Preface to Volume 21

Metals, Microbes, and Minerals: The Biogeochemical Side of Life

Microorganisms are found in almost every conceivable niche of the Earth. Antoni van Leeuwenhoek from Delft, universally acknowledged as the father of microbiology, saw the *animalcules* with his hand-lens microscope in 1674. Through their metabolic activity, they affect the chemistry and physical properties of their surroundings. They play key roles in carbon and nutrient cycling, in animal (including human) and plant health, in agriculture and the global food web. Undoubtedly, microbes played an important role in the evolution of the Earth and its atmosphere. It is the aim of this book to introduce the reader to the world of microorganisms, and to recognize the role they have played in the history of the Earth, and still play in altering our environment.

Studies of microbial interactions with geological media advance the field of *Geomicrobiology*. Most likely life had a rocky start according to expert Robert Hazen. How could *dead minerals* have assisted the emergence of life? The answer is chemistry. Minerals grow from simple molecules into ordered structures; critical transformations might not have been possible without the help of minerals acting as containers, scaffolds, templates, catalysts, and reactants.

Recently, a consortium of scientists published a *Consensus Statement* concerning climate change and microorganisms. It is now well established that human activities cause unprecedented animal and plant extinctions, surprisingly microorganisms are generally not discussed in the context of climate change. They date back to the origin of life on Earth, at least 3.8 billion years ago, and they will likely exist well beyond any future extinction events. Unless humans appreciate the importance of microbial processes, they fundamentally limit their understanding of Earth's biosphere and response to climate change and thus jeopardize efforts to create an environmentally sustainable future.

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Chapter 1 introduces the reader to the complex and fascinating microbial world. As potent chemists and geoengineers, microbes had a significant influence on the history of the Earth. And they still do, in altering our environment. Their presence within geologic media had a profound effect on themselves and on the chemical and physical properties of the surrounding environment. Note that nowadays a remarkable number of microbially catalyzed reactions have been explored down to the level of enzyme structure, active site architecture, and specific roles of neighboring amino acid residues.

Global element cycles are in the focus of *Chapter 2*. Prokaryotes (classical Bacteria and Archaea) enable not only simple exergonic redox reactions to proceed but also couple exergonic with endergonic reactions, to perform biosynthesis. Microbial transformations can be highly specific and can direct reactions towards single types of products, such as the stereospecific production of one enantiomer, an important application in nowadays biotechnology. Therefore, they hold great promise for future applications in degradative and biosynthetic activities.

Chapter 3 emphasizes that biological processes leave an "imprint" in the form of non-equilibrium isotope distributions in metabolites, which have been intensively studied in sediments of various Earth ages. A central finding is that isotope fractionation occurs with high variability. Three different scales are investigated, (i) the enzyme level, (ii) the cell level, and (iii) the ecosystem level. The isotope fractionation of carbon from CO_2 in water oxidizing phototrophs, and the fractionation of sulfur from sulfate during microbial reduction of sulfate to hydrogen sulfide are discussed and fodder for future integration across these scales is provided.

The *in situ* detection and visualization of metals within cells and tissues is addressed in *Chapter 4*. Advances in imaging techniques, notably improved detection sensitivity and spatial resolution, enable metal imaging from the mesoscale down to the nanoscale size regime. The most important techniques for quantifying and visualizing biological metals are reviewed. Direct detection approaches (X-ray fluorescence microscopy, secondary ion mass spectrometry, laser-ablation inductively coupled mass spectrometry) and indirect imaging methods (fluorescence microscopy, magnetic resonance imaging) are discussed in detail.

Metal-bearing minerals are an integral part of almost all "metabolism-first"-type scenarios for the emergence of life as highlighted in *Chapter 5*. Metabolism-first scenarios stand in opposition to primordial soup hypotheses which envisage prebiotic synthesis of organic molecules as building blocks enabling life to come into being. A critical analysis of the historical roots of these emergence of life hypotheses points out fundamental inconsistencies, thus it is necessary to appeal to basic thermodynamic principles to provide rigorous guidelines for developing contradiction-free models. Combining these guidelines with the current understanding of biological energy conversion, arguably the process most fundamental to all life, strongly suggests an expansion of previous mineral-based scenarios.

