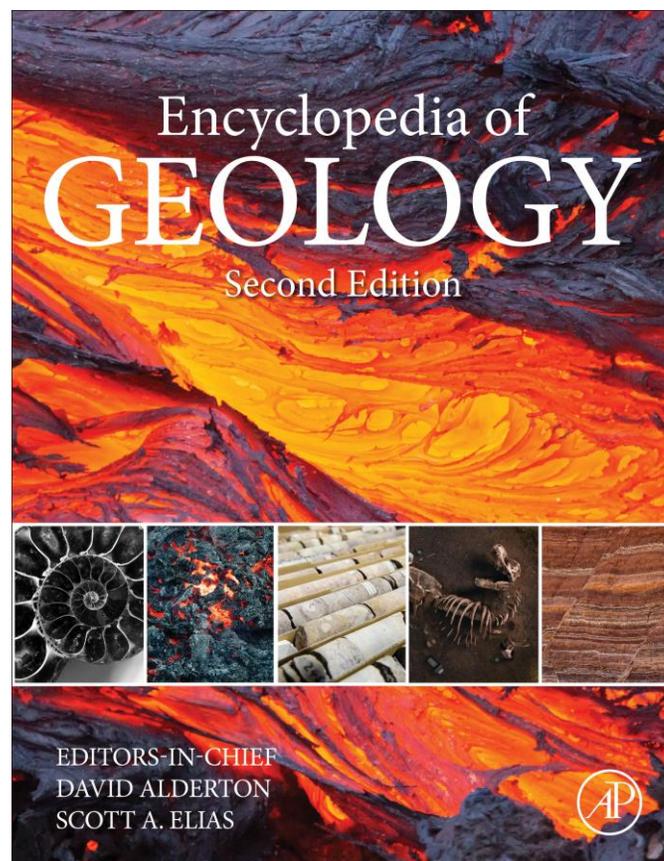


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Robbins Leslie J., and Konhauser Kurt O. (2021) Geobiology and Geomicrobiology. In: Alderton, David; Elias, Scott A. (eds.) *Encyclopedia of Geology*, 2nd edition. vol. 6, pp. 554-568. United Kingdom: Academic Press.

[dx.doi.org/10.1016/B978-0-12-409548-9.12532-1](https://dx.doi.org/10.1016/B978-0-12-409548-9.12532-1)

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## Geobiology and Geomicrobiology

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### Glossary

**Acidophiles** Bacteria capable of living at pH conditions less than 2.

**Adenosine triphosphate (ATP)** A biochemical compound that releases useable free energy when one of its high-energy phosphate bonds is broken.

**Anoxic** Used to define an environment with less than 10 nm dissolved O<sub>2</sub>.

**Archean** 4000–2500 million years before present.

**Biomarkers** Remnants of organic molecules preserved in thermally immature sedimentary units that can be related to a given metabolism or biotic lineage.

**Chelate** Typically an organic compound containing ligand(s) bonded to a central metal atom at two or more points.

**Cryogenian** A period of the Neoproterozoic era that spans 720–635 million years before present.

**Eoarchean** 4000–3600 million years before present.

**Extremophiles** Microbes that are capable of living in extreme surface or subsurface conditions.

**Ga** Billion years (i.e., 10<sup>9</sup>) before present.

**Hadean** The portion of Earth's history from planetary formation to 4000 million years before present.

**Hydrophilic** A substance that is attracted to water molecules and tends to be dissolved in water.

**Hydrophobic** A substance that is repelled by water molecules.

**Hyperthermophiles** Bacteria capable of living at temperatures >80 °C.

**Ka** Thousand years (i.e., 10<sup>3</sup>) before present.

**Ma** Million years (i.e., 10<sup>6</sup>) before present.

**Mesophiles** Microbes that grow between 15 and 40 °C.

**Mesoproterozoic** 1600–1000 million years before present.

**Metalloenzymes** An enzyme that contains a metal ion or cofactor.

**Neoproterozoic** 1000–541 million years before present.

**Oxic** Used to define an environment with greater than 4.5 μM dissolved O<sub>2</sub>.

**PAL** Present atmospheric levels.

**Paleoproterozoic** 2500–1600 million years before present.

**Paleozoic** 541–252 million years before present.

**pH** A scale that denotes the relative acidity of alkalinity of a solution, corresponding to the activity of the hydrogen ion.

pH =  $-\log(\alpha_{\text{H}^+})$ .

**Photosynthesis** A metabolic process involving the utilization of solar energy by plants, algae and certain bacteria for the synthesis of organic molecules.

**Piezophiles** Piezophiles, also known as barophiles, are microorganisms that are capable of living at elevated pressures.

**Plankton** A diverse suite of organisms that live in the water column of freshwater or seawater and are unable to swim against a current.

**Suboxic** Used to define an environment with between 4.5  $\mu\text{M}$  to 10 nm dissolved  $\text{O}_2$ .

**Thermophiles** Microbes that live at temperatures between 45 and 80 °C.

## What Is Geobiology?

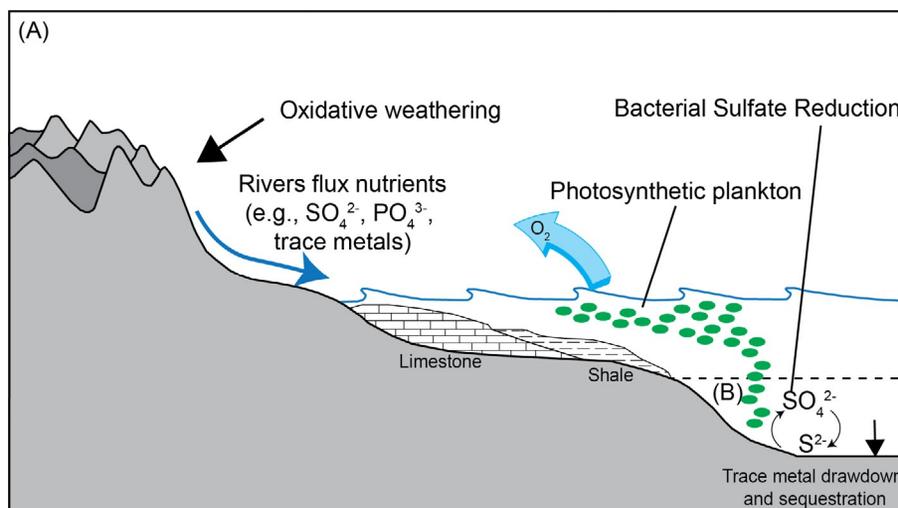
Geobiology (including the subfield of geomicrobiology) explores the relationship between life and the physical Earth. Its origins can be traced to Lourens Baas-Becking's (1934) book *Geobiology*, in which he argued that although microorganisms exist everywhere, the environment selects which species prevail within a given habitat. Since then, geobiology has transformed into its own scientific discipline that considers all aspects of how the biosphere shapes, and is shaped by, Earth's surface and sub-surface environments. The discipline encompasses direct in situ observation, field and laboratory experiments that elucidate how biological and physical processes interact to influence environments, both locally and globally, as well as geological investigations into how Earth and life have interacted over our planet's 4.6 billion year history. A key topic within geobiology encompasses how life controls elemental cycling, from the weathering and dissolution of geological materials to the assimilation of diverse bioessential macro- and micronutrients necessary for life to their long-term incorporation into the sediment record. These processes cover a vast range of spatial scales, from porosity and microfractures in rocks to reservoirs as immense as the oceans. Geobiological processes also operate over a wide range of temporal scales as well, from near instantaneous redox reactions to how life has shaped the composition of Earth's atmosphere over billions of years. The central theme running through all geobiological research is the recognition that life shapes the environment to the same degree that environmental change drives the spatial and temporal distribution of life. Geobiology has demonstrated that life and the Earth are intimately connected and provides a basis through which to quantify and describe the cause and effect relationships and associated feedbacks that connect life to the geosphere.

