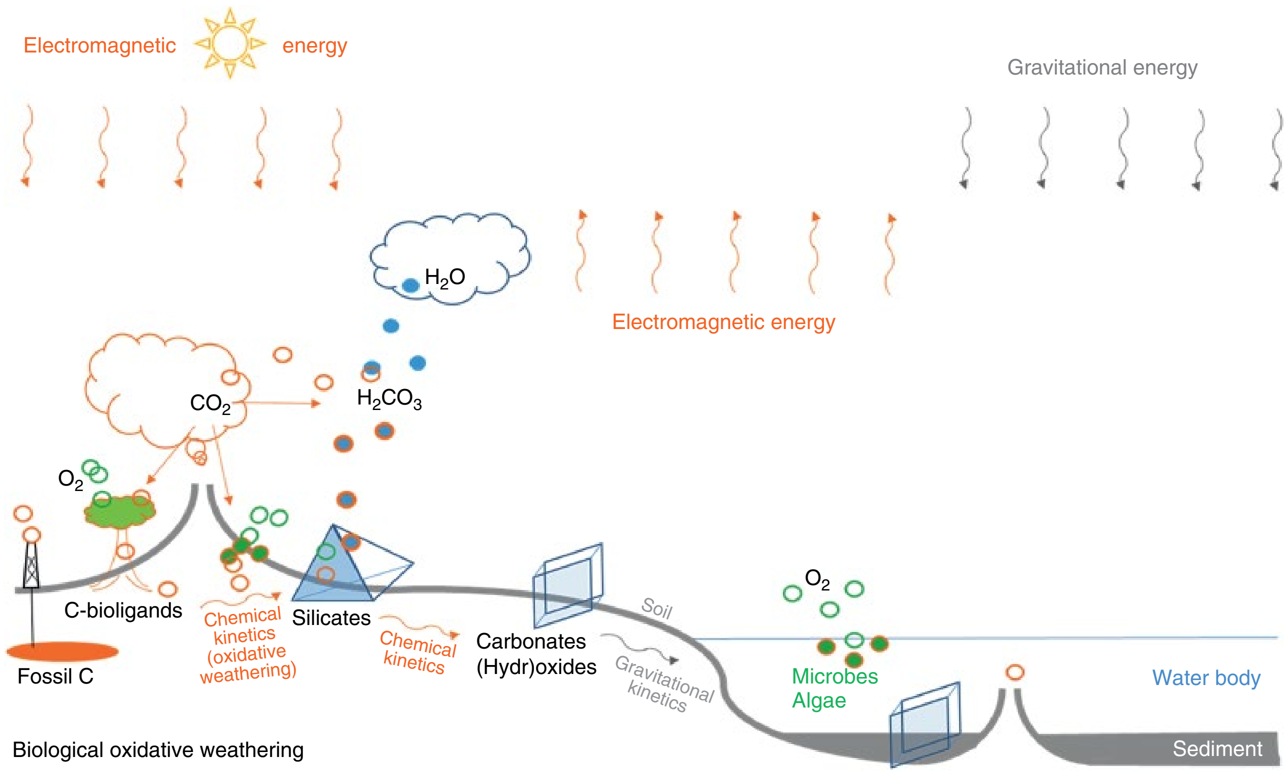

Figure 1.4 Carbon and energy flows on the modern, biosphere-dominated Earth surface. Under modern-day weathering, CO_2 released through mantle degassing (terrestrial and marine), biosphere respiration, or anthropogenic fossil-fuel extraction and burning reacts with rainwater, producing carbonic acid. The biosphere further converts CO_2 to organic acids (through light-harvesting photosynthesis), which together with the carbonic acid and O_2 from the atmosphere react with exposed silicate rock to release chemical elements to flowing water. These elements enter the biosphere and migrate through its different trophic levels as nutrients, are transported to oceans, or precipitate as secondary minerals in soils and sediments.

of the exposed upper crustal environment and the cycles of elements through Earth's solid, fluid, and gaseous reservoirs.

1.5.1. Abiotic Weathering

Disentangling the contribution of various abiotic and biotic factors to weathering in a biosphere-dominated terrestrial world is challenging. Whether living or nonliving factors are the first agents of weathering has been a persistent "chicken-and-egg" question in Earth sciences. Perhaps a good way to approach this problem is by studying incipient weathering and ecosystem colonization of freshly exposed minerals or in recently exposed rock such as volcanic fields, exposed bedrock in the mountains, and landscapes exposed by glacial retreat.

Studies carried out in controlled laboratory settings with unreacted rock exposed to incipient weathering under abiotic conditions have shown an initial spike in solute (anion and cation) export to pore waters (driven by carbonation reactions), which was significantly affected by microbial and plant presence (Burghelea et al., 2018; Zaharescu et al., 2019). This was consistent with early mineral exposure by fracturing and initial mass loss of elements from freshly exposed mineral lattices due to increased exchange at the water–mineral interface, e.g., cracking developed during oxidative/hydration expansion stresses of reduced mineral surfaces under unsaturated pore fluids. Repulsive forces during water–rock interaction have been demonstrated in laboratory experiments (Levenson & Emmanuel, 2017), and field studies have shown evidence of micron-scale surface spalling and loss of Na-containing glass from grain surface to a depth of 250 μm, with minimal secondary mineral deposition in subsurface basalt exposed to subpolar climate (Hausrath et al., 2008).

Temperature has a strong effect on incongruent mineral weathering due to the different activation energies of mineral dissolution; e.g., between pH ~7 and 9, basaltic glass dissolution is faster than embedded minerals at low temperature (~0°C), while basaltic forsterite dissolves more quickly than glass at higher temperatures (~50°C; Bandstra & Brantley, 2008).

Ice nucleation, pervasive over large swaths of the terrestrial surface, particularly at high altitudes and latitudes, and during periods of terrestrial history, e.g., glaciations and Snowball Earth events, is also a major driver of physical and, indirectly, chemical weathering. Studies have shown that active sites of ice nucleation on mineral surfaces generally coincide with sites of incipient chemical weathering in field conditions, e.g., lamellar edges in biotite, cracks, and other mineral defects (Lybrand & Rasmussen, 2014; Murray et al., 2012). Such crystal defects increase the surface area exposed to weathering. Ice nucleation in rock cracks and pores also increases water volume by about 9% (Fahey & Dagesse, 1984), increasing the stresses on minerals making it about three to four times more effective than wetting–drying in disintegrating rock (Fahey, 1983). Cycles of water adsorption on minerals followed by drying, however, have a similar or greater effect on mass loss (leaching) compared to freeze–thaw cycles, releasing ~0.2% of basalt mass after 200 cycles (Yesavage et al., 2015) and up to 3–10% after 25 dry–wet cycles on carbonate rocks (Dunn & Hudec, 1972). Wetting–drying effect on physical disaggregation is enhanced in clays (Dunn & Hudec, 1972) due to their layered structure, which is exposed to repulsive forces when layers adsorb highly polar water molecules in the interspace (Fahey, 1983).

Friction/abrasion of mineral surfaces during gravitational kinetics, e.g., rock transport by rivers and streams (Petrovich, 1981), as well as mechanical fracturing of bedrock during exhumation/orogeny (Holbrook et al., 2019), greatly increase the density of active sites on rock surfaces, and hence the total area available for chemical weathering.

A thermodynamic disequilibrium of crustal materials reaching Earth's surface (degassing spaces, thermal/pressure fractures; Figure 1.5) therefore sets the stage for abiotic weathering. Oxygen and water percolation in developing fractures, strong short-range electrostatic forces on grain surfaces, and weak long-range gravitational gradients further enhance incipient physical and chemical weathering, largely depending on the substrate's physical and geochemical properties and latitudinal/altitudinal location. Zaharescu et al. (2019) estimate that the total global denudation rate of terrestrial surface by abiotic chemistry alone is about 6.1 Tmol year^{-1} of major bedrock cations (Si, Al, Na, K, Ca, Mg, P, Ti, Mn, and Fe).

