MICROBIOLOGY FOR EARTH SCIENTISTS



Matthew F Kirk
Kansas State University

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Microbiology for Earth Scientists

Matthew F Kirk

Kansas State University

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TABLE OF CONTENTS

Licensing

Preface

Table of Figures

1: Earth's Microbiome

- 1.1: Some key features of Earth's Microbiome
- 1.2: Interactions with their environments
- 1.3: Structure of this book
- 1.4: Defining 'geomicrobiology'
- 1.5: Concept Check Questions
- 1.6: References

2: Classification and Phylogeny

- 2.1: Three domains of cellular life
- 2.2: Evaluating phylogeny
- 2.3: What is taxonomy?
- 2.4: Analyzing microbial populations using 16S rRNA genes
- 2.5: Example analysis
- 2.6: Viruses
- 2.7: Concept Check Questions
- 2.8: References

3: Properties of Microorganisms

- 3.1: Components of cells
- 3.2: Cell morphology and size
- 3.3: Gram-positive and gram-negative bacteria
- 3.4: Bacterial sporulation
- 3.5: Biofilms
- 3.6: Cell growth
- 3.7: Virions
- 3.8: Concept Check Questions
- 3.9: References

4: Redox and Mechanism

- 4.1: Redox basics
- 4.2: Balancing redox reactions
- 4.3: Metabolism
- 4.4: Chemotrophy
- 4.5: Phototrophy
- 4.6: Answers to Practice Problems
- 4.7: Concept Check Questions
- 4.8: References

5: Global Biogeochemical Cycles

- 5.1: Carbon cycle
  - 5.1.1: Organic matter
  - 5.1.2: Aerobic and anaerobic respiration
  - 5.1.3: Fermentation and syntrophy
  - 5.1.4: Methanogenesis
  - 5.1.5: Acetogenesis
  - 5.1.6: Methanotrophy
- 5.2: Nitrogen cycle
  - 5.2.1: Nitrogen fixation
  - 5.2.2: Ammonification
  - 5.2.3: Nitrification
  - 5.2.4: Anaerobic ammonia oxidation (anammox)
  - 5.2.5: Denitrification
  - 5.2.6: Dissimilatory nitrate reduction to ammonia (DNRA)
- 5.3: Iron cycle
  - 5.3.1: Ferric iron reduction
  - 5.3.2: Ferrous iron oxidation
- 5.4: Sulfur cycle
  - 5.4.1: Sulfate reduction
  - 5.4.2: Desulfurylation
  - 5.4.3: Oxidation of sulfide and intermediate sulfur compounds
  - 5.4.4: Reduction of intermediate sulfur compounds
  - 5.4.5: Sulfur disproportionation
- 5.5: Concept Check Questions
- 5.6: References

6: Basic Environmental Controls

- 6.1: Categories of controls
- 6.2: Basic properties of the environment
  - 6.2.1: Temperature
  - 6.2.2: Pressure
  - 6.2.3: Oxygen
  - 6.2.4: pH
  - 6.2.5: Water availability
- 6.3: Transport processes
- 6.4: Environment stability
- 6.5: Dispersal mechanisms and barriers
- 6.6: Interactions between controls
- 6.7: Concept Check Questions
- 6.8: References

7: Nutrient and Energy Resources

- 7.1: Nutrients
- 7.2: Extracellular enzymes
- 7.3: Nutrient stoichiometry
- 7.4: Energy sources for phototrophs

- 7.5: Energy sources for chemotrophs
  - 7.5.1: Organic matter
  - 7.5.2: Reduced inorganic components of minerals
  - 7.5.3: Mantle degassing
  - 7.5.4: Serpentinization
  - 7.5.5: Radiolysis of water
  - 7.5.6: Silica radical-based reactions
  - 7.5.7: Trace atmospheric gases
- 7.6: Electroactive organisms
- 7.7: Concept Check Questions
- 7.8: References

8: Thermodynamic Controls

- 8.1: Mass action
- 8.2: Gibbs free energy
- 8.3: Impacts of changes in product and reactant activities
- 8.4: Available, captured, and usable energy
- 8.5: Redox zonation
- 8.6: Characterizing redox processes in aqueous systems
- 8.7: Answers to practice problems
- 8.8: Concept Check Questions
- 8.9: References

9: Kinetic Controls

- 9.1: Role of enzymes
- 9.2: Influence of pH and temperature on enzyme activity
- 9.3: Influence of substrate concentrations
- 9.4: Kinetic rate laws
- 9.5: Thermodynamic constraints on rates
- 9.6: Kinetic constraints on competition between sulfate reducers and methanogens
- 9.7: External controls on microbial reaction rates
- 9.8: Answers to practice problems
- 9.9: Concept Check Questions
- 9.10: References

10: Biological Environment

- 10.1: Microbial interactions
- 10.2: Example interactions
  - 10.2.1: Viral predation/parasitism of bacteria
  - 10.2.2: Mutualisms between plants and soil microorganisms
  - 10.2.3: Interactions of anammox microorganisms with other nitrogen cycles
  - 10.2.4: Interactions among iron and sulfur cycling microorganisms
  - 10.2.5: Interactions among iron reducers, methanogens, and methanotrophs
- 10.3: Spatial scales of interactions
- 10.4: Concept Check Questions
- 10.5: References

11: Mechanisms of Microbial Impacts

- 11.1: Catalyzing reactions
  - 11.1.1: Direct impacts
  - 11.1.2: Indirect impacts
  - 11.1.3: Practice
- 11.2: Generating biomass
- 11.3: Forming minerals
- 11.4: Dissolving minerals
  - 11.4.1: Redox mechanism
  - 11.4.2: Acid mechanism
  - 11.4.3: Chelation mechanism
- 11.5: Answers to practice problems
- 11.6: Concept Check Questions
- 11.7: References

12: Impacts to the Lithosphere

- 12.1: Examples of biomineralization
  - 12.1.1: Carbonates
  - 12.1.2: Amorphous silica
  - 12.1.3: Iron (oxyhydr)oxides
  - 12.1.4: Sulfides
  - 12.1.5: Clay minerals
- 12.2: Microbial influence on marine sediments
- 12.3: Microbial influences on tectonic activity
- 12.4: Mineral evolution
- 12.5: Concept Check Questions
- 12.6: 12.6 References

13: Impacts to the Atmosphere

- 13.1: Oxygen
- 13.2: Trends in greenhouse gases
- 13.3: Carbon dioxide
- 13.4: Methane
- 13.5: Nitrous oxide
- 13.6: Responses of microorganisms to climate change
- 13.7: Managing greenhouse gas emissions
- 13.8: Answers to practice problems
- 13.9: Concept Check Questions
- 13.10: References

14: Impacts to the Hydrosphere

- 14.1: Pathogens
- 14.2: Groundwater quality
  - 14.2.1: Chemical evolution of groundwater
  - 14.2.2: Middendorf aquifer
- 14.3: Surface water quality

- 14.3.1: Connections to groundwater
- 14.3.2: Algal blooms
- 14.4: Examples of microbial impacts to chemical contaminants
  - 14.4.1: Nitrate
  - 14.4.2: Arsenic
  - 14.4.3: Acid mine drainage
  - 14.4.4: Chlorinated solvents
  - 14.4.5: Petroleum hydrocarbons
- 14.5: Applying microbiology to remediate contaminated water
- 14.6: Concept Check Questions
- 14.7: References

15: Appendix A- Thermodynamic Data for Select Reactions

- 15.1: Redox Reactions
- 15.2: Gas Solubility Reactions
- 15.3: Mineral Reactions

Index

Glossary

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Preface

This book aims to increase the ability of earth scientists to understand and use microbiology. Earth scientists work on many of the most pressing issues of our time, including work related to climate change, energy resources, and water. Microorganisms play major roles in these areas, and yet many earth scientists have little exposure to microbiology within their undergraduate training. That was certainly the case for me upon completing a BS in Geological Sciences, and that has also been the case for many of the students who I have taught since becoming a professor. This book can help earth science students and professionals get started with microbiology and show them its vast importance to their area of expertise.

The bias of this book is based on my own experiences and interests. I use many examples from my own research throughout the book. This choice is not because I think my research is superior to other examples, but rather because it is generally a convenient choice for me. Throughout the book, I also emphasize geochemistry. In that regard, microorganisms are largely described based on their function (e.g., sulfate reducers) rather than their taxonomy. Moreover, the book describes some geochemical calculations in detail but only gives a very brief example of how microbial communities are analyzed using molecular techniques. This choice reflects my strengths as a researcher, but it is also a convenient pathway into microbiology for earth scientists, who are generally familiar with geochemistry but not molecular biology.

Most of the topics included in this book are not extensively reviewed. This book is not intended to be a collection of thorough review articles. We bury key messages in the noise when we flood our students with too much information. Instead, for most topics, the book seeks to define key relationships and provide a few concrete examples that can help illustrate those relationships. In short, the idea is to get readers started with microbiology, not to try to tell them everything that is known.

My formal training in microbiology has been modest. I have mostly learned about microorganisms through my research, students, collaborators, and mentors. In that regard, I owe a debt of gratitude to many scientists. As a MS student at the University of Illinois, Craig Bethke and Rob Sanford helped launch my career as a scientist and spark my interest in the world of aquifer microbiology. I also met Qusheng Jin at Illinois, who has been a friend and mentor ever since. As a PhD student at the University of New Mexico, Laura Crossey, Eric Roden, Cristina Takacs-Vesbach, Adrian Brearley, and Cliff Dahm generously helped me integrate microbiology and geochemistry and expand my ability to analyze microbial communities and environmental samples. As a postdoc, I benefited from mentoring by Anna Martini at Amherst College and Susan Altman and Randy Cygan at Sandia National Laboratories.

Since joining Kansas State University, many collaborators have continued my education in biogeochemistry and microbiology, including but not limited to Sharon Billings, Andrea Brookfield, Amy Burgin, Walter Dodds, Ganga Hettiarachchi, Ari Jumpponen, Terry Loecke, Gwen Macpherson, Jesse Nippert, Janet Paper, Prathap Parameswaran, Marcos Sarto, Ben Sikes, Pam Sullivan, Sara Vero, and Lydia Zeglin. I am also grateful for the funding that has made my research and collaborations possible, including support from my home department, the Kansas NSF EPSCoR program, NSF LTER, ACS PRF, and the NSF Geobiology and Low-Temperature Geochemistry program.

In addition to these scientists and funding institutions, I owe a special thanks to the Kansas State University Open/Alternative textbook initiative and in particular, K-State Librarians Gwendolyn Sibley and Carolyn Jackson. The support of this program helped encouraged me to write this book and the efforts of Gwendolyn and Carolyn were instrumental in helping me push it over the finish line.

Finally, it is important to note that most of the contents of this edition of the book have not undergone any peer review. However, I am grateful for generous input from Ben Walters, who read early versions of some chapters while taking my Geomicrobiology course. I am also grateful for valuable input from Qusheng Jin, Karin Goldberg, and Maarten de Moor.

Table of Figures

Figure 1.1: Simple bioreactor design used by Paper et al. (2021)	Section 1.2, Box 1.1
Figure 1.2: Example of the two-way interactions between microorganisms and their environment	Section 1.2, Box 1.1
Figure 2.1: Phylogenetic tree based on the 16S ribosomal RNA (rRNA) gene	Section 2.1
Figure 2.2: Chemical structure of nucleotides and nucleosides	Section 2.2
Figure 2.3: Chemical structure of DNA	Section 2.2
Figure 2.4: Overview of biological information flow	Section 2.2
Figure 2.5: Results of 16S rRNA gene analysis by Kirk et al. (2015)	Section 2.5
Figure 3.1: Comparison of eukaryotic and prokaryotic (bacterial and archaeal) cells)	Section 3.1
Figure 3.2: Examples of cell morphologies	Section 3.2
Figure 3.3: Schematic illustration of the structure of Gram-positive and Gram-negative bacterial cell walls	Section 3.3
Figure 3.4: Image showing endospores within rod-shaped bacteria	Section 3.4
Figure 3.5: Heterogenous composition of microbial biofilm	Section 3.5
Figure 3.6: Cultures containing strains of the bacterium *Zoogloea resiniphila*	Section 3.5
Figure 3.7: Binary fission in a bacterial or archaeal cell	Section 3.6
Figure 3.8: Phases of bacterial growth	Section 3.6
Figure 4.1: Adenosine triphosphate (ATP) molecule with regions highlighted to show adenine, ribose, phosphate molecules, and the high-energy bonds between phosphate molecules	Section 4.4
Figure 4.2: Generalized model of the electron transport chain	Section 4.4
Figure 4.3: Summary of light and dark reactions (rxns) used by (A) oxygenic and (B) anoxygenic photoautotrophs	Section 4.5
Figure 4.4: Grand Prismatic Spring at Yellowstone National Park, USA	Section 4.5
Figure 5.1: Microbial contributions to the global carbon cycle	Section 5.1
Figure 5.2: Illustration of organic matter degradation pathways investigated by Zinke et al. (2019) in Baltic Sea sediment	Section 5.1.3
Figure 5.3: Microbial contributions to the nitrogen cycle	Section 5.2
Figure 5.4: Microbial contributions to the global iron cycle	Section 5.3
Figure 5.5: Potential strategies for extracellular electron transfer	Section 5.3.1
Figure 5.6: Iron (oxhydr)oxides forming on the cut bank of a stream in Starved Rock State Park, Illinois, USA	Section 5.3.2
Figure 5.7: Microbial contributions to the global sulfur cycle	Section 5.4

Figure 6.1: Influence of temperature on growth rate for an individual species	Section 6.2.1
Figure 6.2: Schematic illustration of categories of microorganisms based on oxygen tolerance	Section 6.2.3
Figure 6.3: Schematics showing examples of ways (A) transport and (B) environmental change can serve as environmental controls on microbial populations involved in iron cycling	Section 6.3
Figure 7.1: Simple conceptual diagram of the carbon, nitrogen, and phosphorus (C,N,P) budgets in the shallow terrestrial subsurface	Section 7.1
Figure 7.2: Conceptual diagram illustrating microbial respiration in aquifers fueled by fermentation of organic matter in fine-grained organic-rich confining layers	Section 7.5.1
Figure 7.3: Conceptual diagram showing sources of water and solutes in a terrestrial hydrothermal system	Section 7.5.3
Figure 7.4: Conceptual model of interspecies electron transfer between anaerobic methanotrophs (ANME) and sulfate reducing microorganisms (SRM)	Section 7.6
Figure 8.1: Variation in free energy during an exergonic and endergonic reaction according to transition-state theory	Section 8.2
Figure 8.2: Variation in the Gibbs free energy yield of hematite reduction in response to variation in (A) pH and (B) ferrous iron concentration	Section 8.3
Figure 8.3: Redox zonation illustrated using reaction path modeling	Section 8.5
Figure 8.4: Flowchart for evaluating the dominant redox process in an aqueous system using water chemistry data	Section 8.6
Figure 9.1: Activation energy (EA) of a biological reaction with and without enzymatic catalysis	Section 9.1
Figure 9.2: Schematic illustration of the lock and key model	Section 9.1
Figure 9.3: Relationship between enzyme activity and temperature	Section 9.2
Figure 9.4: Variation in reaction rate with substrate concentration in a hypothetical enzymatic reaction	Section 9.3
Figure 9.5: Results of a kinetic reaction path model of sulfate reduction and methanogenesis	Section 9.6
Figure 9.6: Schematic illustration of microbial reduction of crystalline ferric iron	Section 9.7
Figure 10.1: Types of interactions between two hypothetical species (1 and 2)	Section 10.1
Figure 10.2: Conceptual model of potential interactions among nitrogen cycling microorganisms	Section 10.2.3
Figure 10.3: Conceptual model of potential interactions between	Section 10.2.4

iron reducers and microorganisms associated with the sulfur cycle	
Figure 10.4: Conceptual model of potential interactions between iron reducers, methanogens, and anaerobic methanotrophic (ANME) archaea	Section 10.2.5
Figure 11.1: Confocal microscopic image showing growth of *Pseudomonas fluroescence* biofilm (green) in a capillary tube filled with glass beads (black) and water (red)	Section 11.2
Figure 11.2: Schematic illustration of biomineralization mechanisms	Section 11.3
Figure 11.3: Conceptual diagram of weathering in the subsurface driven by acid production in an overlying soil	Section 11.4.2
Figure 12.1: Diagram of the rock cycle	Chapter 12
Figure 12.2: Examples of carbonate biomineralization	Section 12.1.1
Figure 12.3: Variation in calcium speciation with bicarbonate activity and pH	Section 12.1.1
Figure 12.4: Variation in amorphous silica stability with temperature and dissolved silica activity	Section 12.1.2
Figure 12.5: Examples of amorphous silica precipitation (A) in a hot spring and by (B) diatoms and a (C) radiolarian	Section 12.1.2
Figure 12.6: Examples of iron (oxyhydr)oxide biominerals	Section 12.1.3
Figure 12.7: Examples of sulfide biominerals	Section 12.1.4
Figure 12.8: Schematic illustration of major inputs and reactions that guide marine sediment composition	Section 12.2
Figure 13.1: Estimated variation in the partial pressure of oxygen in the atmosphere over the past four billion years	Section 13.1
Figure 13.2: Sample of 2-billion-year-old banded iron formation (BIF) from the Upper Peninsula of Michigan, USA	Section 13.1
Figure 13.3: Variation with time in the abundance of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide ((N_2O) in the atmosphere	Section 13.2
Figure 13.4: Variation in atmospheric concentrations of the abundance of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) from 2016 to 2020	Section 13.2
Figure 13.5: Variation with pH in the proportions of dissolved inorganic carbon species	Section 13.3
Figure 13.6: Schematic illustration of potentials fates of carbon dioxide produced by organic matter oxidation (C_{org}) during soil respiration	Section 13.3
Figure 13.7: Schematic illustration of the distribution of nitrous oxide (N_2O) sources in one of the watersheds studied by Davidson and Swank (1986) and Davidson et al. (1986)	Section 13.5

Figure 14.1: General trends in groundwater (gw) chemistry along flow	Section 14.2.1
Figure 14.2: Variation along flow in groundwater pH and concentrations of oxygen (O_2), ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and sulfide (S^{2-}) in the Middendorf aquifer as measured by Park et al. (2006)	Section 14.2.2
Figure 14.3: Schematic illustration of groundwater and surface waters coming together within streambeds from Winter et al. (Winter et al., 1998)	Section 14.3.1
Figure 14.4: Landsat 8 satellite image of a harmful algal bloom in the western end of Lake Erie during summer 2019	Section 14.3.2
Figure 14.5: Box plot showing changes in nitrate concentration between the 1970s and 2016 based on data from Lane et al. (2020)	Section 14.4.1
Figure 14.6: Variation with sulfate concentration in total dissolved arsenic, iron, and methane concentrations in the Mahomet aquifer	Section 14.4.2
Figure 14.7: Acid mine drainage flowing away from collapsed entrance to the Davis Mine pyrite mine near Rowe, Massachusetts, USA	Section 14.4.3
Figure 14.8: Schematic illustration pyrite weathering under acidic conditions (e.g., below pH 4.5) by iron- and sulfur-oxidizing microorganisms	Section 14.4.3
Figure 14.9: Schematic illustration of the spreading of light non-aqueous phase liquid (LNAPL) and dense non-aqueous phase liquid (DNAPL) in the subsurface	Section 14.4.4
Figure 14.10: Sequential removal of chlorine during organohalide respiration with dihydrogen as the electron donor	Section 14.4.4
Figure 14.11: Tar bubble in the La Brea Tar Pits in Los Angeles, California, USA	Section 14.4.5
Figure 14.12: Subsurface geochemical zones identified in groundwater and the unsaturated zone at the Bemidji north oil pool site	Section 14.4.5

CHAPTER OVERVIEW

1: Earth's Microbiome

> *"Unlike our universities, nature is not compartmentalized into various departments. The natural sciences have no real boundaries; if you want to question one aspect of science, you really must be educated in ancillary disciplines."*
>
> *—William Schopf*

Microorganisms effectively rule the Earth. Their small size places them beneath our perception, but they are the numerically dominant life form on the planet (Magnabosco et al., 2018; Whitman et al., 1998). It is not possible to know the exact abundance of microorganisms overall on Earth, but it is clearly a vast number. In the oceans alone, for example, estimates suggest that there are 100 million times as many bacteria (13×10^{28}) as stars in the known universe ("Microbiology by numbers," 2011). Although microorganisms are individually small, they are collectively enormous.

But what are microbes? What are they doing? Why is it useful for earth scientists to know about them? In this chapter, we will start to answer these questions by summarizing some important aspects of microbial life. We will also take a look ahead and consider the topics and organization of this book.

1.1: Some key features of Earth's Microbiome

1.2: Interactions with their environments

1.3: Structure of this book

1.4: Defining 'geomicrobiology'

1.5: Concept Check Questions

1.6: References

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1.1: Some key features of Earth's Microbiome

As their name implies, microorganisms are small organisms. They are too small to be seen with the naked eye and exist as single cells, cell clusters, or as viruses. Viruses are not cellular organisms, but they are considered in this book to be microorganisms. Cellular microorganisms can live freely in fluids but also exist within biofilms, which are communities of cells and their extracellular products that form at an interface and often a surface (Costerton et al., 1995). Similarly, viruses can exist independently as viral particles known as virions and also exist within cells of other organisms.

Microorganisms are diverse. They are found across the tree of life, including all Bacteria and Archaea and several groups of Eukaryotes. Many familiar groups of microorganisms are pathogens, microbes that can cause disease. For example, cholera, syphilis, anthrax, leprosy, bubonic plague are all examples of infectious diseases caused by bacteria. There are about 1,400 known species of human pathogens. Although that may seem like a large number, human pathogens account for far less than 1% of the total number of microbial species on Earth ("Microbiology by numbers," 2011). Ecological scaling laws predict that Earth is home to as many as one trillion different microbial species (Locey and Lennon, 2016). Most of the microorganisms that play important roles in natural environments are not pathogens. They are adapted to the conditions of natural environments, which differ significantly from the human body.

These diverse groups drive many of the chemical reactions that occur in low-temperature geochemical systems. They push reactions forward to obtain energy for life functions and to obtain resources from their environments. In fact, many respire oxygen, eat organic carbon, and effectively exhale carbon dioxide, just like us humans. In turn, the reactions they push forward trigger other reactions in geochemical systems. For example, carbon dioxide produced by microbial respiration can dissolve in water and form carbonic acid, which can then react with feldspars to form clay minerals.

Microorganisms exist under a broad range of conditions. Previous research has documented microbial life at temperatures ranging from $-20°C$ to $121°C$, from pH below 0 to 13, under hypersaline conditions, at pressures above 100 MPa, and at heavy metal and radiation levels much greater than those tolerated by humans (Clarke et al., 2013; Pikuta et al., 2007). These characteristics allow them to live in a wide range of environments, which extend from the clouds down to 4 to 5 km into the subsurface (DeLeon-Rodriguez et al., 2013; Gold, 1992).

Microorganisms are capable of rapid growth, but some microbes can also persist over enormous time scales. Morono et al. (2020), for example, recently documented the presence of aerobic bacteria that were able to maintain their metabolic potential under extremely low-energy conditions in marine sediment for up to 101.5 million years. Therefore, microbial life can be difficult to comprehend not only because of their small size and vast abundance but also in terms of the time scales of population turnover, which range from more rapid to far longer than that of humans.

Lastly, microbes are Earth's oldest inhabitants and they have helped transform the Earth over time. Earth formed about 4.5 billion years ago. Early Earth was hot and inhospitable, but as it cooled and differentiated, microorganisms appeared. The exact timing of when or where life on Earth began is unknown but evidence exists in rock record for life by about 3.5 billion years (Schopf et al., 2007) and possibly as old as 4.28 billion years (Dodd et al., 2017). Cyanobacteria were present sometime later, perhaps as early as 3.2 billion years ago (Satkoski et al., 2015), and ultimately caused atmospheric oxygen levels to rise during the Great Oxidation Event, roughly 2.5 to 2.3 billion years ago. Most multicellular microorganism fossils are younger than about 635 million years but some macroscopic organisms may have exist by 1.56 billion years ago (Zhu et al., 2016). Thus, microorganisms have mostly had the planet to themselves throughout Earth's long history.

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1.2: Interactions with their environments

Microorganisms impact the properties of their environments by driving chemical reactions forward, forming biomass, and causing minerals to dissolve and precipitate. In turn, however, environments influence what microorganisms are doing by providing chemical and physical constraints on their activities. Thus, there are two-way interactions between microorganisms and their environments (Box 1.1).

Impacts of microorganisms on their environments are diverse. They help drive the rock cycle and serve as major controls on the composition and quality of our water resources, the abundances of greenhouse gases and oxygen in the atmosphere, the fertility of soils, and more. Microbial impacts to the environment are not just subjects of academic interest, but also societal interest. They affect the habitability of the planet and resources available to human populations.

We can better predict these impacts for natural as well as engineered systems by understanding how environments influence microbial populations. That understanding can also be used to develop strategies to manage microbial populations to achieve favorable outcomes. Microbial biotechnology offers opportunities to generate energy, increase the sustainability and amount of food production, cleanse our water, and more (Bender et al., 2016; Blaser et al., 2016; Newsome et al., 2014). Thus, exciting opportunities can emerge from learning about both sides of the two-way interactions between microbes and their environments.

BOX 1.1 Example Interactions

There are countless examples of the ways that environments and microbial communities interact. However, to provide a concrete example here, we consider results from the bioreactor experiments described in Paper et al. (2021). A bioreactor is a vessel that hosts biological activity and reactions. Bioreactors can take many forms but the design used by Paper et al. (2021) was relatively simple and consisted of a serum bottle containing a solution (or aqueous medium) and some sediment (Fig. 1.1).

During the incubation, microorganisms in the bioreactors primarily survived by 'eating' acetate ($CH3COO^-$) and respiring or 'breathing' ferric iron ($Fe(III)$) and sulfate (SO_4^{2-}). But the proportions of iron and sulfate they respired varied with the pH of the aqueous medium (Fig. 1.2A). In bioreactors supplied with an aqueous medium that had pH 6.0, microorganisms respired two to three times more iron than sulfate. In contrast, in bioreactors with pH 7.5 medium, microorganisms respired iron and sulfate in equal proportions (reaction ratio = 1). Thus, pH influenced the proportions of iron and sulfate that were respired by microbes within the bioreactors.

While pH influenced what reactions the microorganisms were using, those reactions in turn changed the pH of the bioreactors during the incubation. When microorganisms consume ferric iron and sulfate, their reactions also consume hydrogen ions. As such, the reactions cause the pH of the bioreactor water to increase. In the experiments by Paper et al., the amount of pH increase was directly proportional to the amount of acetate that the microbes consumed (Fig. 1.2).

Taken together, the results demonstrate that pH can influence what microorganisms are doing – in this case the proportion of iron to sulfate respiration. However, in turn, microbial activity can alter pH – here by causing it to increase. Thus, the interactions go both ways.

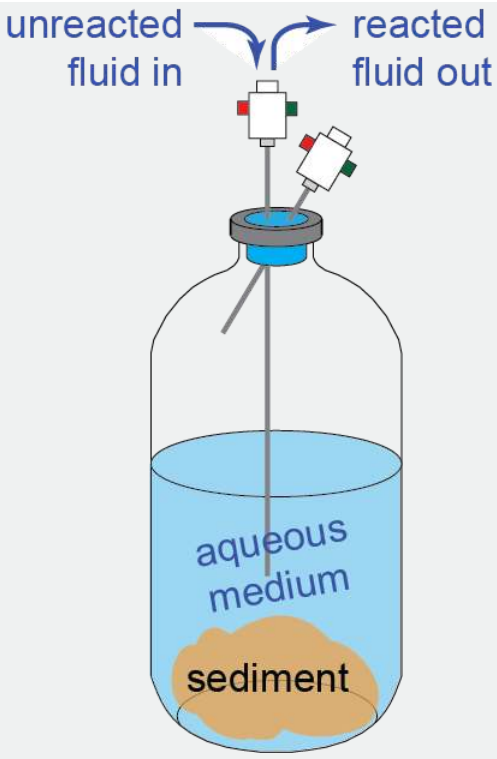


Figure **1.1**: Simple bioreactor design used by Paper et al. (2021)
https://commons.wikimedia.org/wiki/File:Serum_bottle_bioreactor.png

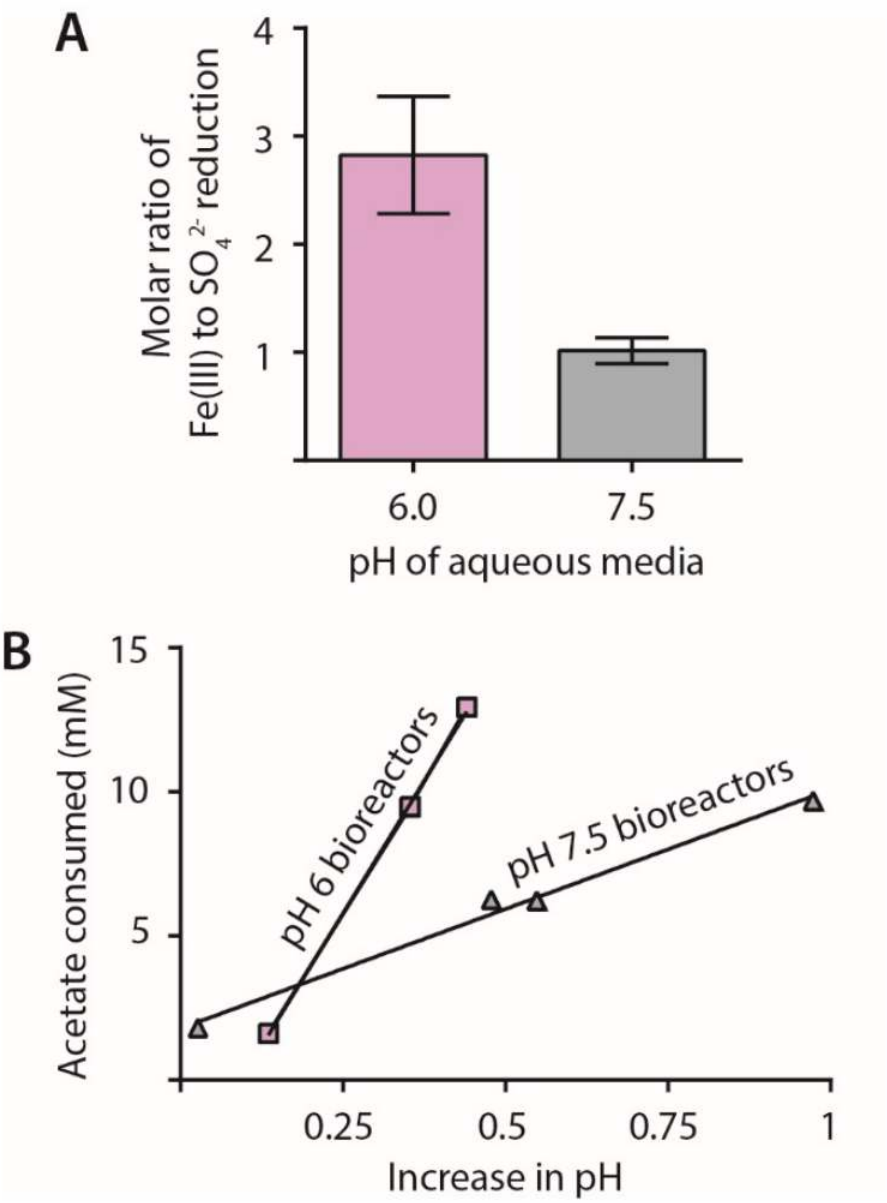


Figure 1.2: Example of the two-way interactions between microorganisms and their environment based on data from bioreactor experiments described by Paper et al. (2021). (Graph A) The pH of the environment helped steer microbial activity by affecting the proportion of iron to sulfate reduction in the experiments. (Graph B) In turn, the microbial reactions caused the pH of the bioreactor solutions to increase. Scatter points show averages for replicate reactors and lines are best-fit results of linear regressions.
https://commons.wikimedia.org/wiki/File:Example_interactions_between_microbial_activity_and_pH.png

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1.3: Structure of this book

To help you organize their thoughts about the interactions between microbes and their environments, this book is divided into three parts:

- **Part 1. Microbes and microbial reactions.** This portion of the book provides basic background information about microorganisms and major biogeochemical cycles.
- **Part 2. Environmental controls on microorganisms.** This part describes ways that environments influence microbial activity. This content can help us understand the patterns in microbial activity and community composition that we see in nature.
- **Part 3. Impacts of microbial activity.** The final part of the book provides examples of ways that microbes impact their environments, with emphasis on environmental concerns.

Chapters within each part expand on many of the topics discussed within this introductory chapter. Those chapters will provide additional details, concrete examples, and opportunities to practice concepts and develop skills. Emphasis is placed on the applications of tools that are familiar to earth scientists, such as the use of geochemical data.

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1.4: Defining ‘geomicrobiology’

The subdiscipline of earth science taken up by this book can best be described as geomicrobiology. Before concluding this introductory chapter, it is useful to consider some context for the field of geomicrobiology. Broadly speaking, geomicrobiology is an area of research that examines the roles of microorganisms in geological processes. It straddles the boundary between earth science and microbiology and integrates concepts from geochemistry, biochemistry, mineralogy, hydrology, microbial ecology, and more. By pulling concepts from these disciplines together, we can develop a more complete understanding of natural systems than is possible within a single discipline. As quoted at the beginning of this chapter, nature is not compartmentalized like our universities. Nature is interdisciplinary.

Multiple areas of geomicrobiology research have emerged over the past few decades. The chapters of this book consider topics that are essential to many of them. Whether your interest is in marine or terrestrial environments, modern systems or deep time, crude oil or drinking water, it will be helpful to understand ways that environments shape microbial activity and mechanisms by which microbes impact their environments.

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1.5: Concept Check Questions

1. What characteristics define microorganisms?
2. Where do we find microorganisms and what are some of the environmental limits on the existence of microbial life?
3. How do microorganisms and their environments interact? Why is it useful to understand those interactions?

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CHAPTER OVERVIEW

2: Classification and Phylogeny

> *"The tree of life as we know it has dramatically expanded due to new genomic sampling of previously enigmatic or unknown microbial lineages."*
>
> *—-Hug et al. (2016)*

Historically, the breadth of microbial life was vastly underestimated. Scientists used microscopes to see microorganisms as early as the 17th century (Gest, 2004) and they developed enrichment culturing techniques by the 19th century (Austin, 2017). Although valuable advancements, the ability of these techniques to survey microbial communities and assess evolutionary relationships is limited. Microorganisms have relatively simple morphologies that poorly reflect their great diversity (Woese, 1987) and the vast majority of microorganisms have not been successfully cultured (Stewart, 2012). However, technological advances in molecular biology in recent decades have helped overcome these limitations and our view of microbial life and its significance is rapidly growing.

This chapter describes some basic concepts necessary to understand the classification microbial life. We will consider the tree of life and the concepts of phylogeny and taxonomy. We will also consider a common approach used to directly analyze microbial communities based on the 16S rRNA gene. Many new and powerful molecular biology techniques have emerged in recent years. This chapter does not attempt to provide a summary of these techniques. Instead, we focus on some basic concepts that will help you understand the breadth of microbial life and relationships between different groups of microorganisms.