Geobiologists today are addressing some of the most compelling of research questions. Many of these studies are by their very nature interdisciplinary, at the intersection of geology and biology, but also increasingly drawing on other fields including astrobiology, climatology, and the medical sciences. As more is learned about how life interacts with the planet, it is becoming increasingly apparent that it is the feedbacks and drivers between life and Earth that are the most critical agents of change. For example, one may ask: How did microbial genetic innovation in the past lead to the biological reactions that modified Earth's surface? Environmental or geological change, through processes such as tectonics, may also influence biology, creating new opportunities for evolutionary innovation—sometimes in unexpected ways.

Perhaps the most obvious illustration of such a complex interrelationship is oxygenic photosynthesis and the redox history of our atmospheres and oceans. Ancient cyanobacteria adapted to split water to produce oxygen and then spread to large portions of the surface ocean. As oxygen accumulated, a protective ozone layer formed around the Earth, allowing microbial life—including those components that respire using oxygen—to expand across the planet's surface. Almost simultaneously, crustal cooling and increased continental emergence facilitated an increase in oxidative weathering that enhanced the supply of bioessential trace elements (e.g., Mo, Cu) to the oceans. As a positive feedback, increased oxidative weathering resulted in even greater nutrient delivery to the ocean, further stimulating primary productivity. However, there is also a negative feedback that applies to this system. As oxidative weathering increased there would have been a greater flux of sulfate from the land to the oceans, leading to increased bacterial sulfate reduction in the remaining anoxic portions of the ocean. The resulting accumulation of hydrogen sulfide would have stripped the trace metals essential for primary production, throttling down oxygenic photosynthesis, and placing cyanobacteria in a state of nutrient limitation. Collectively, these feedbacks modulated the composition of the Earth's atmosphere over hundreds of millions to billions of years (see Fig. 1). This is just one example, at the largest scale, of the complex give-and-take between life and the abiotic Earth that has shaped the evolution of our biosphere. Geobiologists strive for a more complete understanding of the Earth as a dynamic and interconnected system, to know our origins, to predict our future, and to explore for life beyond not only our planet, but our solar system as well.

## Microbial Diversity

Unlike multicellular life that is restricted to the Earth's surface, the adaptable nature of microorganisms has allowed them to inhabit the most diverse and harsh environments imaginable, often representing the only life forms. In most aquatic systems, microbial cell densities are remarkably similar, ranging from  $10^5$ – $10^6$  cells  $\text{mL}^{-1}$ . Such consistency reflects less the overall amount of microbial productivity that can be supported in these environments than it does control by grazing (Fenchel et al., 2000). Much higher cell densities may be observed wherever abundant nutrients and energy are available and in environments where predation is limited.



**Fig. 1** Model of the positive and negative feedbacks arising from the accumulation of dissolved oxygen in association with Archean “oxygen oases”. As oxygen eventually built up in the atmosphere (A)—in association with the Great Oxidation Event at ca. 2.45 billion years ago—its immediate effect was to trigger the evolution of aerobic metabolisms on land, such as the oxidation of reduced sulfur and iron in pyrite. The acid weathering arising led to enhanced chemical weathering, the transport of solutes to the oceans and increased primary production. However, in some basins (B), the amount of sulfate transported by rivers led to sulfate reduction of dead planktonic biomass, and the eventual increase in dissolved sulfide into the water column. This served as a negative feedback in that the dissolved sulfide reacted with dissolved trace metals that were required for metalloenzymes, thus causing their removal from seawater and throttling primary productivity.

Microorganisms define the limits of biological tolerance to physiochemical extremes. This includes environments subject to acute variations in temperature, pressure, and aqueous chemistry. In each of these environments, the indigenous microorganisms have made unique adaptations with regards to metabolic strategies, motility, size, morphology, and many other structural and functional aspects of the cell. Microorganisms inhabiting these environments, referred to as *extremophiles*, often require conditions prohibitive to higher forms of life to survive and are a testament to life’s ability to utilize high specific and restricted surface and subsurface environments. A few examples of the breadth of environmental conditions microbes have evolved to inhabit are presented below.

## Temperature

Each microorganism has a temperature range over which it can grow. Psychrophiles grow best at temperatures  $<15^{\circ}\text{C}$ . In nature, they are commonly found in deep ocean waters or in polar regions. Mesophiles, which grow between  $15$  and  $45^{\circ}\text{C}$ , are the most common types of microorganisms and include most pathogenic species. Thermophiles grow between  $45$  and  $80^{\circ}\text{C}$  and hyperthermophiles grow above  $80^{\circ}\text{C}$ . At high temperatures, subtle changes occur in the configuration of the proteins and nucleic acids causing them to become irreversibly altered. As temperatures approach the surface boiling point of water, monomers that make up the cells begin to hydrolyze; for instance the half-life of adenosine triphosphate (ATP) is less than 30 min at  $100^{\circ}\text{C}$  (Miller and Bada, 1988). To date, the uppermost survival temperature measured is  $121^{\circ}\text{C}$  for an archaeal species, most similar to *Pyrodicticum occultum* and *Pyrobaculum aerophilum*, recovered from an active black smoker vent near the Juan de Fuca Ridge, although cultures exposed to  $130^{\circ}\text{C}$  for 2 h still grew when transferred to fresh medium at  $103^{\circ}\text{C}$  (Kashefi and Lovley, 2003). Given that many amino acids are stable up to  $\sim 150^{\circ}\text{C}$ , a higher temperature threshold may yet be reported (Cowan, 2004).

One principal factor that governs a microorganism’s minimum temperature is whether the cell membrane continues to be fluid, so that its capability for nutrient transport and energy generation remain functional. Experiments with psychrophiles have shown that lipids in their plasma membrane change composition as temperature is decreased by adding an increasing proportion of polyunsaturated and branched fatty acids to maintain fluidity (Gounot, 1986). Other adaptations include increasing the production of extracellular compounds that increase the viscosity of the immediate fluid phase, in essence a natural antifreeze agent (Raymond and Fritsen, 2001). To date, the minimum temperature recorded for actively growing bacteria in culture is  $-20^{\circ}\text{C}$  (Rivkina et al., 2000), while in nature, the minimum temperature observed is  $-17^{\circ}\text{C}$  in snow (Carpenter et al., 2000). At lower temperatures (e.g.,  $-27^{\circ}\text{C}$  in Antarctic permafrost), microorganisms are believed to be in a state of anabiosis, where they are metabolically inactive (Vorobyova et al., 1997).

## Pressure

Microorganisms are the only life forms that can inhabit deep subsurface environments where the pore spaces are only micrometers in scale. The metabolic processes employed by subsurface species are similar to those utilized by surface species, with two major

exceptions. First, light is not available at depth, so photosynthesis is not possible. Therefore, microbial life is dependent upon energy sources available within the sediment or dissolved in circulating fluids. Second, in sediments,  $O_2$  is rapidly depleted in the top few meters, hence anaerobic respiration dominates at depth (Lovley and Chapelle, 1995). In a well-cited study, core samples of marine sediment, collected from >500 m depth, contained viable populations of sulfate-reducing bacteria (SRB) that were observed to slowly metabolize pore water sulfate (Parkes et al., 1994). Based on extrapolation from direct cell counts, the authors estimated that similarly metabolizing populations of buried SRB, growing globally in sediment to depths of 500 m, could constitute up to one-tenth of Earth's living biomass. There is also significant evidence that microorganisms live in deep terrestrial groundwater and within rock matrix pore space and microfractures. The extent to which they can migrate is set by the temperature, assuming that adequate energy supplies are available for microbial life. Therefore, even at the 6 km depth reached in some gold mines of South Africa, fissure waters still support a deep biosphere of hyperthermophilic *Archaea* (Takai et al., 2001).

Life in the deep-sea must also contend with elevated hydrostatic pressures which increases by 1 bar for every 10 m of water column. Therefore, if the deep-sea corresponds to a depth of water in excess of 1000 m, then some 75% of the total oceanic volume is exposed to hydrostatic pressures above 100 bars. The microbes, and higher life forms, that live in the deep-sea display different levels of adaptation to elevated hydrostatic pressures, from the barosensitive to obligate piezophiles (also called barophiles) that require high pressures. Studies on natural piezophilic marine life began in earnest with the discovery of black smokers at the Galápagos Rift (Corliss et al., 1979). Observing an active biological community, including giant tube worms, clams and shrimp, the question arose what comprised the base of the food chain? A major breakthrough came when it was discovered that piezophilic bacteria could survive within the digestive tracts of their animal hosts. Since then, studies have expanded outwards from the hydrothermal vents and demonstrated that piezophilic bacteria survive throughout the abyssal seafloor, including within the world's deepest sediment in the Mariana Trench at nearly 11,000 m (Kato et al., 1998). Remarkably, experiments have even documented that bacteria survive pressures equivalent to a depth of 50 km below the Earth's crust (Sharma et al., 2002).

