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Biogeochemical Cycles

Ecological Drivers and Environmental Impact

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CONTRIBUTORS

Elsa Abs
Ecology and Evolutionary Biology, University of Arizona, Tucson, Arizona, USA; *and* Institute of Biology of Ecole Normale Superieure (IBENS), National Center for Scientific Research (CNRS), INSERM, PSL University, Paris, France

Deonie Allen
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Tomoko Kawaguchi Akitsu
Faculty of Life and Environmental Sciences, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan

Lucas Aschwanden
Institute of Geological Sciences, University of Bern, Bern, Switzerland

Scott W. Bailey
US Forest Service, Northern Research Station, North Woodstock, New Hampshire, USA

Zsuzsanna Balogh-Brunstad
Department of Geology and Environmental Sciences, Hartwick College, Oneonta, New York, USA

Biraj B. Basak
ICAR-Directorate of Medicinal and Aromatic Plants Research (DMAPR), Anand, India

Stéphane Binet
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France; *and* Institute of Earth Sciences, ISTO, University of Orléans, BRGM, Orléans, France

Dipak R. Biswas
Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute (IARI), New Delhi, India

Susan L. Brantley
Earth and Environmental Systems Institute and Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania, USA

Casey Bryce
Geomicrobiology Group, Centre for Applied Geoscience, University of Tübingen, Tübingen, Germany

Carmen I. Burghelea
Biosphere 2, University of Arizona, Tucson, Arizona, USA

Lluis Camarero
Center for Advanced Studies of Blanes, CSIC, Blanes, Girona, Spain

Jon Chorover
Department of Environmental Science, University of Arizona, Tucson, Arizona, USA

Adrien Claustres
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Charles Cockell
UK Centre for Astrobiology, School of Physics and Astronomy, University of Edinburgh, Edinburgh, UK

Luca Da Ros
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

François De Vleeschouwer
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France; and Franco-Argentine Institute for the Study of Climate and its Impacts, University of Buenos Aires, Argentina

Alice Dohnalkova
Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, USA

Katerina Dontsova
Department of Environmental Science, *and* Biosphere 2, University of Arizona, Tucson, Arizona, USA

Ronald I. Dorn
School of Geographical Sciences and Urban Planning, Arizona State University, Tempe, Arizona, USA

Pilar Durantez
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Régis Ferrière
Ecology and Evolutionary Biology, University of Arizona, Tucson, Arizona, USA; *and* Institute of Biology of Ecole Normale Superieure (IBENS), National Center for Scientific Research (CNRS), INSERM, PSL University, Paris, France; *and* International Center for Interdisciplinary and Global Environmental Studies (iGLOBES), CNRS, ENS, University of Arizona, Tucson, Arizona, USA

Didier Galop
GEODE, Geography of the Environment, University of Jean-Jaurès Toulouse, France, and LabEx DRIIHM (ANR-11-LABX-0010), INEE-CNRS,Paris, France

Laure Gandois
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Yves Goddéris
Environmental Geosciences Toulouse, CNRS—Midi-Pyrénées Observatory, Toulouse, France

Sarah Godsey
Department of Geosciences, Idaho State University, Pocatello, Idaho, USA

Sophia V. Hansson
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France; *and* Department of Bioscience – Arctic Research Centre, Aarhus University, Aarhus, Denmark

Marilen Haver
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Elizabeth Herndon
Department of Geology, Kent State University, Kent, Ohio, USA

Séverine Jean
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Lauren Kinsman-Costello
Department of Biological Sciences, Kent State University, Kent, Ohio, USA

Pascal Laffaille
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Hanna Landenmark
UK Centre for Astrobiology, School of Physics and Astronomy, University of Edinburgh, Edinburgh, UK

Gaël Le Roux
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Li Li
Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, Pennsylvania, USA

Stephen Lofts
Centre for Ecology and Hydrology, Lancaster University, Lancaster, UK

Claire Marie-Loudon
UK Centre for Astrobiology, School of Physics and Astronomy, University of Edinburgh, Edinburgh, UK