1.5.2. Microbial Contribution to Weathering

Microbes are a key ecosystem component and one of the most abundant and active biological agents that shape the Earth's surface through weathering processes and carbon burial. Microbial ecosystems including free-living heterotrophic and phototrophic colonizers of bare rock surfaces characterize the first stages of primary succession in terrestrial ecosystems. Rocks and minerals represent an ecological niche, which provides microbes with living habitats and nutrients, while microbes impact primary to secondary mineral weathering rates through their effects on mineral solubility and metal speciation. It is estimated that the microbial parts of terrestrial ecosystems contribute about 11.5% over abiotic rock dissolution globally, or 6.8 Tmol year^{-1} (microbes + abiotic; Zaharescu et al., 2019).

An increasing number of studies during the past two decades lie at the heart of geomicrobiology, an emerging field that studies mineral–microbe interactions at different scales, in different environments, using a multitude of experimental approaches (electron microscopy, atomic force microscopy, spectroscopy, x-ray, molecular, and isotope techniques; Balogh-Brunstad et al., 2020, Chapter 4, this volume; Banfield & Nealson, 1997; Buss et al., 2007; Huang et al., 2014; Miot et al., 2014; Parikh & Chorover, 2005, 2006; Perdrial et al., 2009; Omoike & Chorover, 2004).

Microbes' close association with mineral particles has been reported extensively in the literature as influencing soil genesis, nutrient and lithogenic element cycling, mineral dissolution, CO_2 drawdown, and plant nutrition (Ahmed & Holmström, 2015; Balogh-Brunstad, Keller, Dickinson, et al., 2008; Barker et al., 1998; Cockell et al., 2007; Gadd, 2013; Gislason et al., 2009; Gleeson et al., 2006; Hilley & Porder, 2008; Kinzler et al., 2003; Muentz, 1890; Puente et al., 2009; Uroz et al., 2009, 2011; Wightman & Fein, 2004; Wu et al., 2008). Microbial effects on weathering extend from micro- to global scale with a wide ecological impact on ecosystem services (biogeochemical cycling and atmospheric CO_2 regulation; Bonneville et al., 2009; Hilley & Porder, 2008; Z. Li et al., 2016). In the critical zone, biogeochemical processes controlled by microbes influence the retention and export of organic matter, nutrients and toxic elements, affecting soil fertility and water quality (Brantley et al., 2011; Gadd, 2013).

Microorganisms, inclusive of bacteria, archaea, and fungi are the first to colonize new substrates, promote physical and chemical weathering, and biotransformation of minerals (Balogh-Brunstad, Keller, Dickinson, et al., 2008; Balogh-Brunstad, Keller, Gill, et al., 2008; Balogh-Brunstad, Keller, Bormann, et al., 2008; Brunner et al, 2011; Burford et al., 2003; Dong et al., 2015; Finlay et al., 2009; Gorbushina & Broughton, 2009; Frey et al., 2010; Leake et al., 2008; Z. Li et al., 2016; Seiffert et al., 2014; L.L. Sun et al., 2013; R.R. Wang et al., 2015; W.I. Wang et al., 2015; B. Xiao et al., 2012; L.L. Xiao et al., 2016). Multiple studies showed the role of bacteria and fungi in both mineral formation (Ehrlich, 1999; Gadd, 2007; Gorshkov et al., 1992; Kawano & Tomita, 2001)

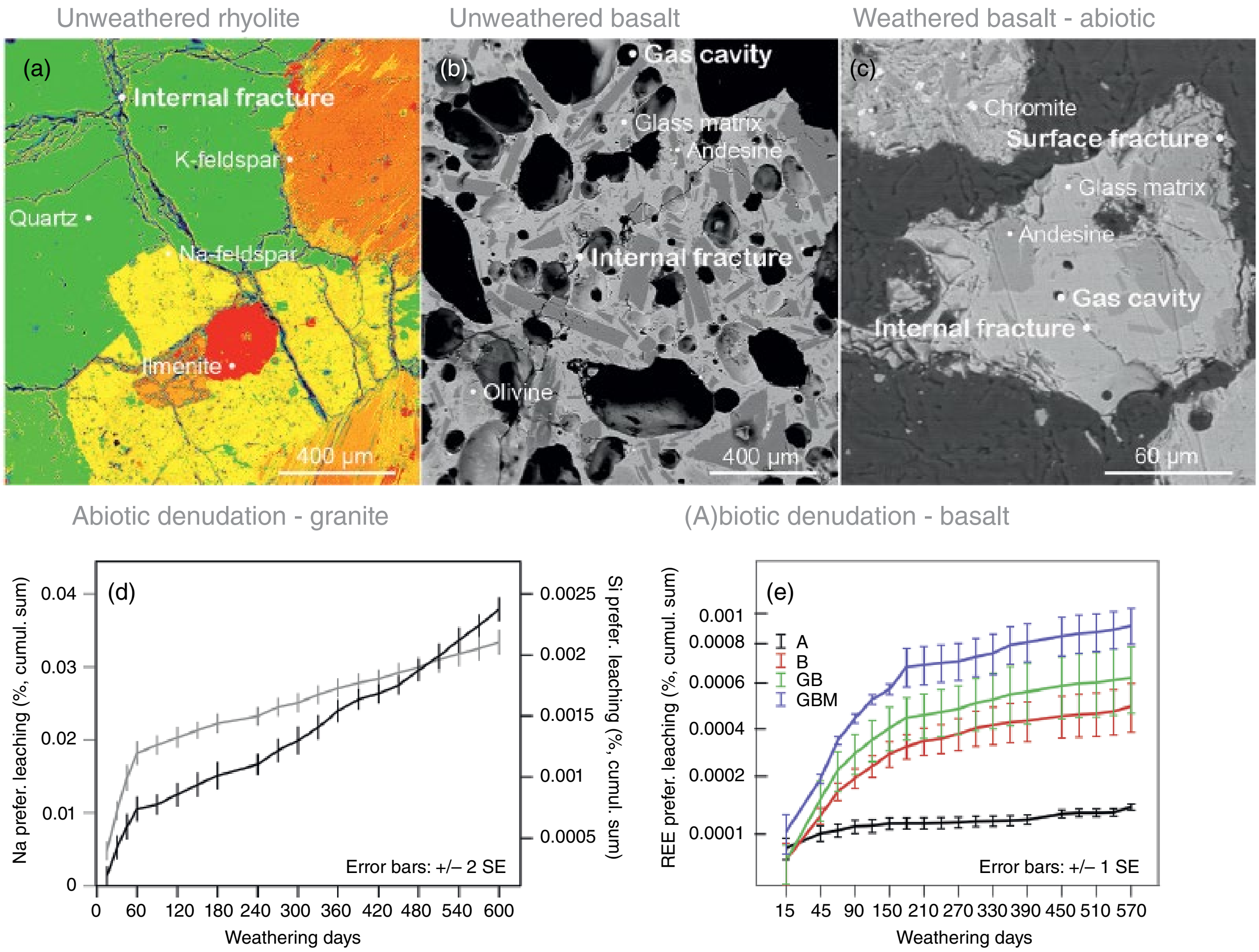

Figure 1.5 Incipient weathering as driven by abiotic and biotic agents. Internal and peripheral fractures set the stage for physical weathering. Electron probe microanalysis showing internal microfractures within and between minerals in (a) rhyolite and (b) basalt, together with (c) surface microfractures on separated rock grains. (a) Color back-scattered electron map; (b) gray-scale back-scattered electrons map. Leaching experiments showing (d) abiotic preferential (normalized to their rock abundances) leaching to pore water of Na (light gray) and Si (dark gray) from granular granite, and (e) rare earth elements (sum) leaching from granular basalt (0.25–0.5mm, Zaharescu et al. 2017, 2019). Treatments were in order of increasing denudation: A, abiotic; B, rock microbes; GB, buffalo grass (*Buchloe dactyloides*) microbes; GBM, grass–microbes–arbuscular mycorrhiza (*Glomus intraradices*).

and dissolution (Bennett et al., 1996; Liermann et al., 2000; O'Reilly et al., 2006; Perdrial et al., 2009; Rosenberg & Maurice, 2003).