## Acidity (pH)

The acidity or alkalinity of a solution is commonly expressed in terms of pH value, where  $pH = -\log_{10}$  of the hydrogen ion concentration in moles per liter. On this logarithmic scale, 7 is neutral, lower values are more acid and higher values more alkaline. For most microorganisms (e.g., the neutrophiles), the external pH range in which growth is possible lies within a pH range of 5–9, although the intracellular pH must remain neutral to prevent the destruction of cytoplasmic macromolecules. Only a few species, acidophiles, are tolerant of pH values below 2. They are generally restricted to mine drainage and geothermal environments, where a number of chemolithoautotrophic Fe(II)- and S-oxidizing bacteria, such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* exist. One archaeal species, *Ferroplasma acidarmanus*, was isolated from biofilms attached to the surface of pyrite ( $FeS_2$ ) in waters with a pH as low as 0 (Edwards et al., 2000). The record for growth at the lowest pH comes from the archaeal species *Picrophilus oshimae* and *Picrophilus torridus*, which were found in hydrothermal waters at a pH of  $-0.2$  (Schleper et al., 1995). Several eukaryotes have also been recovered from waters with a pH lower than 1, including the red alga *Cyanidium caldarium*, the green alga *Dunaliella acidophila*, and several fungi (Zettler et al., 2002). An even more adverse environment than mine drainage is the acidic geothermally heated waters in solfataras (i.e., fumaroles), where pH can drop to values as low as 0, and temperatures can be in excess of 100 °C. The high concentrations of sulfuric acid, coupled with elevated temperatures, limit growth to just a few types of thermoacidophilic *Archaea*, including species from the orders *Sulfolobales* and *Thermoplasmatales* (e.g., Fütterer et al., 2004).

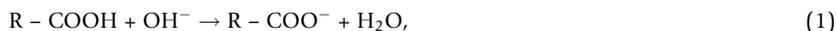
In contrast to low pH environments, a wide variety of microbes can thrive in highly alkaline waters at pH values of 10–11, the so-called alkaliphiles. Some of the most extensively studied alkaline ecosystems are the soda lakes of the Kenyan Rift Valley, where salinities can reach in excess of 30% and pH exceeds 12. Despite these conditions, the high temperatures and daily light intensities make these lakes among some of the most productive naturally occurring aquatic environments in the world (Jones et al., 1998). Massive blooms of cyanobacteria (e.g., species of *Spirulina* and *Anabaenopsis* sp.), photosynthetic bacteria (e.g., *Chromatium* sp.), and sometimes diatoms, represent the primary producers in the less saline lakes, while red anoxygenic, photoautotrophic halophilic (salt-loving) and alkaliphilic *Bacteria* (e.g., *Ectothiorhodospira* sp.) and *Archaea* (e.g., *Natronobacterium*) species thrive in the concentrated brines (Grant and Tindall, 1986).

## Microbial Impacts on the Modern Earth's Surface System

From localized niches, on the order of  $\mu m$ 's, to ecosystems as immense as the oceans, microorganisms are intimately involved in transforming inorganic and organic compounds to meet their nutritional and metabolic needs. As metabolic waste from one species nearly always provides substrates for another, there is a continuous recycling of elements throughout the biosphere. Given sufficient time, the collective metabolic activities of countless microbial communities have the potential to modify the dynamics of the entire Earth, controlling the composition of Earth's atmosphere, the aqueous chemistry of both marine and terrestrial water bodies, and the nature of the soils that support and sustain plant life. Below, we highlight several microbial influences in more detail.

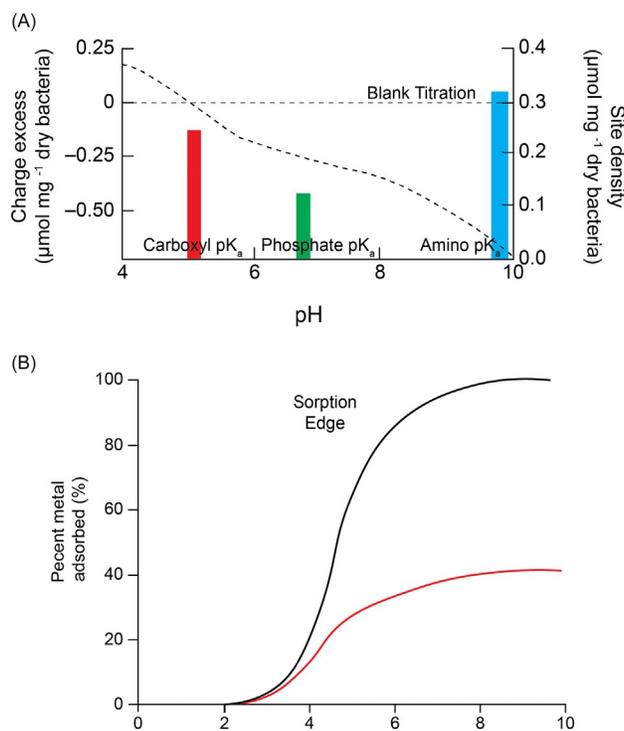
### Sorption of Solutes

Acid-base modeling of bacteria has shown that their cell surfaces—including the peptidoglycan-rich cell wall and various outer layers such as extracellular polysaccharides (EPS)—are dominated by distinct ligands that progressively deprotonate with increasing pH. In their pioneering study, Fein et al. (1997) used intact *Bacillus subtilis* cells to show that three specific ligands could effectively explain the buffering effect provided by the cell wall surfaces. For instance, at low pH, the deprotonation of carboxyl groups could accurately predict the buffering capacity of the biomass from pH 2–6 (reaction 1), while phosphate groups accurately mimicked the titration curves up to pH 7.5 (reaction 2). At pH values above 7.5, a third deprotonation reaction was observed that involved amino groups (reaction 3):



Given the increased deprotonation of cell surface ligands with increased pH, bacterial cells become progressively more anionic as pH increases. In other words, at low pH, when the surface functional groups are fully protonated, bacteria are either neutral or positively-charged, the latter being the result of a cell possessing abundant amino groups. Meanwhile, at the growth pH of most bacteria, cells inherently display a net negative charge and the magnitude of the negativity increases with higher pH values. Therefore, at low pH conditions, most bacterial surfaces behave hydrophobically, but with an increasingly hydrophilic nature at higher pH conditions. The implications of this change in surface reactivity is that bacterial surfaces should intimately interact with soluble metal cations (Fig. 2).

In their pioneering work on metal binding to *B. subtilis*, Beveridge and Murray (1976) proposed a two-step mechanism for the metal adsorption process; the first step in time is an electrostatic interaction between the metal cations and the anionic sites in the cell wall. This interaction then acts as a nucleation site for the deposition of more metal cations from solution, potentially leading to biomineralization. Since those early studies, experiments have begun to place more emphasis on determining the stability constants for metal-organic ligand interactions and in elucidating how metal binding correlates with cell surface reactivity during changes in solution chemistry. The goal for much of this research is to develop geochemical speciation models that describe how microorganisms interact with metals and mineral surfaces under varying geochemical conditions (see Johnson et al., 2007; Flynn et al.,



**Fig. 2** (A) A hypothetical titration profile of a bacterium illustrating charge excess (i.e., net surface charge) resulting from the deprotonation of functional groups and calculated as the difference in proton concentration between the bacterial and blank titrations. The blank titrations are free of functional groups and correspond to the dissociation of water. The site densities of distinct functional groups (drawn as colored bars) are modeled from charge excess and plotted according to the pH at which half are deprotonated, the pKa value. (B) Isotherms showing the adsorption of any given metal cation to bacterial biomass when (i) there are more ligands than metals (black line) which leads to 100% metal adsorption and a steep sorption edge, and (ii) when there are more metals than biomass and the curve plateaus due to the lack of available ligands (red line). On average, carboxyl groups deprotonate over the pH range 2–6, phosphates pH: 5–8, and amino groups pH: 8–11.