Rebecca Lybrand
Oregon State University, Corvallis, Oregon, USA

Ashis Maity
ICAR-National Research Center for Pomegranate, Solapur, India

Laurent Marquer
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France; *and* GEODE, Geography of the Environment, CNRS, University of Jean-Jaurès Toulouse, France

Florence Mazier
GEODE, Geography of the Environment, University of Jean-Jaurès Toulouse, France

Bryan Moravec
Department of Environmental Science, University of Arizona, Tucson, Arizona, USA

Hiroyuki Muraoka
River Basin Research Center, Gifu University, Yanagido, Gifu, Japan

Shin Nagai
Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology, Showamachi, Kanazawa-ku, Yokohama, Kanagawa, Japan; *and* Institute of Arctic Climate and Environment Research, Japan Agency for Marine-Earth Science and Technology, Showamachi, Kanazawa-ku, Yokohama, Kanagawa, Japan

Thomas Nägler
Institute of Geological Sciences, University of Bern, Bern, Switzerland

Kenlo Nishida Nasahara
Faculty of Life and Environmental Sciences, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan

Natasha Nicholson
UK Centre for Astrobiology, School of Physics and Astronomy, University of Edinburgh, Edinburgh, UK

Jose Miguel Sánchez-Pérez
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Thomas Pettke
Institute of Geological Sciences, University of Bern, Bern, Switzerland

Marie-Claire Pierret
Laboratory of Hydrology and Geochemistry of Strasbourg, EOST, Strasbourg University, CNRS, Strasbourg, France

Anne Probst
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Christopher T. Reinhard
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

Thomas Rosset
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Loredana Saccone
Department of Architecture and Civil Engineering, University of Bath, Bath, UK

Taku M. Saitoh
River Basin Research Center, Gifu University, Yanagido, Gifu, Japan

Toby Samuels
UK Centre for Astrobiology, School of Physics and Astronomy, University of Edinburgh, Edinburgh, UK; *and* Institute of Evolutionary Biology, School of Biological Sciences, University of Edinburgh, Edinburgh, UK

Sabine Sauvage
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Dirk S. Schmeller
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Anaelle Simonneau
Institute of Earth Sciences, ISTO, University of Orléans, BRGM, Orléans, France

Kyle Smart
Department of Geology and Environmental Sciences, Hartwick College, Oneonta, New York, USA

Mark M. Smits
Applied Biology, HAS University of Applied Sciences, Hertogenbosch, the Netherlands

Adam H. Stevens
UK Centre for Astrobiology, School of Physics and Astronomy, University of Edinburgh, Edinburgh, UK

Pamela L. Sullivan
College of Earth, Ocean, and Atmospheric Science, Oregon State University, Corvallis, Oregon, USA

Roman Teisserenc
Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, INPT, UPS, Toulouse, France

Igor Villa
Institute of Geological Sciences, University of Bern, Bern, Switzerland; *and* University Center for Dating and Archaeometry, University of Milan Bicocca, Milano, Italy

Andrea Voegelin
Institute of Geological Sciences, University of Bern, Bern, Switzerland

Dragos G. Zaharescu
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

PREFACE

Biogeochemical cycles describe the flow of various elements through Earth's critical zone. These cycles are interconnected and strongly influenced by water and energy fluxes, including chemical energy preserved in organic compounds, which influence and are influenced by ecological processes and climate shifts. This book provides an overview of the current state of knowledge regarding many aspects of biogeochemical cycles in the context of global change. The book also highlights areas of need for forming collaborations and method development to gain a better understanding of the cause and effect relationships between biogeochemical cycling of elements, climate shifts, human impacts and disturbances, and ecological responses. In addition, it is important to place an emphasis on further investigations of the interconnections between traditionally studied natural ecosystems, frontier ecosystems, and managed (agricultural) systems, because they are all part of global cycles and subjected to global changes that affect the biogeochemical cycling of elements.