In terrestrial ecosystems, microbial controls on weathering have been studied in carbonates and silicate rocks (Bennett et al., 2001; Folk, 1993; Lian, 1998; Lian et al., 2002, 2005, 2006, 2008; Viles, 1988). Silicate weathering is of global importance due to its role in soil development, nutrient cycling, and carbon sequestration (Beaulieu et al., 2012; Berner, 1995; Ehrlich, 1998; Shirokova et al., 2012; Schulz et al., 2013; L.L. Sun et al., 2013; White & Brantley, 1995; Wofsy et al., 2001; B. Xiao et al., 2012). Microbes can directly and indirectly impact silicate dissolution and secondary mineral formation (Finlay et al., 2009) through their attachment to the mineral surfaces and their metabolic products, respectively.

Some of the microbial strategies that enhance mineral dissolution and disrupt silicate framework are: mineral–water equilibria alteration at the point of contact, proton and hydroxyl production inducing the formation of mineral surface ion complexes, catalyzing redox reactions, or mediating the formation of secondary mineral phases (Barker et al., 1998; Bennett et al., 2001; Bonneville et al., 2004; Brown et al., 1999; Drever & Stillings, 1997; Duff et al., 1963; Goldstein, 1986; Huang et al., 2014; Hutchens et al., 2003; Kalinowski et al., 2000; Lapanje et al., 2012; Z. Li et al., 2016; Liermann et al., 2000; Rogers & Bennett, 2004; Rogers et al., 1998; Ullman et al., 1996; Wendling

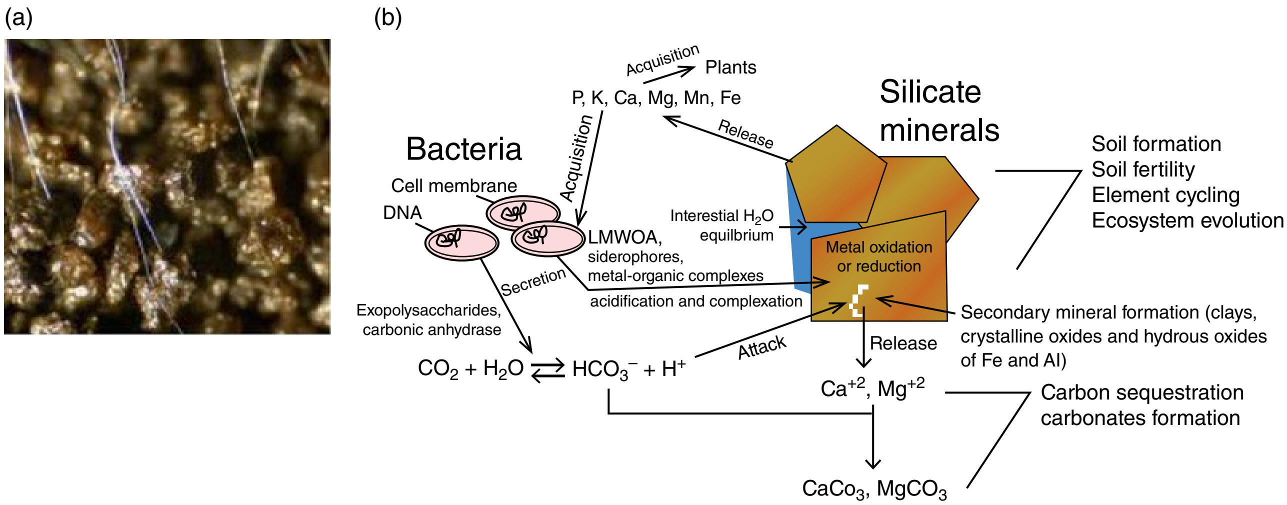

Figure 1.6 Microbes–rock interactions during weathering: (a) fungal hyphae prospecting basalt grains (Zaharescu et al., 2019) and (b) a schematic of mineral weathering by microbes and the affected ecosystem processes. [(a) Zaharescu et al. (2019). Reproduced with permission of Dragos G Zaharescu.]

et al., 2005; L.L. Xiao & Lian, 2016; L.L. Xiao et al., 2014; Yao et al., 2013; Zhao et al., 2013). In addition to enhancing dissolution of crystalline silicates, microorganisms can play a significant role in glass dissolution—glasses being less resistant to chemical weathering than their well-crystallized counterparts (Callot et al., 1987; White, 1983). From silicate minerals and glasses, microbes derive both macro (e.g., N, P, and S) and trace nutrients (e.g., K, Fe, Ni, V, and Mn; Brantley et al., 2001; Valsami-Jones et al., 1998) for their metabolic use and plant growth (Figure 1.6).

Microbial exometabolites (e.g. extracellular polysaccharides, and metal-complexing ligands, such as low-molecular-weight organic acids and siderophores) are important agents in promoting mineral dissolution, oxidation, or reduction of metals at mineral surfaces (Berthelin & Belgy, 1979; Buss et al., 2007; Ivarson et al., 1978, 1980, 1981; Malinovskaya et al., 1990; Neilands, 1995; Welch et al., 1999, 2002). The most common biogenic chelators are siderophores and organic acids, which can act independently or together enhancing mineral dissolution rate 10 to 100 times (Buss et al., 2007; Cama & Ganor, 2006; Reichard et al., 2007).

Organic acids, including heterogeneous condensed compounds of variable charge and solubility, and simple low-molecular-weight organic acids, like phenolic acids secreted by soil bacteria and oxalic acid produced by fungi, are particularly significant in enhancing silicate dissolution rates by decreasing pH, forming framework-destabilizing surface complexes, or by complexing metals in solution (Bennett & Casey, 1994; Blake & Walter, 1996; Cama & Ganor, 2006; Dontsova et al., 2014; Drever & Stillings, 1997; Drever & Vance, 1994; Goyne et al., 2006, 2010; Neaman et al., 2005, 2006; Stephens & Hering, 2004; Stillings et al., 1996; Ullman et al., 1996; Welch & Ullman, 1993; Wieland et al., 1988).

Microbial impacts on mineral surfaces depend on the substrate type, composition, porosity, surface reactivity, surface aging, and microbial adaptability (Hutchens, 2009; Olsson- Francis et al., 2012; Uroz et al., 2012; Wild et al., 2018; Zaharescu et al., 2017). While it is known that minerals control the diversity of bacterial communities in soil (Uroz et al., 2012), questions remain about qualitative and quantitative changes that weathering microbial communities will undergo under global climate change or other human-induced environmental perturbations.

1.5.3. Vascular Plant and Mycorrhizae Effect on Weathering

Plant–soil interactions play a central role in the biogeochemical carbon, nitrogen, and hydrological cycles, with feedbacks to the atmosphere, oceans, and climate. Intense biological activity in soil coupled with the hydrological cycle drives progressive weathering of geological media and affects soil and ecosystem development. Experimental studies combined with field measurements of river nutrient fluxes globally estimate that vascular plants and associated microbial communities together with abiotic leaching add about 6.6 Tmol $year^{-1}$ to the major element cycles, while adding symbiotic fungi would reduce the contribution to about 6.2 Tmol $year^{-1}$ (Zaharescu et al., 2019). This means that plant colonization increases element retention into soil and biomass while microbes and fungi accelerate denudation.