Chapter 6 centers on magnetotactic bacteria, which form so-called magnetosomes, intracellular organelles consisting of ferrimagnetic crystals which sequester and biomineralize large amounts of iron in specific membrane-enclosed compartments. Magnetosome biosynthesis is under spatio-temporal control by specific factors and functions. The resulting cellular dipole moment acts like a compass needle which aligns the cell in the geomagnetic field. Magnetotaxis appears to facilitate the navigation of the actively swimming bacterial cells along vertical redox gradients within stratified sediments of natural waters. Recent knowledge on the diversity and ecology of magnetotactic bacteria is summarized as is the process of magnetosome biomineralization.

Chapter 7 elucidates important aspects of microbial life on iron. Reduced and oxidized iron compounds are present in virtually all of Earth's environments. Fe is essential to all (micro)organisms because it is a key constituent of numerous metalloenzymes. It can be used as an electron donor, or acceptor, by microorganisms for metabolic redox reactions which generate energy and drive growth. In this chapter it is discussed how different types of Fe(II)-oxidizing (aerobic, microaerophilic, anoxygenic phototrophic, anaerobic nitrate-reducing) and Fe(III)-reducing (ammonium-oxidizing, organic matter-oxidizing, methanotrophic, sulfur-oxidizing) microorganisms use the oxidation and reduction of Fe(II) and Fe(III), respectively, to generate energy and to produce biomass.

In *Chapter 8* recent advances in the field of extracellular redox chemistry are summarized. Life depends on metals and their redox transformations within the biologically accessible potential range. These transformations influence their mobility in water, their bioavailability, their toxicity, and their affinity towards biomolecules. The current state of the art is surveyed regarding the interaction between living organisms and metals with respect to the mechanisms of microbial assimilatory metal uptake, with special emphasis on iron. Direct metal uptake by membrane transporters and indirect metal uptake by metallophores are addressed. The implications of the extracellular redox chemistry of microbes for the environment, health, and biotechnology are discussed, including open questions that reveal new possibilities for diverse applications.

Metal ions have driven many of biology's catalytic processes since life first evolved, however, this advantage is a double-edged sword. Some metal ions are essential but also toxic if not processed properly, and others are non-essential but toxic if available. These aspects are in the focus of *Chapter 9*. The molecular methods that microorganisms have developed to deal with toxic metal ions (Cr, Ag, Au, Cd, Hg) are covered as are the toxic effects of the nutrient metals under dis-homeostasis. Toxic but rare or unavailable elements are not covered, yet brief introductions to some non-nutrient but highly toxic metals and metalloids of groups 13–15, Al, Tl, Pb, As, and Bi are included.

Chapter 10 focuses on rare earth elements essential for our daily life. Just think of their use in high technologies like cellular phones and computers, and the use in renewable energy applications. Their interaction with biomolecules and living organisms, and the exploitation of their photo-physical properties for a range of applications in biochemistry and medicine have been studied for many decades. Yet, an entirely new area of research has emerged in the past ten years after it was established that many bacteria utilize certain rare earth elements in their metabolism. The chapter gives an overview on the most recent developments with an account of the more established uses of rare earth elements in biochemistry, biomining, and medicine.

In conclusion, Volume 21 of the *Metal Ions in Life Sciences* series offers a wealth of in-depth information about the world of microorganisms and their important role in all aspects of life. Unique chemical reactions have been discovered which employ novel sophisticated transition metal centers. They have been explored to the level of enzyme structure, active site architecture, and specific roles of neighboring amino acid residues, and can be understood nowadays at atomic resolution.

It is the study of microbial interactions with geological media, which advances the field of *Geomicrobiology*. Significant advances in the understanding of these novel metal centers, such as CuA and CuZ present in nitrous oxide reductase, the coupled siroheme-[4Fe-4S] cluster of dissimilatory sulfite reductase, the super catalyst cytochrome P_{450} heme thiolate, or the Fe- and V,Mo Fe-S clusters of nitrogenase to name a few, have been achieved by the application of powerful spectroscopic and biochemical techniques, as also discussed in greater detail in Volume 20 of *Metal Ions in Life Sciences*, entitled *Transition Metal Ions and Sulfur: A Strong Relationship for Life.*

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