2.1: Three domains of cellular life
2.2: Evaluating phylogeny
2.3: What is taxonomy?
2.4: Analyzing microbial populations using 16S rRNA genes
2.5: Example analysis
2.6: Viruses
2.7: Concept Check Questions
2.8: References

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2.1: Three domains of cellular life

The tree of life (Fig. **2.1**) is a map of evolutionary relationships, known as phylogenetic relationships, among cellular organisms. Branching points are referred to as nodes and represent the most recent common ancestor of the groups on each branch. The length of the lines connecting different groups is typically proportional to the evolutionary difference between the groups. Groups that are more closely related are separated by less distance than those that are less closely related.

Three major groups are visible in the tree – the Bacteria, Archaea, and Eukarya – which are referred to as the three domains of life. Bacteria and Archaea are domains that consist exclusively of microorganisms. Eukaryota includes the macroorganisms (e.g., you are a eukaryote) but also multiple groups that contain microorganisms, including the fungi, protozoa, and algae. Not included in the tree are viruses, which we can think of as a major group or "empire" that is separate from cellular life (Koonin, 2010). We will focus our attention here on cellular organisms but come back to viruses at the end of this chapter.

Bacteria and Archaea share some similar properties, at least superficially. They are similar in size and both lack a nucleus. As such, historically they have been collectively referred to as the prokaryotes. However, Bacteria and Archaea also differ in significant ways. Archaea create membranes from lipids that are different from those used by Bacteria and Eukarya and they create ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) in ways that are more like the Eukarya (Frazer, 2013). In fact, phylogenetic and biochemical results show that Archaea are more closely related to Eukarya than they are to Bacteria, despite their similar physical features (Pace, 2006). We can see this relationship in the tree of life by noting that Archaea and Eukarya share a common ancestral branch that is independent of that giving rise to the Bacteria (Fig. 2.1). Therefore, evolutionary relationships are misrepresented when we refer to Archaea and Bacteria together as prokaryotes.

The phylogenetic tree shown in Figure **2.1** is relatively simple. Its purpose here is to provide a clear illustration of the concepts described above. Recently, Hug et al. (2016) analyzed genetic information from over 1,000 uncultivated and little-known organisms, together with published sequences, to create a more complete picture of the tree of life. Their updated tree, which is freely available online (https://www.nature.com/articles/nmicrobiol201648/figures/1), shows that bacterial diversity far exceeds that of Archaea and Eukarya and illustrates that much of the diversity of microbial life is only accessible by cultivation-independent approaches.

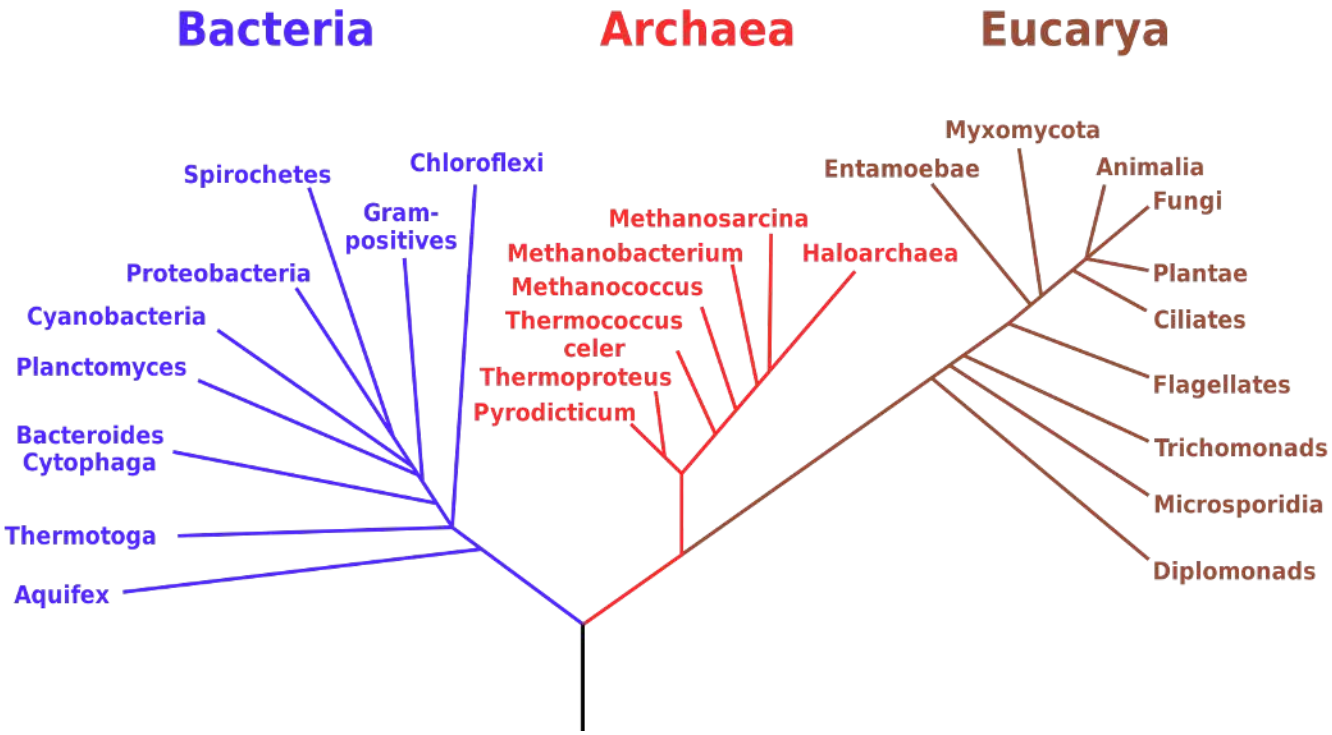


Figure **2.1**: Phylogenetic tree based on the 16S ribosomal RNA (rRNA) gene. The tree shows the three domains of life (Bacteria, Archaea, and Eukarya or Eucarya) and approximate evolutionary distances between them. Groups of organisms listed are not uniform in taxonomic level. Image credit: Eric Gaba. Public domain)
https://commons.wikimedia.org/wiki/File:Phylogenetic_tree_scientific_names.svg

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2.2: Evaluating phylogeny

Phylogeny considers how organisms are related according to the theory of evolution. We can evaluate phylogenetic relationships using information-bearing macromolecules such as genes. The basic idea is that all organisms are connected by a vast phylogenetic tree. Genes change over time. Greater differences in gene composition approximately correspond to more time since two organisms shared a common ancestor. Thus, we can use genes as a molecular clock that provides a measure of relatedness (Woese, 1987). But what are genes? Let's back up and consider some background material related to biological information flow.

DNA contains the plans needed to make cells. It is a polymer of nucleotides, which are molecules consisting of a sugar, a phosphate, and a nitrogenous base (Fig. **2.2**). In DNA, the sugar is deoxyribose and the bases are adenine, guanine, cytosine, and thymine. Nucleotide monomers are joined together to form a strand of DNA through bonds between the phosphate and sugar molecules of each nucleotide (Fig. **2.3**). DNA is double-stranded. Each strand is linked by hydrogen bonds between nitrogenous bases. Portions of an organism's DNA that code for specific proteins or RNA molecules are referred to as genes. All of the genes in an organism are referred to as its genome.

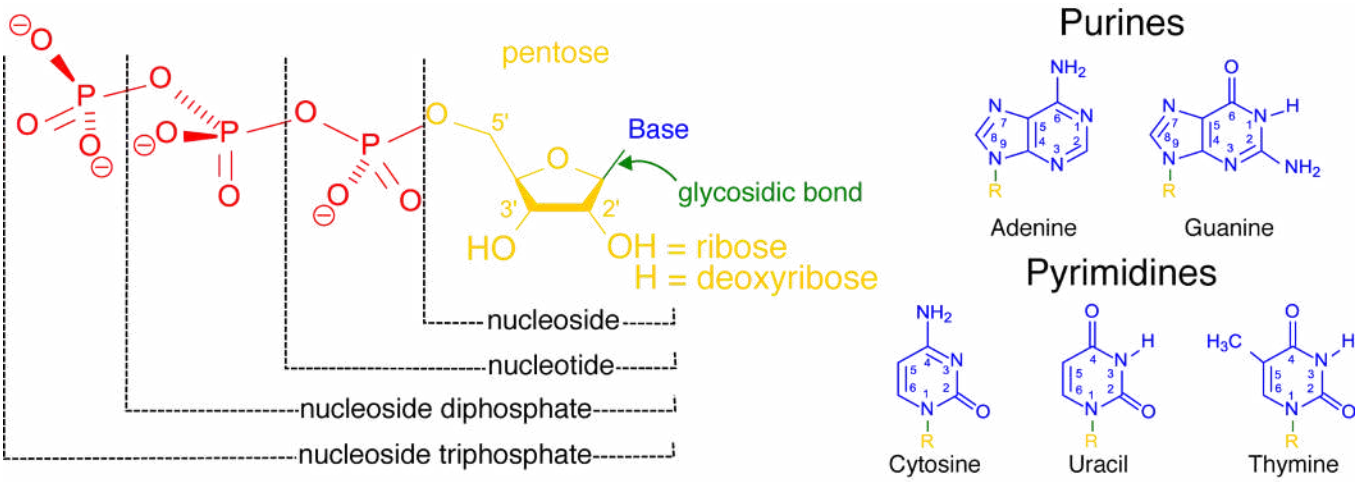


Figure **2.2**: Chemical structure of nucleotides and nucleosides. Public domain. https://commons.wikimedia.org/wiki/File:Nucleotides.png

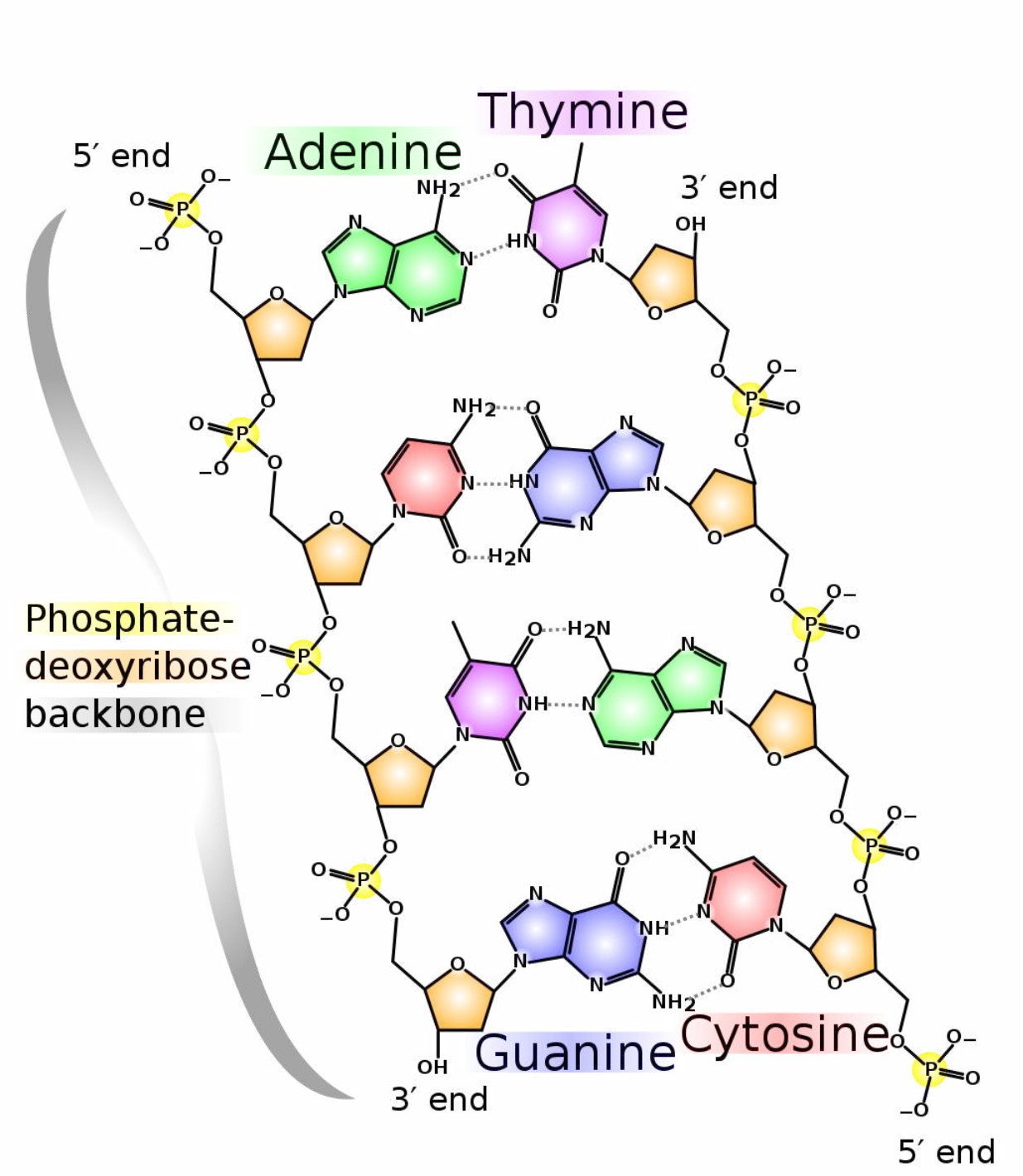


Figure **2.2.2.3**: Chemical structure of DNA. Bonds between the sugar and phosphate groups of each nucleotide form the phosphatedeoxyribose backbone of each DNA strand. Hydrogen bonds between each base, shown as dotted lines, link the two strands of DNA together. Image by Madeleine Price Ball https://commons.wikimedia.org/w/index.php?curid=1848174

The order of nucleotides in a DNA strand is known as the DNA sequence. Among other things, that sequence includes plans for constructing proteins with ribosomes, the protein factories of cells (Fig. **2.4**). Proteins are polymers of amino acids that provide structural functions, form enzymes, conduct messages, help transport atoms and small molecules, and more. Proteins play a central role in cellular life.

Three kinds of RNA are involved in the information flow from DNA to proteins (Fig. **2.4**). Like DNA, RNA is a polymer of nucleotides. However, RNA contains uracil rather than thymine (Fig. **2.2**). Messenger rRNA (mRNA) is a single-stranded working

copy of DNA that delivers the plans for proteins to the ribosomes. The process of making mRNA from DNA is known as transcription. In the ribosome, each group of three nucleic acids in the mRNA, known as codons, are translated into one amino acid, a process known as translation. During translation, transfer RNA (tRNA) brings amino acids to the ribosome and helps match them to the mRNA, so the correct amino acid is added in the appropriate location on the protein. Lastly, ribosomal RNA (rRNA) helps form ribosomes themselves. Ribosomes are composed of two subunits, the large and the small subunit, which are both composed of a mixture of protein and rRNA (Table **2.1**).

So how do we use these molecules to evaluate phylogenetic relationships? We can assess how closely related two organisms are to one another by comparing the composition of molecules associated with biological information flow: DNA, RNA, or proteins. For example, we can compare the nucleic acid sequences of a particular gene possessed by several species of microorganisms. Species that are closely related will have nucleotide sequences that are more similar than the sequences of species that are distantly related. Thus, the extent to which the gene sequences are similar can be used as a measure of relatedness.

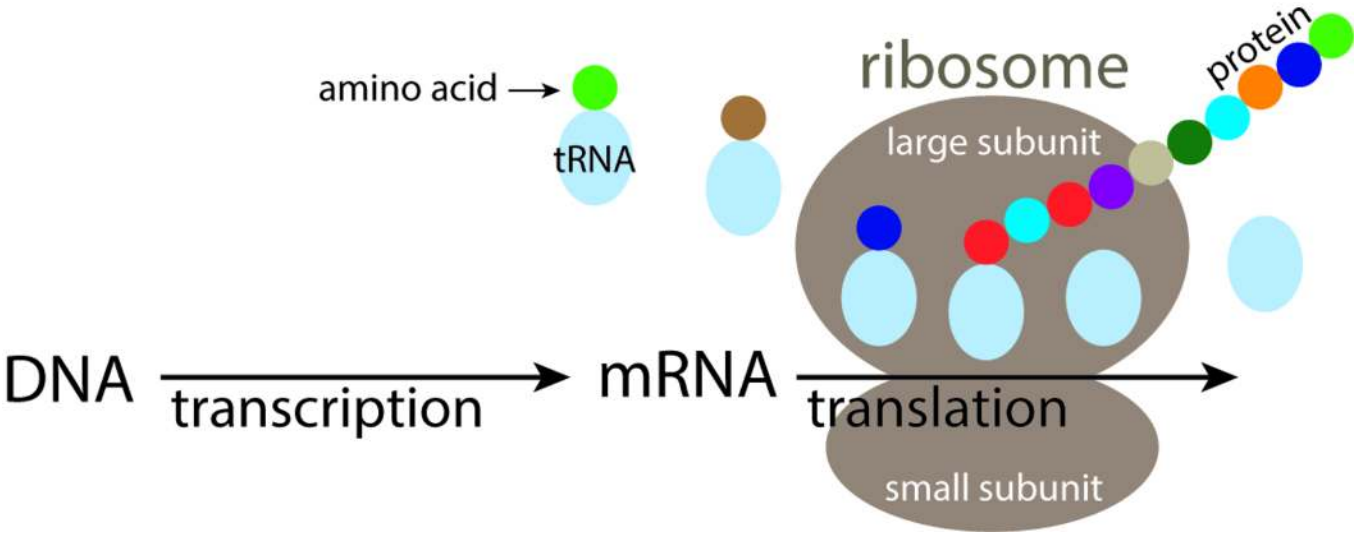


Figure **2.4**: Overview of biological information flow.
https://commons.wikimedia.org/wiki/File:Biological_information_flow.tif

Table **2.1**: Composition of the Ribosome

Domain	Overall size**	Large subunit		Small subunits	
		Total	rRNAs	Total	rRNAs
Archaea, Bacteria	70S	50S	5S, 23S	30S	16S
Eukarya	80S	60S	28S, 5.8S, 5S	40S	18S
*Source: Table 33.2 in Garrett and Grisham (1999).					
**Sizes are expressed in Svedberg units (S), which is a measure of the rate of sedimentation during centrifugation rather than absolute mass or volume.					

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2.3: What is taxonomy?

Whereas phylogeny tells us about the evolutionary relationships between organisms, taxonomy is the classification of life. Taxonomy organizes information about organisms and thus provides an information retrieval system. If you know what group a microbe fits within, you can know some of their characteristics.

The scheme biologists use for classification was defined by Carl Linnaeus in 1735. It is a nested hierarchy consisting of the following groups: domain, phylum, class, order, family, genus, species. Domain is the largest group or 'taxon'. Within each domain, there are several phyla. Within each phylum there can be multiple classes. Within each class there may be multiple orders, and so forth.

You probably can name a few genera or species and perhaps some other taxa as well. For example, *E. coli* is a well-known pathogenic bacterium. The *E* represents the organism's genus, *Escherichia*, and *coli* is the specific name (i.e., the name of the species). Can you name any microorganisms that are not pathogens?

Ideally, microorganisms within the same group would be more closely related to each other than to microbes in other groups at the same level of taxonomy (Hugenholtz et al., 2021; Mayr, 1981). In other words, taxonomy should be built on phylogeny. However, existing taxonomy does not completely achieve this goal in part because the biological community is still grappling with how to develop nomenclature for species that have not been cultured and incorporate them into a stable taxonomic framework (Hugenholtz et al., 2021). Therefore, microbial taxonomy will change alongside advances in our understanding of the microbial world.

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2.4: Analyzing microbial populations using 16S rRNA genes

To further illustrate principles described in this chapter, we can consider the basic steps needed to analyze microbial communities by sequencing the 16S rRNA gene (or 18S rRNA gene in Eukaryotes). The 16S rRNA gene is the DNA that makes the rRNA that composes the small subunit of the ribosome (Table **2.1**). To be clear, 16S rRNA is RNA but the 16S rRNA gene is DNA. Although many new and advanced options exist, the 16S rRNA gene continues to be commonly used by scientists and engineers to analyze microbial communities.

The first step to analyzing a microbial community is to collect a sample. How you accomplish this task will depend on what you are sampling and analyzing. If you are sampling soil or sediment, sampling may simply involve using a sterile scoop to pick up some material and place it in a sterile storage container. Water samples are commonly filtered through a membrane with 0.2 µm pores, a size small enough to capture microbial cells. Once collected, microbial samples are generally stored at cold temperatures to limit further biological activity.

Next, the DNA needs to be extracted from cells within the samples. The basic procedure is to break the cells open and then isolate the DNA from other cellular and environmental debris. These tasks are often accomplished using a commercially available extraction kit, which contains necessary chemical solutions and other consumables, as well as instructions. The end product is typically a buffered solution containing DNA, commonly referred to as DNA extract solution.

The next steps make copies of the 16S rRNA gene using polymerase chain reaction (PCR). PCR can take a small amount of DNA and make millions of copies. To set up a PCR reaction, a solution of ingredients is prepared and mixed with the DNA extract solutions and then incubated in repeating cycles of heating and cooling. Those cycles pull apart the double strands of DNA, allow small segments of DNA (primers) to attach to each strand, and then allow an enzyme (DNA polymerase) to make copies of the DNA. To start copying the DNA, the polymerase requires a section of double stranded DNA, which exists when the primers bind to DNA in the reaction mixture. The primers will only bind to places in the DNA that contain a nucleotide sequence that complements that of the primers. Therefore, the primers determine which region of DNA is copied. Primers can be designed to target specific groups of microorganisms, or they can be compatible with whole domains or multiple domains.

Once the DNA is amplified, the PCR reaction solutions are typically purified, and the DNA concentration is measured. Next, the sequence of nucleotides in the DNA is identified using a process known as DNA sequencing. Several approaches are available now for DNA sequencing and this step is commonly carried out at a sequencing facility.

Once the sequencing data are obtained, the data needs to be processed to remove poor quality data and then it can be analyzed and interpreted. Free, open-source bioinformatics software available for these calculations includes QIIME2 (Bolyen et al., 2019) and Mothur (Schloss et al., 2009; Schloss and McBain, 2020). These software platforms allow researchers to characterize phylogenetic relationships and taxonomy, test relationships between microbial community composition and environmental conditions, and more. As such, this type of microbial community analysis is a powerful tool for shedding light on the interactions between a microbial community and its environment.

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2.5: Example analysis

To provide an example of a microbial community analysis using 16S rRNA gene sequencing, we can consider some of the findings of Kirk et al. (2015). Their study examined variation in the chemistry and microbiology of water and natural gas samples collected from coal-bearing strata in the Cherokee basin in southeastern Kansas, USA. One research question they considered was: how did methane in the coalbed gas form? Some Archaea can form methane by a few different pathways (see Section 5.1.4), but methane can also form abiotically through thermal degradation of organic matter.

The researchers' geochemical analysis indicated that methanogenic microorganisms formed the methane by oxidizing dihydrogen (H_2) and reducing carbon dioxide (CO_2). Consistent with that result, their analysis of 16S rRNA genes in their samples indicated that most of the archaeal sequences were closely related to groups of methanogens that form methane by reducing carbon dioxide. To illustrate, Figure **2.5** shows the relative abundances of sequences that classified within classes of Archaea. The relative abundance of a microbial group (e.g., a genus, a family, or etc.) is the number of sequences that classified within that group divided by the total number sequences obtained for the sample. This value is typically expressed as a percentage. Of the classes identified, only those within *Methanosarcinales* are thought to be capable of producing methane by pathways other than carbon dioxide reduction (Thauer et al., 2008), and these sequences accounted for only a small portion of the sequences overall. Thus, the results from the geochemical and microbial analyses provided strong evidence for understanding how methane formed in the coalbeds.

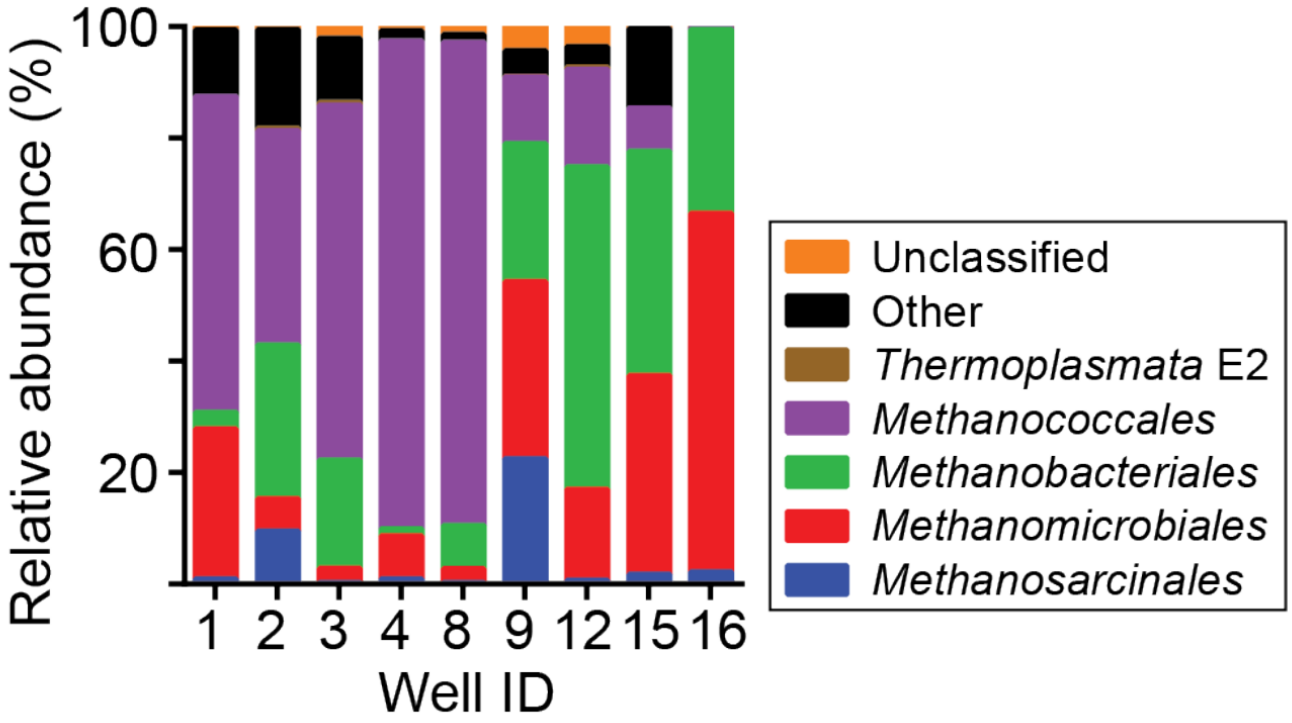


Figure **2.5**: Results of 16S rRNA gene analysis by Kirk et al. (2015). Results are only shown for sequences that classified within orders of Archaea, and only classes with average relative abundance greater than 2% are specifically identified.

In addition to helping reveal the main pathway of methanogenesis in the coalbeds, their analysis also provided insight into potential environmental controls on microbial methane production. They observed that the relative abundance of Methanosarcinales sequences, though small overall, increased significantly with the salinity of the formation water. This result is also consistent with their analysis of gas and water geochemistry. Thus, they concluded that methane formed primarily by carbon dioxide reduction but that the contribution of other pathways increased with the salinity of the formation water. This result indicates that formation water salinity is an environmental control on the overall function of the microbial community in the coalbeds.

For this type of analysis, care should be taken in interpreting the functional capabilities of microorganisms based on their taxonomy. Microbial species can often use more than one type of reaction as a source of energy and just because one species is closely related to another, it does not mean that they would both use the same reaction. Therefore, it is helpful to combine microbial

community analyses with other results that provide constraints on community function, such as results that show how the community is affecting the chemistry of the environment.

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2.6: Viruses

Unlike cellular organisms, viruses do not have both DNA and RNA and they are not able to replicate themselves. They typically have either DNA or RNA, which encodes some proteins necessary for replication, but they do not have the genetic information needed for translation, membrane function, or metabolism (Koonin, 2010). Instead, viruses infect other cells and force them to produce copies of the virus.

Because viruses are unable to independently replicate, some scientists reason that viruses are not living organisms but rather are entities that exist in the gray area between chemistry and life (Villarreal, 2008). Nonetheless, viruses do replicate with assistance within the cellular environment of their host. Moreover, they are more abundant and genetically diverse than cellular organisms (Bergh et al., 1989; Raoult and Forterre, 2008), and they affect all cellular organisms. Thus, we should not overlook their influence on microbial life, whether we consider them to be living organisms or not.

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2.7: Concept Check Questions

1. What are the three domains of life? Which two were traditionally lumped together and referred to as prokaryotes?
2. Does phylogeny affect taxonomy?
3. Why is morphology not a great way to evaluate microbial phylogeny?
4. What is used to evaluate microbial phylogeny?
5. Where does the information that is used to make protein in a cellular organism come from ? Can you explain the steps?
6. How is 16S rRNA different from the 16S rRNA gene?
7. What steps are involved in the analysis of a microbial community using 16S rRNA genes?
8. Is a virus alive? What distinguishes living from nonliving chemicals?

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CHAPTER OVERVIEW

3: Properties of Microorganisms

> *"To be brutally honest, few people care that bacteria have different shapes. Which is a shame, because the bacteria seem to care very much."*
>
> *—Young (2006)*

Microorganisms have relatively simple morphologies relative to their broad genetic and metabolic diversity. While that is true, they do in fact vary in shape and size and can be solitary or aggregated in a variety of ways (Young, 2006). The properties of cells influence their growth and interactions with the environment. This chapter summarizes some of those properties and considers growth cycles of microbial populations. We will also briefly discuss properties of viruses.

3.1: Components of cells
3.2: Cell morphology and size
3.3: Gram-positive and gram-negative bacteria
3.4: Bacterial sporulation
3.5: Biofilms
3.6: Cell growth
3.7: Virions
3.8: Concept Check Questions
3.9: References

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3.1: Components of cells

The cell is described as the most basic unit of life. They are small discrete packages that carry out functional and structural roles of organisms and, aside from viruses, all organisms exist as cells or cell assemblages. Major components of bacterial and archaeal cells include the following (Fig. **3.1**):

- **Cytoplasm:** a mixture of substances and structures that are either dissolved or suspended in water and carry out the functions of the cell. Those substances and structures include macromolecules such as proteins and nucleic acids, ribosomes, small organic molecules that are precursors of macromolecules, and inorganic ions. Within the cytoplasm, raw materials from the external environment are enzymatically degraded and new macromolecules are formed.
- **Cytoplasmic membrane:** a phospholipid bilayer that surrounds the cytoplasm and serves as a permeable barrier. Proteins embedded in the cytoplasmic membrane provide important functions including roles in energy production and the transport of materials in and out of the cell.
- **Ribosome:** small organelle in the cytoplasm that is responsible for protein production in organisms of all three domains of life. See Chapter 2 for additional details.
- **Cell wall:** provides cells with structural support and helps determine cell shape (Beveridge, 1988). Cell walls are found in Bacteria and Archaea but also some plants, fungi, and algae of domain Eukaryota.
- **Cell capsule:** large structure on the outside of some bacterial and archaeal cells that usually consists of polysaccharides. It can help cells resist viruses and toxic chemicals, adhere to surfaces, and remain hydrated.
- **Nucleoid:** a large double-stranded molecule that aggregates to form a visible mass.
- **Flagellum:** lash-like appendage of some cells that is primarily used to help the cell move.
- Pilus: (not shown): hair like structure found on the surface of some bacteria and archaea. Numerous pili can be present on each cell and uses vary. They can be used for electron transfer, adherence to surfaces, conjugation, and more.

Eukaryotic cells contain many of the same components as bacterial and archaeal cells (Fig. **3.1**). In addition, eukaryotic cells have membrane-enclosed organelles such as the nucleus, nucleolus, mitochondria, and chloroplasts. The nucleus houses DNA, which is packed in a very organized state called chromosomes. The nucleolus exists within the nucleus and produces ribosomes. Mitochondria and chloroplasts are organelles that are used in energy production. Aside from these differences, Eukaryotes also have more DNA than Bacteria and Archaea. The genome is all of the genetic material within an organism. The genome of Eukaryotes is typically much larger, by up to several orders of magnitude, than that of bacteria (Theriot, 2013).

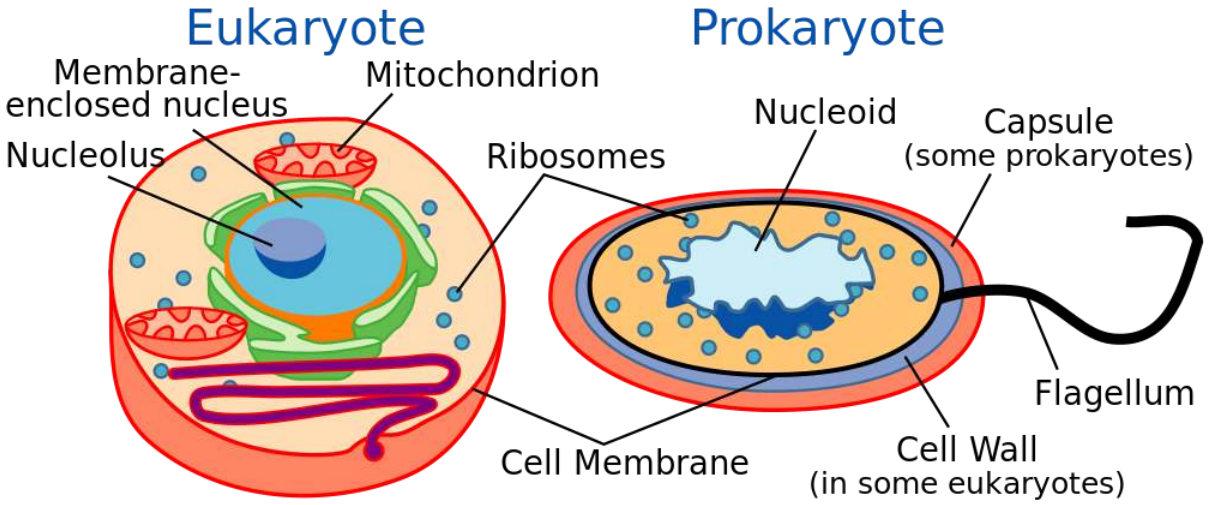


Figure **3.1**: Comparison of eukaryotic and prokaryotic (bacterial and archaeal) cells. Figure is not to scale. Image is public domain. Source: https://commons.wikimedia.org/wiki/File:Celltypes.png

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3.2: Cell morphology and size

Many cell morphologies have been observed, including cells that look like lemons, teardrops, oblong spheroids, flat squares, beans, disks, and more (Young, 2006). However, the most common shapes are bacilli (rods), cocci (spherical), spirilla (curved rods), spirochetes (tightly coiled cells), and filamentous bacteria (long thin cells or chains of cells) (Fig. **3.2**). Selective forces that guide variation in microbial morphology are not well known, but possibilities include nutrient limitations, growth demands, attachment, dispersal effects, motility, and predation (Young, 2006).

Eukaryotic cells are generally much larger than bacterial and archaeal cells. Eukaryotic cells range from about 5 to 100 µm in diameter whereas bacterial and archaeal cell diameters typically range from about 0.5 to 2 µm (Konhauser, 2007). There are exceptions, such as the centimeter-long bacterial cells recently described by Volland et al. (2022). However, microorganisms are generally very small and unable to be seen with the naked eye.

The small size of microorganisms appears to reflect their dependence on diffusion. Virtually all bacteria, even those able to use a flagellum to move, depend on diffusion to bring required compounds to their surface and mix nutrients and other molecules within their cytoplasm (Young, 2006). Smaller cells tend to have larger surface area to volume ratios, allowing more efficient exchanges of nutrients and waste than larger cells. This characteristic can allow smaller cells to have more rapid growth rates than larger cells.