Plant roots influence mineral dissolution and chemical denudation, with consequences for soil formation, soil fertility, its stability, landscape evolution, and long-term productivity of terrestrial ecosystems. The rooting zone is a hot spot where intense gradients in carbon and water are superimposed upon low-temperature geochemical disequilibria. Plants affect weathering through direct contact of roots with mineral surfaces, water redistribution, rhizosphere production of organic and inorganic acids, root and heterotrophic respiration, biorecycling of cations, and formation of biogenic minerals (Bormann et al. 1998; Kelly et al., 1998; Landeweert et al., 2001; Leyval & Berthelin, 1991; Marschner, 2012). It is acknowledged that vascular plants enhance weathering of phosphates (Grinsted et al., 1982; Hinsinger & Gilkes, 1997), carbonates (Jaillard, 1987), and silicates (Burghelea et al., 2015, 2018; Drever, 1994; Hinsinger et al., 2001; Robert & Berthelin, 1986; Zaharescu et al., 2017). Higher plants are efficient rock-weathering agents due to a high mass of fine roots that produce etching and create vast contact areas with minerals (April & Keller, 1990; Berner & Cochran, 1998; Cochran & Berner, 1996). Moreover, plant growth and storage of rock-derived elements can also accelerate weathering (Akter & Akagi, 2006; Bashan et al., 2002, 2006; Berner, 1992, 1995; Drever, 1994; Franklin & Dyness, 1973; Jackson, 1996; Lundström et al., 2000; Pawlik et al., 2016).

Rhizosphere processes, including rhizodeposition of low-molecular-weight organic acids decrease pH, release gases (e.g. CO_2), and enhance availability of cations (e.g. Ca, Mg, and K) in rhizosphere soil solution (Gobran et al., 1998; Gregory, 2006; Griffiths e al., 1994; Marschner, 2012; Yatsu, 1988). The pH in the rhizosphere microenvironment can be as low as 3, whereas in the bulk soil it commonly varies between 5 and 7 (Arthur & Fahey, 1993; Hinsinger, 1998). Additionally, the decay of organic matter produces organic acids and carbonic acid, which also attack mineral surfaces.

When soil resources are limited, plants turn to common symbiotic partners, such as mycorrhizal fungi, to provide them with necessary mineral-derived nutrients otherwise not available to plants and to ensure plant growth, nutrition, and ecosystem productivity (Aghili et al., 2014; Smith & Read, 2008; Treseder, 2004, 2013). The mutualistic relationship efficacy is substrate-dependent, since the costs and benefits depend on resource availability and/or imbalance among the symbionts (Burghelea et al., 2015; Grman & Robinson, 2013; N.C. Johnson et al., 1997, 2010; Rosenstock, 2009).

Laboratory and field studies provide compelling evidence that ectomycorrhizal (ECM) fungi, commonly associated with trees, are able to enhance weathering and extract nutrients such as P, K, Ca, Mg, and Fe from apatite, biotite, feldspars, and other silicates (Balogh-Brunstad, Keller, Gill, et al., 2008; Finlay et al., 2009; Gadd, 2007; Hoffland et al., 2004; Jongmans et al., 1997; Landeweert et al., 2001; Leyval & Berthelin, 1991; Paris et al., 1995; Rosling, Lindahl, and Finlay, 2004; Rosling, Lindahl, Taylor, et al., 2004; Smits et al., 2012; van Breemen, Finlay, et al., 2000; van Breemen, Lundström, et al., 2000; van Schöll et al., 2008; Wallander et al., 1997). A network of hyphae (mycelium) accessing a higher mineral surface area than roots alone extends around the root tips like a sheath, protruding in between the cortical cells of roots, transporting nutrients and water to the plant in exchange for photosynthetically derived carbon (Leake et al., 2004, 2008; Smits et al., 2008). Other mechanisms by which ECM enhance weathering include secretion of organic acids (oxalic and citric acid) and targeted ligands, like siderophores, that form complexes with the metals in solution and on mineral surfaces (Hoffland et al., 2004; Schmalenberger et al., 2009; Y.P. Sun et al., 1999; van Hees et al., 2006). Within fungal mats, the pH of the soil solution is lower by more than 1 pH unit (Cromack et al., 1979) and oxalate concentrations are at least an order of magnitude higher (Griffiths et al., 1994) than in the surrounding soil.

Another type of widespread mycorrhizal fungi (80% of plant species) with indirect effects on weathering is arbuscular mycorrhiza (AM; Taylor et al., 2009). Small diameter fungal hyphae (3–4 μm) are able to penetrate between mineral grains (Figure 1.7), bind mineral particles, extract limiting nutrients (e.g., P and N), and translocate them to the plant through the hyphal invaginations into the root-cell membrane (Hetrick, 1989; Hetrick et al., 1988; Marschner, 1995; Marschner & Dell, 1994). The AM can enhance weathering through selective ion absorption (Lange Ness & Vlek, 2000), increased respiration, alteration of soil pH due to increased uptake of nitrate and ammonium, and stabilization of soil through production of glomalin (Bago et al., 1996; Burghelea et al., 2014, 2018; Johansen et al., 1993; Rillig, 2004; Six et al., 2004; Smith & Read, 2008; Tisdall & Oades, 1982; Zaharescu et al., 2017, 2019).

1.5.4. The Animal World

While plants are the main conduits of chemical energy input into the Earth biogeochemical cycles through photosynthetic carbon fixation that drives lithogenic elements release from the rock during weathering, animals can also contribute towards biogeochemical cycling. A major mechanism of animal effects on weathering involves translocation and mixing of altered minerals and elements released during weathering, as well as incorporation and transformation of organic compounds produced by the plants. Translocation can happen within the soil profile through activity of burrowing animals and on the surface through predation.

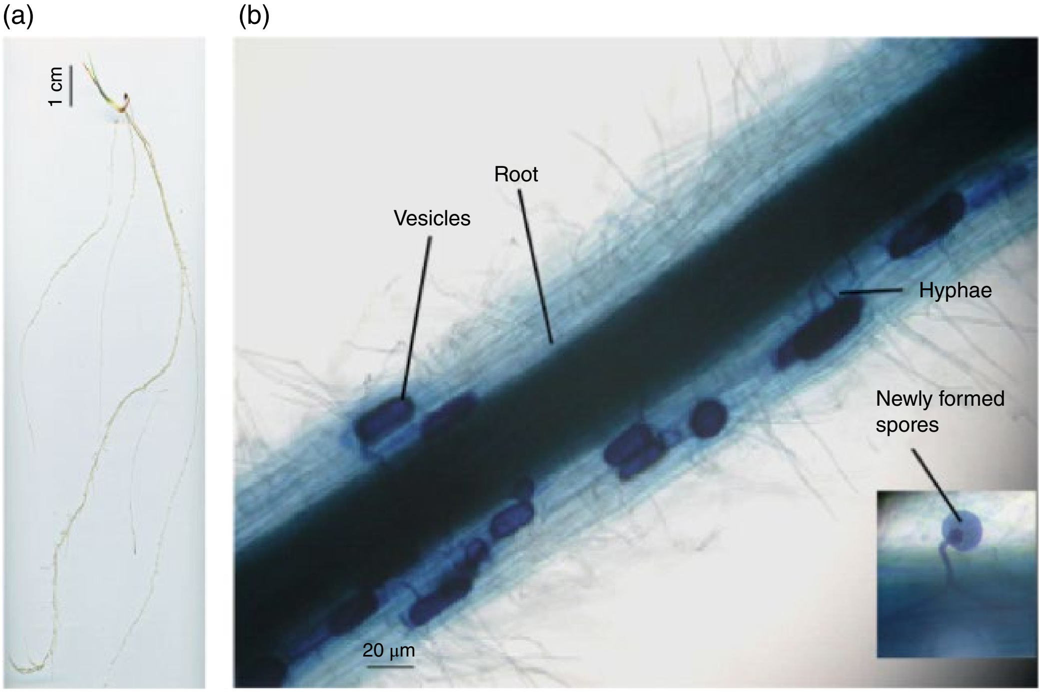

Figure 1.7 Mycorrhiza symbiosis: (a) root of buffalo grass (*Bouteloa dactyloides*) infected by arbuscular mycorrhizae symbiont (*Glomus intraradices*); (b) mycorrhiza reproductive spores (inset).