Most of the current publications in the area of biogeochemical cycles focus exclusively on carbon and how it is influenced by climate change, as well as feedbacks between climate change and biogeochemical processes linked to the fate of carbon. However, other element cycles are equally affected by climate change and other human activities, even if they do not provide direct feedback to the atmospheric concentrations of greenhouse gases and therefore climate change. In the past decade, many research groups around the globe invested in further examination of Earth's critical zone in order to evaluate the effect of the rapidly increasing population and industrialization of developing nations on ecosystems and geochemical cycles. The results showed that Earth undergoes rapid changes in response to human activities and some subsystems are extremely vulnerable to ongoing changes; for example, permafrost, mountain, and desert ecosystems. The warming and drying of these ecosystems causes an increase in carbon release into the atmosphere in the form of CO_2 and methane, which provides positive feedback to global warming and triggers changes in other elemental cycles.

This book is organized into three sections, starting with a summary of all biological drivers of weathering and carbon sequestration (Chapter 1), detailed descriptions of plant-induced rock weathering (Chapter 2) and microbial weathering (Chapter 3), available analytical techniques to study the impact of biological weathering on small-scales (Chapter 4), and modeling approaches to examine changes in CO_2 flux due to respiration as climate changes (Chapter 5). The second section focuses on relationships between structure and function of the critical zone with respect to biogeochemical processes (Chapter 6), on plagioclase weathering and soil formation in ecosystems historically affected by anthropogenic acid deposition (Chapter 7), on molybdenum (Chapter 8) and other trace metal cycling in mountain environments (Chapter 9), and prediction of future changes in the critical zone (Chapter 10). The third section provides some insights into how spatial and temporal variability of vegetation in a changing environment can be quantified (Chapter 11), how permafrost ecosystems respond to changes in climate (Chapter 12), how rock varnish responds to anthropogenic disturbances (Chapter 13), and how natural sources of phosphorus and potassium can improve the sustainability of managed systems (Chapter 14). Lastly, the book summarizes challenges and opportunities of studying the biogeochemical cycles under changing environments (Chapter 15).

This book grew out of the Goldschmidt conference session titled "Ecological Drivers of Biogeochemical Cycles under Changing Environment" held in Yokohama, Japan in 2016. Original research was presented during the conference. However, for the purpose of this book, the editors encouraged the contributors to provide a more inclusive overview and summarize the current state of knowledge in the areas of their expertise.

Katerina Dontsova
University of Arizona, USA

Zsuzsanna Balogh-Brunstad
Hartwick College, USA

Gaël Le Roux
University of Toulouse, France

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Part I
Biological Weathering

1

Biological Weathering in the Terrestrial System: An Evolutionary Perspective

Dragos G. Zaharescu[1], Carmen I. Burghelea[2], Katerina Dontsova[2,3], Christopher T. Reinhard[1], Jon Chorover[3], and Rebecca Lybrand[4]

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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[1] *School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA*

[2] *Biosphere 2, University of Arizona, Tucson, Arizona, USA*

[3] *Department of Environmental Science, University of Arizona, Tucson, Arizona, USA*

[4] *Oregon State University, Corvallis, Oregon, USA*

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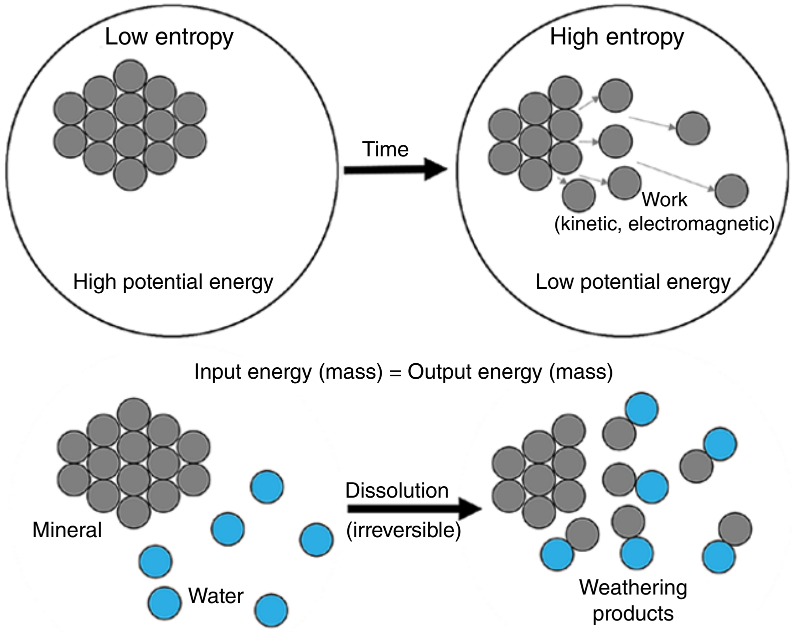