2017). The reactions can be quantified using two different approaches: (1) bulk partitioning relationships or (2) surface complexation models (SCM). In the first instance, partitioning models, such as  $K_d$ , Freundlich and Langmuir isotherms, can easily be applied to complex systems because they do not require a detailed understanding of the nature of the surfaces or the adsorption/desorption mechanisms involved. However, they are system-specific, meaning that the results from a set of experiments on one system can be inapplicable to a different system. In contrast, the SCM takes into account the effects of changing pH, solution composition and ionic strength, the acid-base properties of surface functional groups, competitive sorption with other solutes, and solid-phase reactivity and mineralogy. It then draws upon that information to extrapolate to conditions beyond those tested. Fortuitously, it is now becoming apparent that metal cations display a similar affinity series for a given group of ligands, regardless of whether the ligands exist on the surface of microorganisms or as aqueous organic species. This means that common complexes, such as metal-oxalic acid or metal-acetate aqueous complexes, can be used to predict metal-carboxyl surface stabilities of bacteria for those metals whose bacterial adsorption behavior has not yet been measured directly (e.g., Fein et al., 2001).

### Biominingeralization

Microorganisms form mineral phases throughout nature. This process, termed *biomineralization*, can occur both passively and actively. The first pathway involves mineral formation in the open environment, without any apparent regulatory control. This process was defined by Lowenstam (1981) as “biologically induced biomineralization”. It is not specifically designed for mineralization, but biominerals form as incidental by-products due to the activity of microorganisms and their surrounding environment. Simple perturbations, such as the development of an ionized cell surface, facilitate metal adsorption and promote heterogeneous nucleation by lowering the interfacial energies and stabilizing the nascent nuclei from re-dissolving. Indeed, microorganisms can be likened to mineralizing templates because the composition and structure of their functional groups are ideal for the passive formation of a number of different types of mineral nuclei. Microbial activity can also affect mineral saturation states immediately outside the cell through the excretion of metabolic wastes (e.g.,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ) or enzymatic mediated redox changes (e.g., Fe(II) or Mn(II) oxidation). For example, denitrifying or photosynthetic bacteria promote an increase in solution pH that is supportive of carbonate precipitation; SRB induce the formation of metal sulfides (e.g., pyrite,  $\text{FeS}_2$ ) by generating  $\text{HS}^-$ ; while the release of  $\text{Fe}^{2+}$  by Fe(III)-reducing bacteria may lead to magnetite ( $\text{Fe}_3\text{O}_4$ ) formation.

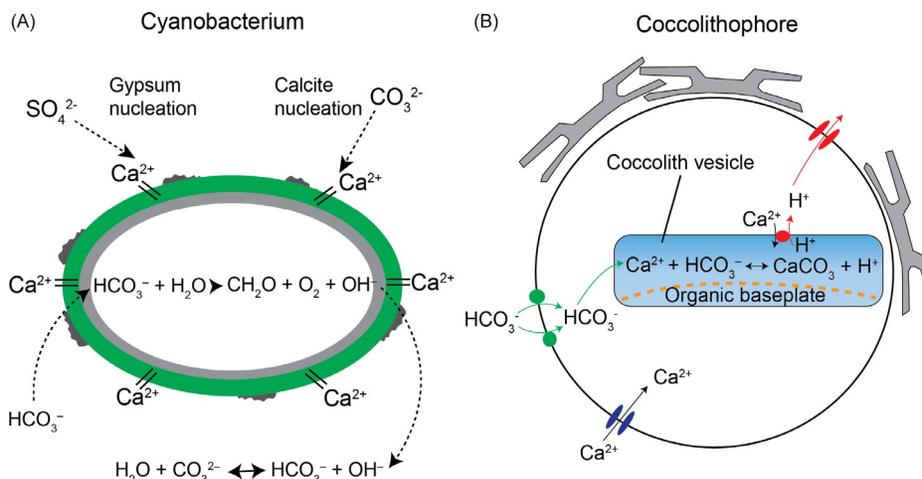
As induced biomineralization is a passive process, dependent upon the chemical composition of the fluids in which they are growing, a particular microorganism will form a mineral phase from the solutes immediately available to it. Conversely, the same microorganism in a different environment would likely form a different mineral phase. Perhaps one of the best examples comes from the “whiting events” associated with cyanobacterial blooms in Fayetteville Green Lake, New York (USA). Under the transmission electron microscope, the unicellular *Synechococcus* sp. is frequently shown to be completely mineralized, yet the type of mineralization is seasonally dependant (Thompson et al., 1990). During the active growth phase of the year, a light rain of plankton encrusted in calcite ( $\text{CaCO}_3$ ) falls to the lake bottom contributing to unconsolidated lime deposition. The role of cyanobacteria in carbonate precipitation is two-fold: metabolic fixation of inorganic carbon tends to increase solution pH and leads to an increase in the saturation state (reaction 4), while adsorption of  $\text{Ca}^{2+}$  to the cell surface promotes heterogeneous nucleation (Fig. 3).



During the cold winter months, when the *Synechococcus* cells become dormant, the non-metabolizing cells develop abundant gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) crystals instead because the lake is characterized by high concentrations of dissolved sulfate throughout the year. Importantly, calcium is bound to the cell surface at all times, thus the authigenic mineral formed is solely the result of the dissolved anions available ( $\text{HCO}_3^-$  vs.  $\text{SO}_4^{2-}$ ); calcite is more insoluble than gypsum so when it is thermodynamically favored it preferentially precipitates.

By contrast, “biologically controlled biomineralization” is completely regulated, allowing the organism to precipitate minerals that serve physiological roles (Mann, 1988). In the initial stages, a specific site within the cytoplasm or on the cell wall is sealed off from the external environment, creating confined geochemical conditions independent from the external milieu. Two common methods of space delineation occur. The first involves the development of intercellular spaces between a number of cells. The second is the formation of intracellular deposition vesicles. Once the organic matrix is formed, the next step entails the cells sequestering specific ions of choice and transferring them to the isolated compartments where their concentrations are increased until a state of supersaturation is achieved. Levels of supersaturation are regulated by managing the rate at which mineral constituents are provided to the compartment via specific transport enzymes. Nucleation is controlled by exposing ligands with distinct stereochemical and electrochemical properties tailored to interact with specific hydrated ions. Moreover, as the mineralization site is isolated from outside the cell by a barrier through which ions cannot freely diffuse, the cellular membrane, internal mineralization may proceed even though external conditions are thermodynamically unfavorable.

Using calcite again as an example, the differences between induced and controlled mineralization are readily evident. Calcium carbonate minerals constitute the largest fraction of known biologically controlled biominerals, with coccolithophores and foraminifera removing vast amounts of calcite from seawater to form their skeletons (e.g., Andrews et al., 2004). Import of  $\text{Ca}^{2+}$  from  $\text{CaCO}_3$ -saturated seawater occurs passively through  $\text{Ca}^{2+}$  channels into the cytoplasm. The  $\text{Ca}^{2+}$  then proceeds against a concentration gradient to get into the vesicle, requiring energy in the form of ATP. To complete calcite formation,  $\text{HCO}_3^-$  is also



**Fig. 3** (A) Significant insights into the mechanisms underpinning freshwater cyanobacterial calcification have been obtained from experiments replicating the activity of *Synechococcus* sp. communities in Fayetteville Green Lake, New York. When the cyanobacteria were cultured in filter-sterilized lake water (pH 7) they began to precipitate gypsum on their surfaces within 4 h of the beginning of the experiment. The biomineralization of gypsum was a two-step process initiated by the binding of  $\text{Ca}^{2+}$  to the cell's S-layer, followed by reaction with dissolved sulfate. Within 24 h, an increase in the alkalization of the microenvironment around the cells pushed the solid mineral stability field towards the formation of calcite. (B) Schematic of the cellular processes associated with the calcification of coccolithophores, including the transport into the cell from the surrounding seawater of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  and the removal of the end product  $\text{H}^+$  from the cell. Note how calcification takes place within an intracellular vesicle where the conditions for mineral formation are cellularly controlled. Modified from (A) Thompson JG and Ferris FG (1990) Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water. *Geology* 18: 995–998; (B) Monteiro FM, Bach LT, Brownlee C, et al. (2016) Why marine phytoplankton calcify. *Science Advances* e1501822, 14 p.

introduced into the deposition vesicle. Because the concentration of  $\text{CO}_2$  in seawater may be limiting for photosynthesis, coccolithophores have the ability to utilize  $\text{HCO}_3^-$  instead, with the net result being the generation of  $\text{OH}^-$ . However, unlike the cyanobacteria that excrete the unwanted  $\text{OH}^-$  ions into the surrounding medium, it appears that in the coccolithophores the  $\text{OH}^-$  ions are neutralized by protons generated from the calcifying vesicle. This maintains the pH within the depositional vesicle at an appropriate level for calcification (Fig. 3). The subtle differences between cyanobacterial and coccolithophore calcification clearly highlight their differing activities; the former is simply photosynthesizing and inducing calcite as a by-product of their metabolism, while the latter controls the process intracellularly.