Bioturbation by both invertebrate and vertebrate animals is one of most studied contributions of animals to biogeochemical cycling of lithogenic elements (Meysman et al., 2006). Bioturbation is soil and sediment mixing by biological agents, such as plants and animals. Invertebrates that contribute to soil mixing include permanent and transient soil inhabitants such as earthworms, nematodes, arachnids (mites), isopods, coleopteran insects (beetles—adults and larvae) that move particles when they borrow, as well as hymenopteran insects (termites, ants, wasps, and bees) that engineer structures within soil. Vertebrates include fish, reptiles, amphibians, and fossorial mammals such as moles and gophers, as well as birds (Gabet et al., 2003).

Burrowing type influences characteristics of soil mixing: animals that burrow horizontal tunnels on slopes, like pocket gophers and some ground squirrels, result in horizontal movement of soils, while prairie dogs and harvester ants result in vertical mixing (Zaitlin & Hayashi, 2012). Most animals, however, prefer the top layer of the soil and generally do not burrow in saprolite. M.O. Johnson et al. (2014) used optically stimulated luminescence (OSL) dates and isotopes (meteoric ^{10}Be) to demonstrate that mixing rate decreases nonlinearly with increasing soil depth in soils of Queensland, Australia. In general, bioturbation results in vertical homogenization of the profile by exposing less-weathered material to weathering, however, vertebrates can increase horizontal soil heterogeneity (patchiness) through burrowing and foraging (Eldridge et al., 2012; Zaitlin & Hayashi, 2012).

Earthworm effects on soil properties have been studied extensively (e.g., Hodson et al., 2014; Shipitalo & Le Bayon, 2004; Swaby, 1949). Charles Darwin observed burial of material deposited on the soil surface over time through soil mixing by earthworms, and he dedicated his last book to the earthworms (Darwin, 1881). Earthworms pass soil through their digestive tract while moving through the soil, producing casts covered in mucus. As a result, they leave macropores that allow rapid, preferential flow of water, increasing soil hydraulic conductivity, with indirect effects on weathering processes, and soil aggregation (Shipitalo & Le Bayon, 2004; Shipitalo & Protz, 1989; Pulleman et al., 2005; Ziegler & Zech, 1992b). This has implications for water holding capacity and potentially organic matter preservation in the soils.

The effect of earthworms on C preservation has been studied extensively (Angst et al., 2017) but no clear trend has been reported. Effect of worms on composition of organic matter is rather limited, plant residues decrease in size as they pass through the digestive tract but do not undergo significant change in chemical composition (Hong et al., 2011; Ziegler & Zech, 1992a;), though there is evidence that earthworms promote formation of organo-mineral complexes (Shipitalo & Protz, 1989; Ziegler & Zech, 1992b). It has been reported that C can be preserved through physical protection of organic matter inside cast aggregates (Angst et al., 2017), but it is not reflected on whole soil C content (Frouz et al., 2014). Similarly, while overall amount of C and N in well-drained silt loam soil from Ohio and their distribution with depth did not change in the presence of earthworms, an increase in water-stable aggregates that are enriched in C and N can preserve them (Ketterings et al., 1997). It was also shown for tropical soils that cast aggregates were enriched in C and N compared to control aggregates of similar size (Hong et al., 2011).

Earthworms play a significant role in soil mixing. In natural northern forest ecosystems, invasive species of the earthworms can significantly affect distribution of C over the soil profile, completely destroying the O-horizon by mixing it with underlying mineral soil and significantly affecting habitat for microorganisms and plants (e.g., Bal et al., 2017; Bohlen et al., 2004; Craven et al., 2017). Vertebral animals that burrow contribute to mixing as well. Gophers, moles, and mountain beavers mix soil while building their burrows or foraging for food (Eldridge et al., 2012). Vertebrate burrows and foraging pits tend to be enriched in organic matter and higher in labile carbon and support greater levels of infiltration.

There is limited information regarding earthworm and bioturbation effect on other chemical properties of the soils. It has been shown that earthworms can form calcium carbonate in the gut (Lee et al., 2008; Robertson, 1936; Versteegh et al., 2014). There also has been some direct evidence of chemical weathering promotion by the earthworms (Carpenter et al., 2007; Hodson et al., 2014). Earthworms also influence mobility of metals (Chen et al., 2019; Duarte et al., 2012; Sizmur & Hodson, 2009; Sizmur et al., 2011), likely through changes in pH and dissolved organic carbon (DOC), as well as P availability (Ros et al., 2017), and affect transformation of the organic contaminants (Chen et al., 2019). Chemistry of hazardous waste sites can be particularly affected by bioturbation, when plants and animals penetrate protective barriers, become exposed to contaminated material themselves. and bring them closer to the surface where other organisms and humans can be exposed (Bowerman & Redente, 1998).

Animals that live on top of soils, both herbivores and carnivores, affect the biogeochemical cycles of C, N, P, and other life essential and nonessential elements through their influence on the plant and animal biomass. Herbivores consume plants affecting ecosystem productivity and carbon inputs into the soil and predators influence herbivore populations (Schmitz et al., 2018; Willoughby, 2018). In general, overall effects of the herbivores on C storage in the ecosystem is negative and predator is positive (Schmitz et al., 2018). There are additional effects, related to soil compaction and temperatures, as well as through effect on composition of organic matter during digestion.

Indirect evidence of the important role of bioturbation in weathering and soil formation is that incorporation of bioturbation in soil-formation models successfully represents soil development. The Model for Integrated Landscape Evolution and Soil Development (MILESD; Vanwalleghem et al., 2013) was successfully applied to a 6.25 km^2 area in the Werrikimbe National Park, Australia, simulating soil development over a period of 60,000 years. Temme & Vanwalleghem (2016) incorporated bioturbation in LORICA—a new model for linking landscape and soil profile evolution. While it has not been tested on a natural system, in the sensitivity analysis, bioturbation was one of the key factors affecting chemical weathering. Carbon fluxes have also been successfully modeled by inclusion of bioturbation (Yoo et al., 2011).

In addition to the role of animals in bioturbation, or mixing of soils and sediments, there are some groups of animals that directly influence geochemical processes. For example, termites and ants have been shown to directly increase weathering through release of organic acids, similar to plants and microorganisms. In fact, effect of ants on weathering has been shown to be much greater than that of plants in some ecosystems (Figure 1.8). Dorn et al. (2014) have shown for six sites in Arizona and Texas that eight different ant species enhanced mineral dissolution by ~50× to 300× over controls. High densities of vesicular-arbuscular mycorrhizal fungi and microbial enrichment have also been associated with the harvester ant mounds (Friese & Allen, 1993), potentially providing another mechanism for increased weathering, as discussed above.

1.5.5. Humans

Humans are part of the animal world but have a disproportionate effect on their environment compared to other animals. They exert the biggest influence on biogeochemical cycles as they not only affect them directly but also influence all other aspects of the environment. Land use, including agriculture and forestry, mining, industry emissions of acid-producing gasses, and now climate change are some of the largest effects of humans on weathering and biogeochemical cycles.