Figure 1.1 The principle of entropy in a theoretical, closed system, and how it applies to open-system natural processes, such as weathering. Initial conditions are characterized by low entropy (e.g., ordered mineral structures, water crystals) and high potential energy. As electromagnetic energy is 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):

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

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,

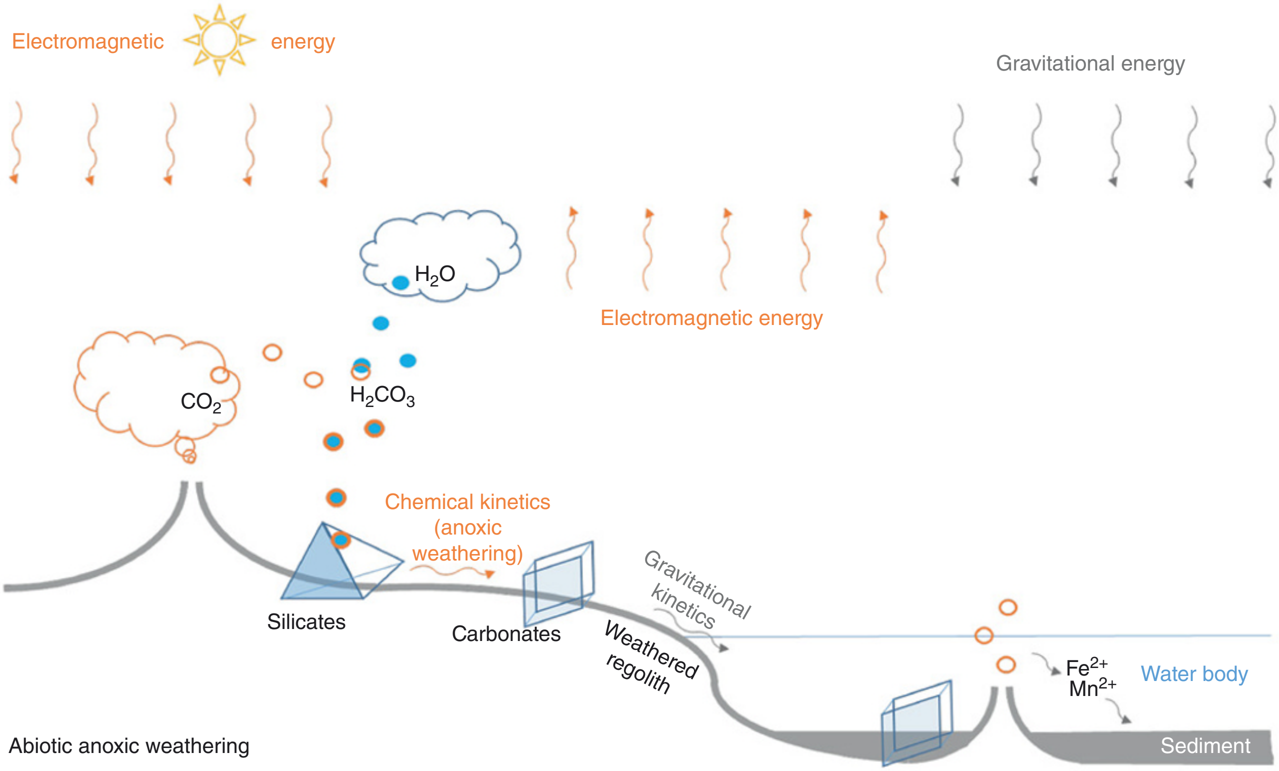

Figure 1.2 Simplified schematic of carbon and energy flows during the Archean Eon (3.5 Ga). Volcanic degassing releases CO_2 (together with other gases and aerosols) to the atmosphere, which