Although small size can provide an advantage, it has its limits. Cells need to be large enough to house the essential stuff the cell needs, such as nucleic acids, ribosomes, proteins, and more (Koch, 1996). Moreover, surface-to-volume ratio seems to be more important in low-nutrient environments (Young, 2006). Where nutrient availability is high, a higher diffusive flux has the potential to allow cells to form larger cells, despite the potential decrease in the surface area to volume ratio.

One environmental implication of the small size of microorganisms is that it makes it possible for them to dominate life in the subsurface. Microorganisms can exist anywhere that macroorganisms are found. But microbes rule in the subsurface, where space available for life is mostly limited to small spaces between mineral grains or along fractures.

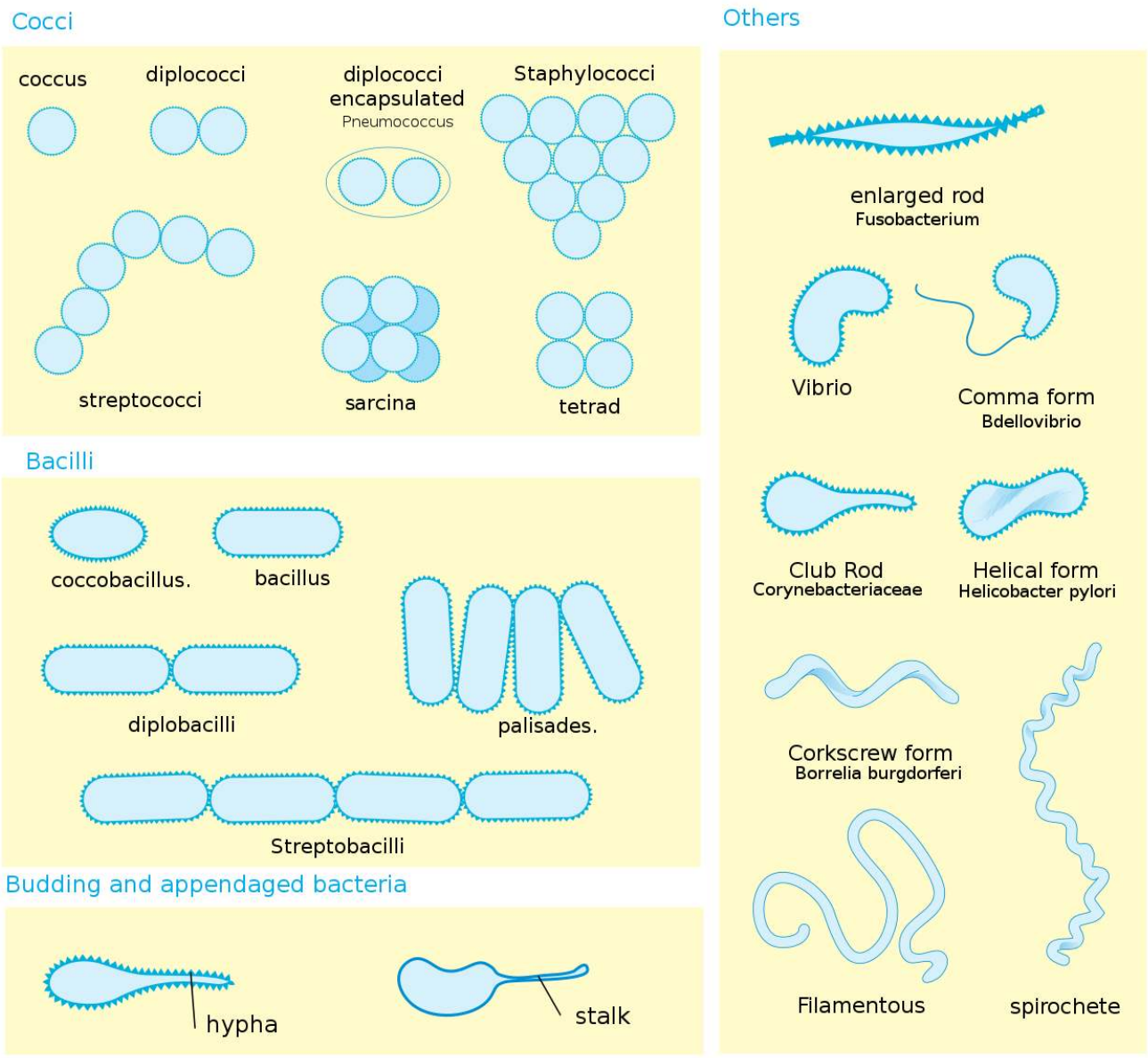


Figure **3.2.** Examples of cell morphologies. Public domain. https://commons.wikimedia.org/wiki/File:Bacterial_morphology_diagram.svg

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3.3: Gram-positive and gram-negative bacteria

The cell walls of Bacteria have a rigid layer composed of peptidoglycan that is the main source of strength of the wall (Madigan et al., 2003). Peptidoglycan is a polymer consisting of sugars and amino acids. For some Bacteria, peptidoglycan makes up as much as 90% of the cell wall. However, for other Bacteria, it makes up only about 10% of the cell wall (Fig. **3.3**).

These two groups of Bacteria can be distinguished based on a staining procedure. By this method, cells are exposed to a stain, crystal violet, that binds to peptidoglycan. Cells with an abundance of peptidoglycan retain more of the stain than those that have little. The cells that retain more stain are referred to as gram-positive cells (i.e., the staining result is positive). Those that bind little stain are referred to as gram-negative cells. This difference in stain retention was traditionally used to help classify Bacteria and was originally developed in the nineteenth century by a Danish scientist, Hans Christian Gram.

Aside from the difference in peptidoglycan thickness, gram-negative cell walls differ from gram-positive cell walls in a few other ways as well. Gram-negative cell walls have an outer membrane. Unlike the cytoplasmic membrane, the outer membrane is not composed entirely of phospholipid but also contains polysaccharide and protein components and can be referred to as the lipopolysaccharide layer (LPS). Moreover, gram-negative cells also contain a thicker periplasm, a gel-like matrix between the inner cytoplasmic membrane and the outer membrane (Fig. **3.3**).

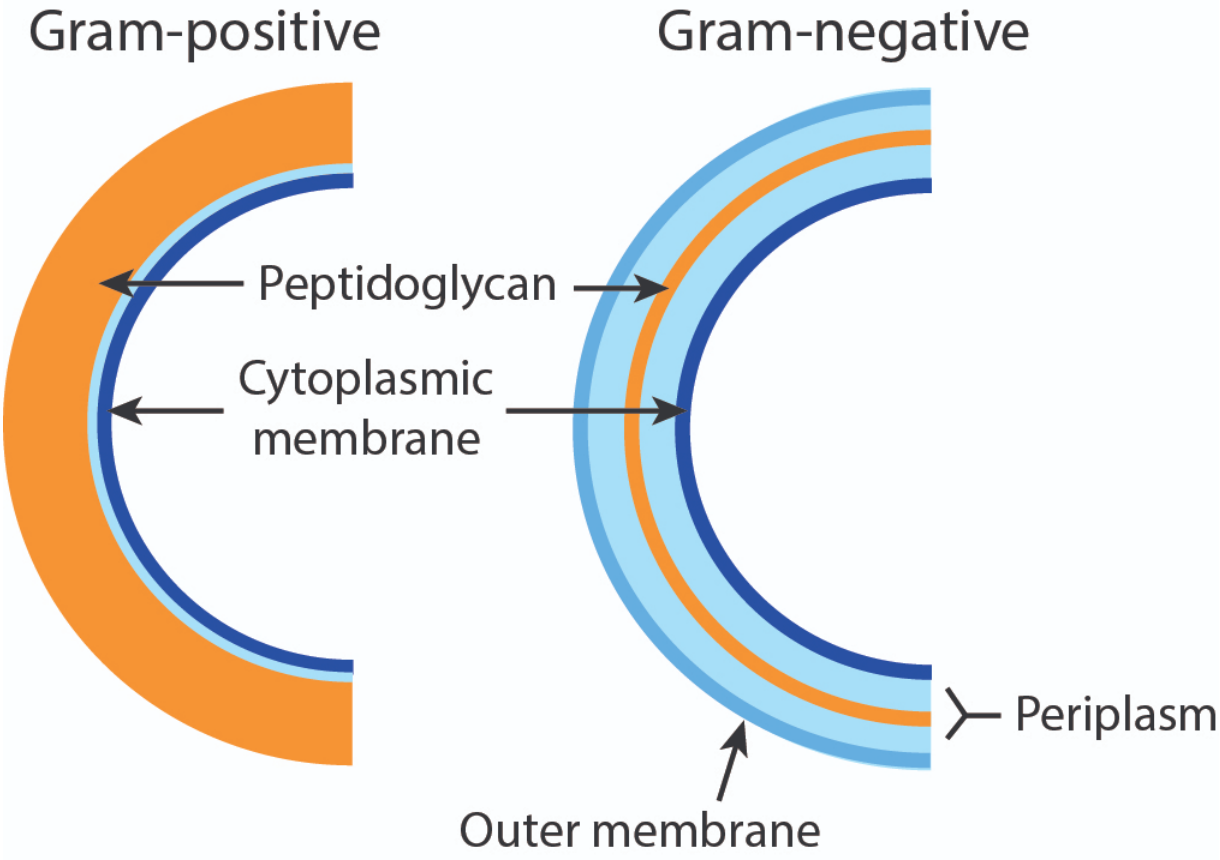


Figure **3.3**: Schematic illustration of the structure of Gram-positive and Gram-negative bacterial cell walls. https://commons.wikimedia.org/wiki/File:Bacterial_cell_walls.jpg

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3.4: Bacterial sporulation

Spores are durable structures that are formed within some Bacteria (endospores; Fig. **3.4**) or on the bacterial surface (exospores). Spore contents include the bacterium's DNA and ribosomes, key ingredients for making a new cell. Bacterial spores are protective spores rather than reproductive spores, which are formed by fungi. Protective spores provide a strategy for surviving harsh conditions. Spores can survive extreme heat, desiccation, UV exposure, and other environmental stressors (Beskrovnaya et al., 2021). In fact, spores have been recognized as the hardiest form of life on Earth (Nicholson et al., 2000). Once favorable conditions return, the spore can then transform back into a cell.

Sporulation, the process of forming spores, has been most thoroughly studied in members of the phyla *Firmicutes*, who make endospores, and *Actinobacteria*, who make exospores, but other groups are also capable of sporulation (Beskrovnaya et al., 2021). Generally, the main driver of spore formation appears to be depletion of nutrients (Higgins and Dworkin, 2012; McCormick and Flärdh, 2012), but drivers vary with the needs of individual species (Beskrovnaya et al., 2021). For example, Mearls et al. (2012) found that a strain of *Clostridium thermocellum* formed spores when exposed to oxygen (O_2). The bacterium is an anaerobe, meaning it exists in environments with little oxygen. As we will discuss in Chapter 6, oxygen is toxic to some anaerobic microorganisms and thus, sporulation provides *C. thermocellum* with a strategy to survive oxygen stress.

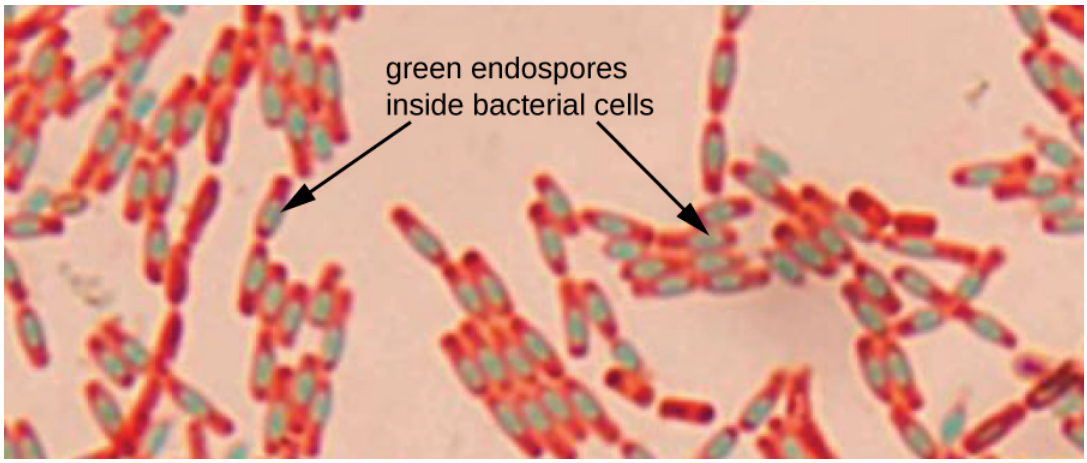


Figure **3.4**: Image showing endospores within rod-shaped bacteria.
https://commons.wikimedia.org/wiki/File:OSC_Microbio_02_04_Endospores.jpg

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3.5: Biofilms

Microorganisms can live planktonically, which is to say they can live freely within solutions. However, biofilms are the dominant mode of microbial life in terms of cell abundance and metabolism in ecosystems that can supply nutrients sufficient for growth (Costerton et al., 1995; Flemming and Wuertz, 2019). A biofilm is a community of microorganisms that is encased in extracellular polymeric substances (EPS) (Fig. **3.5**). Biofilms are often attached to a solid surface or an interface, such as the interface between air and water. Biofilms can also be dispersed in solutions. Where that is the case, they can be referred to as flocs or granules (Davey and O'Toole, 2000) (Fig. **3.6**).

Life within a biofilm provides cells with a more secure existence. Microbial biofilms are diverse in terms of their composition and morphology and usually house a mixture of species (Flemming and Wingender, 2010). Cells within biofilms are physiologically distinct from free-living cells of the same species (Costerton et al., 1995). The biofilm provides these cells with shelter that helps minimize exposure to environmental stresses (Hall-Stoodley et al., 2004). In addition, biofilms help cells maintain proximity to extracellular resources (Flemming and Wingender, 2010).

As an example of the sheltering effect of biofilms, research on microbial aspects of geological carbon storage indicates that biofilms can help subsurface microorganisms endure the stress of exposure to high levels of carbon dioxide. During geological carbon storage, carbon dioxide is captured at a point source, compressed, and injected into a rock layer within the subsurface (Bickle, 2009). Over time, the carbon dioxide will react with groundwater and minerals in the bedrock, causing it to become trapped as dissolved inorganic carbon and carbonate minerals.

Microorganisms catalyze many of the reactions that occur in the subsurface, so numerous recent studies have considered how high pressure carbon dioxide will affect subsurface microbial communities and how those communities might ultimately affect the fate of carbon dioxide (Kirk et al., 2016; Mu and Moreau, 2015). Those studies have shown that microorganisms that live within biofilms, as well as those with gram-positive cell walls and the ability to form spores, can better endure the stress associated with high levels of carbon dioxide (Bertoloni et al., 2006; Furukawa et al., 2004; Mitchell et al., 2008; Watanabe et al., 2003; Zhang et al., 2006). Thus, these properties of cells may help determine how microbial communities change after carbon dioxide injection in carbon storage reservoirs.

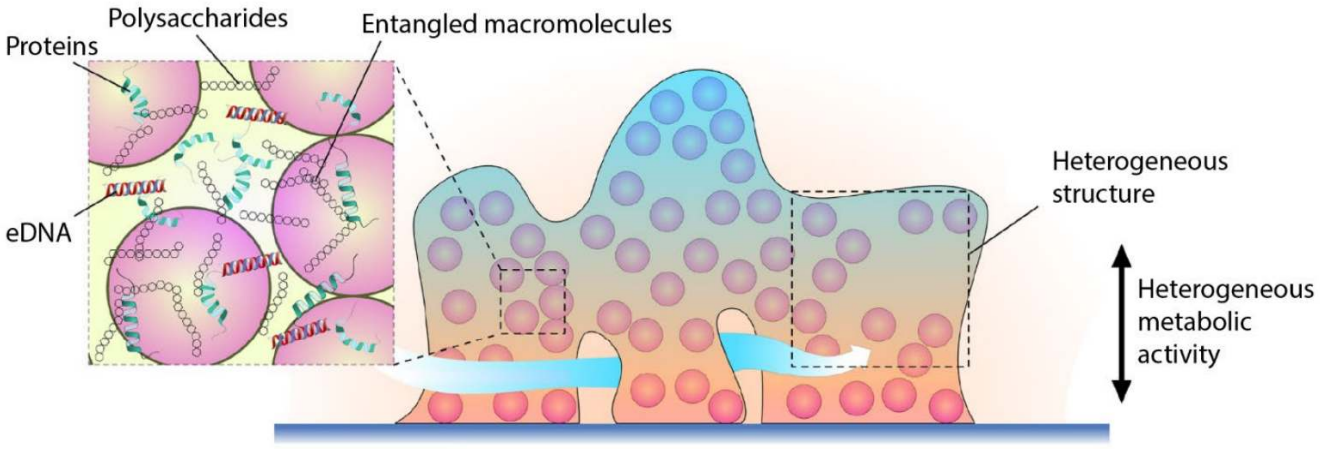


Figure **3.5**: Heterogenous composition of microbial biofilm. Biofilms are composed of microorganisms encased within their extracellular polymeric substances (EPS). Compositional gradients in species composition and distribution occur alongside gradients in nutrient supply and redox conditions. Numerous components are found within the matrix, including polysaccharides, proteins, and environmental DNA (eDNA). Entanglement of these components helps provide cohesion. Image modified from Boudarel et al., (2018).

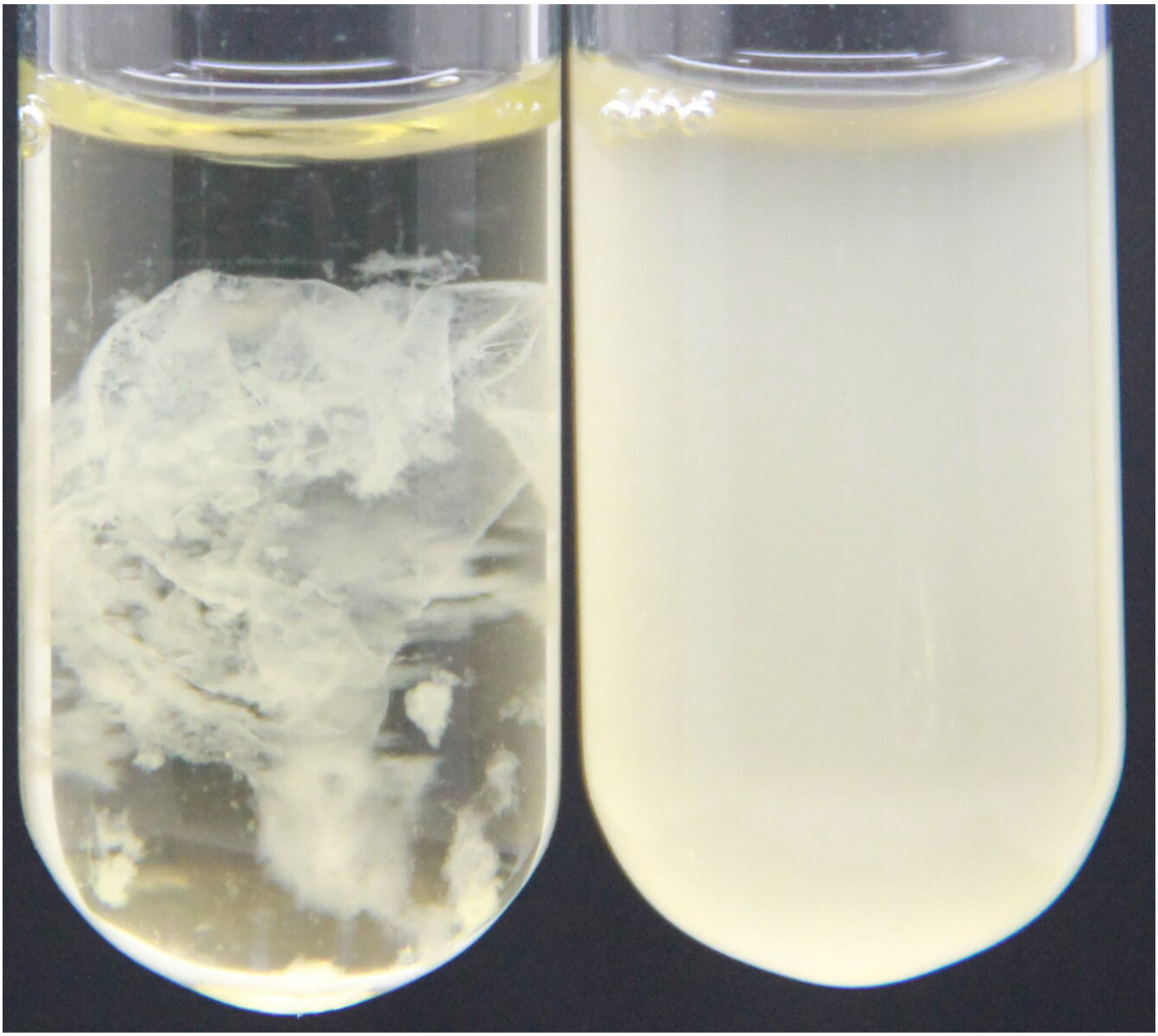


Figure 3.6: Cultures containing strains of the bacterium *Zoogloea resiniphila*. The culture on the left contains floc formed by a strain of *Z. resiniphila* that was isolated from a sludge wastewater treatment reactor. The culture on the right contains a mutant version of the bacterium that has lost the ability to form a floc. Instead, the cells are suspended in the culture solution, causing it to become turbid. This photo was taken by Ms. Na Gao for the purpose of donation to the public domain. Public Domain, https://commons.wikimedia.org/w/index.php?curid=74138940

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3.6: Cell growth

Bacterial and archaeal cells grow by binary fission, in which each individual cell divides into two cells. The two cells are identical unless there is some genetic mutation that occurs when the cell's genome is replicated. To carry out the process, the cells elongate, increase abundance of all cellular components, and then form a partition via inward growth of the cell membrane (Fig. **3.7**).

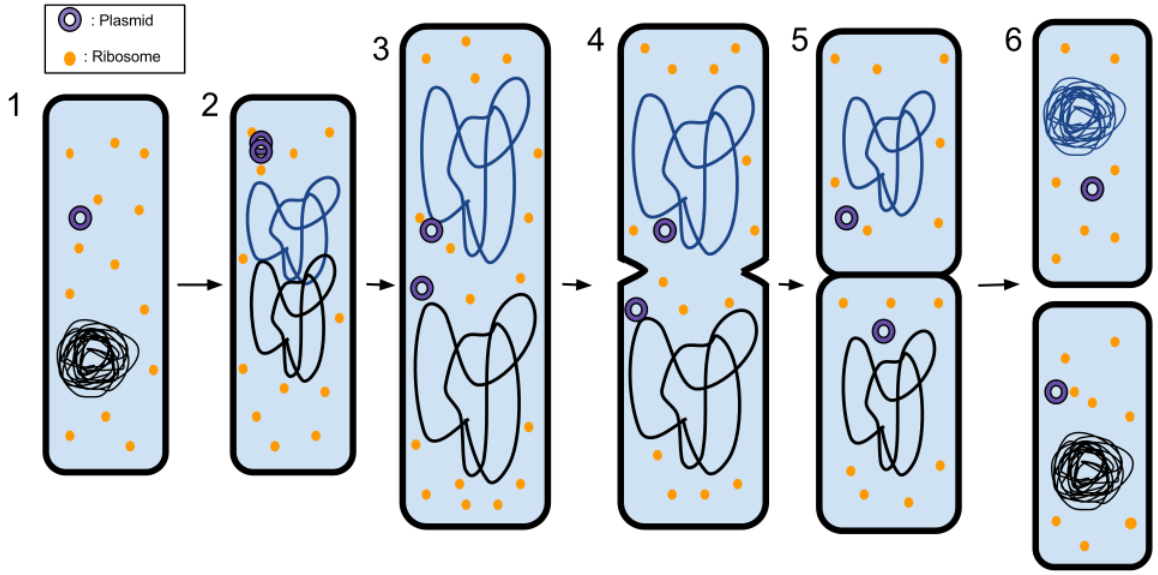


Figure **3.7**: Binary fission in a bacterial or archaeal cell. (1) The initial cell contains tightly coiled DNA. (2) The cell's DNA is replicated and then (3) pulled into separate ends of the elongating cell. (4) A new cell wall starts to grow and then (5) fully develops, allowing the cells to separate (6). Image source: https://commons.wikimedia.org/wiki/File:Binary_Fission_2.svg

Growth rate refers to the change in number cells or cell mass over time. When bacterial cells are introduced to a culture, the following sequence of phases can result (Fig. **3.8**):

1. **Lag phase.** Initially, little growth may occur. During this period, cells may be adapting to conditions, gathering materials, and healing.
2. **Exponential growth phase.** During this phase, cells are in their healthiest state and the rate of increase in cell abundance is proportional to the size of the population. This increase in cell count reflects growth by doubling. One cell becomes two (2^1), which then become four (2^2), then 8 (2^3), then 16 (2^4), and so forth. We can represent this relationship as

$$N = N_0 2^n \tag{3.6.1}$$

   where N is the population size, N_0 is the initial population size, and n is the number of generations that have occurred during the period of exponential growth (Madigan et al., 2003)
3. **Stationary phase.** No net growth occurs because cell growth balanced by cell death. This phase may occur if the environment is running out of essential resources and/or accumulating too much of the waste products of the population.
4. **Death phase.** During the death phase, the rate of cell death is greater than the rate of growth so population size decreases. This phase may occur if resources are exhausted and/or waste levels are too high or if there are significant changes to environmental conditions that limit growth or stress cells such as changes in temperature or pH.

These phases are not always observed (Monod, 1949). For example, if system were open to inflow of critical resources and outflow of waste, population turnover may persist, preventing the occurrence of a death phase. The illustration of growth phases shown in Figure **3.7**, therefore, is an idealized model.

Lastly, we should consider the question: are these phases observed in cultures relevant to microbial populations in natural environments? Natural environments are commonly not steady-state systems (Schlesinger and Bernhardt, 2013), meaning that controls on population growth are not stable over time. They change with the seasons, the daily cycle of the sun, hydrological variability, and more. When favorable conditions emerge, a population is not necessarily going to launch immediately into exponential growth. There may be a lag phase when they heal and gather resources. And their growth may not extend without limit.

Eventually the population may exhaust its resources or the environment may accumulate too much waste. Thus, the answer to our question is yes, the pattern observed in cultures does have relevance to microbial populations in nature.

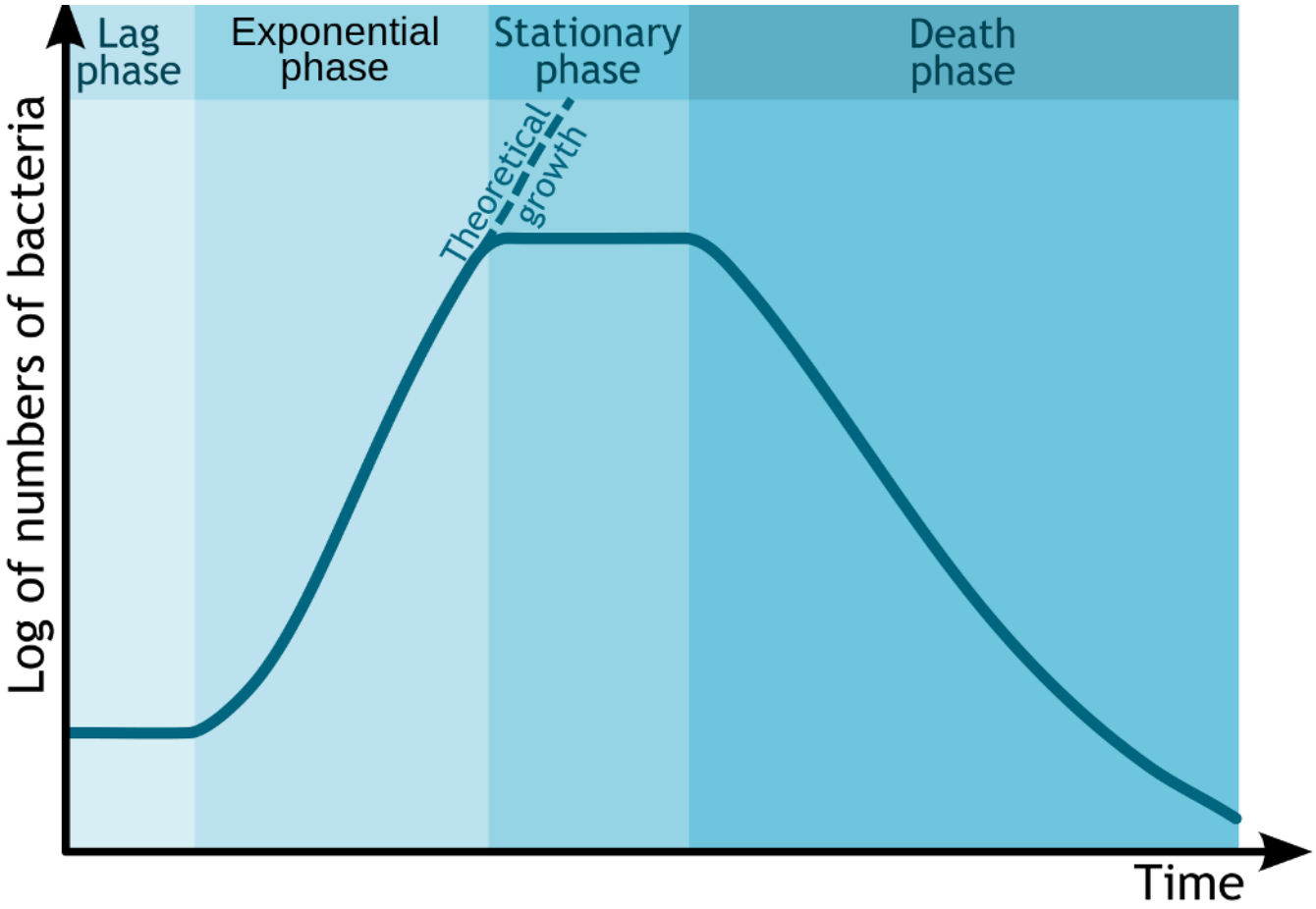


Figure **3.8**: Phases of bacterial growth. Image: https://en.Wikipedia.org/wiki/Bacterial_growth

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3.7: Virions

Viruses, when not within a host cell, exist as viral particles known as virions. A virion consists of some genetic material (DNA or RNA), a protein coat known as a capsid which protects the genetic material, and in some cases an outside envelope of lipids. Shapes are variable and size is typically on the order of $\frac{1}{100}$ the size of bacterial cells.

Unlike Bacteria and Archaea, viruses do not grow by cellular division. Viruses do not have cells. Instead, they rely on their host cell to make copies of the virus, as noted at the end of Chapter 2. Their life cycle begins when they attach to a host cell and gain access to the cell interior. Next, they remove their capsid and release their DNA or RNA, which causes the host to replicate viral genetic material and proteins. Lastly, the viral particles assemble and can be released from the host cell.

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3.8: Concept Check Questions

1. Are you familiar with the basic components of cells, including the cell wall, cytoplasmic membrane, ribosomes, nucleoid, and cytoplasm?
2. How do gram-positive cell walls differ from gram-negative cell walls and how might this difference affect the durability of bacterial cells?
3. Can you describe ways in which the archaeal and bacterial cells differ from eukaryotic cells?
4. What is meant by exponential growth? What does ‘exponential’ mean?
5. Consider an open system where nutrients and energy resources are resupplied, and waste is removed over time. How could the growth cycles of microbes in that system differ from the growth cycle of a population in a closed system where resources are not refreshed and waste accumulates?

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CHAPTER OVERVIEW

4: Redox and Mechanism

Microorganisms drive oxidation-reduction reactions (i.e., redox reactions) forward to obtain energy for life functions and to obtain nutrients needed to make biomass. Those reactions play a central role in the two-way interactions between microbes and their environments. Environments influence what redox reactions are available to the microbial community, and by driving the reactions forward, the microbes influence the geochemical evolution of the system.

Because of these relationships, understanding redox chemistry is essential to developing a strong foundation for geomicrobiology. We begin this chapter by reviewing some of the basics of redox reactions and then discuss the major categories of microbial metabolisms.

4.1: Redox basics
4.2: Balancing redox reactions
4.3: Metabolism
4.4: Chemotrophy
4.5: Phototrophy
4.6: Answers to Practice Problems
4.7: Concept Check Questions
4.8: References

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4.1: Redox basics

Consider the following chemical reactions:

$$Fe^{3+} + 3\ H_2O \longleftrightarrow Fe(OH)_3\ (s) + H^+ \tag{4.1.1}$$

$$2\ Mn^{2+} + 2\ H_2O + O_2 \longleftrightarrow 2\ MnO_2\ (s) + 4\ H^+ \tag{4.1.2}$$

Only one of them is a redox reaction. Which one and how do you know? This first section will help you answer these questions. We will consider how to identify redox reactions and how to write balanced redox reactions, as a way of reinforcing redox concepts.

The defining feature of redox reactions is the transfer of an electron or electrons from one element or compound to another. When an element loses an electron, it is said to be oxidized. When an element gains an electron, it is said to be reduced.

Electrons are negatively charged. Therefore, we can identify whether an element has gained or lost an electron by examining its oxidation state on both sides of the reaction. If an element's oxidation state increases as the reaction moves forward, then electrons must have been removed. The element has been oxidized. If the oxidation state decreases as the reaction moves forward, then electrons have been added or in other words the element has been reduced. Lastly, if the oxidation state does not change, the element does not participate in redox in the reaction.

Oxidation state or oxidation number is the charge that an atom would have if it existed as a monatomic ion. The rules for identifying the oxidation state of an element follow in Table 4.1. The first rule refers to elements in elemental form. To clarify, an element in elemental form is one that is not combined with other elements to form a compound. Instead, it exists in a free, uncharged state. Also, the last rule in the list refers to polyatomic ions. A polyatomic ion is a set of two or more atoms bonded covalently to form a single compound, which has a net charge. Hence, the compound is an ion.

To determine the oxidation states of elements in polyatomic ions, it is helpful to use a simple algebraic approach. For example, what is the oxidation state of sulfur in sulfate (SO_4^{2-})? The oxidation state of sulfur can range from -2 to $+6$. The overall charge on the ion is -2 and, based on the rules listed in Table 4.1, the oxygen atoms each have a charge of -2. Therefore, we can calculate the charge on the sulfur (S) as:

$$-2 = S + 4(-2) \tag{4.1.3}$$

Solving for S, we conclude that the oxidation state is $+6$.

Table 4.1: Rules for Identifying Oxidation States

Rule	Examples (ox. state)	Exceptions
Atoms in elemental form have an oxidation state of zero.	O_2, H_2, N_2 Fe metal (0)	
Monatomic ions have an oxidation state equal to the charge on the ion.	Fe^{2+}, Mn^{2+}	
Hydrogen in most compounds has an oxidation state of +1.	H in H_2O and OH^{-1} (+1)	Elemental H (0) and H in hydrides (−1)
Oxygen in most compounds has an oxidation state of −2.	O in H_2O and OH^{-1} (−2)	Elemental O (0) and O in hydrogen peroxide (−1)
Halogens in most compounds have an oxidation state of −1.	F^-, Cl^-, Br^- (−1)	Elemental forms of halogens (0)
Atoms in compounds and polyatomic ions have an oxidation state that equals the sum of the overall charge on the compound and the oxidation numbers of each atom in the compound.	S in SO_4^{2-} (+6)	

Applying these rules to the reactions above (equations 1 and 2), we determine that, in the first reaction, none of the oxidation states have changed between the reactant and product side of the reaction (Table **4.2**). Therefore, the reaction does not include redox.