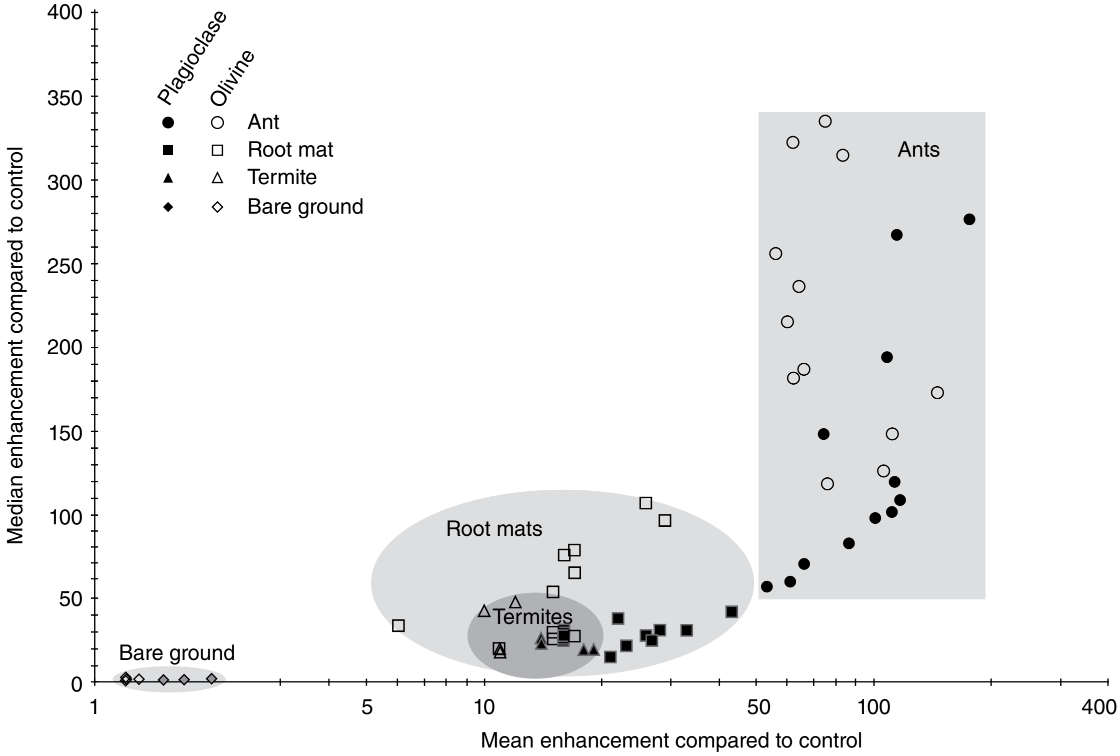

Figure 1.8 Mineral dissolution enhancements during 25-year experiments at six field settings in Texas and Arizona (USA). Samples of emplaced basalt grains containing plagioclase and olivine were extracted from ant nests, termite nests, root mats of trees, bare-ground settings, and a control consisting of basalt grains in plastic pipes exposed only to infiltrating precipitation. [Dorn (2014). Reproduced wih permission of Geological Society of America.]

1.5.5.1. Land Use

Change in land use through agriculture and animal husbandry has multiple effects on biogeochemical cycles. One of them is use of mineral fertilizer, which significantly affects nutrient fluxes. At the same time, removal of the crop biomass depletes nutrient store in the soils, possibly promoting weathering.

Other processes involved include change in water fluxes and erosion rates. About a quarter of land used in agriculture is affected by water and wind erosion (Hurni et al., 2008). Generally, intensive agriculture can increase soil erosion removing weathered, productive top layer high in organic matter and clays with high capacity to hold cations on exchange sites. Increase in erosion has been linked to acceleration of weathering processes (Dixon et al., 2012; Dixon & von Blanckenburg, 2012; Ferrier & Kirchner, 2008; Larsen et al., 2014; Stallard & Edmond, 1987). Irrigated agriculture can often result in soil degradation due to salt accumulation (Vlek et al., 2008).

A number of studies showed differences in weathering fluxes between agricultural and nonagricultural watersheds (Barnes & Raymond, 2009; Fortner et al., 2012; Liu et al., 2000; Oh & Raymond, 2006; Weller et al., 2003), with increased weathering in watersheds used as cropland. Fortner at al. (2012) showed evidence that nitrification of nitrogen added as fertilizer increases soil acidity and promotes weathering. Another explanation of increased weathering in cropland is the increase in plant productivity and exudation (Raymond and Cole, 2003).

Land-use conversion from forest to cultivation has been shown to impact root density and exudation of organic compounds that promote weathering even 70 years after the area was reforested again (Billings et al., 2018). At the Calhoun Critical Zone Observatory in the USA's Southern Piedmont, in cultivated plots, root densities approached zero at depths > 70 cm, while in forested plots, root density declined with depth to 200 cm; and below 70 cm, root densities in old-growth forests averaged 2.1 times those in regenerating forests. This root distribution influenced microbial community composition, as well as relative abundance of root-associated bacteria, which was greater in old-growth soils than in regenerating forests. Soil respiration and salt-extractable organic C, a proxy for organic acids, both factors in biological weathering, were significantly greater at 3–5 m depth in old forests relative to regenerating forests and cultivated plots. Forested sites that are used to harvest lumber can also be subject to acidification due to removal of the basic cations with the harvest (McGivney et al., 2019).

1.5.5.2. Mining

Mining results in excavation of the ore material and often deposition of the finer material remaining after ore enrichment on the soil surface, where it is at disequilibrium with the atmospheric conditions. Because of this mining strongly promotes weathering processes (Ross et al., 2018). In pyrite, an iron ore, as well as accessory mineral during coal mining, Fe and S are present in reduced form. When residual pyrite in the ore is exposed to atmospheric levels of O_2, it is oxidized resulting in soluble forms of iron and decrease in solution pH. The produced sulfuric acid can then oxidize and dissolve various elements including toxic metals (Blodau, 2006; Cravotta, 1991). Acid mine drainage due to pyrite in coal accounts for 28–40% of total riverine sulfate derived from pyrite oxidation (Raymond & Oh, 2009). The legacy of trace metal contamination as result of mining activities can persist for a very long time after mining has been discontinued (Le Roux et al., 2020).

1.5.5.3. Rain Acidification

While a decreasing concern now (Engardt et al., 2017), rain acidification can have a direct effect on weathering and element cycles in the environment. Rainfall at equilibrium with ambient CO_2 (410 ppm) would have pH of 5.61. An increase in the partial pressure of CO_2 in the atmosphere due to burning of fossil fuels decreases the pH of rainwater. However, burning fossil fuels, particularly coal, can also release N, and particularly S, oxides, which when combined with water in the air form strong acids (Driscoll et al., 2001). In mid-1970s—at the height of the crisis—rainfall acidity value averaged pH 4 in the industrial NE of the United States (Likens and Bormann, 1974). Passing of The Clean Air Act (42 U.S.C. §7401 et seq., 1970) and installation of scrubbers in the coal burning power plants and later shift to gas-burning power plants decreased importance of these processes. Increase in acidity of the rainfall increases leaching of basic cations from the soils, mobility of Al, and S and N content (Driscoll et al., 2001). Modeling of the effect of acid rain on weathering of the soils was not definitive due to opposite effects of pH and soluble Al on rock weathering (McGivney et al., 2019), but measurements indicate increased weathering due to atmospheric deposition of S (N.M. Johnson et al., 1972; Lerman et al., 2007; S.-L. Li et al., 2008; Xu & Liu, 2007). Bailey (2020) showed increase in Ca export normalized to Na through the 1960s with maximum in the 1970s in Hubbard Brook Experimental Forest, New Hampshire, USA due to acid deposition.

1.5.5.4. Climate Change

Climate change caused by combustion of the fossil fuel is affecting every aspect of the environment. The increases in temperature and partial pressure of CO_2 in the atmosphere not only influence biogeochemical cycles directly by affecting weathering reaction rates but they also cause changes in geochemical cycles by affecting ecological processes that influence weathering. Increases in temperature can accelerate weathering by influencing the kinetics of reactions, but weathering reactions are typically exothermic and therefore elevated temperatures can also shift the equilibrium of these reactions towards reactants. Whether dissolution would increase or decrease with temperature increase would depend on whether kinetics or thermodynamics of the reaction controls weathering, which would depend on the residence time of the water relative to time needed to achieve equilibrium (Maher, 2011). Multiple studies demonstrated an increase in weathering with temperature (Dessert et al., 2003; G. Li et al., 2016; Turner et al., 2010; White & Blum, 1995), indicating net kinetic control of dissolution processes and that further increase in temperature with climate change will potentially further increase weathering. However, temperature increase is also often accompanied by changes in microbial activity and plant productivity (Phillips et al., 2011). The net effect can be positive or negative depending on initial conditions (Feeley et al., 2007; Melillo et al., 2017), with increases in both biomass production and soil respiration measured for cold systems and decreases for the tropical ecosystems. As shown in previous sections of this chapter, increase in plant and microbial activity accelerate weathering. Therefore, increase in temperature can indirectly influence weathering through change in biological activity, providing a feedback loop, as weathering processes sequester more or less carbon in inorganic form either in soils or in the oceans.