reacts with water vapor to produce carbonic acid. In an anoxic atmosphere, silicate rocks exposed through tectonic 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;

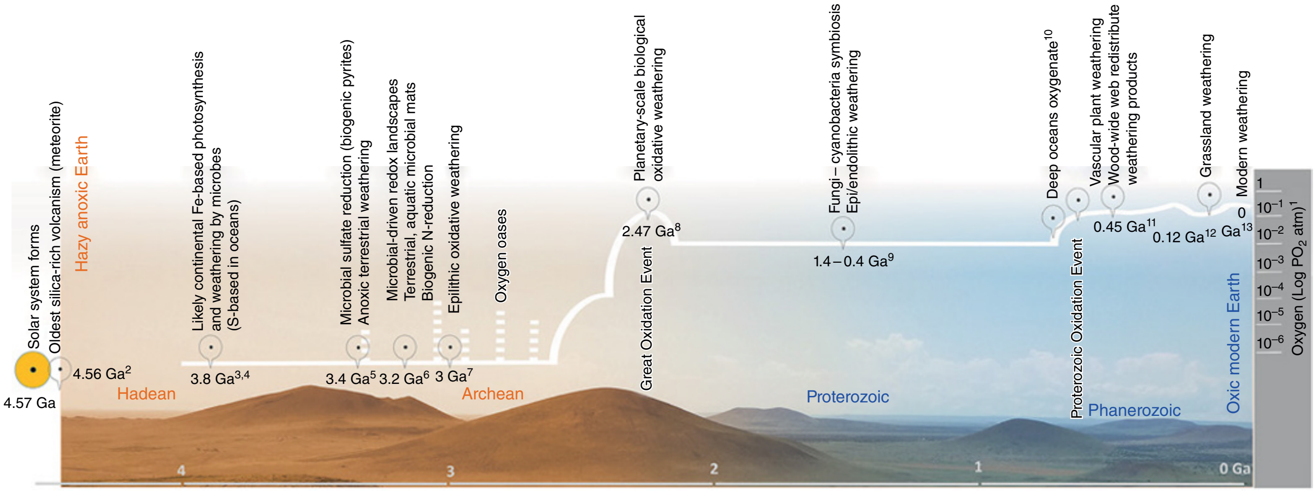

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Figure 1.3 Timeline of major events in the geosphere–atmosphere–biosphere interactions and how they shaped Earth system evolution, including a fundamental shift in its surface thermodynamic disequilibrium attained during The Great Oxidation Event.

Sverjensky & Lee, 2010), phosphates, and new carbon-based biominerals such as organic biominerals and biocarbonates (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