Table **4.2**: Oxidation States of Elements in Polyatomic Ions in Reaction **4.1.1**

(Oxidation state)	**Fe (+3)**		**H (+1), O (−2)**		**Fe (+3), O (−2), H (+1)**		**H (+1)**
Reaction **4.1.1**	**Fe^{3+}**	+	**3 H_2O**	↔	**$Fe(OH)_3$ (*s*)**	+	**3 H^+**

For the second reaction, however, oxidation states of both manganese and oxygen change between the reactant and product side of the reaction (Table **4.3**). Therefore, the reaction does include redox. The manganese oxidation state increases, consistent with the loss of electrons, which we refer to as oxidation. Those electrons must have gone somewhere and indeed, the reaction includes changes in the oxidation state of oxygen. Specifically, each oxygen in **O_2** on the reactant side must gain two electrons because all of the oxygens on the product side have a **−2** oxidation state. Thus, oxygen has been reduced.

Table **4.3**: Oxidation States of Elements in Polyatomic Ions in Reaction **4.1.2**

(Oxidation state)	**Mn (+2)**		**H (+1), O (−2)**		**O (0)**		**Mn (+4), O (−2)**		**H (+1)**
Reaction **4.1.2**	**Mn^{2+}**	+	**2 H_2O**	+	**O_2**	↔	**2 MnO_2 (*s*)**	+	**4 H^+**

This simple example illustrates that being able to evaluate oxidation states correctly is a key to identifying redox reactions and analyzing them. Thus, it is important to practice this concept if you are unsure.

✔ Practice 4.1.1

A. Determine the oxidation state of nitrogen in the following: **NH_4^+**, **N_2**, **NO_3^-**, **NO_2^-**

B. Determine the oxidation state of carbon in the following: **$CHOO^-$**, **CHOOH**, **CH_4**, **CO_2**

✔ Practice 4.1.2

Which of the following reactions are redox reactions? For each redox reaction, identify which element has been oxidized and which has been reduced.

A. **$Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3 + H^+$**

B. **$NO_3^- + 2\ H^+ + 4\ H_2\ (aq) \leftrightarrow NH_4^+ + 3\ H_2O$**

C. **$HCOO^- + H^+ + H_2AsO_4^- \leftrightarrow HCO_3^- + As(OH)_3\ (aq)$**

D. **$H^+ + HS^- \leftrightarrow H_2S\ (aq)$**

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4.2: Balancing redox reactions

Learning how to write balanced redox reactions by hand is an effective way to reinforce redox concepts. To start with, consider the following simple redox reaction:

$$\mathrm{Zn}\ (s) + \mathrm{Ag^+} \longleftrightarrow \mathrm{Zn^{2+}} + \mathrm{Ag}\ (s) \tag{4.2.1}$$

Is this reaction balanced? In terms of elements, yes, but there is more to it than that. Redox reactions must also be balanced in terms of charge. The amount of oxidation must equal the amount of reduction. In other words, electron donation must equal electron acceptance. Electrons do not just swim about freely in aqueous solutions.

Redox reactions can be quite difficult to balance, but there is an easy procedure that you can follow to write and balance simple redox reactions. For the purposes of this book, we will use the following steps:

1. Write half reactions in term of oxidation and reduction.
2. Balance electrons and the species being oxidized and reduced.
3. Combine half reactions.
4. Balance oxygens by adding water molecules and then balance hydrogens by adding hydrogen ions ($\mathrm{H^+}$)
5. Confirm charge and elemental balance.

For our first example, let's apply these rules to the reaction above (4.2.1).

1. Write half reactions in term of oxidation and reduction. For this step, you need to identify oxidation states for each element in the reaction. In doing so, we can see that the oxidation state of zinc increases from 0 to +2, indicating that it loses two electrons as the reaction goes forward. Similarly, we can see that the oxidation state of silver decreases from +1 to 0 as the reaction goes forward, indicating that it gains one electron. Based on this information, we can write the following half reactions:

$$\text{Oxidation half} \qquad \mathrm{Zn} \longleftrightarrow \mathrm{Zn^{2+}} + 2\ e^- \tag{4.2.2}$$
$$\text{Reduction half} \qquad \mathrm{Ag^+} + e^- \longleftrightarrow \mathrm{Ag} \tag{4.2.3}$$

2. Balance electrons and the species being oxidized and reduced. We notice that the oxidation half reaction includes two electrons as written and the reduction half includes only one. Therefore, we need to multiply the reduction half reaction by two:

$$\text{Oxidation half} \qquad \mathrm{Zn} \longleftrightarrow \mathrm{Zn^{2+}} + 2\ e^- \tag{4.2.4}$$
$$\text{Reduction half} \qquad 2\ \mathrm{Ag^+} + 2\ e^- \longleftrightarrow 2\ \mathrm{Ag} \tag{4.2.5}$$

3. Combine half reactions by adding them together. The two electrons on the product side cancel out with the two electrons on the reactant side.

$$\mathrm{Zn^{2+}} + 2\ \mathrm{Ag^+} \longleftrightarrow \mathrm{Zn^{2+}} + 2\ \mathrm{Ag} \tag{4.2.6}$$

4. Balance oxygens and hydrogens. None are present in this reaction so we can skip this step.
5. Confirm charge balance. The net charge on both the reactant and product sides of the equation is +2. Balance in charge and quantities of elements helps us confirm that we have balanced the reaction correctly.

For a second example, we consider a more complicated reaction in which the carbon in acetate ($\mathrm{CH_3COO^-}$) is oxidized to bicarbonate ($\mathrm{HCO3^-}$) and iron in the mineral goethite (FeOOH) is reduced to ferrous iron ($\mathrm{Fe^{2+}}$). This reaction is used by some metal-reducing microorganisms as a source of energy.

1. Define the half reactions. In the oxidation half reaction, acetate includes two carbons and bicarbonate includes one. As such, two bicarbonates are needed in the products for every acetate in the reactants. The carbons have an average oxidation state of 0 in acetate and +4 in bicarbonate. Therefore, carbon releases eight electrons overall in the oxidation half reaction. In the reduction half, the oxidation state of iron in goethite is +3. Therefore, it must gain one electron to become $\mathrm{Fe^{2+}}$

$$\text{Oxidation half} \qquad \mathrm{CH_3COO^-} \longleftrightarrow 2\ \mathrm{HCO_3^-} + 8\ e^- \tag{4.2.7}$$
$$\text{Reduction half} \qquad \mathrm{FeOOH} + e^- \longleftrightarrow \mathrm{Fe^{2+}} \tag{4.2.8}$$

2. Balance the electrons by multiplying the reduction half reaction by eight.

$$\text{Oxidation half} \qquad CH_3COO^- \longleftrightarrow 2\ HCO_3^- + 8\ e^- \tag{4.2.9}$$
$$\text{Reduction half} \qquad 8\ FeOOH + 8\ e^- \longleftrightarrow 8\ Fe^{2+} \tag{4.2.10}$$

3. Combine the half reactions.

$$CH_3COO^- + 8\ FeOOH \longleftrightarrow 2\ HCO_3^- + 8\ Fe^{2+} \tag{4.2.11}$$

4. Balance the oxygens first by adding water and then balance the hydrogens. In reaction (4.2.11), there are 18 oxygens on the reactant side and only six on the product side. Therefore, we can balance oxygens by adding 12 waters to the product side.

$$CH_3COO^- + 8\ FeOOH + 15\ H^+ \longleftrightarrow 2\ HCO_3^- + 8\ Fe^{2+} + 12H_2O \tag{4.2.12}$$

5. Do charges and elements balance? Yes, the net charge is $+14$ on each side of the reaction and the elements are balanced.

For a third and final example, we consider oxidation of elemental hydrogen (H_2) coupled with reduction of oxygen (O_2), with water as the product in both half reactions.

1. Define the half reactions. In the oxidation half reaction, the oxidation state of each hydrogen goes from 0 to $+1$ and there are two hydrogens on each side. Therefore, two electrons are released in the oxidation half reaction. In the reduction half, the oxidation state of oxygen goes from 0 to -2 and there are two oxygens on each side. Therefore, four electrons are gained in the reduction half reaction.

$$\text{Oxidation half} \qquad H_2 \longleftrightarrow H_2O + 2\ e^- \tag{4.2.13}$$
$$\text{Reduction half} \qquad O_2 + 4\ e^- \longleftrightarrow 2\ H_2O \tag{4.2.14}$$

2. Balance the electrons by multiplying the reduction half reaction by two.

$$\text{Oxidation half} \qquad 2\ H_2 \longleftrightarrow 2\ H_2O + 4\ e^- \tag{4.2.15}$$
$$\text{Reduction half} \qquad O_2 + 4\ e^- \longleftrightarrow 2\ H_2O \tag{4.2.16}$$

3. Combine the half reactions.

$$2\ H_2 + O_2 \longleftrightarrow 2\ H_2O \tag{4.2.17}$$

4. Balance the oxygens and then hydrogens. In reaction (4.2.17), there are two oxygens on the reactant side and four on the product side. Therefore, two waters must be added to the reactant side.

$$2\ H_2 + O_2 + 2H_2O \longleftrightarrow 4\ H_2O \tag{4.2.18}$$

   In reaction (4.2.18), there are eight hydrogens on the reactant side and eight on the product side, so hydrogen is already balanced.
5. Do charges and elements balance? Yes, the net charge is 0 on each side of the reaction and the elements are balanced. However, before we finalize this reaction, we can simplify it by removing some of the waters. Water molecules are present in both the product and reactant side of the reaction. We can delete two on each side to eliminate the redundancy. Doing so, gives us the following reaction, which is balanced:

$$2\ H_2 + O_2 \longleftrightarrow 2\ H_2O \tag{4.2.19}$$

Practice 4.2.1

Write redox reactions defined by the following electron transfers:

1. Reduction of Fe in $Fe(OH)_3$ to Fe^{2+} coupled with oxidation of C in CH_4 to HCO_3^-
2. Reduction of S in SO_4^{2-} to H_2S coupled with oxidation of C in CH_4 to HCO_3^-
3. Reduction of N in NO_2^- to N_2 coupled with oxidation of H in H_2 to H_2O
4. Reduction of O in O_2 to H_2O coupled with oxidation of N in NH_4^+ to NO_3^-

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4.3: Metabolism

Metabolism is the name given to all of the chemical reactions within cells that are necessary to sustain life. Metabolism involves reactions that provide cells with energy as well as those that transform nutrients into biological molecules such as nucleic acids, proteins, lipids, and more. How redox reactions are involved depends on the type of metabolism.

A wide diversity of metabolic strategies is possible among microorganisms. To help organize our knowledge about metabolisms, we can classify organisms based on how they obtain energy and carbon. Based on energy sources, major categories of organisms are chemotrophs and phototrophs (Table 4.4). Chemotrophs generate energy by catalyzing redox reactions whereas phototrophs generate energy from light. Based on carbon source, major categories of organisms are heterotrophs and autotrophs. Heterotrophs obtain carbon for biomass from organic compounds whereas autotrophs obtain carbon from inorganic compounds (e.g., CO_2, HCO_3^-). Both chemotrophs and phototrophs can be either heterotrophic or autotrophic. In addition to these major categories, mixotrophs are organisms that can use a mix of different sources of energy and carbon rather than a single category (e.g., use of both heterotrophic and autotrophic pathways).

Chemotrophs are also commonly further classified based on the nature of the electron donor (i.e., what is being oxidized) in their redox reaction. If the electron donor is an organic compound (e.g., acetate, lactate, glucose), they can be described as chemoorganotrophs. If the electron donor is inorganic (e.g., H_2, H_2S, Fe^{2+}, NH_4^+), they can be described as chemolithotrophs. Note that here, the reference to inorganic and organic carbon does not indicate the type of carbon used to make biomass. Instead, it reflects the energy source used by the microorganism.

Lastly, you may also encounter the terms assimilatory and dissimilatory metabolism. Some inorganic compounds such as nitrate, ferric iron, sulfate, and carbon dioxide can be reduced when they are used as electron acceptors in chemotrophic reactions that generate energy. When that is the case, those compounds are said to be dissimilated. However, they can also be reduced for use as a nutrient source in biosynthesis. When that is the case, they are said to be assimilated.

Table 4.4: Classification of organisms based on energy and carbon sources

Classification	Subgroup	Energy Source	Carbon Source
Chemotroph	Chemoheterotroph	Redox reaction	Organic
	Chemoautotroph	Redox reaction	Inorganic
Phototroph	Photoheterotroph	Solar radiation	Organic
	Photoautotroph	Solar radiation	Inorganic

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4.4: Chemotrophy

Chemotrophic metabolic reactions can be divided into two major categories, catabolism and anabolism. Catabolic reactions are redox reactions that the organism uses to obtain energy and anabolic reactions are reactions that the organism uses to synthesize biological molecules. When the catabolic reaction includes an electron donor and an electron acceptor that are separate molecules, chemotrophic catabolism is referred to as respiration. For example, the following reaction can describe respiration by the yeast *Saccharomyces cerevisiae*:

$$C_6H_{12}O_6 + 6\ O_2 \longleftrightarrow 6\ CO_2 + 6\ H_2O \tag{4.4.1}$$

The carbon in glucose ($C_6H_{12}O_6$) is oxidized and molecular oxygen is reduced. Therefore, we can say that glucose is the electron donor and oxygen is the electron acceptor in the catabolic reaction. Since they are separate molecules, the reaction is an example of respiration.

In contrast, when the catabolic reaction oxidizes and reduces portions of a single molecule, the chemotrophic catabolism is referred to as fermentation. For example, reaction (4.4.1) is used by *Saccharomyces cerevisiae* when molecular oxygen is available. However, when oxygen is not available, *Saccharomyces cerevisiae* cells can ferment glucose and produce ethanol (CH_3CH_2OH):

$$C_6H_{12}O_6 \longleftrightarrow 2\ CH_3CH_2OH + 2\ CO_2 \tag{4.4.2}$$

This reaction is an example of alcohol fermentation. Two of the carbons in glucose are oxidized (0 to +4) to make carbon dioxide and four are reduced (0 to −2) to make ethanol. The carbons that were oxidized each donate four electrons for a total of eight (2 carbons × 4 electrons/carbon). The carbons that were reduced each accept two electrons also for a total of eight (4 carbons × 2 electrons/carbon). Thus, charge balance is maintained.

The two components of chemotrophic metabolism, catabolism and anabolism, are linked by the molecule adenosine triphosphate (ATP), which can be thought of as the energy currency of cells. ATP consists of a sugar, a nitrogenous base, and three phosphate molecules (Fig. 4.1). The bonds between the two outermost phosphate groups are high-energy anhydride bonds. As such, energy is effectively stored by creating the bonds through catabolic reactions. That energy can then be released by breaking the bonds in anabolic reactions.

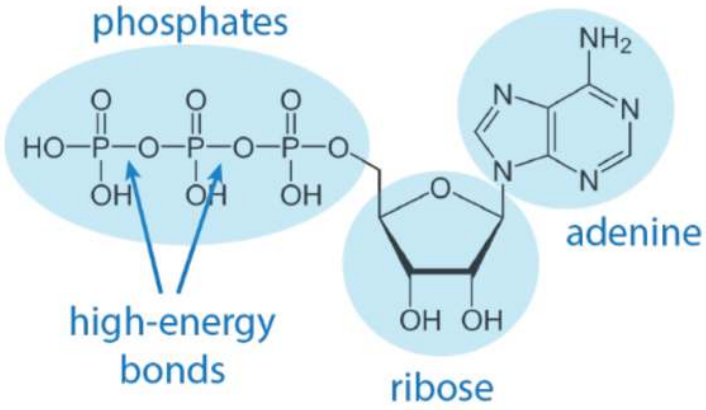


Figure 4.1: Adenosine triphosphate (ATP) molecule with regions highlighted to show adenine, ribose, phosphate molecules, and the high-energy bonds between phosphate molecules.
ATP illustration source: https://commons.wikimedia.org/wiki/File:Adenosintriphosphat_protoniert.svg

Chemotrophic organisms generate ATP using two different strategies: substrate-level phosphorylation and oxidative phosphorylation. During substrate-level phosphorylation, a phosphate is added to adenosine diphosphate (ADP) from a high-energy phosphorylated organic compound that is produced when the organism catalyzes its catabolic reaction. During oxidative phosphorylation, ADP is phosphorylated via the electron transport chain. Respiring chemotrophic microorganisms typically generate ATP from oxidative phosphorylation whereas fermenters generally use substrate-level phosphorylation.

To further illustrate how energy can be captured from a redox reaction, we can consider oxidative phosphorylation in more detail. The electron transport chain is a series of proteins embedded in the cytoplasmic membrane of Bacteria and Archaea or the inner membrane of eukaryotic mitochondria. Electrons that are removed from the organism's electron donor are deposited on the chain,

often via an intermediate electron carrier molecule. Once deposited on the electron transport chain, the electrons flow from one protein to the next, ultimately making their way to the organism's electron acceptor. We can think of the electron acceptor as a drain, which helps pull the electrons through the chain (Fig. 4.2).

As electrons flow along the electron transport chain, ions are pumped across the membrane. Usually those ions are hydrogen ions (i.e., protons). Because ions are being pumped across the membrane, electron flow along the transport chain works to increase the concentration of the ions on one side relative to the other. This gradient in ion concentration effectively provides a source of chemical potential energy that can be used to phosphorylate ADP and make ATP. This gradient is often specifically referred to as the proton motive force.

ADP phosphorylation occurs at a special protein in the membrane known as ATP synthase. At the protein, hydrogen ions flow back across the membrane, which allows a phosphate to be added to ADP:

$$\mathrm{ADP^{2-} + H_2PO_4^- \longleftrightarrow ATP^{3-} + H_2O} \tag{4.4.3}$$

Under the conditions within cells, the forward direction of this chemical reaction is not favorable. However, the chemical energy derived from the ion gradient allows the enzyme to push the reaction forward. Thus, in summary, an ion gradient forms as a result of a redox reaction, and that gradient allows respiring organisms to produce ATP, which is then used as fuel for anabolic reactions.

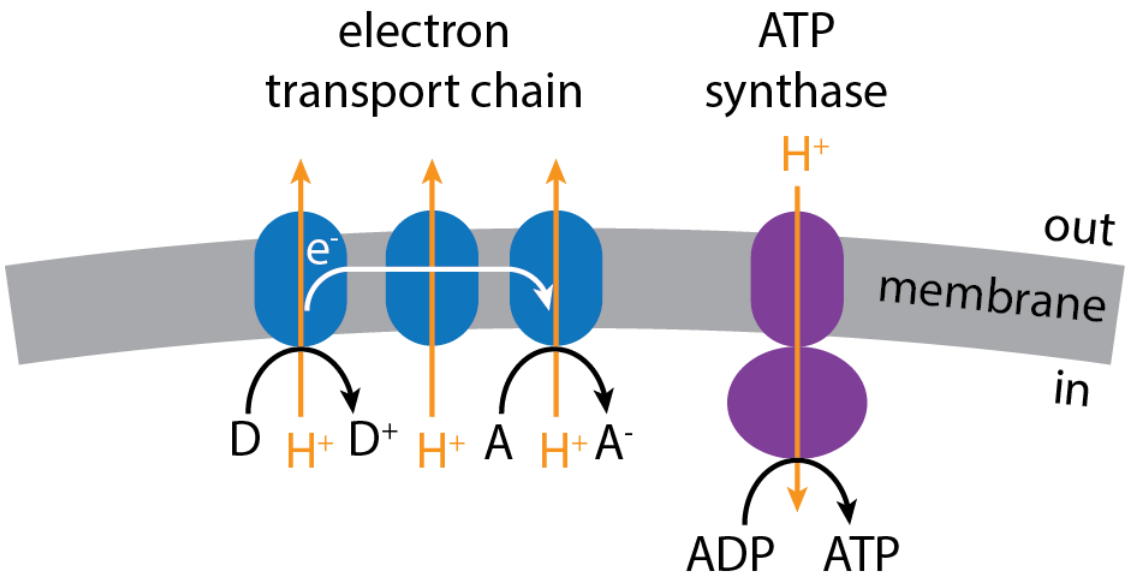


Figure 4.2: Generalized model of the electron transport chain. D and D^+ represent reduced and oxidized forms, respectively, of an electron donor or carrier, whereas A and A^- represent oxidized and reduced forms, respectively, of an electron acceptor. Electrons are transferred from the donor to the acceptor along three proteins. As the electrons move along the proteins, hydrogen ions are pumped outside of the membrane. Hydrogen ions move back to the interior at ATP synthase, allowing the enzyme to catalyze phosphorylation of ADP. Note that the make-up and configuration of the electron transport chain varies among metabolic groups. This figure is based on figure 1 of Jin and Bethke (2002).
https://commons.wikimedia.org/wiki/File:Electron_transport_chain.png

Practice 4.4.1

Identify whether each of the following chemotrophic reactions is a respiration or fermentation reaction:

1. $\mathrm{C_6H_{12}O_6 \longleftrightarrow CH_3CHOHCOOH + C_2H_5OH + CO_2}$
2. $\mathrm{C_6H_{12}O_6 + 4\ H_2O \longleftrightarrow 2\ CH_3COO^- + 2\ HCO_3^- + 4\ H^+ + 4\ H_2}$
3. $\mathrm{CH_3COO^- + 4\ H_2O \longleftrightarrow 4\ H_2 + 2\ HCO_3^- + H^+}$
4. $\mathrm{CH_3COO^- + H^+ \longleftrightarrow CH_4 + CO_2}$
5. $\mathrm{CO_2 + 4\ H_2 \longleftrightarrow CH_4 + 2\ H_2O}$
6. $\mathrm{Fe^{2+} + 1.2\ H^+ + 0.2\ NO_3^- \longleftrightarrow Fe^{3+} + 0.1\ N_2 + 0.6\ H_2O}$

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4.5: Phototrophy

As noted above, phototrophs use solar radiation rather than redox reactions to make ATP. However, redox reactions still play an important role in their metabolism. They use redox reactions to fix carbon, or in other words, convert it from an inorganic to organic form. For example, a phototroph that fixes carbon by converting carbon dioxide into glucose would need to add four electrons to each carbon dioxide from some electron source. Electrons are transferred in the reaction and thus it is a redox reaction.

We can divide phototrophic reactions into two major groups, the light and dark reactions. Light reactions are those that generate ATP, and dark reactions use ATP and fix carbon. Note that solar radiation is necessary for light reactions and sometimes also used in dark reactions, despite their name.

ATP is generated in light reactions through photophosphorylation, which is similar to oxidative phosphorylation. Electrons flow down an electron transport chain embedded in a membrane. A key difference is the source of electrons. The electrons are supplied by a redox reaction in chemotrophs but in phototrophs, the electrons are generated when solar radiation is absorbed by a pigment, such as chlorophyll, that is created by the phototroph.

Two major groups of phototrophs are defined based on whether their dark reactions generate molecular oxygen (O_2). Oxygenic phototrophs produce molecular oxygen, whereas anoxygenic phototrophs do not. The difference between the two groups reflects the ultimate source of electrons in the dark reactions. If the electrons used to reduce carbon are produced by splitting water, molecular oxygen is produced and the phototrophy is oxygenic (Fig. **4.3A**). However, instead of water, the electrons can ultimately come from reduced sulfur or iron, which can be dissolved or within a mineral (Bose et al., 2014; Guzman et al., 2019) (Fig. **4.3B**). In that case, oxidized sulfur or iron is generated rather than oxygen and therefore the phototrophy is anoxygenic.

Some examples of oxygenic phototrophs are plants, algae, and cyanobacteria. At least six groups of Bacteria use anoxygenic phototrophy: green sulfur and non-sulfur bacteria, purple sulfur and non-sulfur bacteria, *Heliobacteria*, and *Chloroacidobacteria* (Tang et al., 2011). Pigments generated by phototrophic organisms, together with minerals that may form alongside their growth, provide some of the most vivid displays of microbial growth in nature (Fig. **4.4**).

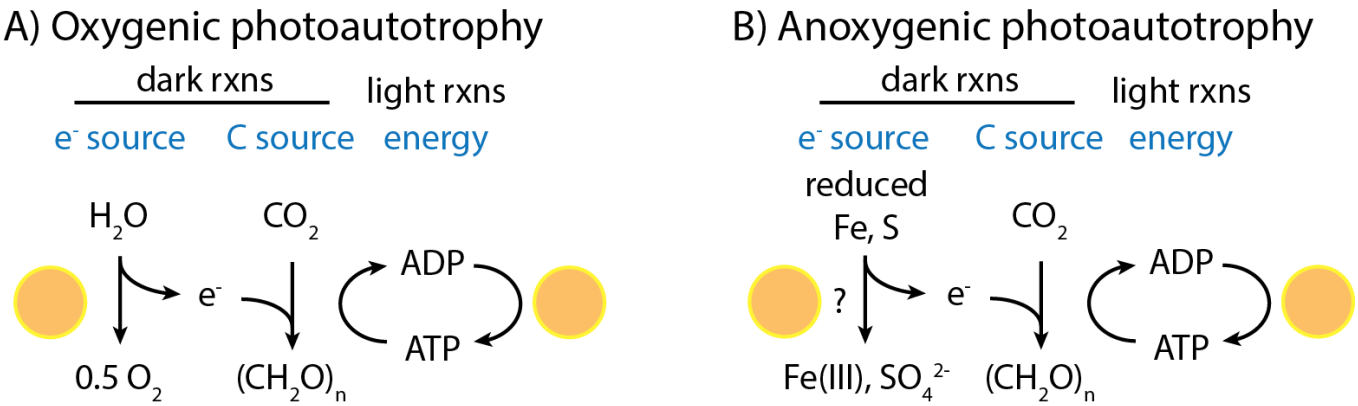


Figure **4.3**: Summary of light and dark reactions (rxns) used by (A) oxygenic and (B) anoxygenic photoautotrophs. The question mark next to the sun in (B) indicates that only some anoxygenic phototrophs use oxygen in their dark reactions. Biomass is represented by the general formula for a carbohydrate ($(CH_2O)_n$). This figure is based on Figure 17.2 of Madigan et al. (2003). https://commons.wikimedia.org/wiki/File:Photoautotrophy.png



Figure 4.4: Grand Prismatic Spring at Yellowstone National Park, USA. The spring is a famous example of the bright colors that can be produced by phototrophic microorganisms. The middle portion of the pool is sterile because it is too hot for microorganisms, but the water cools enough for microbial growth along the edges, where the banding reflects differences in microbial community composition. Microbes that require warmer water grow further from the edge than those that require cooler water. These different populations produce distinct pigments, including chlorophylls (green) and carotenoids (red). Image from Brocken Inaglory. https://en.Wikipedia.org/wiki/File:Grand_Prismatic_Spring_and_Midway_Geyser_Basin_from_above.jpg

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4.6: Answers to Practice Problems

4.1.1. Identifying oxidation states.

A. NH_4^+ (N = −3), N_2 (N = 0), NO_3^- (N = +5), NO_2^- (N = +3)

B. $CHOO^-$ (C = +2), CHOOH (C = +2), CH_4 (C = −4), CO_2 (C = +4)

4.1.2. Identifying redox reactions.

A. Not redox

B. Redox with N in NO_3^- reduced and H in H_2 oxidized

C. Redox with As in $H_2AsO_4^-reducedand\(C$ in $HCOO^-$ oxidized

D. Not redox

4.2.1. Balancing redox reactions.

1. $8\ Fe(OH)_3\ (s) + 15\ H^+ + CH_4 \longrightarrow 21\ H_2O + 8\ Fe^{2+} + HCO_3^-$
2. $H^+ + CH_4 + SO_4^{2-} \longrightarrow H_2S + H_2O + HCO_3^-$
3. $3\ H_2 + 2\ H^+ + 2\ NO_2^- \longrightarrow N_2 + 4\ H_2O$
4. $NH_4^+ + 2\ O_2 \longrightarrow H_2O + 2\ H^+ + NO_3^-$
5. $NH_4^+ + 1.5\ O_2 \longrightarrow H_2O + 2\ H^+ + NO_2^-$
6. $NH_4^+ + NO_2^- \longrightarrow 2\ H_2O + N_2$
7. $8\ Fe(OH)_3\ (s) + 14\ H^+ + H_2S \longrightarrow 20\ H_2O + 8\ Fe^{2+} + SO_4^{2-}$

4.4.1. Respiration and fermentation.

1. Fermentation
2. Fermentation
3. Fermentation
4. Fermentation
5. Respiration
6. Respiration

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4.7: Concept Check Questions

1. What is the defining feature of a redox reaction?
2. How do you identify whether an element has been oxidized or reduced in a chemical reaction?
3. Can you write a balanced redox reaction?
4. What are the categories of metabolism based on energy and carbon sources?
5. What is ATP and what is its connection to catabolism and anabolism?
6. Can a phototroph be a heterotroph?
7. How does ATP generation by phototrophs differ from ATP generation by chemotrophs?
8. How does oxidative phosphorylation differ from substrate level phosphorylation?
9. What is the difference between fermentation and respiration?
10. How is the metabolism of oxygenic phototrophs different from the metabolism of anoxygenic phototrophs?
11. What is the purpose of redox reactions used by phototrophs? How does this compare to chemotrophs?

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CHAPTER OVERVIEW

5: Global Biogeochemical Cycles

In biogeochemical cycles, elements are transformed among multiple oxidation states by biotic and abiotic reactions. In the iron cycle, for example, iron can be transformed back and forth between ferric iron (Fe(III)) and ferrous iron (Fe(II)). Although some reactions in the iron cycle can occur without microbial catalysis, other reactions require it. As such, microbial populations play essential roles in turning the iron cycle, and the same is true for the other cycles we will consider.

Microorganisms mediate reactions in biogeochemical cycles to obtain energy and fix nutrients or for no reason at all. In the latter case, microbes just happen to provide necessary ingredients that allow the reaction to occur. Regardless of why, their activities can drive a wide variety of reactions and thus microorganisms help cycle many elements on a global scale. However, here we focus our efforts on understanding microbial contributions to cycling just four elements – carbon, nitrogen, iron, and sulfur. These elements are among the most abundant redox active elements in Earth's crust. We discuss the biogeochemical cycling of these elements individually in this chapter, but they are connected in nature. As you read, you might try to find those connections.

This chapter focuses on the microbial contributions to each cycle. In Part 2 of this book (Chapters 6-10), we consider how environments help link those microbial contributions together and turn cycles. In Part 3 (Chapters 11-14), we focus our attention on how these microbial contributions impact their environments.

5.1: Carbon cycle
- 5.1.1: Organic matter
- 5.1.2: Aerobic and anaerobic respiration
- 5.1.3: Fermentation and syntrophy
- 5.1.4: Methanogenesis
- 5.1.5: Acetogenesis
- 5.1.6: Methanotrophy

5.2: Nitrogen cycle
- 5.2.1: Nitrogen fixation
- 5.2.2: Ammonification
- 5.2.3: Nitrification
- 5.2.4: Anaerobic ammonia oxidation (anammox)
- 5.2.5: Denitrification
- 5.2.6: Dissimilatory nitrate reduction to ammonia (DNRA)

5.3: Iron cycle
- 5.3.1: Ferric iron reduction
- 5.3.2: Ferrous iron oxidation

5.4: Sulfur cycle
- 5.4.1: Sulfate reduction
- 5.4.2: Desulfurylation
- 5.4.3: Oxidation of sulfide and intermediate sulfur compounds
- 5.4.4: Reduction of intermediate sulfur compounds
- 5.4.5: Sulfur disproportionation

5.5: Concept Check Questions

5.6: References

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5.1: Carbon cycle

The global carbon cycle includes carbon compounds with oxidation states ranging between **+4** and **−4** (Fig. **5.1**). Organisms contribute to the cycle by fixing carbon to generate biomass and using carbon compounds in catabolic reactions. Geological processes help drive the cycle through weathering, mineral deposition, burial, metamorphism, subduction, and volcanism. Moreover, humans help drive the cycle by altering the land surface, combusting fossil fuels, and other activities. Together these coupled biotic and abiotic processes transform carbon among various states on timescales ranging from hours to millions of years (Berner, 2003).

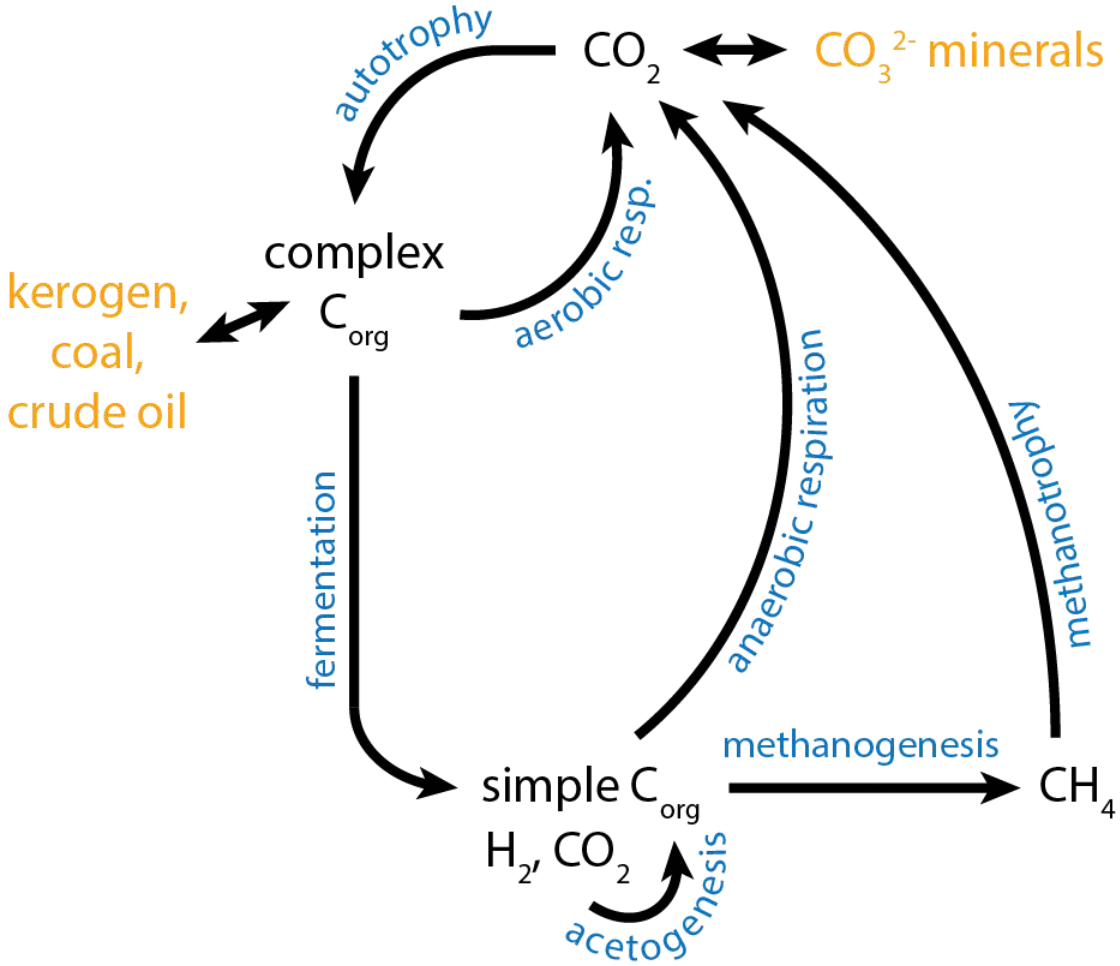


Figure **5.1**: Microbial contributions to the global carbon cycle. Microbial reactions are labeled in blue font and solid phases are in orange font. C_{org} represents carbon in organic compounds. Figure based on figure 1 of Ferry (2010).
https://commons.wikimedia.org/wiki/File:Carbon_cycle.png

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5.1.1: Organic matter

Figure **5.1**, on the main page for section 5.1, refers to “complex” organic matter and “simple” organic matter (C_{org}). We can think of complex organic matter as the biomass of dead organisms. From these high molecular-weight compounds, relatively simple low molecular-weight organic compounds can be produced through respiration and fermentation reactions, as discussed below.