## Weathering

Weathering of the Earth's upper crust includes two major types of reactions, mineral dissolution and mineral oxidation. Microorganisms—bacteria and fungi in particular—play a fundamental role in both processes. They attach to exposed mineral surfaces, coat them with EPS and physically disrupt the grains in their attempt to gain access to nutrients and energy in the underlying substrate. At the same time, they create a complex microenvironment at the mineral-water interface, where metabolically catalyzed redox reactions and the generation of acids and complexing agents lead to pH and concentration gradients markedly different from those in the bulk solution. The majority of organic acids they generate are by-products of fermentation and/or various intermediate steps of the aerobic respiration of glucose, but some microorganisms further excrete organic acids when growth is limited by the absence of an essential nutrient. Many of the fungal acids contain multiple carboxyl groups that dissociate at circumneutral pH. For example, oxalic acid has two dissociation constant ( $K_a$ ) values at pH 1.3 and 4.2, while citric acid is a tricarboxylic acid with three  $\text{p}K_a$  values at 3.1, 4.7 and 6.4. The low  $\text{p}K_a$  values makes both citric and oxalic acids fairly strong acids. The organic acids increase mineral dissolution in two ways, directly and indirectly. In the first instance, the organic acids dissociate and the released protons attack minerals directly by complexing with ligands at the mineral surface (i.e., protonation reactions), weakening, for example, metal-oxygen bonds, and facilitating the release of a metal cation from the surface (e.g., Welch and Ullman, 1993). Intact organic ligands may also complex with metals at the mineral surface, similarly, destabilizing the metal-oxygen bonds, and promoting dissolution through the formation of a metal-chelate complex (e.g., Liermann et al., 2000). Deprotonated organic anions (e.g., oxalate, citrate) indirectly affect dissolution rates by complexing with metal cations in solution, thereby lowering the mineral's saturation state (e.g., Bennett et al., 1988). Some organic anions are very strong chelators and depending on the relative concentration of the anions and metal cations in solution, pH and the stability constants of the various complexes, they can effectively partition a metal cation that has dissolved from the mineral into an organo-metallic complex.

Siderophores are another example of multidentate organic ligands that form strong complexes with metal cations. They are by definition Fe(III) specific and show higher association constants than low molecular weight organic acids, such as oxalic acid. They are also found in reasonably high abundance, averaging micromolar concentrations in soil pore water (Hersman, 2000) to

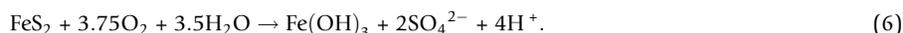
nanomolar concentrations in seawater (Vraspir and Butler, 2009). Siderophores play an important role in the dissolution of Fe-bearing minerals, with for example, a fivefold increase in Fe release and a doubling of cell mass in hornblende-containing cultures relative to control cultures with *Streptomyces* only (Liermann et al., 2000).

Microbes also play a critical role in mineral weathering and soil formation simply through aerobic respiration. The combination of respired CO<sub>2</sub> with water forms carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Despite being a relatively weak acid, it can still accelerate the dissolution of some soluble mineral phases, such as calcite or aragonite (reaction 5).

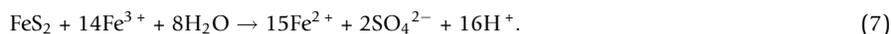


The ability of carbonic acid to cause carbonate mineral weathering can be exemplified with two examples. At current atmospheric pCO<sub>2</sub> levels (approximately  $3 \times 10^{-4}$  atm), and in the presence of calcium carbonate, the equilibrium pH is 8.3, and the concentrations of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> are 10<sup>-3.30</sup> M (20 mg/L) and 10<sup>-3.00</sup> M (60 mg/L), respectively. At pCO<sub>2</sub> levels of  $3 \times 10^{-2}$  atm, characteristic of soil pore waters where biological activity greatly enhances the production of CO<sub>2</sub>, the pH after carbonate dissolution decreases to 7.0, and the concentrations of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> increase to 10<sup>-2.65</sup> M (90 mg/L) and 10<sup>-2.36</sup> M (266 mg/L), respectively.

A number of metal sulfides have the propensity to undergo chemical oxidation when subjected to surface conditions. Of those minerals, pyrite, is arguably the most important environmentally because it is an extremely common constituent in coal seams and ore bodies. The overall process describing the initiation of pyrite oxidation is commonly given by the following reaction:



At first when the pH is still above 4.5, the ferrous iron exposed during the initial reactions spontaneously oxidizes in air to form Fe<sup>3+</sup>, where it is hydrolyzed and re-precipitated as ferric hydroxide. However, as the acid load from the oxidation of the reduced sulfur and iron is allowed to build-up in concentration, the pH of the waters can drop to values below 4.5. When that happens, the role of soluble ferric iron becomes much more important as the pyrite oxidizing agent (Moses et al., 1987):



Indeed, at pH <3, Fe<sup>3+</sup> is the only important oxidizer of pyrite. But, in acid waters, pyrite can reduce ferric iron to ferrous iron faster than the ferrous iron can be regenerated into ferric iron by oxygen. Accordingly, the pyrite will simply reduce all the ferric ions and the reaction will stop. Thus, the ferrous to ferric iron oxidation is considered the rate-determining step in the inorganic oxidation of pyrite (Singer and Stumm, 1970). However, acidophilic bacteria oxidize Fe<sub>(II)</sub> as an energy-generating process, and in doing so foster greater acidification of their local environment. In fact, these bacteria can generate Fe<sup>3+</sup> some 5–6 orders of magnitude faster relative to abiotic conditions (e.g., Lacey and Lawson, 1970).

Aside from its localized effect on degrading individual mineral grains or even entire rock outcrops, microbial weathering has profoundly influenced the Earth's surface environment over geological time. Microorganisms have expedited soil formation since their evolution onto land during the Archean and it has even been suggested that some of the earliest evidence for oxidative weathering is attributable to the metabolic activities of benthic microbial communities (Lalonde and Konhauser, 2015). While soil profiles have developed through microbial influences, the solute-rich leachate has affected the chemical composition of the hydrosphere, from micro-scale soil pore waters to the vastness of the oceans. Additionally, the biochemical weathering of some silicate minerals, and the subsequent deposition of calcium carbonate on the seafloor, are linked through a feedback cycle that impacts on atmospheric CO<sub>2</sub> levels, and ultimately the global climate (e.g., Urey, 1952) (reaction 8).