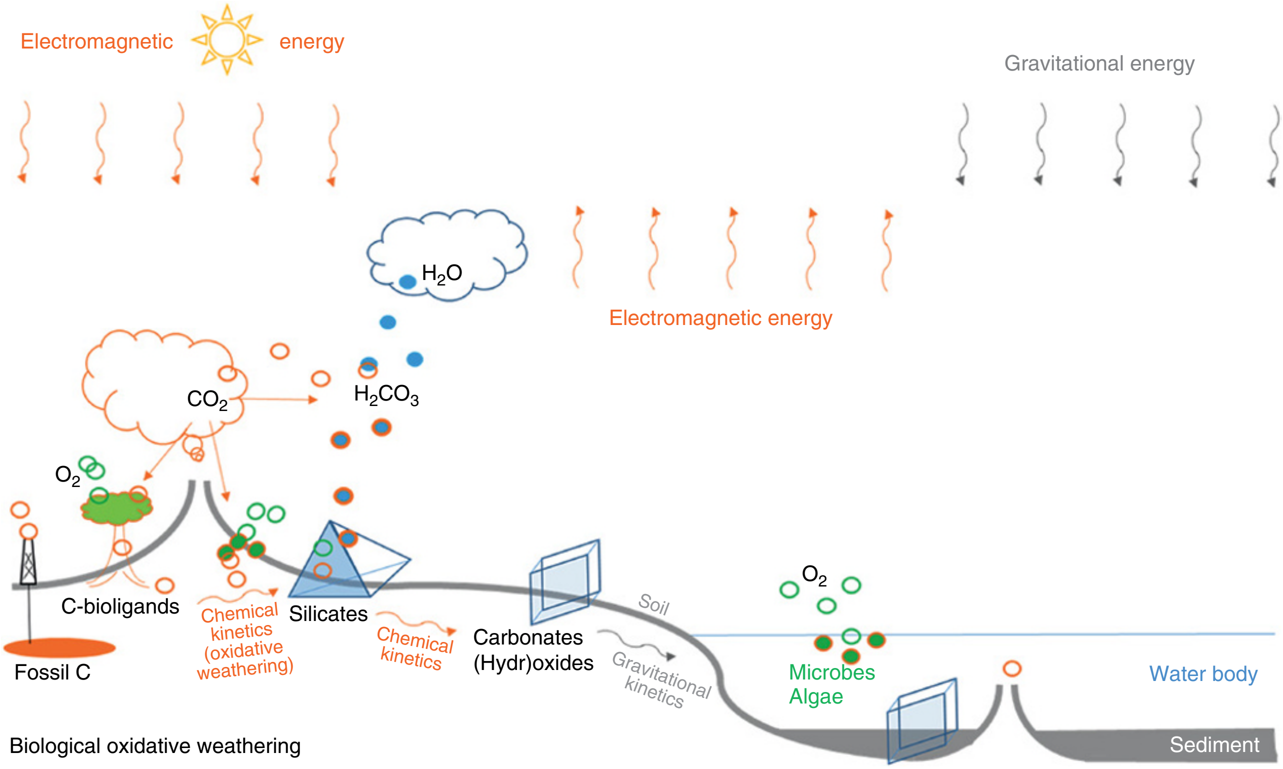

Figure 1.4 Carbon and energy flows on the modern, biosphere-dominated Earth surface. Under modern-day weathering, CO_2 released through mantle degassing (terrestrial and marine), biosphere respiration, or anthropogenic fossil-fuel extraction and burning reacts with rainwater, producing carbonic acid. 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 non-living 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)