A wide range of organic compounds exist in natural environments. In part, this characteristic stems from the fact that organic matter is not simply composed of the element carbon. It includes carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur as major components and other elements as well. These elements are combined in many ways to make complex organic molecules such as carbohydrates, proteins, nucleic acids, fats, oils, and waxes. Secondly, different organisms produce different assortments of organic compounds. For example, one of the largest sources of complex organic matter in terrestrial environments is plant material consisting of rigid polymers such as cellulose and lignin (De Leeuw and Largeau, 1993). However, in marine environments, the bulk of biomass is produced by single-celled organisms that are rich in lipids and nitrogenous compounds (Burdige, 2007). Third, in addition to biologically produced compounds, organic compounds can also form abiotically (McDermott et al., 2015; Reeves and Fiebig, 2020). Thus, organic compounds form along diverse biotic and abiotic pathways.

Adding to this variability, organic compounds found in sedimentary environments have commonly undergone some amount of degradation. In marine environments, for example, most of the organic matter produced by organisms is rapidly consumed before it is able to settle on the seafloor (Hedges and Keil, 1995). As a second example, kerogen is solid-phase organic matter in sedimentary rocks that forms by biological and thermal degradation pathways. It is thought to be the most abundant form of organic matter on Earth, with a mass of about 15,000,000 gigatons in the subsurface (Falkowski et al., 2000). Degradation produces new compounds and can leave residual complex organic matter altered relative to its initial state.

For detailed information about organic matter composition, De Leeuw and Largeau (1993) provide a thorough review of macromolecular organic compounds and their role in kerogen, coal, and crude oil formation. Arndt et al. (2013) reviews organic matter in marine sediments. Lastly, Hedges et al. (1997) and Kandasamy and Nagender Nath (2016) consider inputs of terrestrial organic matter to the oceans.

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5.1.2: Aerobic and anaerobic respiration

In environments where the availability of molecular oxygen (O_2) is relatively high (i.e., oxic or aerobic environments), microorganisms can oxidize organic matter and reduce oxygen in respiration reactions. In other words, they can use organic matter as their electron donor and oxygen as their electron acceptor, which is a form of aerobic respiration. In contrast, where oxygen availability is very low (i.e., anoxic or anaerobic environments), aerobic respiration is limited by oxygen supply. Instead, respiring microorganisms may primarily use alternative electron acceptors, such as nitrate (NO_3^-), ferric iron ($Fe(III)$) sulfate (SO_4^{2-}), and carbon dioxide. Use of these alternative electron acceptors represent different forms of anaerobic respiration.

Aerobic microorganisms have a powerful suite of enzymes that allow them to degrade complex organic matter (Konhauser, 2007). Some anaerobic denitrifying microorganisms can also degrade complex organic compounds (Pang and Wang, 2021). However, most anaerobic microorganisms lack the powerful enzymes necessary to degrade complex organic compounds and instead rely on help from fermenting and syntrophic microorganisms. As described below, fermenters and syntrophs degrade complex organic matter into simpler compounds that can then be used as electron donors for anaerobic respiration.

In many environments, multiple electron acceptors may be available for microbial respiration. Where this is the case, microbial communities preferentially respire the electron acceptor(s) that provide the most advantages in terms of energy production and reaction rate. In Part 2 of this book, we expand on this topic, but for now, we can assume that microbial communities tend to respire molecular oxygen if it is available because it provides organisms with energetic and kinetic advantages. Where oxygen is not available, nitrate is generally the next best electron acceptor. Where neither oxygen nor nitrate are available, electron acceptor preferences vary with environmental conditions.

Box 5.1: Describing Redox State

Many researchers use the terms ‘aerobic’ and ‘anaerobic’ to describe metabolisms whereas they use ‘oxic’ and ‘anoxic’ to describe conditions of the environment, with ‘suboxic’ as an intermediate. Environmental conditions for oxic, suboxic, and anoxic environments can be defined based on dissolved oxygen concentrations and associated microbial metabolisms as shown in Table 5.1.

It is useful to be able to qualitatively describe redox, but these terms can be a source of confusion. For one reason, microbial metabolisms do not consistently align with oxygen concentrations used to define oxic, suboxic, and anoxic environments (Canfield and Thamdrup, 2009). Furthermore, these terms have not been used consistently in the scientific literature. ‘Anaerobic’ has historically been used to describe metabolisms and environments (e.g., Balch and Wolfe, 1976). The meaning of suboxic has also evolved (Canfield and Thamdrup, 2009). As such, these terms can take on different meanings to different people.

To limit ambiguity, one approach is to describe the redox state of the environment in terms of the specific metabolism(s) it hosts, as recommended by Canfield and Thamdrup (2009). For example, locations where microorganisms are mainly using iron and sulfate as electron acceptors could be simply described as iron- and sulfate-reducing environments. We can also use quantitative measures of redox state such as oxygen concentration as well as Eh, pe, etc. However, when doing so, we need to remember that these parameters do not consistently align with metabolisms and that their values depend on how they were measured or calculated. Absolute values of redox state calculated for an environment based on the Nernst equation, for example, vary with the choice of redox couple used for the calculation (Lindberg and Runnells, 1984). Third, we can also explicitly identify the approach taken or boundaries assumed for each particular application. For this book, anaerobic can be applied to organisms and environments, and the term suboxic is not used. Anaerobic or anoxic environments are simply those where oxygen levels are low and anaerobic respiration can occur.

Table 5.1: Redox states defined for sedimentary environments

Category	O_2 (aq) concentration*	Metabolisms**
Oxic	$> 30\ \mu M$	Oxygen reduction
Suboxic	$1 - 30\ \mu M$	Reduction of nitrate, manganese, iron
Anoxic	$< 1\ \mu M$	Sulfate reduction, methanogenesis

*Oxygen concentration ranges are from Berner (1981) and Anderson et al. (1994) as summarized by Langmuir (1997)

**Metabolisms associated with each redox zone are described in Canfield and Thamdrup (2009).

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5.1.3: Fermentation and syntrophy

Degradation of complex organic matter in anaerobic environments typically begins with the activity of fermenting microorganisms. Primary fermenters excrete enzymes that hydrolyze organic polymers and catabolize the resulting monomers to alcohols and fatty acids. The reactions also generate dihydrogen ($HH2$) and carbon dioxide. The following reactions are examples of glucose ($C_6H_{12}O_6$) fermentation (Conrad, 1999):

$$\text{glucose} \longleftrightarrow 2\ \text{lactate} + 2\ H^+ \tag{5.1.3.1}$$
$$\text{glucose} \longleftrightarrow 2\ \text{ethanol} + 2\ CO_2 \tag{5.1.3.2}$$
$$\text{glucose} \longleftrightarrow \frac{2}{3}\ \text{butyrate} + \frac{2}{3}\ \text{acetate} + 2\ CO_2 + 4\ H_2 \tag{5.1.3.3}$$
$$\text{glucose} \longleftrightarrow \frac{4}{3}\ \text{propionate} + \frac{2}{3}\ \text{acetate} + \frac{2}{3}\ CO_2 + 2\ H^+ + \frac{2}{3}\ H_2O \tag{5.1.3.4}$$

Products of those reactions can be consumed by respiring microorganisms. The alcohols and fatty acids produced by the reactions may also be further fermented by syntrophic bacteria, as illustrated by the following example reactions (Jin and Kirk, 2016):

$$\text{acetate} + 4\ H_2O \longleftrightarrow 4\ H_2 + 2\ HCO_3^- + H^+ \tag{5.1.3.5}$$
$$2\ \text{lactate} + 4\ H_2O \longleftrightarrow 2\ \text{acetate} + 4\ H_2 + 2\ HCO_3^- + 2\ H^+ \tag{5.1.3.6}$$
$$\frac{4}{3}\ \text{propionate} + 4\ H_2O \longleftrightarrow \frac{4}{3}\ \text{acetate} + 4\ H_2 + \frac{4}{3}\ HCO_3^- + \frac{4}{3}\ H^+ \tag{5.1.3.7}$$
$$2\ \text{butyrate} + 4\ H_2O \longleftrightarrow 4\ \text{acetate} + 4\ H_2 + 2\ H^+ \tag{5.1.3.8}$$
$$2\ \text{ethanol} + 2\ H_2O \longleftrightarrow 2\ \text{acetate} + 4\ H_2 + 2\ H^+ \tag{5.1.3.9}$$

In general, syntrophy occurs when one species consumes the metabolic product of another and together the species perform an overall reaction that neither could accomplish on their own. In terms of the reactions above, the amount of energy released by the reactions decreases sharply as dihydrogen concentrations increase (Schink and Friedrich, 1994). Reactions that are not thermodynamically favorable cannot be used by a microorganism as a source of energy, as discussed in Chapter 8. Therefore, syntrophic microorganisms can only remain active if they are partnered with other microorganisms that consume the dihydrogen produced by the reaction and thereby limit its accumulation. This type of syntrophic interaction is called interspecies hydrogen transfer.

Putting this all together, in anoxic environments, primary fermenters and syntrophs degrade complex organics to simpler compounds that can be consumed by respiring microorganisms. By working together, these groups of microorganisms transform organic carbon back to inorganic carbon.

To help illustrate pathways of organic matter degradation and nutrient extraction, consider Figure **5.2**, which depicts pathways of organic matter degradation in the Baltic Sea sediment. Numerous microorganisms break down complex organic matter in the sediment to extract energy and nutrient resources that support microbial respiration. Zinke et al. (2019) examined which pathways of organic matter degradation were present and likely active using detailed analysis of sequence data obtained from sediment samples. They then connected these heterotrophic metabolisms to sediment facies and geochemistry to develop a more complete understanding of microbial controls on sediment carbon cycling.

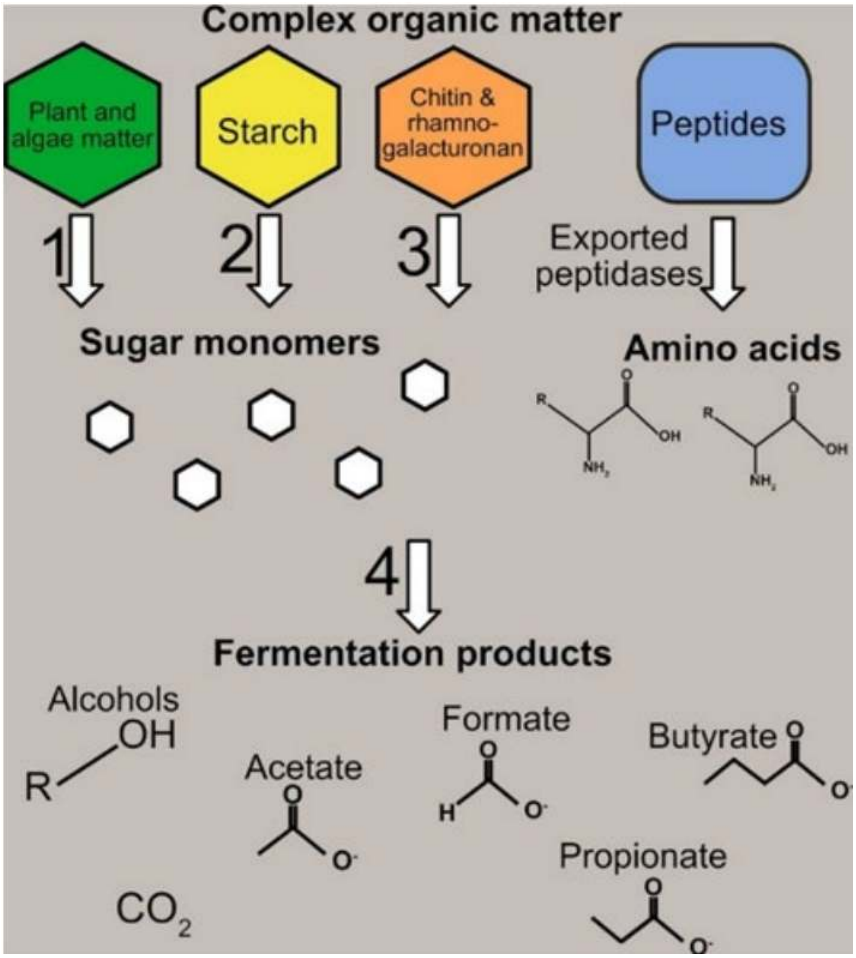


Figure 5.2: Illustration of organic matter degradation pathways investigated by Zinke et al. (2019) in Baltic Sea sediment. Complex polysaccharides are broken down into sugar and amino acid monomers, which can then be fermented into relatively simple organics (alcohols, acetate, formate, propionate, butyrate), H_2, and CO_2.

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5.1.4: Methanogenesis

Microbial methanogenesis refers to methane production by microbial reactions. For the purposes of this book, we specifically refer to methanogens as microorganisms that form methane for energy production. In addition to these groups, there are also microorganisms that form methane as byproduct of their activities, which are discussed in Section 13.4.

Methanogenesis is traditionally assumed to occur where electron acceptors other than carbon dioxide are not available, although that appears to be an oversimplification. For example, several studies have found methanogenesis active alongside microbial iron reduction (Marquart et al., 2019). As a second example, methanogenesis and sulfate reduction have also been observed to coexist when substrates are available that one group can consume but the other cannot (Oremland and Polcin, 1982). Either way, use of methanogenesis as an energy source is thought to be limited to anoxic environments, including anoxic microenvironments within systems that are otherwise oxic (Angle et al., 2017).

All known microorganisms that use methanogenesis as an energy source are classified in Domain Archaea, Kingdom *Euryarchaeota*. Six orders within *Euryarchaeota* are long recognized to contain methanogens (Whitman et al., 2006): *Methanococcales*, *Methanopyrales*, *Methanobacteriales*, *Methanosarcinales*, *Methanomicrobiales*, *Methanocellales*. More recently, *Thermoplasmatales* has also been shown to contain methanogens (Borrel et al., 2013). Methanogens are thought to use a relatively small number of electron donors (Costa and Leigh, 2014). They can make methane by oxidizing dihydrogen (H_2) or formate ($HCOO^-$) and reducing carbon dioxide to methane (CH_4):

$$HCOO^- + H^+ \longleftrightarrow 0.25\ CH_4 + 0.75\ CO_2 + 0.5\ H_2O \quad (5.1.4.1)$$

$$H_2 + 0.25\ CO_2 \longleftrightarrow 0.25\ CH_4 + 0.5\ H_2O \quad (5.1.4.2)$$

This pathway is known as carbon dioxide reduction or hydrogenotrophic methanogenesis and most methanogens are thought to be capable of it.

Secondly, methanogens can make methane from acetate:

$$CH_3COO^- + H^+ \longleftrightarrow CH_4 + CO_2 \quad (5.1.4.3)$$

The reaction, known as acetoclastic methanogenesis, splits acetate into a carboxyl group, which is oxidized to carbon dioxide, and a methyl group, which is reduced to methane. Only members of the order *Methanosarcinales* can catalyze the reaction. About 1 gigaton of methane is estimated to be generated each year and roughly two-thirds of that sum is thought to be produced by acetoclastic methanogenesis (Thauer, 1998). Thus, *Methanosarcinales* species appear to be the biggest producers of microbial methane on Earth.

Lastly, methanogens can also make methane from methyl compounds such as methanol, methylamines, and dimethylsulfide. An example reaction with methanol (CH_3OH) is as follows:

$$CH_3OH \longleftrightarrow 0.75\ CH_4 + 0.25\ CO_2 + 0.5\ H_2O \quad (5.1.4.4)$$

Use of methyl compounds to make methane is known as methylotrophic methanogenesis.

These three pathways are thought to be the main pathways of methanogenesis as a form of catabolism. However, it can be hard to generalize about the capabilities of microorganisms. They can do many things, and much remains to be learned. Kurth et al. (2021) recently demonstrated that a strain of *Methermicoccus shengliensis* was able to make methane by consuming methoxylated aromatic compounds, which are widespread in the subsurface. In addition, methanogens can also receive electrons from other microorganisms through direct interspecies electron transfer (DIET). In the latter case, electrons are transferred from one group to the methanogen via conductive pili and direct contact between cells (Rotaru et al., 2014b, 2014a). Both of these pathways have the potential to have broad environmental significance, but whether that is the case has not yet been demonstrated. Either way, these examples are good reminders that the three main pathways are not the only options available for methanogenic catabolism.

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5.1.5: Acetogenesis

Acetogenesis refers to production of acetate by microorganisms. Some fermenters and syntrophs produce acetate as illustrated in Section 5.1.3. However, microorganisms that are specifically referred to as acetogens are strictly anaerobic organisms that are able to reduce carbon dioxide to acetate via the acetyl coenzyme A (acetyl-CoA) pathway (=Wood-Ljungdahl pathway) (Müller, 2003). They are also sometimes referred to as "homoacetogens", which refers to the fact that they produce acetate as their only fermentation product (Ragsdale and Pierce, 2008).

Acetogens can grow using a variety of electron donors, including dihydrogen, carbon monoxide, formate, and glucose. Example reactions with dihydrogen and glucose follow (Ragsdale and Pierce, 2008):

$$2\ CO_2 + 4\ H_2 \longleftrightarrow \text{acetate} + H^+ + 2\ H_2O \tag{5.1.5.1}$$

$$\text{glucose} \longleftrightarrow 3\ \text{acetate} + 3\ H^+ \tag{5.1.5.2}$$

Most acetogens are classified in phylum *Firmicutes*. However, other groups that contain acetogens include *Spirochaetes*, *Deltaproteobacteria*, and *Acidobacteria* (Ragsdale and Pierce, 2008).

The activity of acetogens can increase the significance of microbial pathways that consume acetate. In methanogenic systems, for example, the activity of acetogens has the potential to increase the importance of aceticlastic methanogenesis relative to hydrogenotrophic methanogenesis (Conrad, 1999).

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5.1.6: Methanotrophy

Methanotrophy occurs when microorganisms use methane as their electron donor and sole source of carbon. Methane oxidation can be coupled to oxygen (O_2) reduction, as shown in the following example reaction:

$$CH_4 + 2\ O_2 \longleftrightarrow 2\ H_2O + CO_2 \tag{5.1.6.1}$$

Aerobic methanotrophs belong to the bacterial phyla *Proteobacteria* and *Verrucomicrobia* (Guerrero-Cruz et al., 2021).

In the absence of oxygen, anaerobic oxidation of methane (AOM) can be coupled to reduction of nitrite, nitrate, manganese, iron, and sulfate (Guerrero-Cruz et al., 2021) as illustrated in the following example reactions:

$$CH_4 + 1.6\ H^+ + 1.6\ NO_3^- \longleftrightarrow 2.8\ H_2O + CO_2 + 0.8\ N_2 \tag{5.1.6.2}$$
$$3\ CH_4 + 8\ H^+ + 8\ NO_2^- \longleftrightarrow 10\ H_2O + 3\ CO_2 + 4\ N_2 \tag{5.1.6.3}$$
$$CH_4 + 8\ Fe^{3+} + 2\ H_2O \longleftrightarrow CO_2 + 8\ Fe^{2+} + 8\ H^+ \tag{5.1.6.4}$$
$$CH_4 + H^+ + SO_4^{2-} \longleftrightarrow 2\ H_2O + CO_2 + HS^- \tag{5.1.6.5}$$

Anaerobic oxidation of methane coupled with sulfate reduction is catalyzed through the combined effort of anaerobic methanotrophic (ANME) archaea and sulfate-reducing bacteria. The anaerobic methanotrophic archaea oxidize the methane and transfer the electrons to the sulfate reducers, who put them on sulfate (Boetius et al., 2000; Martens and Berner, 1974; Timmers et al., 2016). Anaerobic methanotrophic archaea are related to methanogens of orders *Methanosarcinales* and *Methanomicrobiales*. The reaction catalyzed by anaerobic methanotrophic archaea uses the same biochemical pathway as methanogenesis, but in reverse (Timmers et al., 2017).

Similarly, bacteria and archaea can also both be involved in AOM coupled to nitrate reduction. Members of the archaeal family *Methanoperedenaceae* (formerly ANME group 2d) are capable of coupling anaerobic oxidation of methane to the reduction of nitrate to ammonia (Haroon et al., 2013), and bacteria in the candidate genus *Methylomirabilis* can couple anaerobic oxidation of methane to nitrite reduction (Versantvoort et al., 2018). The nitrite used by *Methylomirabilis* can be produced as an intermediate in nitrate reduction by *Methanoperedenaceae*, although the nitrate could come from other sources as well. Thus, the two groups do not necessarily need to work together, as is the case for anaerobic oxidation of methane coupled with sulfate reduction.

Where nitrate is not available, members of archaeal family *Methanoperedenaceae* are also capable of coupling anaerobic oxidation of methane to reduction of iron and manganese in ferrihydrite and birnessite, respectively (Ettwig et al., 2016). As with anaerobic oxidation of methane coupled to nitrate reduction, their activity is not dependent on a bacterial partner.

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5.2: Nitrogen cycle

In the nitrogen cycle, microorganisms cycle nitrogen among compounds with oxidation states ranging from -3 to $+5$. As discussed in Chapter 14, high concentrations of nitrogen compounds, especially nitrate, are a major water quality concern worldwide (Bijay-Singh and Craswell, 2021; Burgin and Hamilton, 2007). Denitrification is one of the main pathways of nitrate removal from aqueous systems (Fig. 5.3). As such, the pathway has received a lot of attention from the scientific community. However, to understand the fate of nitrogen in aqueous systems and improve water resource management, we need to consider the full range of microbial nitrogen transformations (Burgin and Hamilton, 2007).

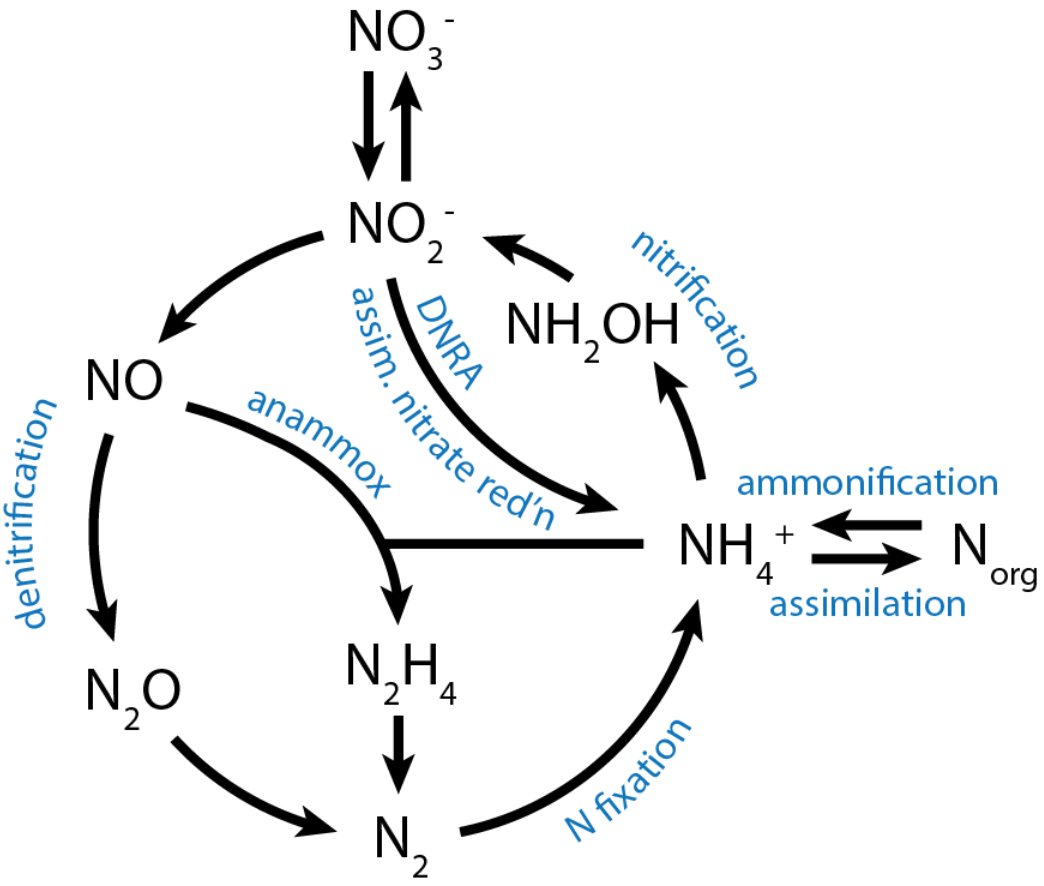


Figure 5.3: Microbial contributions to the nitrogen cycle. Figure after Fig. 1 of Jetten (2008). Microbial reactions are identified in blue font. N_{org} represents nitrogen in organic compounds.
https://commons.wikimedia.org/wiki/File:Microbial_nitrogen_cycle.png

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5.2.1: Nitrogen fixation

Nitrogen-fixation occurs when microorganisms convert dinitrogen (N_2) to ammonia (NH_3) as illustrated in the following half reaction:

$$N_2 + 8\ H^+ + 8\ e^- \longleftrightarrow 2\ NH_3 + H_2 \tag{5.2.1.1}$$

Electrons necessary to reduce dinitrogen are provided by an electron carrier molecule, reduced ferrodoxin. The reaction is catalyzed by the nitrogenase complex, which consists of two proteins: a reductase and a nitrogenase. During the reaction, the electrons are deposited on the reductase, an iron protein, and then transferred to nitrogenase, a molybdenum-iron protein, where nitrogen is reduced to ammonia (Berg et al., 2002).

Only some bacteria and archaea are able to catalyze nitrogen fixation. The reaction does not provide them with energy. Instead, they have to use energy to drive the reaction forward (16 mol ATP per mol of N_2). Why would they do it?

Ammonia as well as nitrate are important sources of nitrogen for plants and microorganisms and organisms need quite a lot of nitrogen. In fact, nitrogen is the fourth most abundant element in biomass (see Chapter 7). Thus, by fixing nitrogen, the microorganisms provide themselves and other organisms with a nutrient that is critical for synthesizing biomass.

Some nitrogen fixers live symbiotically with plants. Examples of symbiotic bacteria include *Rhizobium*, *Frankia*, and some species of *Azospirillum*. These species enter the roots of host plants, where they multiply and stimulate formation of root nodules, which provide a shelter for the microorganisms. The plants benefit from interactions with the nitrogen fixers because they obtain usable nitrogen. The microorganisms benefit because they receive sugars produced by the plant via photosynthesis.

In addition to symbiotic nitrogen fixers, some nitrogen fixers are free-living. They live in close proximity to plant roots and also consume some of the sugar produced by plants. As such, free-living nitrogen fixation may be considered a subcategory of symbiotic nitrogen fixation, although the species involved are distinct and more diverse than plant-hosted nitrogen fixers (Smercina et al., 2019). Bacterial phyla that are known to contain some free-living nitrogen fixers include *Alphaproteobacteria*, *Betaproteobacteria*, *Deltaproteobacteria*, *Gammaproteobacteria*, *Firmicutes*, *Cyanobacteria*, and green-sulfur bacteria (Gaby and Buckley, 2015).

The symbiotic relationship between nitrogen fixers and some plants provides the basis for crop rotations. By this approach, plants hosting nitrogen fixers are grown periodically to increase the quantity of biologically available nitrogen in the crop soil. For example, farmers in the Midwestern US often rotate soybeans and corn. Soybean plants form root nodules that host nitrogen fixers. As such, they increase soil nitrogen content, which helps offsets the nitrogen demand of corn the following year(s).

Farmers have used crop rotations for thousands of years and continue to do so. However, early in the twentieth century, the Haber-Bosch process was developed, which is a chemical means of fixing nitrogen. Widespread use of nitrogen fertilizer produced by this process has greatly boosted food production worldwide but also greatly altered nitrogen cycling. Fluxes of nitrogen from Haber-Bosch as well as fossil fuel combustion have caused a doubling of the turnover rate for the global nitrogen cycle (Gruber and Galloway, 2008).

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5.2.2: Ammonification

Ammonia supplied by nitrogen-fixing microorganisms is not the only source of biologically available nitrogen available in soils and sediments. Another option is the organic nitrogen in dead biomass and animal waste (e.g., amino acids and nucleic acids; represented as N_{org} in Fig. 5.3). During ammonification, microorganisms use enzymes to extract amino groups (NH_2) of organic nitrogen and convert them to ammonia.

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5.2.3: Nitrification

During nitrification, ammonium is ultimately oxidized to nitrate with oxygen as the electron acceptor. The reaction is catalyzed by aerobic microorganisms and has two parts, which were previously thought to be catalyzed exclusively by different groups of microbes (Fig. 5.3). For the first part, ammonium is oxidized by nitrite with hydroxylamine (NH_2OH) as an intermediate, according to the following net reaction.

$$NH_3 + 1.5\ O_2 \longleftrightarrow NO_2^- + H^+ + H_2O \tag{5.2.3.1}$$

The reaction is catalyzed by ammonia-oxidizing bacteria (AOB) and archaea (AOA) (Könneke et al., 2005; Purkhold et al., 2000; Tourna et al., 2011). For the second part, nitrite is oxidized to nitrate:

$$NO_2^- + 0.5\ O_2 \longleftrightarrow NO_3^- \tag{5.2.3.2}$$

The reaction is catalyzed by nitrite oxidizing bacteria (NOB), which are mainly classified in genera *Nitrobacter* and *Nitrococcus*.

More recent work has shown that at least at least two *Nitrospira* species can do both steps themselves (van Kessel et al., 2015). The complete oxidation of ammonia to nitrate in one organism is referred to as comammox (complete ammonia oxidation).

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5.2.4: Anaerobic ammonia oxidation (anammox)

Anammox provides an anaerobic pathway for ammonia oxidation. In the reaction, nitrite produced during nitrification (reaction (5.2.3.1)) is reduced with ammonia as the electron donor, as shown in the following example reaction:

$$\mathrm{NH_4^+ + NO_2^- \longleftrightarrow N_2 + 2\ H_2O} \tag{5.2.4.1}$$

The reaction proceeds through two intermediate compounds, nitric oxide (NO) and hydrazine ($\mathrm{N_2H_4}$) (Kartal and Keltjens, 2016; van Niftrik and Jetten, 2012) (Fig. 5.3). Interestingly, hydrazine is used as a rocket fuel.

So far, anammox has only been demonstrated in members of the *Brocadiales*, a bacterial order within phylum *Planctomycetes* (Jetten et al., 2010; Strous et al., 1999). Their metabolism is chemolithotrophic and has been documented in a wide range of environments, including marine sediments, aquifers, and freshwater aquatic habitats. In marine environments, it has been shown to be capable of consuming more than 50% of the fixed nitrogen in dead biomass (Dalsgaard et al., 2003; Kuypers et al., 2005; Thamdrup and Dalsgaard, 2002). As a second example, Kumar et al. (2017) found that anammox was response for 83% of the nitrogen loss from low-oxygen zones of a pristine limestone aquifer in Germany.

Anammox involves both oxidized and reduced forms of nitrogen and may be particularly common near transitions between oxic and anoxic conditions (Kuenen, 2020; Zhu et al., 2013). The nitrite can be generated by nitrification and denitrification and the ammonium from ammonification, nitrogen fixation, and dissimilatory nitrate reduction to ammonia (DNRA).

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5.2.5: Denitrification

Nitrate can be reduced for assimilatory or dissimilatory purposes. For assimilatory nitrate reduction, nitrate is reduced to ammonia, which can then be used to build biological molecules that contain nitrogen (N_{org}) (Fig. 5.3). For dissimilatory reduction, there are two pathways: denitrification and dissimilatory nitrate reduction to ammonia (DNRA; see section 5.2.6).

Denitrification involves the reduction of nitrate via a chain of microbial reactions ultimately to dinitrogen ($\mathbf{N_2}$), as illustrated by the following reduction half reactions:

$$\mathbf{NO_3^- + 2\ H^+ + 2\ e^- \longleftrightarrow NO_2^- + H_2O} \quad (5.2.5.1)$$

$$\mathbf{NO_2^- + 2\ H^+ + e^- \longleftrightarrow NO + H_2O} \quad (5.2.5.2)$$

$$\mathbf{2\ NO + 2\ H^+ + 2\ e^- \longleftrightarrow N_2O + H_2O} \quad (5.2.5.3)$$

$$\mathbf{N_2O + 2\ H^+ + 2\ e^- \longleftrightarrow N_2 + H_2O} \quad (5.2.5.4)$$

Denitrifying microorganisms can reduce nitrate rapidly to dinitrogen under favorable conditions. However, the chain of reactions may also stop at one of the intermediate nitrogen species such as nitrous oxide ($\mathbf{N_2O}$) or nitric oxide ($\mathbf{NO}$). Electrons necessary to drive the reduction reactions can come from a wide range of organic compounds as well as dihydrogen ($\mathbf{H_2}$), ferrous iron ($\mathbf{Fe(II)}$), reduced sulfur compounds (e.g., sulfide, elemental sulfur, and thiosulfate), iron sulfide solid-phases (e.g., $\mathbf{FeS}$), arsenite ($\mathbf{As(III)}$), and reduced manganese ($\mathbf{Mn(II)}$) (Pang and Wang, 2021). Denitrification is thought to primarily occur in anoxic environments. However, some bacteria can use the reaction in oxic environments (Ji et al., 2015).

Denitrification can be carried out by numerous groups of Bacteria, including organotrophs, lithotrophs, phototrophs (Eldor, 2015) as well as Archaea and Eukaryotes. Some eukaryotic microorganisms are able to store nitrate intracellularly and even use it for dissimilatory nitrate reduction where oxygen is not available (Kamp et al., 2015)

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5.2.6: Dissimilatory nitrate reduction to ammonia (DNRA)

DNRA is a two-step reaction in which nitrate is reduced to nitrite and then nitrite is reduced to ammonium, as illustrated in the following reduction half-reactions:

$$\mathrm{NO_3^-} + 2\ \mathrm{H^+} + 2\ e^- \longleftrightarrow \mathrm{NO_2^-} + \mathrm{H_2O} \tag{5.2.6.1}$$

$$\mathrm{NO_2^-} + 8\ \mathrm{H^+} + 6\ e^- \longleftrightarrow \mathrm{NH_4^+} + 2\ \mathrm{H_2O} \tag{5.2.6.2}$$

Like denitrification, the reaction occurs in anoxic environments and can be catalyzed by a wide range of microorganisms, including Bacteria and Archaea, with organic compounds, dihydrogen, ferrous iron, and sulfide as electron donors (Bu et al., 2017; Kuypers et al., 2018; Pan et al., 2020).

DNRA appears to be less common than denitrification in natural environments. One environmental factor that helps determine which type of nitrate reduction occurs is the carbon/nitrogen ratio of the environment (Hardison et al., 2015; Kraft et al., 2014; Rivett et al., 2008; Rütting et al., 2011; van den Berg et al., 2017). DNRA bacteria appear to have an advantage if nitrate supply is limited but electron donors are abundant. However, if electron donor supply is low relative to nitrate supply, denitrification appears to be favored.