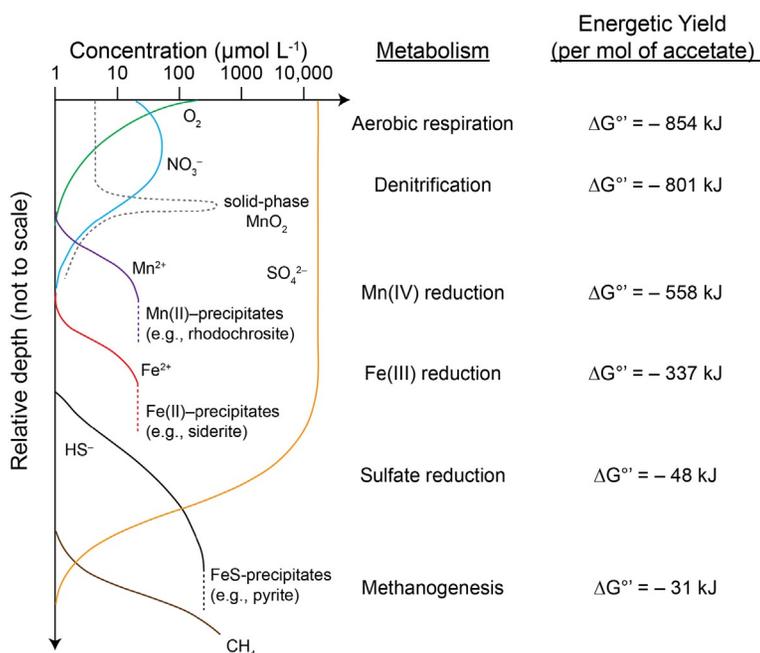
## Redox Reactions

Microorganisms are the major recyclers of organic carbon on Earth; recycling as much as 99% of organic carbon globally in modern marine systems (e.g., Raven and Falkowski, 1999). They fulfill both the role of primary producers, through the conversion of inorganic carbon during photosynthesis and chemolithoautotrophy, and as the major degraders of that biomass, gaining energy and carbon for growth from its transformation to CO<sub>2</sub> or CH<sub>4</sub>. Intimately tied to these opposing processes is the fate of an entire suite of major elements and trace metals that either provide nutrition or function as electron donors or acceptors in the litany of metabolic pathways that microbes are capable of gaining energy from. Elemental cycling occurs within every conceivable environment, from those within μm-thick biofilms, to soils and sediment, to those on spatial scales as large as the continents or oceans. In the case of the latter, after sediment is deposited on the seafloor, a complex suite of physical, chemical, and biological processes modify the unconsolidated material into a sedimentary rock. Typically, the more labile materials are degraded in near-surface sediments on time scales of days to years, more refractory materials are broken down deeper in the sediment on time scales of decades, while the most resistant materials, i.e., the precursors to fossil fuels, are transformed only on timescales of millions of years. The amount of refractory material left after microbial attack will depend on the nature of the primary producers and the degree of processing that has taken place in the river catchment area or oceanic water column. In the end, <1% of the original material buried into sediment may ultimately contribute to the sedimentary organic geochemical record (e.g., Emerson and Hedges, 1988).

Concomitant with the decrease in organic matter with burial is a progressive change in its composition, perhaps most evident in the residual C:N:P ratio. Although the C:N:P ratio of the organic matter input will depend on the relative contribution of terrestrial and marine material, as well as the amount of alteration during descent in the water column, there are still recognizable trends with depth in a given sediment. For example, the preferential stripping of the N from amino acids into solution causes the C:N ratio of the sediment to increase with depth (Macko et al., 1993). The C:P ratio is variable and depends on whether there is preferential stripping of P via biological uptake (Ramirez and Rose, 1992) or if P is lost to the sediment pile via precipitation as diagenetic calcium fluorapatite or its adsorption onto ferric oxyhydroxides (Ingall and Jahnke, 1997).

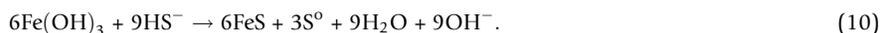
Porewater and mineralogical changes during diagenesis are also directly related to bacterial reduction of soluble ( $O_2$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CO_2$ ) or solid-phase ( $MnO_2$  and ferric oxyhydroxides) components in the sediment. The terminal electron accepting processes that occurs in any given layer depends on what oxidants are available and, in the situation when multiple electron acceptors are present (as in the uppermost sediment layers), on the free energy yield of the specific reaction (Fig. 4). Thus, the decomposition of freshly deposited organic material in sediments proceeds in a continuous sequence of redox reactions, with the most electropositive oxidants being consumed at, or near the surface, and progressively poorer oxidants being consumed at depth until the labile organic fraction is exhausted and the deeper sediments are left with a composition very different from the sediments originally deposited. This sequence of redox reactions is manifest in a biogeochemically-zoned sediment, with characteristic porewater patterns that reflect the dominant microbial assemblages growing at a particular depth of sediment (e.g., Froelich et al., 1979). For instance, sediments are broadly defined as "oxic," "suboxic" and "anoxic" by the levels of dissolved  $O_2$  in the pore waters that, in turn, are directly influenced by microbial respiration.

Inorganic by-products of chemoheterotrophy (e.g.,  $HCO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $NH_4^+$ ,  $NO_2^-$ ,  $HS^-$ ,  $HPO_3^{2-}$  and  $CH_4$ ) seldom accumulate. Physical and macrofaunal processes will cause the net transport of these reduced species from the deeper layers towards the sediment surface, where residing chemolithoautotrophic bacteria use them as metabolic reactants. Alternatively, their presence in pore waters may either trigger important abiotic reactions between the solid and dissolved phases leading to secondary mineral formation. Perhaps one of the best examples is the cementation of loose sediment by various carbonate mineral phases, the most abundant generally being calcite, due to the increased alkalinity derived from organic carbon oxidation (Irwin et al., 1977). Interestingly, the various carbonate phases tend to have characteristic stable carbon isotopic compositions ( $\delta^{13}C$  values). Manganese and ferric iron reduction produce rhodochrosite ( $MnCO_3$ ) and siderite ( $FeCO_3$ ), respectively, with increasingly negative  $\delta^{13}C$  character (typically  $-10$  to  $-2\%$ , respectively) due to the incorporation of an increasing component of biogenic carbonate that has a  $\delta^{13}C$  signature of  $-30$  to  $-20\%$ . Sulfate reduction produces non-ferroan calcite because any available iron reacts preferentially with sulfide. These calcites have an even more negative  $\delta^{13}C$  signature (typically around  $-15\%$ ). Finally, below the zone of sulfate reduction, methanogenesis leads to the production of carbonates with a characteristic positive  $\delta^{13}C$  signature due to the loss of isotopically light C in the form of methane gas (Curtis et al., 1986). Pyrite is another authigenic mineral characteristic of diagenesis. Its formation is indirectly linked to the activity of dissimilatory sulfate reduction which couples the oxidation of simple organic molecules to the reduction of sulfate, thereby generating dissolved hydrogen sulfide (Rickard, 1969). In sediments, this initial



**Fig. 4** Idealized pore water and solid-phase profiles based on the successive utilization of terminal electron acceptors during the decomposition of marine sedimentary organic matter. Adapted from Konhauser KO (2007) *Introduction to Geomicrobiology*. Oxford, UK: Blackwell Science Ltd.

mineralization stage is driven by two separate pathways. One pathway involves dissolved ferrous iron, produced during dissimilatory Fe(III)-reduction, diffusing down from the suboxic layers into the sulfate reduction zone, where it inorganically reacts with pore water at the top of the anoxic zone (reaction 9). The second pathway (reaction 10) involves dissolved sulfide, from the underlying sulfate-reducing sediments, diffusing upwards where it is removed more slowly, but in greater amounts, by inorganic reaction with ferric iron minerals (Canfield, 1989).



## Geobiology of Past Environments

Geobiology has played a fundamental role in building our understanding of how life has evolved over time and how biology has shaped Earth's surface environments and the composition of the atmosphere. Studies focused on elucidating the origins of life, the cycling of major and trace elements, isotopic fractionations induced by biological processes, and the preservation of fossilized life have all proven critical in constructing our narrative about life on Earth has evolved over the past 4.6-billion-years.