Elevated CO_2 has a direct effect on weathering (Berner, 1992), as a reactant in the carbonation reaction; however, it also can have indirect effect by increasing productivity of autotrophs (CO_2 fertilization). A number of greenhouse (Barron-Gafford et al., 2005), covered field (Osborne et al., 1997), and Free Air Carbon-dioxide Enrichment (FACE) studies (Ainsworth and Long, 2005) confirm increase in plant productivity and soil respiration (King et al., 2004). A change in weathering at elevated CO_2 has been demonstrated in laboratory studies (Bruant et al., 2003; Lagache, 1965; Navarre-Sitchler & Thyne, 2007; Osthols & Malmstrom, 1995) but has not been demonstrated conclusively in the field because of inherent soil heterogeneity (Andrews & Schlesinger, 2001; Cheng et al., 2010). However, modeling of the past climates demonstrated a strong relationship between atmospheric CO_2 and biological activity and feedbacks to atmospheric CO_2 resulting both from plant uptake during photosynthesis and enhanced weathering driven by plant activity (Taylor et al., 2012).

Change in precipitation type, amount, distribution, and intensity (Dore, 2005; Trenberth, 2011) is also a part of the climate change that influences fluxes of water through the soils and as a result affects biogeochemical cycles. Another effect of the changing climate on biogeochemical cycles is melting of the permafrost that makes C stored there available to heterotrophic microorganisms (Douglas et al., 2014). Along with C, other elemental cycles are also affected by permafrost melting. For example, reduced conditions resulting from water saturation of warmed soils changes Fe oxidation state and behavior (Herndon et al., 2020).

Under natural conditions, a number of environmental factors can be changing at the same time. For instance, in a field case study in the Pyrenees mountains, Zaharescu, Hooda, Burghelea, Polyakov, et al. (2016), showed that climate-change nested variables, such as increases in temperature and spring freezing altitude, a reducing snow cover (earlier and larger unfrozen surfaces), a general increase in the frequency of drier periods, and changes in the frequency of winter freezing days since the early 1980s, accelerated the weathering of naturally metal-rich mountain topography, with several variables showing a multiannual lagged response (Figure 1.9). Such increased weathering released potentially harmful elements such as As and Ni at levels of concern for ecosystem and human populations in the area and further afield.

1.6. LIFE AND MATTER INTERACTIONS ACROSS SCALES

A complex interplay between abiotic and biotic factors at the Earth surface drive the breakdown of exposed crustal materials, which feeds the geochemical cycles of elements supporting life. This massive thermodynamic process is governed by an energy cascade extending from planetary to molecular scales (Figure 1.10). A gradual loss of gravitationally induced heat left over from the planet formation, together with radioactive decay of isotopes (^{238}U, ^{232}Th, ^{40}K) in the mantle and crust (amounting to ~44.2 Tw, in equal proportion; Stacey & Davis 2008), put in motion plate tectonics through energy dissipating convective cells. Such a process continuously surfaces fresh crust in rift areas, buries bedrock and sediments in subduction zones at an inferred rate of 0.01–22.72 cm $year^{-1}$ (Zahirovic et al., 2015), ultimately exposing new rock materials during crustal uplift, e.g., mountain chains and volcanoes. At the same time, the daily external input of electromagnetic radiation from the Sun (about 1.361 kw m^{-2} of total solar irradiance during a solar minimum, amounting to 173,000 Tw globally; Archer, 2009; Kopp & Lean, 2011), keeps the Earth surface at temperatures suitable for liquid water. The transfer of solar energy through Earth's gaseous and liquid reservoirs stimulates turbulent

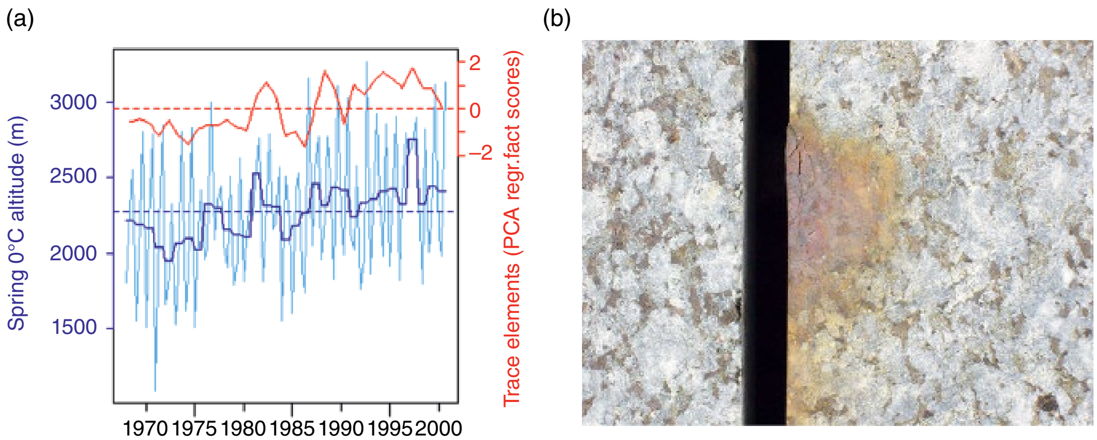

Figure 1.9 Climate change effect on weathering. (a) A generally upward trend and step changes in spring freezing level during 1972–2006 period coincided with changes in trace-metal deposition in a sediment core from Lake Bubal (central Pyrenees, Spain). The lake drains waters from a metal-rich granitic and metamorphic basin, and the climate effect (Pearson $r = 0.6$, $p < 0.05$) is lagged by 4 years. Arsenic, Co, Cr, Cu, Mn, Ni, Pb and Zn concentrations were summarized into one trace element variable (as regression factor [regr. fact.] scores) by principal component analysis (PCA), while the broad variability line in the climate variable was obtained using a locally estimated scatterplot smoothing (LOESS fit line). Horizontal lines are set at variable averages. [Adapted from Zaharescu, Hooda, Burghelea, Polyakov, et al. (2016).] (b) Pyrite mineral in a building granite slab (similar in mineralogical composition to catchment bedrock in (a)) with visible signs of physical (spalling), chemical (reduced Fe oxidation and sulfuric acid staining) and biological (microbial/algae growth) weathering due to exposure to climate agents during the 1999–2009 period.