Which form of dissimilatory nitrate reduction occurs, denitrification or DNRA, will determine if the nitrate N remains in the system and widely available to the microbial community (e.g., as $\mathrm{NH_4^+}$) or if the nitrate nitrogen can be lost from the environment as a nitrogen gas (Burgin and Hamilton, 2007). Thus, there is much interest in knowing environmental controls on the two microbial metabolic pathways.

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5.3: Iron cycle

The iron cycle is relatively simple in some ways, given that it only involves two oxidation states, $+2$ and $+3$, which we can specifically refer to as ferrous iron and ferric iron, respectively, or $\mathrm{Fe(II)}$ and $\mathrm{Fe(III)}$ (Fig. 5.4). However, the cycle typically involves mineral phases, which introduce some complexity to the geochemical and microbial aspects of the cycle.

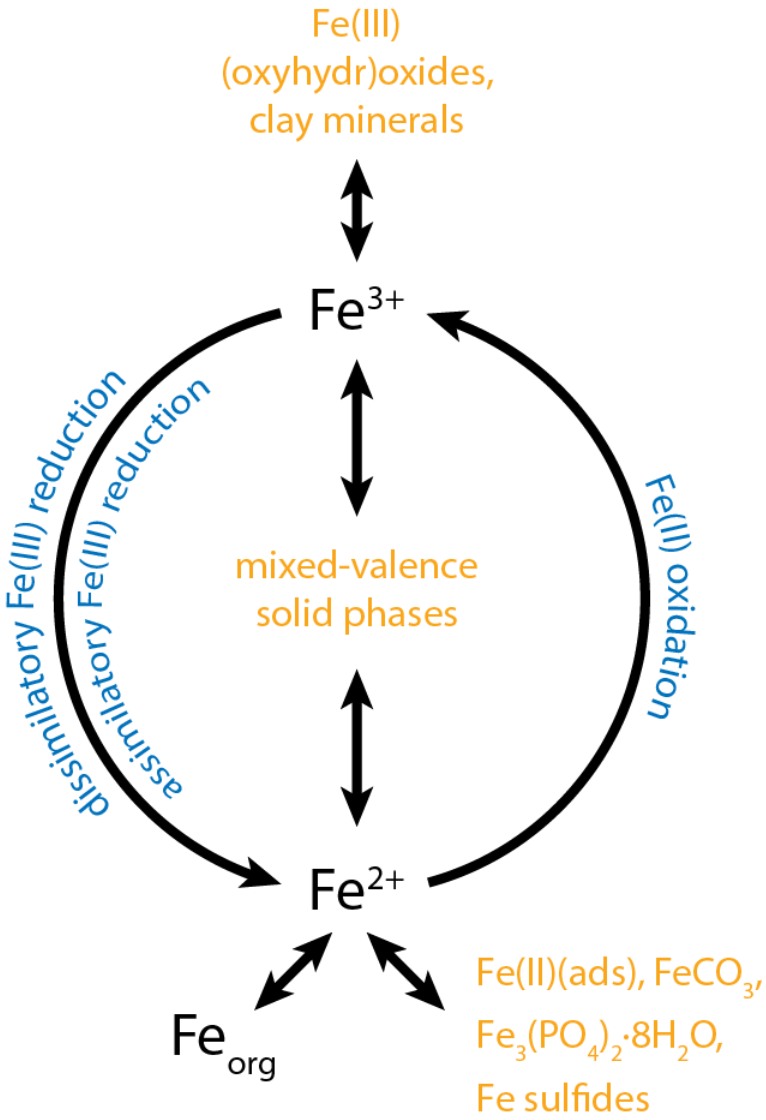


Figure 5.4: Microbial contributions to the global iron cycle. Microbial reactions are labeled in blue font and solid phases are in orange font. Fe_{org} represents iron in organic compounds, $Fe(II)_{ads}$ is adsorbed ferrous iron whereas $\mathrm{FeCO_3}$ and $\mathrm{Fe_3(PO_4)_2 \cdot 8H_2O}$ are chemical formulas for siderite and vivianite, respectively. This figure is based on figure 1 of Schröder et al. (2003). https://commons.wikimedia.org/wiki/File:Microbial_iron_cycle.png

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5.3.1: Ferric iron reduction

Microorganisms can reduce ferric iron ($Fe(III)$) to ferrous iron ($Fe(II)$) for dissimilatory or assimilatory purposes. Assimilatory iron reduction provides iron needed to form proteins that are then used to build some essential enzymes (Ferousi et al., 2017; Schröder et al., 2003). In fact, Ferousi et al. (2017) notes that iron is the most abundant transition metal in organisms. Reflecting this need, some microorganisms can also store iron in the form of ferritin and bacterioferritin (Andrews, 1998).

Dissimilatory iron reduction typically occurs in anoxic environments that lack nitrate. Electron donors that can be used by iron-reducing microorganisms include simple organics and dihydrogen (H_2) (Weber et al., 2006). In addition, ferric iron can also be reduced by reacting with sulfide or reduced humic substances (Canfield, 1989; Lovley et al., 1996; Pyzik and Sommer, 1981; Roden et al., 2010). The sulfide and reduced humic substances that can reduce ferric iron are often products of microbial reactions. However, reduction of iron by these compounds is typically referred to as abiotic iron reduction because the iron reduction reaction itself is not directly catalyzed by microorganisms.

At pH greater than 3, ferric iron solubility is low (Bird et al., 2011). Thus, instead of respiring dissolved ferric iron, the ferric iron available for dissimilatory metabolism commonly exists as a solid phase, including ferric hydroxide, oxide, and oxyhydroxide phases, which are hereafter referred to as (oxyhydr)oxide minerals. In addition to these minerals, microorganisms can also reduce ferric iron in some clay minerals (Dong et al., 2009). The following example reactions include acetate as the electron donor and some common (oxyhydr)oxide minerals (hematite (Fe_2O_3), goethite ($FeOOH$), ferrihydrite (approximated here as $Fe(OH)_3$):

$$CH_3COO^- + 15\ H^+ + 4\ Fe_2O_3 \longleftrightarrow 2\ HCO_3^- + 8\ H_2O + 8\ Fe^{2+} \quad (5.3.1.1)$$

$$CH_3COO^- + 15\ H^+ + 8\ FeOOH \longleftrightarrow 2\ HCO_3^- + 12\ H_2O + 8\ Fe^{2+} \quad (5.3.1.2)$$

$$CH_3COO^- + 15\ H^+ + 8\ Fe(OH)_3 \longleftrightarrow 2\ HCO_3^- + 20\ H_2O + 8\ Fe^{2+} \quad (5.3.1.3)$$

In general, poorly crystalline phases such as ferrihydrite tend to have higher surface areas and solubilities than more stable phases, such as goethite and hematite. These differences can affect the rate at which microorganisms can use them as electron acceptors. Specifically, iron reduction rates have been found to increase with (oxyhdr)oxide surface area and solubility (Bonneville et al., 2009, 2004; Cutting et al., 2009; Larsen and Postma, 2001; Roden, 2006, 2003).

Reflecting these relationships, some previous studies have found that (oxhydr)oxide phases with high crystallinities, such as goethite and hematite, can only support small amounts of microbial iron reduction. However, ferric (oxyhydr)oxide reactivity varies widely, reflecting variation in mineral properties as well as environmental conditions (Konhauser et al., 2011). For example, recent laboratory studies found low rates of goethite reduction in bioreactors with basic pH but in complementary reactors with acidic pH, extensive goethite reduction occurred (Kirk et al., 2013; Marquart et al., 2019; Paper et al., 2021). These differences may reflect the influence of environmental pH on the free energy yield of goethite reduction as well as changes in reaction mechanisms, as discussed in chapters 8 and 10. Either way, the results show that environmental pH can influence the extent to which microorganisms can reduce highly crystalline (oxhydr)oxides. Caution should be taken in extending conclusions drawn from iron-reducing cultures with basic pH to systems with acidic pH.

Solid-phase sources of ferric iron cannot be transported into the cell. Therefore, in order to use them as electron acceptors, iron-reducing microorganisms have to be able to transfer electrons outside of the cell. Microorganisms can transfer electrons externally through proteins on their surface, through electrically conductive pili (e-pili), by cycling electron shuttle compounds, and by forming chelators that solubilize ferric iron (Fig. 5.5). Electron shuttle compounds include flavins, phenazines, and humic substances (Lovley and Holmes, 2021; Piepenbrock et al., 2014). The microorganism transfer electrons to the shuttle, which can then transfer the electrons to the mineral. Chelators are organic compounds that tightly bind to ferric iron and other metal ions, allowing them to become soluble.

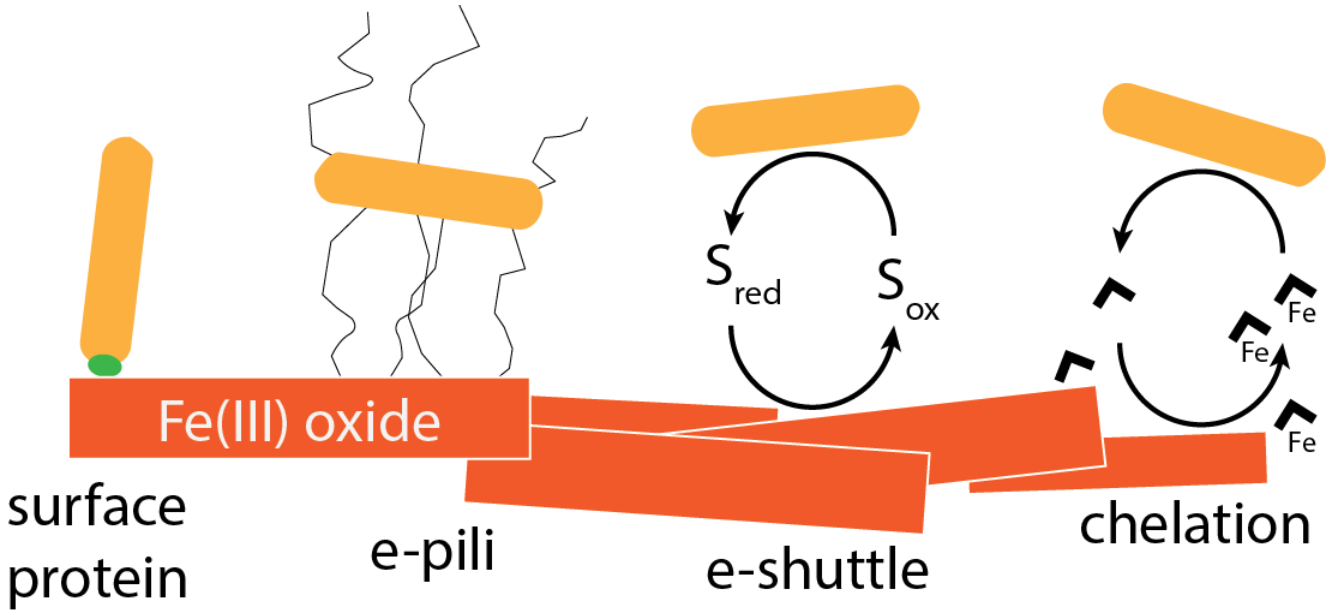


Figure 5.5: Potential strategies for extracellular electron transfer. The surface protein is represented by the green oval. S_{red} and S_{ox} represent reduced and oxidized electron shuttle compounds, respectively. Figure based on figure 1 of Gralnick and Newman (2007) and figure 4 of Lovely and Holmes (2021).
https://commons.wikimedia.org/wiki/File:External_electron_transfer_strategies.png

Regardless of the mechanism, ferrous iron is ultimately produced by ferric iron reduction. Some of the ferrous iron may accumulate in solution, reflecting its high solubility compared to ferric iron. It can adsorb onto what remains of the ferric mineral and other minerals in the environment (Benner et al., 2002; Roden and Urrutia, 1999; Urrutia et al., 1999) $(Fe(II)_{ads}$ in Fig. 5.4). It can also precipitate as a mineral. Example minerals that can form as a result of iron reduction include mackinawite (FeS) and other sulfide minerals, siderite ($FeCO_3$), vivianite ($Fe_3(PO_4)_2 \cdot 8\,H_2O$), and mixed-valence phases including magnetite (Fe_3O_4) and green rust. We will discuss further aspects of microbial mineral precipitation in Chapter 12.

Lastly, many different species of microorganisms are able to use ferric iron reduction as a source of energy (Hori et al., 2015; Lentini et al., 2012; Weber et al., 2006). Among the most widely studied are *Geobacter metallireducens* and *Shewanella putrefaciens*. Some microorganisms that can reduce iron can also use other electron acceptors including sulfur compounds and uranium (Holmes et al., 2004; Lovley et al., 1993). Some can also partner with methanogens and help produce methane via interspecies electron transfer (Rotaru et al., 2014a, 2014b). In this case, rather than transfer the electrons to a ferric iron mineral, the 'iron reducer' transfers electrons to a methanogen, which uses them to reduce carbon dioxide and make methane.

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5.3.2: Ferrous iron oxidation

Microorganisms can oxidize ferrous iron to ferric iron a few different ways. Chemolithotrophic microorganisms can couple ferrous iron oxidation with reduction of oxygen or nitrate, as shown in the following reactions:

$$Fe^{2+} + H^+ + 0.25\ O_2 \longleftrightarrow Fe^{3+} + 0.5\ H_2O \quad (5.3.2.1)$$

$$Fe^{2+} + 1.2\ H^+ + 0.2\ NO_3^- \longleftrightarrow Fe^{3+} + 0.1\ N_2 + 0.6\ H_2O \quad (5.3.2.2)$$

Iron oxidation coupled with oxygen reduction (reaction (5.3.2.1)) is not always biologically catalyzed. The reaction can occur at a rapid pace in solutions with relatively high oxygen concentrations and near-neutral pH. Thus, use of that reaction by microorganisms is largely limited to environments that contain water with low oxygen content and/or acidic pH (Bird et al., 2011; Emerson, 2012; Sobolev and Roden, 2001). Similarly, ferrous iron can also abiotically react with nitrite produced during nitrate reduction (Klueglein Nicole et al., 2014).

In addition to chemolithotrophs, anoxic phototrophs can oxidize ferrous iron to provide electrons for carbon fixation, as discussed in Chapter 4. An example reaction with biomass represented as CH_2O follows:

$$HCO_3^- + 4\ Fe^{2+} + 5\ H^+ \longleftrightarrow CH_2O + 4\ Fe^{3+} + 2\ H_2O \quad (5.3.2.3)$$

Many microorganisms are capable of driving these reactions forward. Some chemolithotrophic species capable of iron oxidation include *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Gallionella ferruginea*. Phototrophic iron oxidation has been documented in purple nonsulfur, purple sulfur, and green sulfur bacteria (Bird et al., 2011). For more details, Bryce et al. (2018) and Emerson et al. (2010) provide recent reviews of the ecology of iron oxidizers.

In solutions with pH greater than 3, the ferric iron these iron-oxidizing microorganisms generate is largely insoluble and forms iron (oxyhdr)oxide minerals, as discussed in Chapter 12 and mentioned in Section 5.3.1. For this reason, iron oxidation may often be catalyzed outside of the cell to avoid clogging as well as acidifying the cytoplasm (Bird et al., 2011; Cosmidis and Benzerara, 2022). Also, in environments where ferrous iron oxidation occurs, the upper surface of the solution often has an oily sheen (Fig. 5.6). That sheen is actually a film of nanocrystalline (oxyhydr)oxide minerals, which is known as schwimmeisen.



Figure **5.6**: Iron (oxhydr)oxides forming on the cut bank of a stream in Starved Rock State Park, Illinois, USA. Ferrous iron is likely being generated by ferric iron reduction in the subsurface adjacent to the stream. Groundwater flow is then transporting dissolved ferrous iron to the streambed, where it is oxidizing and precipitating.
https://commons.wikimedia.org/wiki/File:Metal_oxidation_on_a_cut_bank.jpg

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5.4: Sulfur cycle

In the sulfur cycle, microorganisms cycle sulfur among compounds with oxidation states ranging from -2 and $+6$. Reflecting this broad range of oxidation states, sulfur compounds participate in a wide variety of oxidation reduction reactions, which results in a complex cycle (Fig. 5.7).

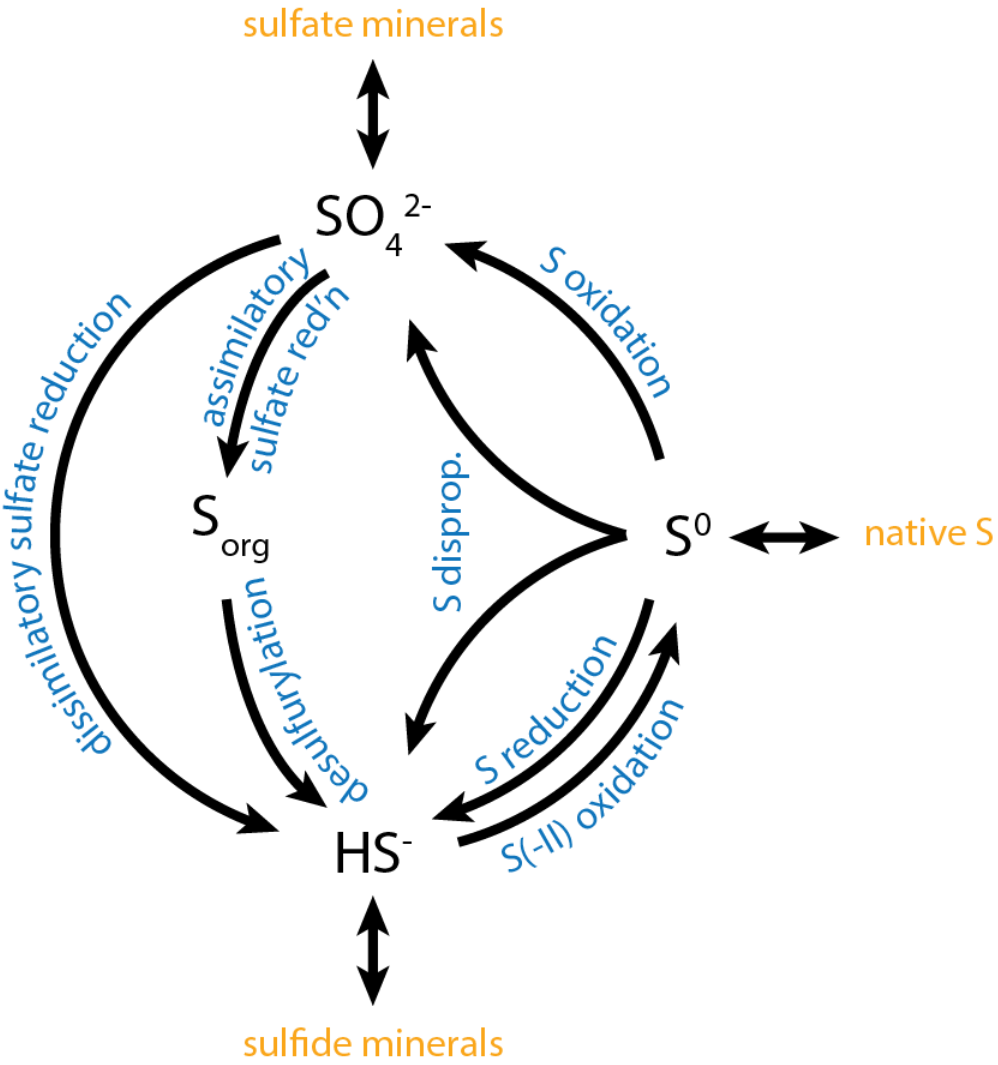


Figure 5.7: Microbial contributions to the global sulfur cycle. Microbial reactions are labeled in blue font and solid phases are in orange font. S_{org} represents sulfur in organic compounds. For simplicity, elemental sulfur (S^0) represents one of several sulfur compounds with oxidation state between -2 and $+6$ that can form during sulfide oxidation. At least some of these intermediate sulfur species can be disproportionated into sulfate and sulfide. Figure based on figure 1 of Barton et al. (2014) and figure 2 of Muyzer and Stams (2008).
https://commons.wikimedia.org/wiki/File:Microbial_sulfur_cycle.png

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5.4.1: Sulfate reduction

Microorganisms can reduce sulfate to sulfide ($S(-II)$) for assimilatory or dissimilatory purposes. During assimilation, the sulfide is incorporated into sulfur-containing amino acids: methionine, cysteine, homocysteine, and taurine (Brosnan and Brosnan, 2006). During dissimilatory sulfate reduction, the sulfide is released into the environment, where it can speciates among H_2S, HS^-, and S^{2-} and other aqueous species as determined by solution pH and composition. Assimilatory sulfate reduction occurs in anoxic and oxic environments. However, dissimilatory sulfate reduction primarily occurs in anoxic environments that lack nitrate, much like ferric iron reduction.

Dissimilatory sulfate reduction is a major driver of the global carbon cycle. In marine sediments, for example, it is estimated to account for more than 50% of the organic matter oxidation (Jorgensen, 1982). Electron donors used by sulfate-reducing microorganisms include dihydrogen and simple organics produced by fermenting and syntrophic microbes, such as ethanol, formate, lactate, pyruvate, malate, succinate, acetate, benzoate, and phenol (Muyzer and Stams, 2008). Some example reactions follow:

$$4\ H_2 + SO_4^{2-} + H^+ \longleftrightarrow 4\ H_2O + HS^- \quad (5.4.1.1)$$

$$2\ HCOO^- + SO_4^{2-} + H^+ \longleftrightarrow 2\ HCO_3^- + HS^- \quad (5.4.1.2)$$

$$CH_3COO^- + SO_4^{2-} \longleftrightarrow 2\ HCO_3^- + HS^- \quad (5.4.1.3)$$

$$2\ CH_3CHOHCOO^- + SO_4^{2-} \longleftrightarrow 2\ CH_3COO^- + 2\ HCO_3^- + HS^- + H^+ \quad (5.4.1.4)$$

$$4\ CH_3CH_2COO^- + 3\ SO_4^{2-} \longleftrightarrow 4CH_3COO^- + 4\ HCO_3^- + 3\ HS^- + H^+ \quad (5.4.1.5)$$

$$CH_4 + SO_4^{2-} \longleftrightarrow HCO_3^- + HS^- + H_2O \quad (5.4.1.6)$$

Some sulfate reducers degrade organics completely to carbon dioxide/bicarbonate whereas others degrade organic compounds incompletely to acetate (reactions (5.4.1.4) and (5.4.1.5)).

The sulfide produced by dissimilatory sulfate reduction can accumulate in solutions and gas phases. It may also form sulfide minerals. Sulfide can precipitate with numerous transition metals and metalloids. Precipitation with iron is common in the terrestrial subsurface, where iron is commonly present and iron reduction may also be occurring (Berner, 1970; Kirk et al., 2016; Postma and Jakobsen, 1996). Typically, the first iron-sulfide to form in low-temperature systems is mackinawite (FeS), which can transform into greigite (Fe_3S_4) and then pyrite (FeS_2) over time (Benning et al., 2000). More information about sulfide biomineralization is available in Section 12.1.4.

Numerous organisms can use sulfate reduction as a source of energy. Many of the groups that are capable of sulfate reduction include ‘desulf’ in their name. For example, *Desulfovibrio* is a well-known genus of gram-negative bacteria that can use sulfate reduction in dissimilatory metabolism (Devereux et al., 1990). Most microorganisms capable of sulfate reduction belong to five lineages of Bacteria and two lineages of Archaea (Muyzer and Stams, 2008). Bacterial groups include genera within *Deltaproteobacteria*, *Clostridia*, *Nitrospirae*, *Thermodesulfobacteria*, and *Thermodesulfobiaceae* (Muyzer and Stams, 2008). Archaeal groups include the genus *Archaeoglobus* in *Euryarchaeota* and the genera *Thermocladium* and *Caldirvirga* in *Crenarchaeota* (Muyzer and Stams, 2008). However, more recent research by Anantharaman et al (2018) indicates that, in addition to these well-recognized groups, many other lineages contain species capable of dissimilatory sulfate reduction.

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5.4.2: Desulfurylation

Desulfurylation occurs when microorganisms break down sulfur-containing proteins in dead biomass and produce sulfide (Fig. 5.7).

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5.4.3: Oxidation of sulfide and intermediate sulfur compounds

Reduced sulfur compounds are those in which sulfur has an oxidation state less than $+6$. That includes the sulfide produced by dissimilatory sulfate reduction and desulfurylation reactions as well as sulfur compounds with intermediate oxidation states (between -2 and $+6$) such as elemental sulfur (S^0), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}), dithionite ($S_2O_4^{2-}$), tetrathionate ($S_4O_6^{2-}$), and polysulfide compounds (S_n^{2-}). Intermediate sulfur species are collectively represented by S^0 in Figure 5.7 and can be produced by incomplete oxidation of sulfide.

Chemotrophic and phototrophic microorganisms can use reduced sulfur species as electron donors in reactions that supply energy and fix carbon, respectively. Potential electron acceptors in the reactions include oxygen (O_2), nitrate, and ferric iron. Some example reactions with oxygen as the electron acceptor follow:

$$H_2S + 2\ O_2 \longleftrightarrow SO_4^{2-} + 2\ H^+ \quad (5.4.3.1)$$

$$S_2O_3^{2-} + H_2O + 2\ O_2 \longleftrightarrow 2\ SO_4^{2-} + 2\ H^+ \quad (5.4.3.2)$$

$$SO_3^{2-} + 0.5\ O_2 \longleftrightarrow SO_4^{2-} \quad (5.4.3.3)$$

$$S^0 + H_2O + 1.5\ O_2 \longleftrightarrow SO_4^{2-} + 2\ H^+ \quad (5.4.3.4)$$

Microorganisms capable of sulfur oxidation are found within all three domains of life. Among Bacteria, well-recognized groups that contain species capable of chemotrophic sulfur oxidation include *Thiobacillaceae* and *Beggiatoaceae* (Ehrlich and Newman, 2009). Filamentous members of the *Desulfobulbaceae*, known as cable bacteria, can oxidize sulfide by transferring electrons from sulfide to oxygen or nitrate over centimeter distances in sediments (Müller et al., 2020; Sandfeld et al., 2020). Thus, they can help cycle sulfur by forming an electrical connection across redox zones. Anoxygenic phototrophic Bacteria capable of sulfur oxidation have been identified have been identified in four groups: green sulfur bacteria (*Chlorobiaceae*), purple sulfur and non-sulfur bacteria, Gram-positive *Heliobacteria*, and filamentous and gliding green bacteria (*Chloroflexaceae*) (Barton et al., 2014). Among Archaea, *Sulfolobus* and *Acidianus* are widely studied groups capable of sulfur oxidation (Ehrlich and Newman, 2009). Lastly, some fungi are also able to oxidize sulfur (Li et al., 2010).

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5.4.4: Reduction of intermediate sulfur compounds

In addition to serving as electron donors, intermediate sulfur compounds can also serve as electron acceptors in anaerobic microbial reactions. Some example reactions with dihydrogen (H_2) as the electron donor follow:

$$S_2O_3^{2-} + 4\ H^+ \longleftrightarrow 3\ H_2O + 2\ HS^- \quad (5.4.4.1)$$

$$SO_3^{2-} + 3\ H_2 + H^+ \longleftrightarrow HS^- + 3\ H_2O \quad (5.4.4.2)$$

$$S^0 + H_2 \longleftrightarrow HS^- + H^+ \quad (5.4.4.3)$$

Some sulfate-reducing Bacteria can use intermediate sulfur compounds as an electron acceptor. However, the ability to use sulfate as an electron acceptor does not guarantee the ability to use intermediate sulfur species (Ehrlich and Newman, 2009). *Shewanella putrefaciens* and some *Clostridia*, for example, cannot reduce sulfate but can reduce some intermediate sulfur compounds.

Similarly, many microorganisms that are capable of using ferric iron as their electron acceptor can also use intermediate sulfur compounds. Examples include some species within *Shewanella*, *Desulfuromonas*, *Geobacter*, and *Pelobacter* (Flynn et al., 2014; Lovley et al., 1995).

In addition to Bacteria, some Archaea and Eukaryotes can also reduce intermediate sulfur compounds. Some thermophilic Archaea can grow autotrophically on sulfur using dihydrogen or methane as their electron donor (Ehrlich and Newman, 2009; Stetter et al., 1986). Among Eukaryotes, some fungi can reduce intermediate sulfur species. For example, Ehrlich and Fox (1967) identified two strains of *Rhodotorula* and one of *Trichosporon* in acid-mine drainage that could reduce sulfur to sulfide with glucose as the electron donor.

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5.4.5: Sulfur disproportionation

A disproportionation reaction is a type of redox reaction in which one compound of intermediate oxidation state is converted into two compounds, one that is more reduced and one that is more oxidized than the initial compound. Thus, fermentation is a type of disproportionation (Bak and Cypionka, 1987). Disproportionation reactions are also sometimes referred to as dismutations.

Some chemolithotrophic microorganisms can disproportionate sulfur compounds with intermediate oxidation states, as shown in the following example reactions with thiosulfate $(S_2O_3^{2-})$, sulfite (SO_3^{2-}), and elemental sulfur (S^0) (Bak and Cypionka, 1987; Finster, 2008; Thamdrup et al., 1993):

$$S_2O_3^{2-} + H_2O \leftrightarrow SO_4^{2-} + HS^- + H^+ \quad (5.4.5.1)$$

$$4\ SO_3^{2-} + H^+ \leftrightarrow 3\ SO_4^{2-} + HS^- \quad (5.4.5.2)$$

$$4\ S^0 + 4\ H_2O \leftrightarrow SO_4^{2-} + 3\ HS^- + 5\ H^+ \quad (5.4.5.3)$$

The reactions are essentially a combination of the microbial reactions in the two sections immediately above: intermediate sulfur species are both oxidized and reduced. Microorganisms that have found to be capable of using these reactions to support growth are primarily within bacterial class *Deltaproteobacteria*, including *Desulfobacter*, *Desulfococcus*, *Desulfotomaculum*, *Desulfovibrio*, *Desulfomonile*, *Desulfobulbus*, *Desulfofustis*, and *Desulfocapsa* (Finster, 2008).

The extent to which elemental sulfur disproportionation can occur appears to depend on the availability of elements that can scavenge sulfide. Thamdrup et al. (1993) found that elemental sulfur disproportionation only proceeded significantly if a sulfide sink such as iron or manganese were present, which can cause precipitation of metal sulfide phases. Similarly, Müller et al. (2020) found that cable Bacteria of family *Desulfobulbaceae* were only able to disproportionate elemental sulfur and thiosulfate if low sulfide concentrations were maintained by ferrous iron. Low sulfide concentrations help ensure that the reaction remains thermodynamically favorable.

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5.5: Concept Check Questions

1. How does the carbon cycle connect to the nitrogen, iron, and sulfur cycles?
2. What role does bacterial fermentation and syntrophy play in methanogenesis by Archaea?
3. What microbial reactions can remove biologically available nitrogen from a system? Do any do it without generating greenhouse gas?
4. What are the two pathways of nitrate reduction? How do they differ?
5. What microbial reactions oxidize nitrogen? Can these reactions occur in an anoxic environment?
6. Is nitrogen fixation a catabolic reaction?
7. If iron reduction were occurring, how would the mineralogy of an environment change?
8. How can microorganisms respire solid phases?
9. What electron acceptors can be used by iron-oxidizing microorganisms?
10. Under what environmental conditions does abiotic iron oxidation occur rapidly? Are microorganisms typically involved in iron oxidation under such conditions? Why or why not?
11. How would you expect use of ferrous iron to differ between *Gallionella ferruginea* and purple nonsulfur bacteria?
12. What are two reasons microorganisms may catalyze sulfur oxidation?
13. Have you ever detected sulfate reduction without any analytical instruments?
14. What microbial contribution to the sulfur cycle both oxidizes and reduces sulfur?

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CHAPTER OVERVIEW

6: Basic Environmental Controls

> *"... as we continue to explore biogeochemical cycling we become increasingly aware of the subtle influences shaping these processes."*
> *- Kappler and Bryce (2017)*

As discussed in Chapter 5, microorganisms play many roles in driving the global biogeochemical cycles. You may be wondering what connects all of these contributions together and causes microbial communities to transition between different roles or functions. Why might microbial communities catalyze denitrification at one location but nitrification in another, for example? You may also be wondering what controls the identity of the microbial species that are catalyzing the reactions. Numerous species can catalyze denitrification, for example. Why might those responsible differ between environments?

Generally, there are no simple answers to these questions. To understand patterns of microbial activity in the environment, we need to consider the wide variety of ways that environments influence microbial communities. The chemical composition of an environment impacts physiological constraints on microorganisms and the thermodynamic and kinetic controls on their reactions. Biological interactions between species affect their ability to grow. Transport of mass in and out of microbial habitats impacts resource supply and waste accumulation. Among other potential controls, the stability of an environment, the extent to which conditions change over time, is also influential.

Part 2 of this book (Chapters 6-10) will help you start to make sense of these relationships and connect the various contributions of microorganisms within the global biogeochemical cycles. We begin with an overview of controls and then, in the next few chapters, turn our attention to nutrient and energy resources, thermodynamics, kinetics, and biological controls. Factors that influence the distribution of microbial activity are superimposed on one another and can be challenging to pull apart and yet, by doing so, we can better understand and potentially alter patterns of microbial activity in the environment.

6.1: Categories of controls
6.2: Basic properties of the environment
6.2.1: Temperature
6.2.2: Pressure
6.2.3: Oxygen
6.2.4: pH
6.2.5: Water availability
6.3: Transport processes
6.4: Environment stability
6.5: Dispersal mechanisms and barriers
6.6: Interactions between controls
6.7: Concept Check Questions
6.8: References

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6.1: Categories of controls

We can define two categories of processes that control microbial community assembly: deterministic and stochastic controls (Dini-Andreote et al., 2015; Ning et al., 2019). Deterministic controls are nonrandom and include basic physical and chemical properties of the environment (e.g., pH, temperature, water availability, salinity) and biological interactions. In contrast, stochastic controls are random. The outcome of an individual event cannot be predicted whereas the frequency of outcomes over numerous events follows a predictable distribution. Stochastic controls include random birth-death events, random chance for colonization, and random changes in organism abundances (i.e., ecological drift). In addition, geological processes such as fracture activity also have the potential to serve as stochastic controls (e.g., Zhang et al., 2022).

Part 2 of this book largely focuses on deterministic controls. We can think of them as environmental control knobs. However, we need to remember that even if we know approximately how a control knob will impact a community, the outcome of turning a knob may not always be identical because of stochastic processes. Both deterministic and stochastic processes influence the composition of microbial communities and the relative influences of each vary with time and location and among systems (DiniAndreote et al., 2015)

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6.2: Basic properties of the environment

The basic properties of an environment help determine who exists within the environment and their levels of activity. Those environmental properties include temperature, pH, salinity, and the availability of oxygen and water. Individual species can only grow within some fraction of the range of conditions where microbial life exists. Thus, these properties impact the distributions of microbial species on and within Earth. We consider the limits these parameters place on microorganisms in this chapter. These parameters also influence the thermodynamics and kinetics of microbial reactions, which we discuss in chapters 8 and 9, respectively.

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6.2.1: Temperature

The temperature range of microbial life approximately coincides with the temperature range at which water can exist as a liquid under near surface conditions. Microbial growth has been documented at temperatures as low as −20°C (Rivkina et al., 2000). On the high end, microbial growth has been observed at and just above 120°C (Beulig et al., 2022; Kashefi and Lovley, 2003; Takai et al., 2008).