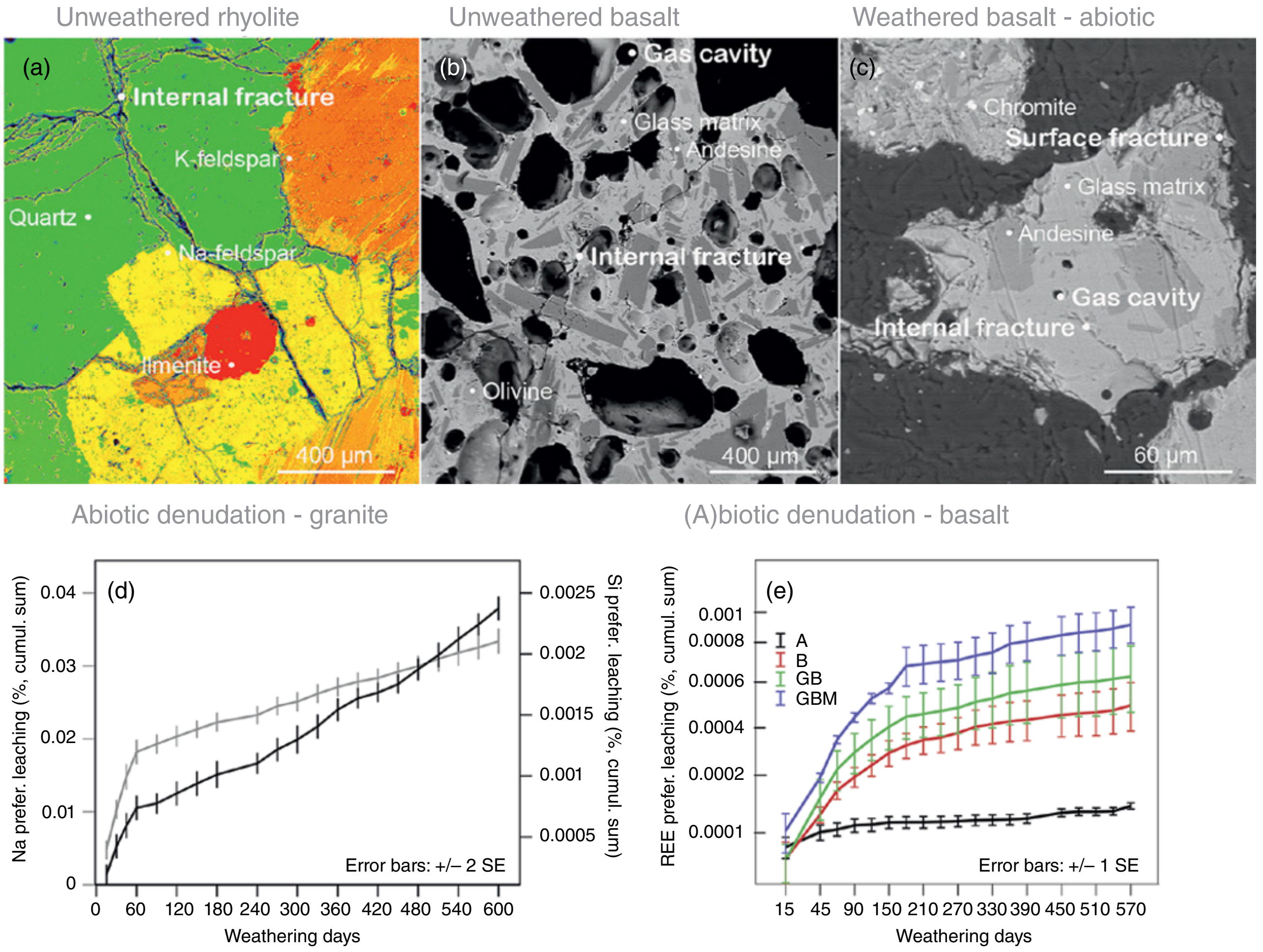

Figure 1.5 Incipient weathering as driven by abiotic and biotic agents. Internal and peripheral fractures set the stage for physical weathering. Electron probe microanalysis showing internal microfractures within and between minerals in (a) rhyolite and (b) basalt, together with (c) surface microfractures 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