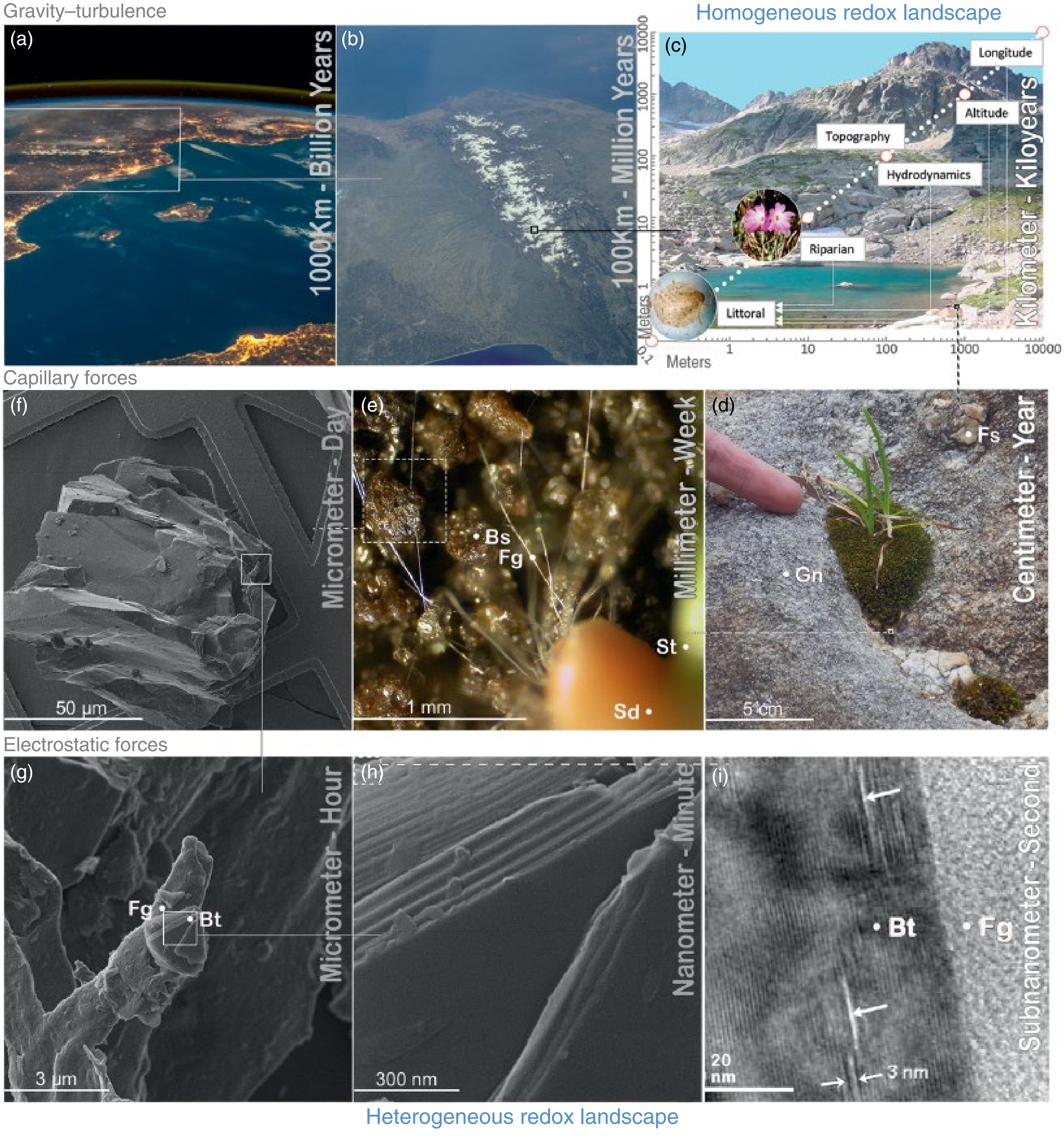

Figure 1.10 Weathering across scales. Interaction among Earth's solid, liquid, gaseous, and living systems from planetary to nanoscale, with changes in the dominant forces and the oxidative landscape included. (a) Earth view from the International Space Station showing the interface between atmosphere, hydrosphere, geosphere (Pyrenees Mountains are highlighted) and anthroposphere. (b) Pyrenees Mountains as seen by NASA mission STS-51 in 1993. (c) Differential effect of catchment components on littoral macroinvertebrates community composition at different scales. (d) Grass and moss growing on a granite bolder. (e) Arbuscular mycorrhiza connecting basalt grains with seedling of buffalo grass (*Bouteloua dactyloides*). (f–h) A biotite grain attached to a fungal hyphae as shown by He-ion microscopy. (i) A transmission electron microscopy (atomic lattice-resolution) image of a fungal hyphae (Fg) interacting with biotite mineral (Bt), showing 3-nm-wide disruption in the mineral sheet stacking. [(c)Adapted from Zaharescu, Burghela, et al. (2016). (i) Bonneville et al. (2009). Reproduced with permission of Geological Society of America.]

mixing of air and water, and results in the patterns of weather and climate we observe (Houze Jr, 2014). Earth's gravity, on the other hand creates buoyancy gradients for air gases and conduits for the turbulent movement of fluids on the terrestrial surface from continental scales down to Kolmogorov microscales, where turbulent kinetics is lost due to drag, and gives off to viscosity (Kantha & Clayson, 2000). At micro- and nanoscales, short-range interactions, such as capillarity and electrostatic forces, and Brownian kinetics become critical. Such an energy cascade across the planetary surface gives birth to erosional and accretion structures along fractal lines of development, from the largest mountains to the smallest soil aggregates (Figure 1.10).

Chemical interactions between air, liquid water, biota and freshly exposed mineral surfaces are critical to driving the nutrient cycles along the energy conduit mentioned above. Such biogeochemical reactions spontaneously consume reactive minerals, oxygen, and atmospheric acidity (as rainwater-dissolved CO_2) to start the cycle of chemical elements through oxidative weathering (Burghelea et al., 2015; Zaharescu et al., 2019). Surface interactions between microbes, plant roots, fungi, animals, and mineral grains create structures (pore spaces, mineral–organic aggregates) and micro- and macrohabitats within soil and sediment matrices, which in turn dictate redox gradients, and nutrient exchanges with water, minerals, and biota. These stabilize soils on hillslopes, and stimulate the colonization and development of various ecosystems. Species assemblages of such ecosystems depend on the structure and composition of nutrient sources in the bedrock, their position in the landscape, and their connection and feedback relationships with the flows of matter and energy in the wider hydrosphere and atmosphere (Figure 1.10; Zaharescu, Burghela, et al., 2016; Zaharescu et al., 2017), ultimately directing the coevolution of the biosphere–geosphere system.

1.7. FUTURE DIRECTIONS

We presented an integrated overview of the various living and nonliving actors that control the breakdown of upper crustal materials when they become exposed to the thermodynamic disequilibrium at the interface with air, water, and life. We further highlight major steps in the evolution of Earth weathering, and how small-scale interactions on mineral surfaces connect with planetary-scale fluxes of energy and matter. With recent advances in high-energy spectroscopy, microscopy, molecular biology, remote sensing, and modelling, there are great opportunities for further research that could improve our picture of the coevolution of life and its life-support system, particularly in the context of sustainable development of human civilization and understanding its place in the Earth system and beyond. We therefore recommend:

1. Increased transdisciplinary efforts including inputs from fields such as physics, mathematics, computing, material sciences, to better constrain key factors directing Earth biogeochemical evolution.
2. Recognition of turbulence as the major paradigm of complex nonlinear multi-scale systems, such as natural processes. Understanding the role of turbulence mixing in transporting mass and energy across the terrestrial surface during abiotic and biotic transformation of the upper crust remains an unknown quantity.
3. Working to understand dominant processes at fundamental scales of interactions, e.g., grain/aggregate scales in soils/sediments, and interface processes at nano- to atomic scales.
4. Closing critical knowledge gaps regarding weathering in Earth evolution context and throughout the solar system, and the development of new methodologies and space missions to target such questions.
5. Developing improved proxies for individual geochemical transformations to aid in better characterizing weathering.
6. Distinguishing and defining geochemical signatures of biosphere interactions with the geomedia, as well as with the liquid and gaseous reservoirs at the planetary surface.
7. Development of complete biogeochemical cycles of all elements and linking them to the evolution of key life functions.
8. Identifying biosphere's keystone species capable of large cascade effects in surface biogeochemistry.
9. Better understanding of the role of deep biosphere in crustal evolution.
10. Better constraining the contribution of ocean, lake, and river floor weathering to global element cycles.
11. Developing a more complete understanding of the effects of climate change on biogeochemical cycles, particularly as it relates to trace-metal weathering—which can have potentially detrimental consequences for the ecosystem and human health.
12. A better understanding of the relationship between the limits of nutrient replenishment through weathering and limits of human and ecosystem growth.

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