### Sedimentological and Microfossil Evidence for Early Life

Life was almost certainly established on Earth by 4 Ga, but pinpointing the exact timing of life's appearance remains difficult because physical evidence from that time (e.g., rocks) are limited to a few mineral grains (e.g., zircons) that have survived (Bell et al., 2015). Similarly, understanding what constituted the earliest life on Earth comes from a combination of both sedimentological and geochemical lines of evidence of rocks aged ca. 3.8 Ga (e.g., from Australia, Canada and Greenland), but it too is often complicated by a number of factors including poor preservation of the original chemical and physical features due to billions of years of alteration. These challenges to positively identifying signs of ancient life have been recently reviewed by Javaux (2019), and notably include (i) positively demonstrating both the biogenicity and syngenicity of microfossils or biogenic structure, (ii) assigning some level of taxonomic affinity, and (iii) reasonably constraining the geological age. Each of these factors, in themselves, can present a serious challenge and must be satisfactorily addressed in order to positively detect signs of life in sediments from Earth's most ancient geological successions. As a result, much of the earliest evidence for life remains controversial, being variously ascribed to both biotic and abiotic processes, or troubled by a lack of robust geological age constraints.

The earliest evidence, although certainly some of the most controversial, includes the identification of graphite in a Hadean zircon from the 4.1 Ga Jack Hills zircons that has been interpreted to reflect organic carbon (Bell et al., 2015). Additional evidence for early life on Earth includes the identification of putative Eoarchean microfossils from the  $\geq 3.77$  Ga Nuvvuagittuq Supracrustal Belt in Canada (Dodd et al., 2017), as well as stromatolites from the  $>3.7$  Ga Isua Supracrustal Belt in Greenland (Nutman et al., 2016). However, the biogenic origin of both the putative microfossils from Nuvvuagittuq and the Isua stromatolites have recently been challenged and ascribed to abiological processes (e.g., Wacey et al., 2018).

Perhaps the oldest unambiguous evidence for life on Earth comes from the Pilbara Craton of western Australia, where 3.45 Ga microfossils and biofilms have been identified in the Strelley Pool Formation (Allwood et al., 2007). Similarly, remnants of both shallow marine and terrestrial microbial communities have been identified in the 3.22 Ga Moodies Group in the Barberton Greenstone Belt, South Africa (e.g., Homann, 2019). Given the complex history of Archean supracrustal belts, it is unsurprising that many of the first sedimentological and geochemical indicators for life remain controversial and key areas of research for the geobiology community. Yet, studies such as these play a foundational role in our understanding of the origins of life and the subsequent evolution of more complex life that has shaped Earth's surface environments and atmosphere.

### Biomarkers

Additional constraints on the emergence and evolution of life have been garnered from biomarkers—which are effectively, chemical fossils. While previous studies applied the search for biomarkers to Archean successions, a large-scale reassessment demonstrated that biomarkers from that time are unlikely to reflect primary signals (French et al., 2015). Instead, it appears that previous reports of Archean biomarkers reflect contamination during sample collection, handling, or subsequent analysis. As such, the focus on biomarkers in ancient settings has recently shifted to the Neoproterozoic where the emergent view is that the biomarker record supports the rise of eukaryotes to ecological dominance in the Cryogenian, between 659 and 645 Ma (Brocks et al., 2017). This rise in eukaryotic dominance is reflected through an increase in the sterane to hopane ratios recorded in Cryogenian sedimentary units and is supported by a concomitant shift in the Zn-isotope record of both sulfides and organic matter (Isson et al., 2018). Biomarkers additionally record the appearance of sponges during the Cryogenian (Love et al., 2009) marking some of the earliest evidence for animal life.

## The Evolution of Atmospheric Oxygen

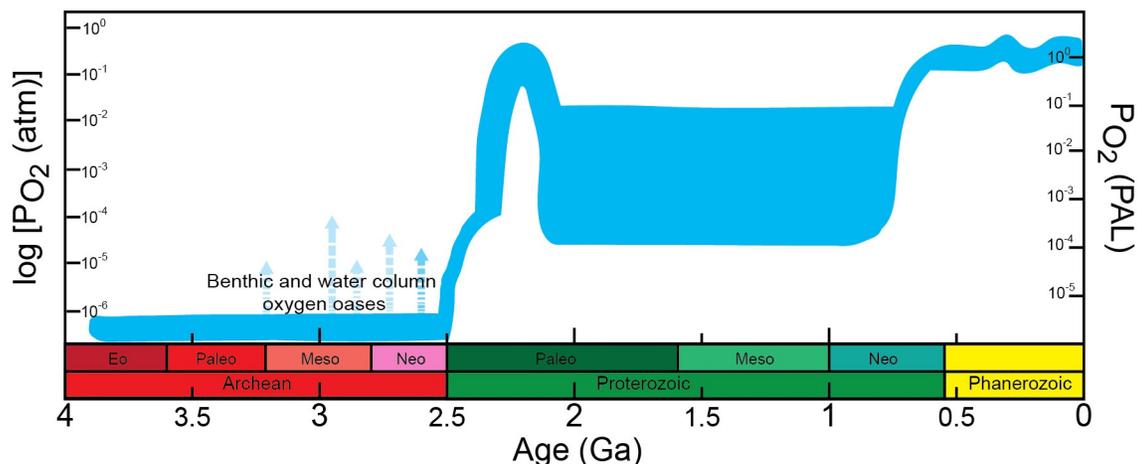
An area of geobiology that has arguably received the greatest attention has been constraining the onset, timing, and tempo of the oxygenation of Earth's atmosphere and oceans (see Lyons et al., 2014; Fig. 5). While phylogenomic reconstructions for the origins of oxygenic photosynthesis remain debated (e.g., Shih et al., 2016; Magnabosco et al., 2018), geochemical evidence points to a dominantly anoxic Archean atmosphere, with some oxidative, possibly transient, element cycling by 3.0 Ga, if not earlier (e.g., Planavsky et al., 2014). This was followed by the Great Oxidation Event (GOE) in the Paleoproterozoic which represents the first permanent rise in oxygen in Earth's atmosphere (e.g., Konhauser et al., 2011). The GOE is perhaps best reflected in the loss of mass independent sulfur isotope fractionation (S-MIF) from sedimentary successions around ~2.3 Ga, although the onset and timing may be more spatially and temporally complex than initially suspected (e.g., Farquhar et al., 2011; Philippot et al., 2018). Following a period of low O<sub>2</sub> in the Mesoproterozoic, the rise to near modern levels of O<sub>2</sub> in the terminal Neoproterozoic to early Paleozoic is reflected in compilations of several redox sensitive trace elements (e.g., Mo, V, and U; Sahoo et al., 2012; Partin et al., 2013).

Despite extensive work, the history of Proterozoic oxygen remains extensively debated. Recent efforts to reconstruct the history of Proterozoic oxygenation have relied on two methods: (1) the use of non-traditional metal stable isotopes, and (2) Earth Systems models. Approaches using non-traditional metal stable isotopes have been fuelled by advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). For instance, Cr isotopes have been used by various research groups to elucidate insights into the history of Proterozoic oxygenation. While Cr isotopes in iron formations and shales have been argued by Planavsky et al. (2014) and Cole et al. (2016) to reflect Proterozoic atmospheric oxygen being <1% of present atmospheric levels (PAL), measurements of Cr isotopes in carbonate and shale successions have also been used to argue for elevated oxygen conditions of >1% PAL during the same period (Gilleaudeau et al., 2016; Canfield et al., 2018). This could reflect either (i) spatial and temporal variability in the oxygenation of Earth's surface environments during the Mesoproterozoic, or (ii) that despite the advances in mass spectrometry that have allowed for these isotopic measurements to be made, there are subtleties that exist within these proxy records that remain to be fully understood.

In recent years, variously complex Earth Systems models and redox balance calculations have also provided insights into how the oxygenation of Earth's atmosphere and oceans may be held in steady state by nutrient limitation—notably by phosphorus—for prolonged periods (e.g., Laakso and Schrag, 2014). Several of these models converge on a scenario whereby Earth's oxygenation state is held at constant, but at low levels, due to nutrient limited primary productivity in the Mesoproterozoic. This is consistent with the view that phosphorus is the limiting nutrient on geological timescales (Tyrrell, 1999), that a fundamental shift in the phosphorus record occurred during the Cryogenian period in the lead up to the Cambrian faunal explosion (Reinhard et al., 2017), and a recently proposed collapse in primary productivity following the GOE (Hodgskiss et al., 2019). This collapse in primary productivity has recently been quantified, through the measurement of triple oxygen isotopes in Paleoproterozoic successions (Hodgskiss et al., 2019), and has been proposed to reflect a >80% collapse in primary productivity. Such a collapse following the GOE would undoubtedly have profound effects on the cycling and continued oxygenation of Earth's surface environments.