Within these temperature limits, individual species have their own temperature needs. Species each have a temperature optimum at which their growth rate can be highest and a temperature minimum and maximum beyond which their growth is not possible (Fig. 6.1). Collectively, we can refer to these temperature values as the 'cardinal temperatures' for the species. Maximum and minimum temperature values for a species are typically separated by about 30°C (Madigan et al., 2003).

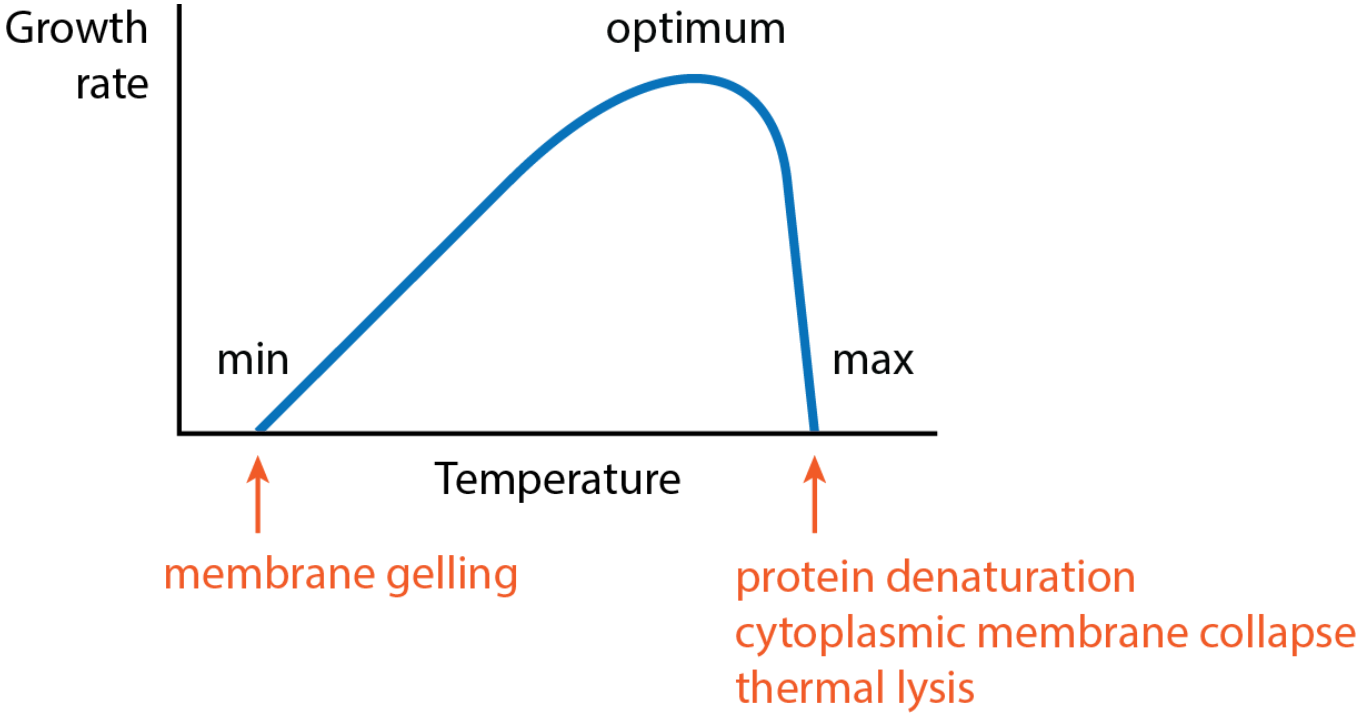


Figure 6.1: Influence of temperature on growth rate for an individual species. Figure based on 6.16 of Madigan et al. (2003). https://commons.wikimedia.org/wiki/File:Temperature_and_growth_rate.png

The cardinal temperatures for an individual species reflect the stability and functional limits of their biomolecules. At the upper limit, for example, a cell's enzymes may lose their form and ability to function, and its membranes may become too diffusive, allowing the cell to rupture or lyse. At the lower limit, a cell's membranes may gel, causing insufficient transport of components in and out of the cell interior.

These thermal traits can be used to characterize microbial species. Microorganisms that grow well under relative cold conditions are referred to as psychrophiles ('cold loving'). Microorganisms that grow well under hot conditions are described as thermophiles ('heat loving'). Whereas those that grow well under moderate temperatures are referred to as mesophiles ('middle loving'). Growth ranges for each category are listed in Table 6.1. Optimal temperatures for species within each category would fall within that range.

For microorganisms that live under extreme conditions, it is important to remember that these species are not just tolerant of these extremes but actually require them (Madigan et al., 2003). For example, one of the ways that psychrophiles adapt to low temperatures is by having a high percentage of unsaturated fatty acids in their plasma membrane (Madigan et al., 2003). More unsaturated fatty acids help the membrane remain fluid and functional at low temperatures. However, this membrane composition is poorly suited for life at high temperatures, where it would be too fluid to serve as an effective permeability barrier. Thus, you would not be helping out a psychrophile by giving it a warmer place to live. Instead, you would be preventing its growth or even causing it to split open, a process known as thermal lysis.

Table 6.1: Categories of microorganisms based on temperature preferences

Category	Temperature Range
Psychrophiles	< 0 to 20°C
Mesophiles	15 to 45°C
Thermophiles	45 to 80°C
Hyperthermophiles	> 80°C
*Temperature ranges are based on those listed in Konhauser (2007).	

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6.2.2: Pressure

Microbial life can exist over multiple orders of magnitude in pressure. Most species that have been tested do not grow at pressures below $0.0025\ \mathrm{MPa}$, although growth has been observed for a few species at $0.0007\ \mathrm{MPa}$, a pressure within the range measured on the surface of Mars (Verseux, 2020). At the high end, microorganisms capable of growing at $100\ \mathrm{MPa}\ (=1000\ \mathrm{atm})$ have been isolated from water samples collected at a 10.5 km depth in the ocean (Yayanos et al., 1979) and mud samples from the Mariana Trench (Takami et al., 1997). Laboratory studies have found that cell viability decreases sharply at pressures ranging from about 100 to $150\ \mathrm{MPa}$ (Picard and Daniel, 2013), suggesting that the upper limit for growth may be within or near that range.

Life at each extreme provides unique challenges. Low pressure can inhibit growth by causing cells to dry out (i.e., desiccate) or by limiting the supply of a necessary gas such as carbon dioxide or oxygen (Verseux, 2020). At high pressure, lipid volumes decrease, which impacts membrane fluidity and function (Pikuta et al., 2007).

Based on their pressure requirements, individual species can be described as barotolerant microorganisms, barophiles, and extreme barophiles. Barotolerant microorganisms can grow at $0.1\ \mathrm{MPa}\ (\ 1000\ \mathrm{atm})$ but cannot grow at pressures above $50\ \mathrm{MPa}$ (Madigan et al., 2003). Barophilic microorganism can also grow at $0.1\ \mathrm{MPa}$ but have optimal growth at pressures greater than $40\ \mathrm{MPa}$ (Madigan et al., 2003; Pikuta et al., 2007; Zobell and Johnson, 1949). Extreme or obligate barophiles require high pressure for growth. They do not grow at pressures below about $40\ \mathrm{MPa}$ (Madigan et al., 2003).

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6.2.3: Oxygen

Dioxygen or simply oxygen (O_2) serves as an environmental control in at least two ways. First, it is used as an electron acceptor by aerobic organisms. Thus, the supply of oxygen influences where aerobes may be active. Secondly, oxygen is also a source of stress for cells. Oxygen toxicity for some cells can occur because cells contain oxygen-sensitive molecules, and the cells may lack the protective enzymes that detoxify reactive oxygen species (ROS) generated by oxygen metabolism. These ROS include the superoxide anion (O_2^{2-}), hydrogen peroxide (H_2O_2), and hydroxyl radical (OH) (Fridovich, 1999).

As described by Madigan et al. (2003), there are three main categories of microorganisms based on their response to oxygen availability (Fig. 6.2). Aerobes are capable of using oxygen in environments with atmospheric levels of oxygen. Microaerophiles are microorganisms that can use oxygen only when it is present at low levels relative to the atmosphere. And lastly, anaerobes are microorganisms that cannot use oxygen.

Among these classes, we can further subdivide aerobes and anaerobes (Madigan et al., 2003). Aerobes can be facultative aerobes, which can grow with or without oxygen, or obligate aerobes, which can only grow aerobically. Similarly, anaerobes can be aerotolerant anaerobes, which can tolerate and grow in the presence of oxygen, or obligate anaerobes, which are inhibited or killed by oxygen exposure.

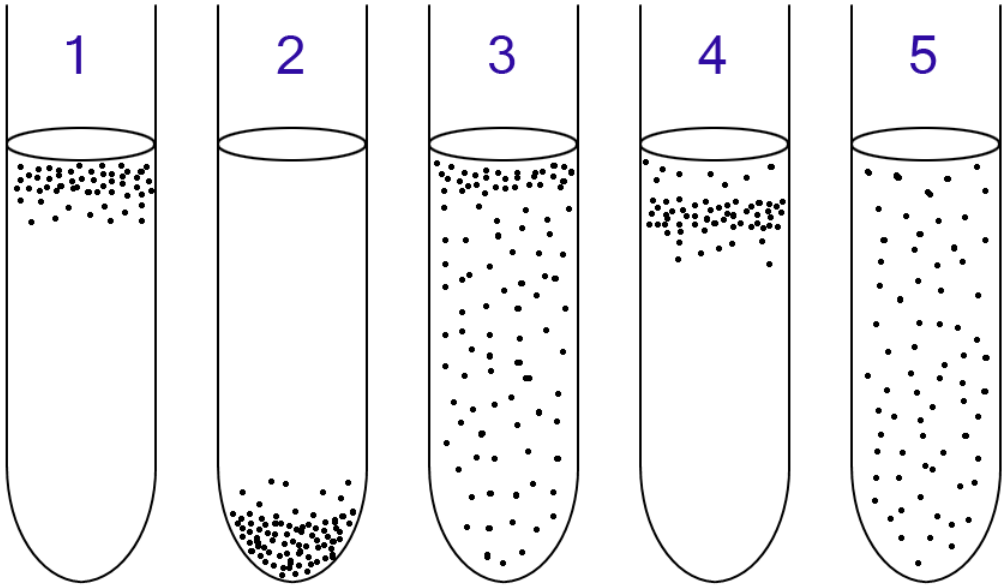


Figure 6.2: Schematic illustration of categories of microorganisms based on oxygen tolerance. The tubes show liquid cultures of microorganisms with a gradient from high dissolved oxygen concentration near the interface between gas and liquid to anoxic conditions at the bottom of the tube.
Tube 1: Obligate aerobes concentrate near the interface between water and gas where dissolved oxygen concentration is highest.
Tube 2: Obligate anaerobic microorganisms gather at the bottom to limit exposure to dissolved oxygen.
Tube 3: Facultative aerobes gather mostly at the top, where they can best take advantage of dissolved oxygen, but they are located throughout the tube.
Tube 4: Microaerophiles gather near the top of the tube but not at the interface.
Tube 5: Aerotolerant anaerobes are not affected by oxygen and disperse throughout the tube.
https://commons.wikimedia.org/wiki/File:Anaerobic.png

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6.2.4: pH

pH tells us the extent to which an environment is acidic or basic. Similarly to pressure, microbial life extends over a broad pH range. Only a few species can grow in environments with pH less than 2 and above 10 (Madigan et al., 2003), but microbial growth has been demonstrated at external pH as low as 0 and as high as about 13 (Pikuta et al., 2007; Roadcap et al., 2006; Schleper et al., 1995). To fully appreciate the extent of this range, we have to recall that pH is calculated as the negative log (base 10) of hydrogen ion activity:

$$\mathrm{pH} = -\log\left[\mathrm{H}^{+}\right] \tag{6.2.4.1}$$

Thus, for each pH unit, hydrogen ion activity changes by a factor of ten. In other words, microbial life extends over at least 13 orders of magnitude in hydrogen ion activity.

Within these extremes, most individual species can only grow over a pH range of three to four pH units (Rosso et al., 1995). Neutrophiles grow optimally at pH levels between 5 and 9 (Konhauser, 2007). Acidophiles grow best at pH less than 5 and alkaliphiles grow best at pH greater than 9 (Baker-Austin and Dopson, 2007; Horikoshi, 1999). The pH requirements for growth of these groups represents the pH of the external environment. Internal pH, the pH of a cell's cytoplasm, is typically near neutral values, even for acidophiles and alkaliphiles (Lowe et al., 1993).

External pH influences microbial communities in several ways. As summarized by Jin and Kirk (2018a, 2018b), pH affects geochemical reactions that affect the salinity and composition of aqueous solutions and the bioavailability of nutrients, it impacts the function and activity of microbial enzymes and other biomolecules, and it affects the amount of energy released by microbial reactions and reaction rates because many microbial reactions include hydrogen ions either as a product or reactant.

Reflecting these impacts, many studies have found that pH is a significant environmental control on microbial community composition. As an example, Fierer and Jackson (2006) examined microbial communities in 98 soil samples from across North and South America. They considered environmental factors that influenced microbial community diversity, which includes richness (the number of different species) and evenness (distribution of abundance across the species). Their analysis showed that soil pH was a more important driver of diversity than even mean annual temperature and other factors that typically predict plant and animal diversity. They also found that soil pH was the strongest predictor of microbial community composition. As a second example, Power et al. (2018) examined microbial communities in 925 geothermal springs in New Zealand. The springs had pH ranging from < 1 to 9.7 and temperature ranging from 13.9-100.6°C. They found that pH was the primary driver of diversity in springs with temperature below 70°C. Above 70°C, temperature became a significant driver.

In both of these studies, species richness was found to be greatest at near-neutral pH. Similarly, Thompson et al. (2017) observed the same result in an even larger scale study, which examined bacterial and archaeal rRNA gene sequences collected from sites around the world. Their analysis included 3,986 samples collected mostly from freshwater and soil environments. Taken together, the results indicate that most bacterial and archaeal species are neutrophiles.

Lastly, the extent to which pH impacts soil microbial communities appears to be greater for bacteria than fungi. Rousk et al. (2010) examined microbial communities in soils from a long-term field experiment where soil microbes were exposed to pH ranging from 4 to 8.3. The relative abundance and diversity of bacteria in the community were significantly related to pH. In contrast, they found that the relative abundance of fungi was unaffected by pH and fungal diversity was only weakly related to pH. They interpreted that differences in the response of bacteria and fungi to pH may reflect narrower pH ranges for bacterial species than fungal species within the communities

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6.2.5: Water availability

Water is the solvent of life (Madigan et al., 2003). A solvent is a substance that can dissolve other molecules or compounds, which we refer to as solutes. Many of the reactants and products in microbial reactions are soluble in water, the main component of a cell's cytoplasm. Water also helps microbial reactions occur by serving as transport agent for reactants and products (Konhauser, 2007).

The availability of water for these needs depends not only on the amount of water present (i.e., how wet or how dry) but also the salinity of the water (i.e., the concentration of solutes that are dissolved in the water) (Madigan et al., 2003). Thus, environmental processes such as evaporation, mixing of water masses, and addition of salt mass to aquatic habitats (e.g., road salt) all have the potential to alter the availability of water for microbial populations.

The salinity of an environment affects pressure within cells. Typically, the cytoplasm of cells has higher salinity than the environment (Madigan et al., 2003). This difference in solute concentrations favors flow of water into the cell through a process known as osmosis, which gives the cell a positive pressure. As the salinity of an environment increases, however, it can eventually become more saline than the cytoplasm, which makes it favorable for water to flow out of the cell.

Most microorganisms are not able to grow in environments with high salinity (Madigan et al., 2003), and accordingly humans have long used salt as a food preservative. Halotolerant microorganisms are those that can tolerate some increase in salinity but typically grow best at low salinity (Madigan et al., 2003). Halophilic microorganisms require elevated salinity, with the amount depending on the species (Madigan et al., 2003). These microorganisms can adapt to high salinity by making their cytoplasm saltier, an approach known as the salt-in strategy (Oren, 1999). Cells can also maintain low salt concentrations in their cytoplasm and balance osmotic pressure with organic-compatible solutes (Oren, 1999).

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6.3: Transport processes

Transport processes such as advection and diffusion move nutrients, energy resources, waste products, and other chemicals related to microbial reactions, as well as microbial cells themselves. As a result, transport is often an important environmental control on the distribution and activities of microbial populations.

To illustrate, we first consider a hypothetical situation in which groundwater passes through a volume of aquifer where anaerobic microbes are driving iron reduction (Fig. **6.3A**). Iron reduction generates ferrous iron (**Fe(II)**), which is relatively soluble (Section 5.3.1). Therefore, ferrous iron concentrations can increase in groundwater as it flows through a zone of iron reduction. Where that groundwater discharges at the surface, the ferrous iron it carries would then be exposed to oxygen, which can allow growth of iron-oxidizing microorganisms and cause ferric (oxyhydr)oxide minerals to form. In such a setting, mass transport by groundwater promotes iron reduction in the subsurface by removing ferrous iron waste (Roden and Urrutia, 1999) and it promotes iron oxidation at the surface by suppling the electron donor (i.e., ferrous iron).

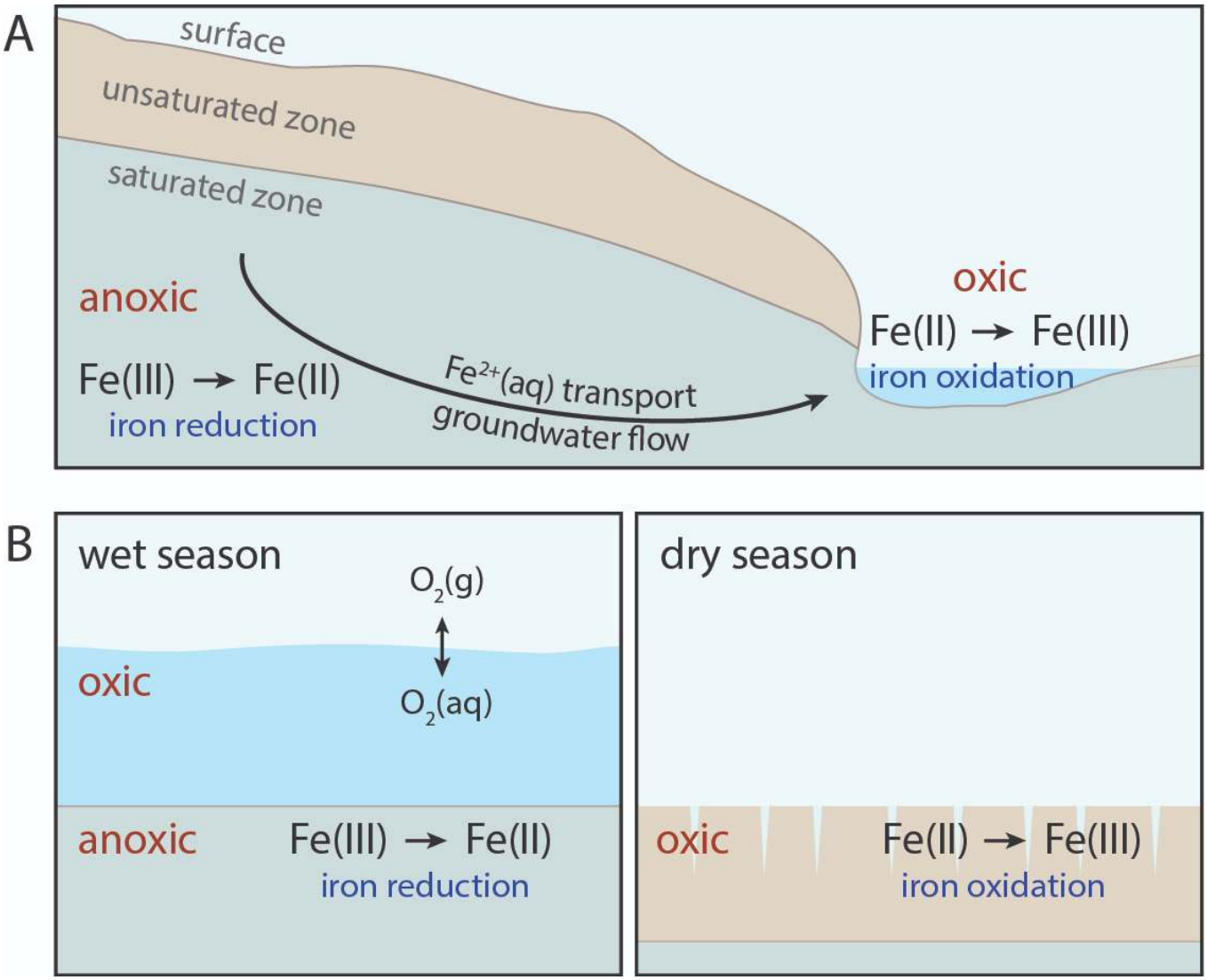


Figure **6.3**: Schematics showing examples of ways (A) transport and (B) environmental change can serve as environmental controls on microbial populations involved in iron cycling. Part (A) depicts microbial reduction of ferric iron (**Fe(III)**) within an anoxic zone of an aquifer. The ferrous iron (**Fe(II)**) produced by iron reduction is relatively soluble. As such, some of it can be transported by groundwater flow to a discharge zone at the surface, where oxygen is available and iron oxidation can occur. The iron oxides shown in Figure 5.6 appear to have formed because of this very situation. Part (B) depicts the impact of seasonal variation in precipitation as a control on the water saturation and redox state of a wetland soil. During the wet season, water limits the oxygen supply at depth, allowing microbes to use ferric iron minerals as electron acceptors in the soil. During the dry season, the soil dries, exposing formerly anoxic portions of the soil to oxygen. As a result, ferrous iron (**Fe(II)**) produced in the wet season can then be oxidized.
https://commons.wikimedia.org/wiki/File:Biogeochemical_cycle_turn_over.jpg

As a second example, we consider results from Burrows et al. (2021), which examined rates of methane oxidation and microbial community composition at methane seeps in the Condamine River in eastern Australia. At the study area, methane-rich gas bubbles discharge from the subsurface into oxic river water, creating create conditions favorable for growth of methanotrophic microorganisms. Rates of methane oxidation in the river sediment varied with the rate of gas bubble discharge into the river and the amount of water flowing in the river. Thus, transport influences methanotrophy in two ways. First, it makes methanotrophy possible by supplying methane to an oxic environment and secondly, transport and dispersal of methane by streamflow helps to determine reaction rate.

As a third example, studies by Zarnetski et al. (2012, 2011) showed that the residence time of water in hyporheic zones influences the proportions of nitrification and denitrification that occur there. The hyporheic zone is the porous media beneath and adjacent to a stream where groundwater and surface water mix. The residence time of water in the hyporheic zone is the amount of time

required for the hyporheic zone pore space to be replaced by inflowing water. Inflowing streamwater transports oxygen into the hyporheic zone and thus, water residence time influences oxygen availability (Triska et al., 1993; Valett et al., 1996). The more rapidly hyporheic zone water is replaced, the more rapidly oxygen can be added to the hyporheic zone. As such, the likelihood that oxygen can be supplied at a rate greater than it can be consumed increases as the residence time of the water in the hyporheic zone decreases. Consistent with these relationships, Zarnetski et al. found that denitrification, an anaerobic process, was dominant where residence times were long and oxygen availability low and nitrification, an aerobic process, was dominant where residence time was short and oxygen availability high. Thus, the residence time of water in the hyporheic zone influenced oxygen supply, which in turn influenced the function of the microbial community and the fate of nitrogen.

A fourth and final example illustrates similar phenomena in soils. In soils, the amount of water can alter the rate of respiration but also oxygen transport (Tiedje et al., 1984). Increasing soil moisture stimulates aerobic respiration until water saturation begins to fill pores and limit oxygen transport to diffusion, at which point anaerobic processes such as denitrification begin to increase (Linn and Doran, 1984; Skopp et al., 1990). Soils fall along a continuum from those that are flooded and continuously anaerobic (e.g., wetland soils) to those that are well drained and unlikely to host large zones of anaerobic respiration (Tiedje et al., 1984). Similarly, soil clay content also influences the connectivity of pores and oxygen transport in soils. As clay content increases, connectivity decreases and anaerobic microenvironments increase in abundance even in otherwise well aerated upland soils (Keiluweit et al., 2018).

Taken together, these examples illustrate that transport may be important in many settings, including a variety of aquatic habitats, the subsurface, and soils. Within these environments, transport can deliver energy and nutrient resources to microorganisms and thereby influence community function and composition. It can affect the concentrations of those resources and thus rates of metabolic reactions. Moreover, transport can remove waste products and thus help sustain microbial reactions.

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6.4: Environment stability

Disturbances, events that disrupt the stability of an environment, have the potential to be a major environmental control on microbial populations. Disturbances can directly alter a community but they may also alter the environment in a way that indirectly affects the community (Shade et al., 2012). Specifically, if the physical and/or chemical properties of a system change as a result of a disturbance, those changes can in turn alter the biological activity within the system.

As an example, consider the impact of water level fluctuations in wetlands (Fig. 6.3B). Anaerobic metabolisms, such as microbial iron reduction, may be favorable within water-saturated anoxic wetland soil. Some of the ferrous iron produced by iron reducers in such an environment could accumulate within the pore water. It could also adsorb to mineral surfaces and precipitate as ferrous iron minerals. However, if the environment dries and the soil becomes oxic, microorganisms may be able to oxidize the ferrous iron back to ferric iron and thus complete the iron cycle. Changes in conditions within this hypothetical environment, therefore, would directly affect the availability of oxygen and indirectly affect which components of the iron cycle were being catalyzed.

Disturbances may have a greater influence on microbial communities at or near the surface than they do deep in the subsurface. Earth's surface is dynamic. Conditions change over the course of a day and with the seasons because of the rotation of the Earth, the tilt of its axis, and its orbit around the Sun. Conditions can change in hours or less in response to changing weather, floods, fires, landslides, volcanic eruptions, and other events. Therefore, there are many sources of potential disturbances at the surface. These events would also impact the shallow subsurface, but their effects would attenuate with depth. As such, the deep subsurface is likely much more stable than the surface and shallow subsurface.

The stability of a microbial community is characterized by its resistance, the degree to which the community is insensitive to the disturbance, and its resilience, the rate at which a community returns to pre-disturbance condition (Shade et al., 2012). A community's stability in the face of disturbance can be measured in terms of whether the function of the community changes and/or whether the composition of the community changes. Communities with greater functional redundancy (i.e., the coexistence of multiple species that carry out the same metabolic function) may see compositional changes without functional changes (Allison and Martiny, 2008; Konopka, 2009).

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6.5: Dispersal mechanisms and barriers

Dispersal is the movement and successful establishment of a species from one location to another (Hanson et al., 2012). Population size influences dispersal rate. Specifically, larger populations have the potential to disperse more rapidly than smaller populations. However, dispersal rates are also influenced by properties of the species (e.g., cell morphology, metabolism, ability to form spores) as well as properties of the environment (e.g., availability of space and resources, geomorphic features, presence or absence of transporting agents). Thus, environments can influence distributions of microbial populations through dispersal limitations.

Population distributions can reflect the dispersal properties of environments as the exist today as well as historical legacies. For example, Takacs-Vesbach et al. (2008) examined the distribution of distinct sequences of the bacterial genus *Sulfurihydrogenibium* in springs within Yellowstone National Park, USA. Their analysis showed that the distribution of these sequences was not correlated to variation in spring geochemistry or geographic distance but that there was a strong relationship to past geological events. Specifically, sites within the boundary of the Yellowstone caldera as it existed two million years ago contained sequences that were more closely related to one another than they were to sequences in sites located outside of the caldera boundary. The past history of volcanism, therefore, seemed to define the current geographic ranges of *Sulfurihydrogenibium* sequences.

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6.6: Interactions between controls

We have looked at some environmental controls on an individual basis in this chapter and will consider additional controls in the chapters ahead. One thing to bear in mind as you learn about these controls is that they can interact. An interaction effect occurs when the effect of one variable on a system depends on the state of a second variable.

As an example, it has long been known that the effect of pressure on microbial growth for some species depends on the temperature of the environment. In early research on this topic, Zobell and Johnson (1949) studied the effects of pressure and temperature on several species of microorganisms isolated from marine and terrestrial environments. Relationships varied between isolates, but for many, they found that the isolates were better able to grow at higher pressures if temperature was also higher. Thus, the response to high pressure depended on temperature for those isolates.

As a second example, research has shown that the activities of enzymes used by soil microorganisms to degrade organic matter are sensitive to temperature. Min et al. (2014) investigated how that sensitivity varies with the pH of the environment for two enzymes, one that soil microbes use to obtain carbon (BGase; liberates glucose carbon from cellulose) and one used for nitrogen (NAGase; liberates nitrogen-acetylglucosamine from chitin). They found that the temperature sensitivity of BGase differed significantly with pH whereas that of NAGase did not vary with pH. As a result, an increase in temperature can cause changes in flows of carbon and nitrogen during organic matter decay but the nature of those changes is dependent on the pH of the environment. Their results have implications for changes in nutrient availability in soils in response to climate change (Min et al., 2014; Souza and Billings, 2022). We will more broadly consider nutrient availability as a control on microorganisms in the next chapter (Chapter 7).

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6.7: Concept Check Questions

1. Microbial life has been identified at temperatures as high as 121°C. Can liquid water be present at that temperature?
2. Explain how temporal and spatial variation in microbial activity and community composition could be related to temperature.
3. Where would you expect microbial life to extend deeper into the subsurface, within the sinking plate of a subduction zone or near a divergent plate boundary?
4. How are psychrophiles adapted to life at cold temperatures?
5. Would you expect that an organism that is adapted to life under high temperature (e.g., optimum 80°C) to be able to live at a more comfortable temperature of 20°C)? Why or why not?
6. Under what pH conditions do we tend to see the most diverse populations of soil microorganisms? How does pH compare to water and temperature as controls on the diversity of soil microbial communities?
7. How might groundwater flow influence microbial activity in an aquifer?
8. If you place a cell from a freshwater environment into a saline environment, its cell wall may rupture. Why?
9. Where would disturbance have the greatest impact on a microbial community? Rank the following in order of decreasing impact of disturbance: (a) floodplain soil, (b) 10-meter depth in the subsurface of the floodplain, and (c) 100-meter depth in the subsurface of the floodplain.

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CHAPTER OVERVIEW

7: Nutrient and Energy Resources

> *"Microbial life exists in all the locations where life can survive, that would mean all the locations that have a chemical energy supply and that are at a temperature below the maximum one to which microbes can adapt"*
>
> *—Thomas Gold, PNAS 1992*

> *"Life will find a way"*
>
> *—Michael Crichton, Jurassic Park*

The abundance and types of nutrient and energy resources in an environment can influence many aspects of that environment's microbial activity. Nutrient and energy resource availability helps determine what types of microbial reactions can be present and the extent to which microbes driving those reactions can be active. Nutrient and energy resource availability also affects the composition of the microbial community. If the chemicals an organism needs from the environment for their metabolism are not available, then that organism cannot live there. However, other organisms may have different needs and can survive or even thrive in that same environment.

For the purposes of this chapter, we will consider energy sources to be sources of electrons. For phototrophic organisms, electrons are discharged when light is absorbed by specialized pigments such as chlorophyll (Section 4.5). So, we can think of light as their ultimate energy source. For chemotrophs, we can consider their electron donors to be their energy sources.

7.1: Nutrients
7.2: Extracellular enzymes
7.3: Nutrient stoichiometry
7.4: Energy sources for phototrophs
7.5: Energy sources for chemotrophs
7.5.1: Organic matter
7.5.2: Reduced inorganic components of minerals
7.5.3: Mantle degassing
7.5.4: Serpentinization
7.5.5: Radiolysis of water
7.5.6: Silica radical-based reactions
7.5.7: Trace atmospheric gases
7.6: Electroactive organisms
7.7: Concept Check Questions
7.8: References

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7.1: Nutrients

Nutrients are chemicals that organisms need to create their biological molecules but cannot make themselves. As such, they obtain them from their environment. Nutrients can be divided into two broad categories: macronutrients and micronutrients. Macronutrients are substances needed in relatively high abundance. Carbon, nitrogen, and phosphorus are the macronutrients needed in the largest abundance, and those we focus on here (Fig. **7.1**). Micronutrients are nutrients needed only in trace quantities, although they are certainly still essential.

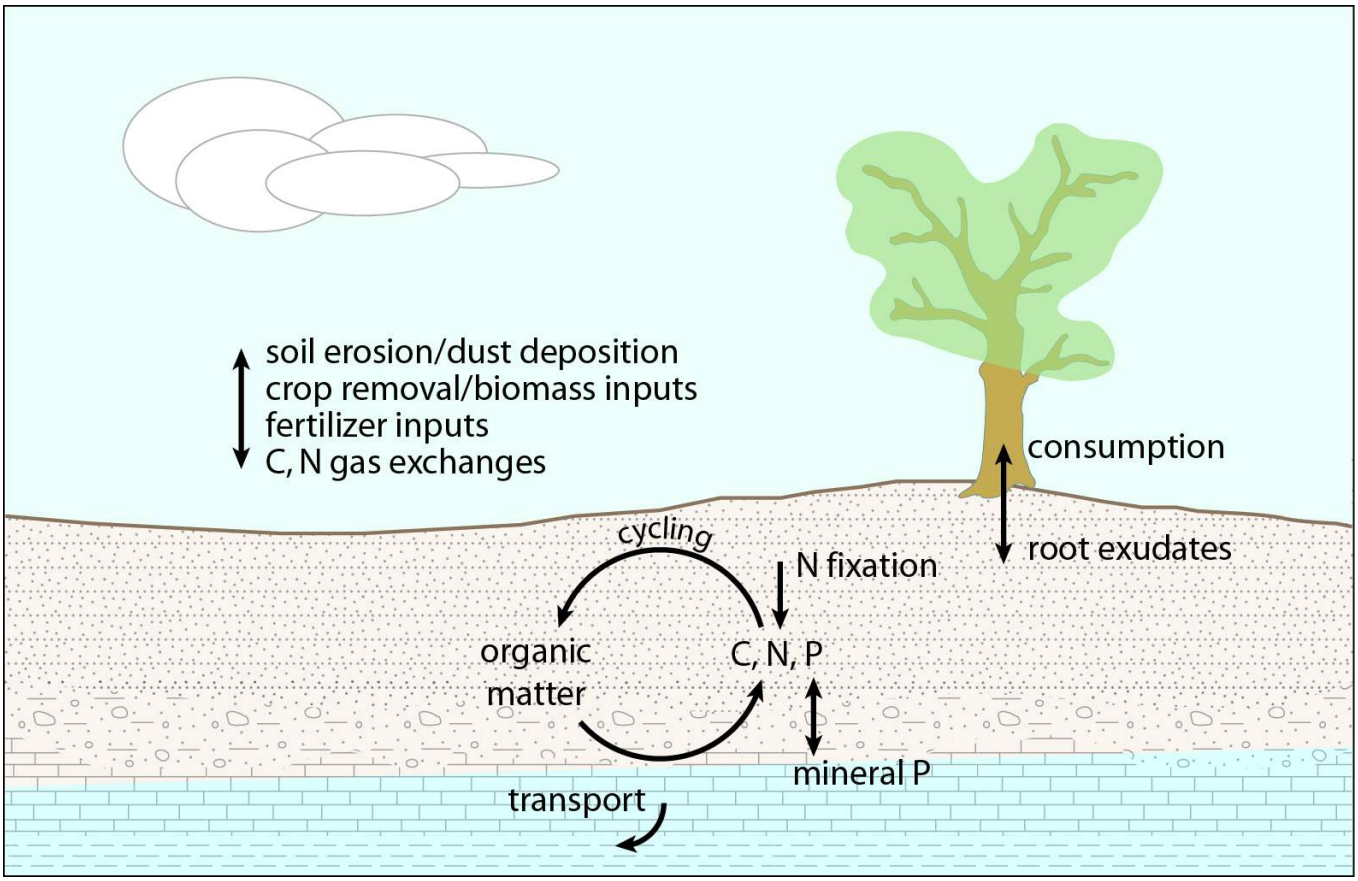


Figure **7.1**: Simple conceptual diagram of the carbon, nitrogen, and phosphorus (C,N,P) budgets in the shallow terrestrial subsurface. Organisms recycle nutrients when they degrade organic matter and form new organic compounds. Nutrients can also be added externally or removed from the soil, as shown in the figure. The tree represents plants in general, not just woody vegetation. Root exudates from plants include sugars, amino acids, and organic acids (Canarini et al., 2019). Dust can serve as a major nutrient source for soil, particularly where nutrients have been depleted from the underlying bedrock by intense weathering (Aciego et al., 2017; Pett-Ridge, 2009). Fertilizer inputs include both chemical fertilizers as well as animal wastes. Subsurface transport represents leaching of nutrients and other compounds as water passes through soil. Mineral phosphorus represents primary and secondary phosphate minerals as well as phosphorus that is adsorbed to mineral surfaces.
https://commons.wikimedia.org/wiki/File:Soil_nutrient_budget.jpg

Carbon is the major element in all biological macromolecules and accounts for about 50% of the dry mass of cells (Madigan et al., 2003). Autotrophs assimilate carbon mainly from carbon dioxide. In contrast, heterotrophs assimilate carbon from organic sources and have been observed using a wide variety of organic compounds, including amino acids, fatty acids, organic acids, sugars, nitrogen bases, aromatic compounds, and more (Madigan et al., 2003).