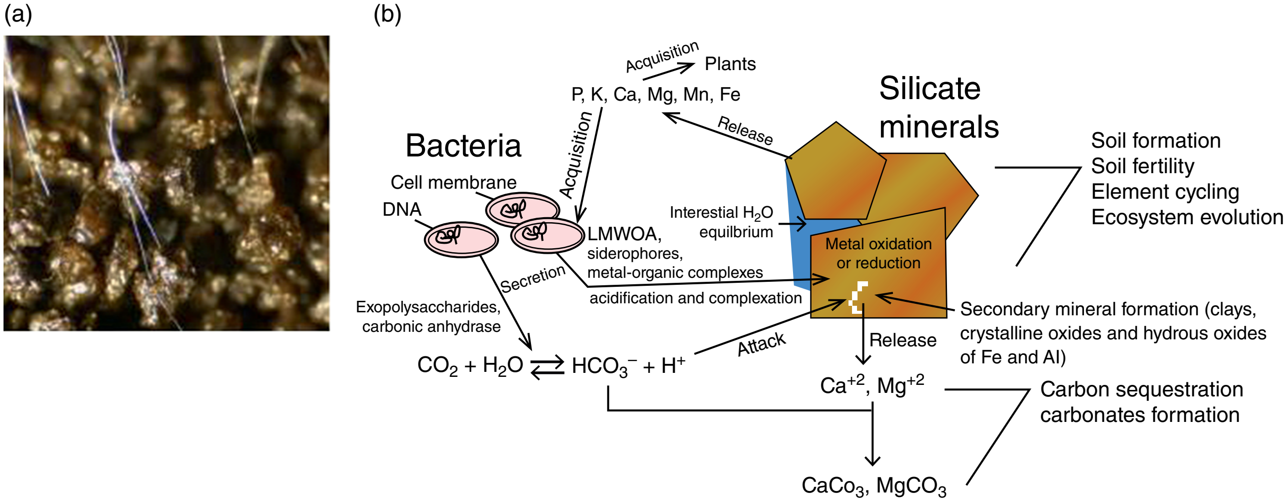

Figure 1.6 Microbes–rock interactions during weathering: (a) fungal hyphae prospecting basalt grains (Zaharescu et al., 2019) and (b) a schematic of mineral weathering by microbes and the affected ecosystem processes. [(a) Zaharescu et al. (2019). Reproduced with permission of Dragos G Zaharescu.]

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.

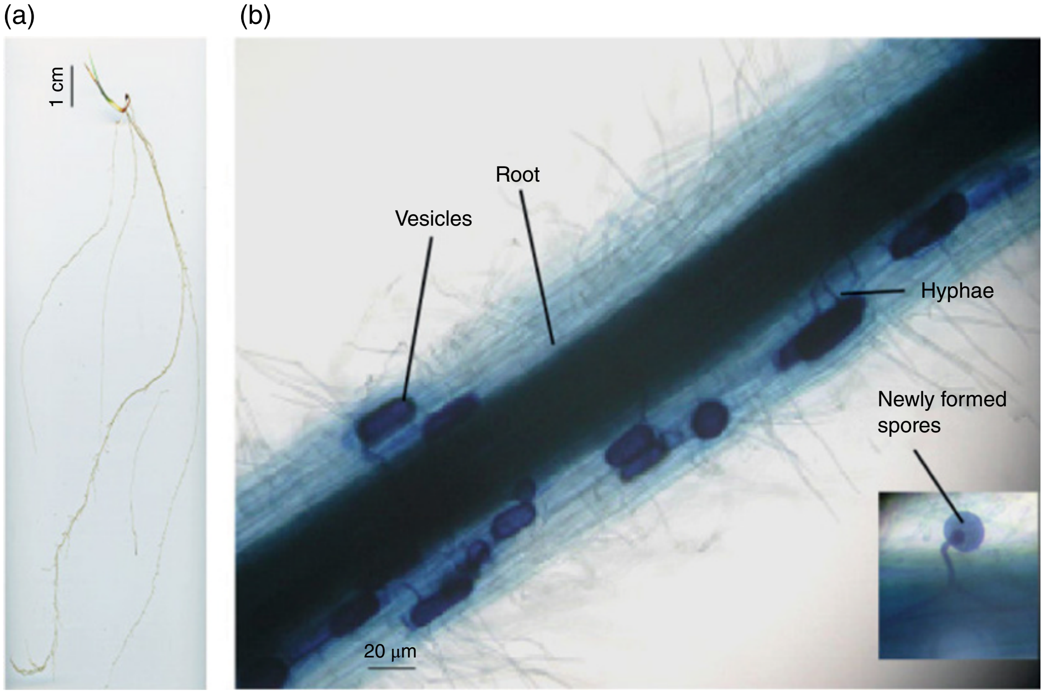

Figure 1.7 Mycorrhiza symbiosis: (a) root of buffalo grass (*Bouteloa dactyloides*) infected by arbuscular mycorrhizae symbiont (*Glomus intraradices*); (b) mycorrhiza reproductive spores (inset).

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.