## Trace Metal Cycling and Evolution

It has long been recognized that transition metals play a critical role in biology, fulfilling roles as both structural components and reactive centers in metalloenzymes. It has been variously proposed (e.g., Anbar and Knoll, 2002; Konhauser et al., 2009; Dupont et al., 2010) that the trace metal inventory of microbial enzymes reflects the availability of trace metals in marine systems, and that



**Fig. 5** A recently refined view on the evolution of oxygen levels in the atmosphere-ocean system through time as described Lyons et al. (2014) and Robbins et al. (2016). Whiffs of oxygen prior to 2.7 Ga may be attributed to the photosynthetic activity of benthic microbial mats as per Lalonde and Konhauser (2015) and water column oxygen oases as per Olson et al. (2013).

changes in aqueous concentrations may either drive trace metal acquisition (an increase) or lead to the marginalization of microbial communities (a decline). As such there has been a concerted effort to reconstruct the cycling of trace metals in deep time and examine their relation to the trajectory of biological evolution. This has included a number of investigations into chemical sedimentary records including shales, iron formations, carbonates, and sedimentary to early diagenetic pyrite (see review in Robbins et al., 2016). While there are certainly a number of instances where it appears that biological utilization of trace metals is clearly controlled by the availability in aqueous systems and changes over geological time, these studies have yielded several surprising results; for instance, both Zn and Cu are characterized by relatively static records in both shales and banded iron formations (Scott et al., 2013; Robbins et al., 2013; Chi Fru et al., 2016), running counter to previous predictions about the trajectory of their abundances and roles in controlling eukaryotic evolution (e.g., Dupont et al., 2010). These studies hint at the possibility that some trace metals may be buffered in concentration over geological time by the activity of the biosphere or that biological use in metalloenzymes may reflect more intrinsic biological processes rather than solely environmental availability in some instances. In either event, geobiology has established a wealth of research linking the evolution of the biosphere to temporal patterns observed within the trace metal records of chemical sediments from the Archean onwards.

### The Rise of Complex Life and Phanerozoic Mass Extinctions

The terminal Neoproterozoic was set against a backdrop of some of the most extreme climatic and geochemical perturbations in Earth history, the *Snowball Earth* events (e.g., Hoffman et al., 2017) where there were at least two instances where the Earth's surface was effectively entirely glaciated. These events occurred in the Cryogenian between ~717–659 Ma and 645–635 Ma and are referred to as the Sturtian and Marinoan glaciations, respectively. Interestingly, these Snowball Earth events closely precede the appearance of metazoan life, i.e., the Doushantuo and Ediacaran fauna at 600 and 580 Ma, respectively (e.g., Erwin, 2015). The mode of preservation of these enigmatic soft-bodied fossils in Ediacaran-aged strata remains debated (e.g., Tarhan et al., 2016; Liu et al., 2019), but mark an important transition in the structure of the biosphere in the lead up to the Cambrian faunal explosion.

The Cambrian faunal explosion represents the sudden appearance of most animals, and it set off a string of evolutionary events in the Phanerozoic that ultimately shaped the Earth's modern biosphere. This includes the five most severe mass extinctions recorded in Earth's history, i.e., events during Latest Ordovician, Late Devonian, Permian-Triassic, Latest Triassic, and Cretaceous-Tertiary time (e.g., Raup and Sepkoski, 1982). Current understanding of the impact that these extinction events and of evolutionary events, such as the Great Ordovician Biodiversity Event (GOBE), had on biodiversity is currently undergoing a reappraisal that is benefiting from new approaches such as the incorporation of advanced modeling techniques (e.g., network analysis; Muscente et al., 2018). In terms of the ecological impact, while it appears that the GOBE may have had a greater impact, the Permian-Triassic extinction stands out among the extinction events as the most severe (Muscente et al., 2018). The Permian-Triassic event, when ~90% of marine taxa on Earth went extinct, corresponds to the eruption of the Siberian Trap volcanism, which resulted in a major injection of CO<sub>2</sub> and CH<sub>4</sub> to the atmosphere that, in turn, caused global warming and the onset of marine anoxia (e.g., Erwin, 1994; Song et al., 2013). The final of these mass extinctions, which marks the Cretaceous-Tertiary boundary, corresponds to the large bolide impact at Chicxulub, Mexico (e.g., Schulte et al., 2010).

### Climate Change and Characterizing Past Climate States

One of the most pressing problems facing society today is anthropogenic climate change. A critical aspect of understanding future climate projections, and assessing their sensitivity, is the validation of Earth System models against proxy record data for past climatic events and perturbations. This has resulted in a large focus on the development of proxy records for Cenozoic climate events. The reconstruction of Cenozoic climate events often relies on geochemical measurements taken from biological records, including measurement of O-isotopes ( $\delta^{18}\text{O}$ ) measurements on benthic foraminifera, B-isotopes ( $\delta^{11}\text{B}$ ) on foraminifera and corals, and C-isotope ( $\delta^{13}\text{C}$ ) for biomarkers such as alkenones (e.g., Pagani, 2002; Zachos et al., 2008; Foster and Rae, 2016). Reconstructions of more recent climate events also rely heavily on CO<sub>2</sub> and  $\delta^{18}\text{O}$  measurements from ice cores (e.g., Dansgaard et al., 1993; Bereiter et al., 2015); however, these records can only be used to constrain the last 800 Ka or so.

Given the rapid, and continuing rise in greenhouse gases, researchers are now turning to the geological record to identify periods in Earth history that may represent appropriate analogues for future climate states. For instance, Burke et al. (2018) used a combination of three separate Earth System models to compare past Cenozoic climate reconstructions with future projections. In doing so, the authors utilized two scenarios for representative concentration pathways (RCPs)—RCP 4.5 and RCP 8.5. The RCPs are established by independent groups and provide a means by which to test future climate predications against a consistent set of scenarios. For example, RCP 4.5 represents a stabilization of radiative forcing by the year 2100, whereas RCP 8.5 reflects continued increases in greenhouse gas emissions. In their analysis, Burke et al. (2018) found that the Pliocene (5.3–2.6 Ma) and Eocene (56.0–33.9 Ma) provide the best analogues for Earth's projected climate states and warming of between 2 and >10 °C. Most troubling perhaps is that their analysis of RCP 8.5 identifies a subset of scenarios (~9%) that have no geological analogue for the future climate projections. This indicates that the anthropogenic release of greenhouse gases could be pushing Earth's climate system into a state that is not reflected in geological record of the last 65 million years. Equally troubling, is the analogy of future climate scenarios with the Eocene, a period in Earth's history where temperatures in the Arctic were much higher, rainforest-like environments existed at high latitudes and supported a diverse group of animal life, including abundant mammals and even alligators (e.g., Eberle and Greenwood, 2012). Implications for warmer temperatures are numerous, but in terms of geobiology,

some of the most relevant are global species diversification, changing ocean currents and phytoplankton community structure. This is where geobiological research on paleo-environments will serve us well as ancient sediments preserve a record of the biosphere, hydrosphere, and atmosphere during such warming intervals.

## Future Directions

As geobiology continues to benefit from advances in microscopy and instrumentation, researchers in the field are increasingly seeking to answer a much broader set of questions about how life and the Earth interact. At present, geobiologists have the ability to address questions pertaining to how life and the Earth co-evolved over geological time and how environmental and industrial problems may be addressed, but also the ability to contribute to other, farther reaching fields. For instance, geobiologists are now using tools traditionally applied to characterize geological or microbial samples and their isotopes but are applying them to address medical problems (e.g., Kopf et al., 2016). Geobiologists are also working to inform the search for life on Mars (e.g., Fernández-Remolar et al., 2005), how life on other exoplanets may be remotely detected (e.g., Schwieterman et al., 2018), and how the Earth will continue to be affected by anthropogenic driven climate change (Schrag, 2012). It is clear that geobiologists today and in the future are poised to answer a wide array of truly interdisciplinary questions, that will undoubtedly continue to refine our understanding of how the Earth and the biosphere have evolved in concert and continue to interact.

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