Nitrogen is the next most abundant element in biological macromolecules. It accounts for about 12% of the dry weight of cells and is needed to make proteins, nucleic acids, and more. The most abundant nitrogen sources are ammonia, nitrate, and dinitrogen. Most bacteria can obtain nitrogen from ammonia, some can use nitrate, and only nitrogen fixing bacteria can use dinitrogen. Ammonia can be supplied from nitrogen fixation, dissimilatory nitrate reduction to ammonia (DNRA), or ammonification, nitrate can be supplied by nitrification, and both ammonia and nitrate can be supplied by fertilizers.

Phosphorus is primarily used to make nucleotides and phospholipids. Phosphorus is ultimately derived from mineral sources such as apatite ($Ca_5(PO_4)_3(F, Cl, OH)$), which are not generally abundant in natural environments. Therefore, microbial communities recycle phosphorus from decaying biomass and this source accounts for most of the phosphorus used by plants and the microbiomes of most ecosystems unless phosphorus is supplied as chemical fertilizer (Turner, 2008). Where organic sources of phosphate are limited and fertilizers are not applied, microorganisms must acquire phosphate from minerals (Welch et al., 2002) (Fig. 7.1). Such conditions are common during the early stages of rock weathering (Welch et al., 2002).

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7.2: Extracellular enzymes

Enzymes play major roles in biological reactions as catalysts. We will consider enzymes more broadly in Chapter 9: Kinetic Controls. However, for this chapter, we briefly consider how extracellular enzymes help supply nutrients and energy resources.

Extracellular enzymes, also known as exoenzymes or ecoenzymes, are enzymes that are not contained by the membranes of living cells. Microorganisms release them into the environment to degrade organic matter and release nutrients. They help deconstruct plant and microbial cell walls, depolymerize biological macromolecules such as proteins and lipids, and ultimately produce soluble compounds that can be assimilated by microbes (Burns et al., 2013; Sinsabaugh et al., 2009). Thus, extracellular enzymes play significant roles in supplying microbial communities with nutrients and turning the biogeochemical cycles (Fig. 7.1).

Enzymes that are commonly assayed by researchers to better understand microbial resource extraction are summarized in Table 7.1. Lignocellulose is the most abundant product of terrestrial primary production, but it does not contain nitrogen or phosphorus. So, other biological molecules are degraded for those compounds. Proteins, chitin, and peptidoglycan are major sources of nitrogen whereas nucleic acids, phospholipids, and other ester phosphates are major sources of phosphate.

Table 7.1: Examples of extracellular enzymes and their functions*

Enzyme	Function
B-1,4-glucosidase	Cellulose degradation; hydrolyzes glucose from cellobiose
B-1,4-n-acetylglucosaminidase	Chitin and peptidoglycan degradation; hydrolyzes glucosamine from chitobiose
Leucine aminopeptidase	Proteolysis: hydrolyzes leucine and other hydrophobic amino acids from the N terminus of polypeptides
Phosphatase	Hydrolyzes phosphate from phosphosaccharides and phospholipids

*Source: Sinsabaugh et al. (2009)

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7.3: Nutrient stoichiometry

Stoichiometry essentially means ratio. Thus, nutrient stoichiometry simply refers to the ratios or proportions of nutrients in an environment. Nutrient stoichiometry is a major control on structure and function of ecosystems (Cleveland and Liptzin, 2007; Schlesinger and Bernhardt, 2013). A microorganism's nutrient demand is determined by the proportions of nutrients in its biomass relative to the availability of those nutrients in the environment (Sinsabaugh et al., 2009). If one nutrient is not available in sufficient supply relative to others required by the organism, it may be a growth limiting factor. For example, if an organism's biomass has a $\mathbf{N:P}$ ratio of $\mathbf{16:1}$, but the environment's $\mathbf{N:P}$ ratio is $\mathbf{32:1}$, then phosphorus supply may limit that organism's growth.

As an example of this relationship, in marine environments, biological productivity is often limited by nitrogen, which is supplied by nitrogen fixation. However, rates of nitrogen fixation are limited by the availability of iron, a critical ingredient needed to make nitrogenase, the enzyme that organisms use to fix nitrogen (Section 5.2.1). As a result, over large areas of the ocean, iron that blows in from the land controls marine productivity. In general, productivity can sometimes be increased by adding limiting nutrient itself or some trace element that helps the organism obtain the limiting nutrient from environment (Schlesinger and Bernhardt, 2013).

In addition to overall productivity, nutrient stoichiometry can influence which species are able to grow because different species have different biomass stoichiometries. Moreover, different species may vary in their preferred forms of nutrients. Some groups may prefer nitrogen delivered as ammonium, for example, whereas others prefer nitrate. As an example study, Andersen et al. (2020) examined impacts to algal communities of seasonal variation in $\mathbf{N:P}$ ratios and nitrogen form (nitrate vs ammonium) in a hyper-eutrophic reservoir. Their results showed that algal growth in the reservoir was limited by phosphorus in the spring fall, but nitrogen was limiting during the summer. During periods of phosphorus limitation, the relative abundances of chlorophytes and diatoms increased within the algal community. However, during periods of nitrogen limitation, the proportion of cyanobacteria in the community increased. Moreover, while nitrogen limited, study results indicated that chlorophytes and cyanobacteria were more strongly stimulated by ammonium addition whereas diatoms were more strongly stimulated by nitrate addition.

Changes in nutrient proportions in an environment can occur in response to natural processes and human activities. As an example of natural processes, widespread weathering of pyrite and other sulfide minerals has been proposed to have increased fluxes of phosphorus, iron, and sulfur to the oceans between about $\mathbf{2.22}$ and $\mathbf{2.06\ Ga}$ (Bekker and Holland, 2012). According to the hypothesis, increased availability of these nutrients stimulated growth of cyanobacteria, which led to anomalously high burial of organic matter in marine sediments. Similarly, nutrients supplied by windblown volcanic ash inputs have also been proposed as a mechanism for stimulating marine biological productivity and organic matter burial during the Cretaceous (Lee et al., 2018). An example of human impacts to nutrient availability is the massive application of fertilizer to crop areas, much of which makes its way to the oceans (Gruber and Galloway, 2008).

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7.4: Energy sources for phototrophs

Phototrophic reactions are generally limited to soils and aqueous environments that receive light from the sun. Light cannot penetrate deeply into soils. For example, in a study of 19 different soils with a range of textures by Ciani et al. (2005), the maximum light penetration depth measured was $300\ \mu m$. Thus, in soils, active microbial phototrophy would be limited to the upper surfaces of the soil. In contrast, light penetrates more deeply into aqueous systems, creating a large volume of potential habitat for phototrophs. In the oceans, for example, significant light can extend as deep as $200\ m$, and phototrophic microorganisms are abundant down to about $100\ m$ depth (Falkowski, 2012).

In addition to the sun, other sources of electromagnetic radiation have the potential to fuel phototrophs. Consistent with this possibility, Beatty et al. (2005) isolated an anaerobic green sulfur bacterial species from a deep-sea hydrothermal vent. The organism was obligately phototrophic and could grow on extremely low levels of light. The only source of light at the site is geothermal radiation, which included wavelengths that could be absorbed by the photosynthetic pigments of the organism. The organism was not found in surrounding waters, indicating that it uses radiation and reduced sulfur compounds from the vent to generate energy and fix carbon, respectively.

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7.5: Energy sources for chemotrophs

Chemotrophic reactions can occur on Earth's surface and within the upper 5 km or so of the subsurface (Akob and Kuesel, 2011). Chemotrophs that use organic electron donors are known as chemoorganotrophs and those using inorganic electron donors are known as chemolithotrophs (Section 4.3). Chemorganotrophic microbial reactions are widespread and likely occur wherever organic matter is available and the properties of the environment are conducive to microbial life. Chemolithotrophs are also widespread. Major inorganic electron donors include dihydrogen (H^2), carbon monoxide (CO), ammonium (NH_4^+), ferrous iron (Fe^{2+}), sulfide (H_2S), and sulfur compounds with intermediate oxidation states (Jannasch and Mottl, 1985), but many other possibilities exist.

Electron donors used by chemotrophs can come from many sources. First, dead biomass and plant roots can supply electron donors to organotrophs but also lithotrophs, given that dihydrogen is produced during organic matter fermentation. Moreover, in many cases, inorganic electron donors are ultimately produced by organotrophs. For example, ferrous iron generated by organotrophic iron reduction can be exposed to lithotrophic iron oxidation as a result of aqueous transport or environmental change, as illustrated in Figure 6.3. Secondly, organic and inorganic electron donors can also be supplied by 'geologic' or 'lithogenic' sources, including reduced inorganic components of minerals, outgassing of the mantle, serpentinization, radiolysis of water, and silica radical-based reactions. Lithogenic sources appear to play a particularly prominent role in fueling Earth's deep hot biosphere (Colman et al., 2017; Gold, 1992). And third, microorganisms are very resourceful can even use trace amounts of gases in the atmosphere as electron donors. The subsections below discuss these energy sources in more detail.

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7.5.1: Organic matter

In our discussion of the carbon cycle (Section 5.1.1), we described complex organic matter as the biomass of dead organisms. That organic matter can be degraded through microbial fermentation and respiration reactions and thus serves as fuel for the microorganisms that catalyze those reactions. It can also be thermally degraded, which becomes increasingly important as temperature increases above 50°C (Beulig et al., 2022). Products of thermal degradation can include petroleum, methane, acetate, and dihydrogen, which then have the potential to feed microbial populations where conditions are suitable for growth (Horsfield et al., 2006; Parkes et al., 2007). Lastly, in addition to dead biomass, plants can also add organic electron donors directly to soils through their roots. In fact, plants may release up to 20% of their photosynthesis products into soils, thus providing a substantial energy and carbon source for soil microorganisms (Haichar et al., 2008; Martinović et al., 2022).

The total abundance of organic matter in soils and sediment varies widely. Factors that affect organic matter abundance include the rate at which the organic matter is produced by autotrophs, the rate at which can be degraded, as well as the rate at which the organic matter is diluted by mineral sedimentation. Rates of organic matter production vary with factors such as climate and nutrient supply. One of the major factors that influences degradation rate is oxygen availability. Anaerobic degradation is typically slower than aerobic degradation in response to inhibition of oxidative enzymes and the lower energy yield of anaerobic respiration (Arndt et al., 2013; Freeman et al., 2001; Keiluweit et al., 2017; Naughton et al., 2021). In addition to oxygen availability, degradation rates also vary with organic matter composition, soil/sediment mineralogy, climate, water availability, pH, and microbial community composition (Schmidt et al., 2011).

In subsurface sediments and sedimentary rocks, organic carbon levels tend to be higher in fine-grained layers than coarse-grained layers. However, organic matter degradation within both can be linked. For example, McMahon and Chapelle (1991) analyzed concentrations of fermentation products in Atlantic coastal plain sediments in South Carolina, USA. Their results showed that fermentation was dominant in the fine-grained confining layers, resulting in a net accumulation of simple organic compounds within them. In coarse-grained aquifers, however, concentrations of simple organic compounds were lower and microbial respiration was dominant. They concluded that diffusion of fermentation products from the confining layers fueled respiration in the aquifers (Fig. 7.2). Other studies that have observed similar phenomena include Krumholz et al. (1997), who examined geochemistry and sulfate-reducing activity in alternating layers of Cretaceous shale and sandstone, and Aeppli et al. (2022), who analyzed geochemistry and microbial community composition in column reactor experiments designed to model alluvial aquifers.

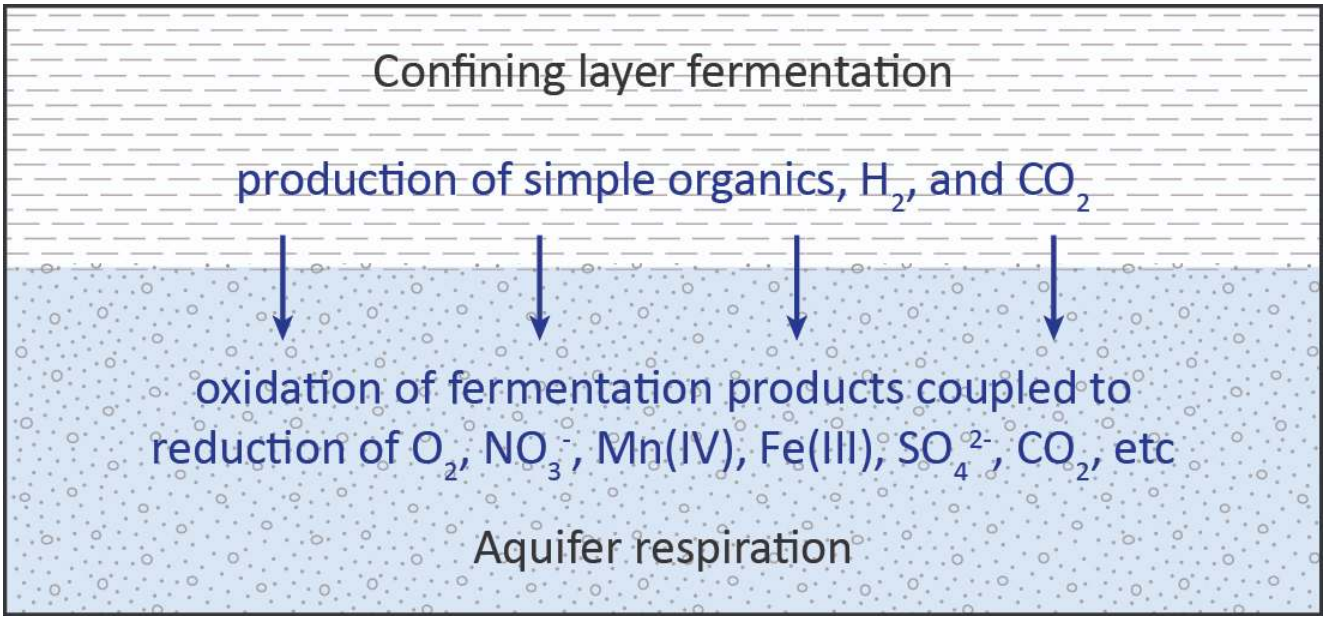


Figure 7.2: Conceptual diagram illustrating microbial respiration in aquifers fueled by fermentation of organic matter in fine-grained organic-rich confining layers.
https://commons.wikimedia.org/wiki/File:Aquifer_microbiology.jpg

Lastly, when measured, concentrations of fermentation products (i.e., simple labile organic compounds and dihydrogen) are often found to be at relatively low concentrations. In the study by McMahon and Chapelle (1991), for example, the highest concentrations of acetate and formate that they measured in the aquitards were about 45 and $65\ \mu\mathrm{M}$, respectively. Does this mean they are not that important as energy resources? Not necessarily. Flux is important to consider when interpreting concentrations. A solute may be produced at a high rate but found to be low in concentration if the solute is produced and consumed at similar rates. Moreover, small concentrations of electron donors, even if supplied by low rates, have the potential to be important over long time scales.

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7.5.2: Reduced inorganic components of minerals

In addition to organic compounds, reduced inorganic components within rocks and sediment, such as ferrous iron and sulfur, can also serve as energy sources for chemolithotrophic microorganisms if suitable electron acceptors are available such as oxygen or nitrate. For example, studies have shown that microorganisms can use ferrous iron and sulfur in pyrite as an energy source (Baker and Banfield, 2003; Percak-Dennett et al., 2017) as well as ferrous iron in basalt, siderite, biotite, olivine, and hornblende (Edwards et al., 2003; Napieralski et al., 2019; Popa et al., 2012; Shelobolina et al., 2012).

Such energy sources have the potential to be important in marine environments where basalt is exposed to seawater containing oxygen and/or nitrate. Santelli et al. (2008) estimated that reduced inorganic components of upper ocean crust can support 10^7 to 10^9 cells per gram of rock, which corresponds well to measured cell densities on basalt. Moreover, iron-oxidizing chemolithotrophs isolated from deep sea environments have been shown to be capable of growing on basalt and causing increased basalt weathering (Edwards et al., 2004, 2003).

They also have the potential to support microbial ecosystems in terrestrial environments where reduced components in bedrock are exposed to oxic or nitrate-bearing solutions. For example, Napieralski et al. (2019) demonstrated that iron-oxidizing bacteria inhabit the weathering rind of a quartz diorite in Puerto Rico and have the capability of using mineral-derived ferrous iron as their primary energy source. Culturing experiments indicate that their activities increase the rate at which the bedrock weathers. Additional information about mineral weathering is available in Section 11.4.

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7.5.3: Mantle degassing

Mantle volatiles degas through conduits and vents in the Earth's crust and can include potential energy sources for microorganism such dihydrogen, reduced sulfur compounds, carbon monoxide, and methane, as well as carbon dioxide and water (Crossey et al., 2016; Jannasch and Mottl, 1985). Along with these compounds, deeply derived fluids can also deliver solutes leached from deep bedrock and capable of serving as energy sources, such as reduced metals (Jannasch and Mottl, 1985).

These fluids and gases discharge into diverse oceanic and continental settings. In the oceans, volatiles and hydrothermal fluids discharge at deep-sea vents located along oceanic ridges formed by divergent plate boundaries. In continental settings, volatiles can discharge at springs and fumaroles in extensional environments as well as volcanic arcs at convergent boundaries and hotspot volcanoes. Continental extensional environments are analogous to oceanic ridges but the greater thickness of continental crust compared to oceanic crust causes the deep fluids and gases emitted there to be more diffuse and compositionally variable (Crossey et al., 2016).

At oceanic ridges and continental volcanic settings, magma is found at relatively shallow depth within the subsurface. Heat supplied by the magma drives circulation of groundwater, which in turn helps transport solutes and gases to the land surface or seafloor. Drivers, conduit systems, and transit times for transfer of volatiles and deep fluids through continental extensional settings are less clear (Crossey et al., 2016). Deeply derived fluids with mantle volatiles may be hot/warm but they can also be cool. For example, carbonic travertine-depositing springs transfer mantle volatiles to the surface in extensional settings across the western USA (Newell et al., 2005). Many of these springs are cool. Thus, thermal gradients help transport mantle volatiles through the crust but other drivers, such as regional groundwater flow, are also likely involved.

To help illustrate mantle degassing as an energy source for microbial communities, we can consider recent work by Colman et al. (2019) at Yellowstone National Park, USA. Their study examined microbial communities across a range of conditions and highlighted the influence of vapor phase separation on community composition and function. As depicted in Figure **7.3**, vapor phases that separate from deep hydrothermal fluids can transport sulfide toward the surface, where it can interact with oxic groundwater and form sulfate and acid. Springs that do not receive vapor phase inputs tend to have higher pH and lower sulfate concentrations. Thus, vapor phase separation is a major control on spring geochemistry, which in turn can influence the composition and function of microbial communities. In addition to vapor-phase separation, water-rock interactions and mixing also create variation in spring geochemistry (Shock et al., 2010).

Based on their findings, Colman and co-authors divided Yellowstone hot springs into three broad categories:

- **Acidic sulfur-rich springs influenced by vapor-phase inputs**
  Microorganisms in acidic springs were generally adapted to include sulfur in their energy metabolisms.
- **Moderately acidic gas-rich hot springs that receive meteoric water and condensed vapor**
  Microorganisms from these springs were generally capable of using volcanic gases, including dihydrogen and methane, as energy sources.
- **Springs with near-neutral to basic pH that primarily receive aqueous phase hydrothermal inputs**
  Microorganisms within these springs appear to have been adapted to heterotrophic metabolism involving nitrate/nitrite, oxygen, or sulfate as electron acceptors.

They concluded that subsurface geological processes, especially phase separation of rising hydrothermal water, shapes the ecology of thermophilic communities at Yellowstone by influencing availability of nutrients and energy resources.

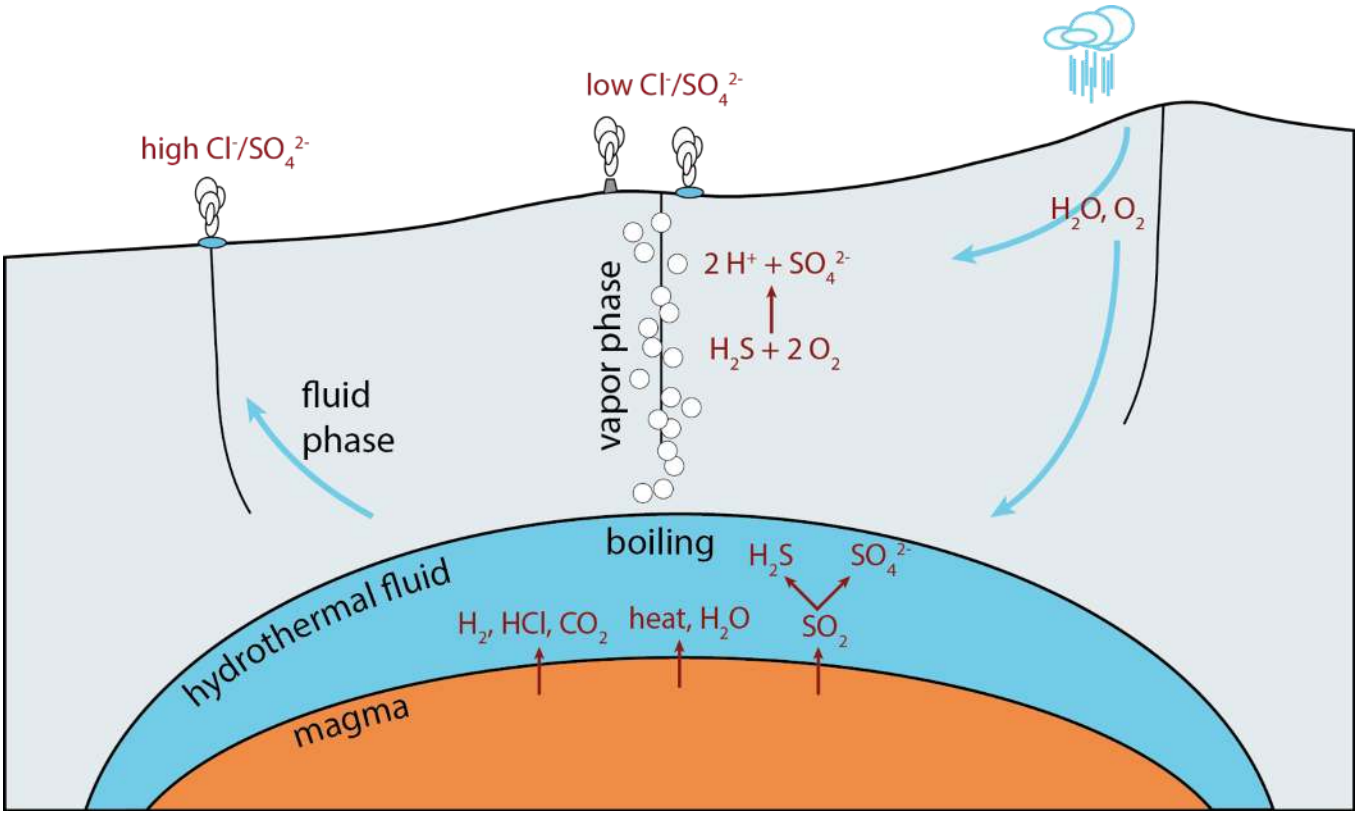


Figure **7.3**: Conceptual diagram showing sources of water and solutes in a terrestrial hydrothermal system. The diagram depicts groundwater circulation driven by shallow magma at an extensional setting or hot spot. The heated water contains dissolved magmatic gas, including sulfur dioxide ($SSOO2$), which can disproportionate into sulfide and sulfate in high temperature aqueous solutions. As the solutions flow toward the surface along faults and joints, decompression boiling can liberate a gas phase enriched in sulfide. As the vapor approaches the surface, exposure to oxic groundwater can cause the sulfide to oxidize, producing sulfate and acid. Springs that primarily receive vapor phase inputs tend to be acidic with low concentration of chloride relative to sulfate. Springs that primarily receive fluid phase inputs tend to have near neutral to basic pH with high concentrations of chloride relative to sulfate. This figure and accompanying text are modified from figure 1 of Colman et al. (2019)
https://commons.wikimedia.org/wiki/File:Hydrothermal_system.png

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7.5.4: Serpentinization

Serpentinization is the hydration and oxidation of ultramafic rocks to produce serpentinites, which are composed of serpentine group minerals with varying amounts of brucite, magnetite, and/or ironnickel alloys (Sleep et al., 2004). Ultramafic rocks are mainly composed of olivine and pyroxene. Alteration of these minerals creates strongly reducing conditions that can generate dihydrogen, methane, and other low-molecular weight organic compounds, which can be used as energy sources by chemotrophs (Proskurowski et al., 2008; Sleep et al., 2004).

The overall process of serpentinization can be illustrated by the following reaction (McCollom and Seewald, 2013):

$$\begin{aligned} &\text{Olivine} + \text{pyroxene} + \mathrm{H_2O} \\ &\leftrightarrow \text{serpentine} + / - \text{brucite} + / - \text{magnetite} + / - \mathrm{H_2} \end{aligned} \tag{7.5.4.1}$$

The reaction is largely restricted to environments with temperatures below 330 to $400°C$ because at higher temperatures, olivine is stable in the presence of water (McCollom and Bach, 2009). During serpentinization, dihydrogen is produced because the olivine and pyroxene contain ferrous iron, which can oxidize to ferric iron and reduce water as illustrated in the following reaction (McCollom and Seewald, 2013):

$$3\ \left(\mathrm{Fe^{2+}O}\right)_{\text{rock}} + \mathrm{H_2O} \leftrightarrow \left(\left(\mathrm{Fe^{2+}}\right)\left(\mathrm{Fe^{3+}}\right)_2\mathrm{O_4}\right)_{\text{rock}} + \mathrm{H_2} \tag{7.5.4.2}$$

Magnetite can serve as a sink for the oxidized iron. The iron can also reside in the serpentine minerals. The fate of the iron is important, from the perspective of microbiology, because it helps determine the amount of dihydrogen that is produced during serpentinization (McCollom and Bach, 2009).

You may be wondering how organic compounds are produced? The dihydrogen produced from serpentinization can in turn form methane and other organics through abiotic reactions with carbon dioxide:

$$\mathrm{CO_2} + 4\ \mathrm{H_2} \leftrightarrow \mathrm{CH_4} + 2\ \mathrm{H_2O} \tag{7.5.4.3}$$

This reaction is equivalent to that catalyzed by hydrogenotrophic methanogens (reaction 5.1.4.2). In a system hosting serpentinization, the reaction can occur abiotically because of the elevated temperatures and strongly reducing conditions. However, the reaction becomes slow without catalysis at temperatures below about $350°C$ (Seewald et al., 2006). Therefore, the temperature influences the extent to which serpentinization generates potential organic electron donors.

Microbial communities can only be supported by serpentinization where ultramafic rocks are exposed to aqueous alteration. This includes a significant portion of the seafloor (Brazelton et al., 2013). Formation and exposure of ultramafic rocks is most common along the axes of slow spreading ocean ridges where the mantle is too cool to form basalts (Dick et al., 2003; Sleep et al., 2004). About 10% of the oceanic crust forms along these locations (Dick et al., 2003). In addition to marine environments, serpentinization also occurs on portions of each continent (Brazelton et al., 2013). Thus, serpentinization has the potential to support microbial communities across a wide range of settings.

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7.5.5: Radiolysis of water

Radioactive decay of isotopes such as uranium-238, uranium-235, and potassium-40 releases alpha, beta, and gamma radiation. Energy from this radiation excites and ionizes water molecules, producing several chemical species including dihydrogen, which can be used as an energy source for microbial communities (Dzaugis et al., 2016).

This source of energy can help sustain microbial populations in subsurface oceanic and continental crust and sediment. In continental crust, Lin et al. (2006) found that sulfate-reducing microorganisms in 2.8 km deep Archaean metabasalt could be sustained for millions of years on radiolytic dihydrogen. In marine environments, Sauvage et al. (2021) estimated that the global rate of radiolytic dihydrogen production in marine sediment is about 1-2% of the global organic flux to the seafloor and may be the main energy source for microbes in sediment older than a couple of million years. Similarly, Dzaugis et al. (2016) concluded that radiolytic dihydrogen is likely more important than iron oxidation as an energy source in basalts older than 10 million years. Taken together, these findings indicate that radiolysis of water is an important and widespread energy source for subsurface microorganisms.

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7.5.6: Silica radical-based reactions

Mechanical shearing of silicate minerals can produce silica radicals such as $\mathrm{Si}\cdot$ that can react with water to produce hydrogen radicals as illustrated in the following reaction (Kita et al., 1982):

$$\mathrm{Si}\cdot + \mathrm{H_2O} \longleftrightarrow \mathrm{SiOH} + \mathrm{H}\cdot \tag{7.5.6.1}$$

Hydrogen radicals produced by these reactions can then form dihydrogen according to the following reaction:

$$\mathrm{H}\cdot + \mathrm{H}\cdot \longleftrightarrow \mathrm{H_2} \tag{7.5.6.2}$$

As such, the reactions have the potential to fuel microbial activity in environments where silicate minerals are being sheared, such as within faults and subglacial environments.

Dunham et al. (2020) recently tested this possibility by analyzing the microbial communities and geochemistry of two glaciated study sites, one located on basaltic and rhyolitic bedrock and the other located on carbonate bedrock with some interbeds of shale, siltstone, and sandstone. They found that dissolved dihydrogen concentrations were an order of magnitude higher at the site with basaltic and rhyolitic bedrock than the carbonate-dominated site and that microorganisms at the basalt/rhyolite site appeared to be better adapted to use of dihydrogen as an energy source in chemolithoautotrophic metabolism. In addition to a greater abundance of silica minerals, the basalt/rhyolite study area also had higher abundance of iron, which can also generate dihydrogen through reduction of water, as described previously (reaction 7.5.4.2). Nonetheless, the results are consistent with the possibility that dihydrogen production by silica shearing can serve as an important energy source.

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7.5.7: Trace atmospheric gases

As mentioned above in the context of fermentation products, small concentrations of potential electron donors should not be overlooked. Atmospheric trace gases as energy resources provides another example that small concentrations can be important. Here, we focus on trace gases in the atmosphere, but similar findings have also recently been documented for the oceans (Lappan et al., 2023).

Potential energy sources such as methane and dihydrogen are present within the atmosphere but at very low concentrations. The bottommost layer of the atmosphere, the troposphere, is mostly composed of nitrogen (78%), oxygen (21%), and argon (0.9%). The remaining 0.1% includes numerous other gases, including water vapor, nitric oxide, nitrous oxide, carbon dioxide, carbon monoxide, carbonyl sulfide, methane, dihydrogen, and more. Among these, some recent studies highlight potential use of methane and dihydrogen, although use of others is possible as well, as reviewed by Conrad (1996).

Recent metagenomics studies that found evidence for use of atmospheric dihydrogen include Bay et al. (2021) and Ortiz et al. (2021). Bay et al. examined microbial communities in topsoil and biological soil crusts along a precipitation gradient in the Negev Desert in Israel. Ortiz et al. analyzed microbial communities in Antarctic desert soils. Both studies used metagenomics to show that the most abundant microbial populations in the soils had the capacity to use atmospheric dihydrogen in aerobic respiration and to support carbon fixation.

Evidence that soil microorganisms can use atmospheric methane as an energy source has also been observed by multiple studies (Conrad, 2009). Recent findings by Tveit et al. (2019) suggest that the capacity to grow aerobically using atmospheric methane as an energy and carbon source is more widespread than previously recognized. They isolated a bacterium closely related to *Methylocapsa gorgona*, which can grow on atmospheric methane. Based on an analysis of publicly available 16S rRNA gene amplicon datasets collected from locations around the world, species closely related to *M. gorgona* are widespread and can provide a significant sink for atmospheric methane.

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7.6: Electroactive organisms

Electroactive microorganisms are those that can exchange electrons from their extracellular environment (Lovley and Holmes, 2021). Some have the ability to export electrons whereas other species have the ability to accept electrons from extracellular sources. For example, as illustrated in Chapter 5, many iron-reducing microorganisms can transfer electrons extracellularly to ferric iron minerals, and some iron reducers can also transfer electrons to methanogens via direct interspecies electron transfer (DIET) (Rotaru et al., 2014a, 2014b). There are also phototrophic electroactive microorganisms that use reduced solid-phases as sources of electrons for carbon fixation (Bose et al., 2014). Thus, extracellular electron exchange can serve diverse roles in microbial metabolism.

For microorganisms that accept electrons from other cells and use them in energy metabolism, the electrons or electron donating cells are essentially their energy source. The electrons may ultimately originate from organic or inorganic chemicals, but they are directly delivered to the cells as electrons and thus this interaction does not fit neatly within the categories of energy sources that are defined above. Thus, we highlight them briefly here before concluding this chapter.

One consequence of these interactions is that the species involved may have access to a wider range of electron donors and acceptors than they would have individually. To illustrate, we can consider the example of methane oxidation coupled with sulfate reduction from Chapter 5:

$$CH_4 + H^+ + SO_4^{2-} \leftrightarrow 2\ H_2O + CO_2 + HS^- \tag{7.6.1}$$

Catalysis of the reaction has not been demonstrated for an individual species. However, it has been shown that anaerobic methanotrophic archaea (ANME) can work together with sulfate-reducing bacteria to push the reaction forward (Scheller et al., 2016; Timmers et al., 2016). The methanotrophs oxidize the methane and pass the electrons to the sulfate reducers, which use them to reduce sulfate (Fig. **7.4**). Through this cooperation, the sulfate reducer has access to an energy resource (methane) that would be inaccessible otherwise, and the methanotroph has access to sulfate as an electron sink.

For a much more comprehensive summary electroactive microbiology than provided here, some recent reviews include Lovley and Holmes (2021), Rotaru et al. (2021), Shen et al. (2016), and Lovley (2017).

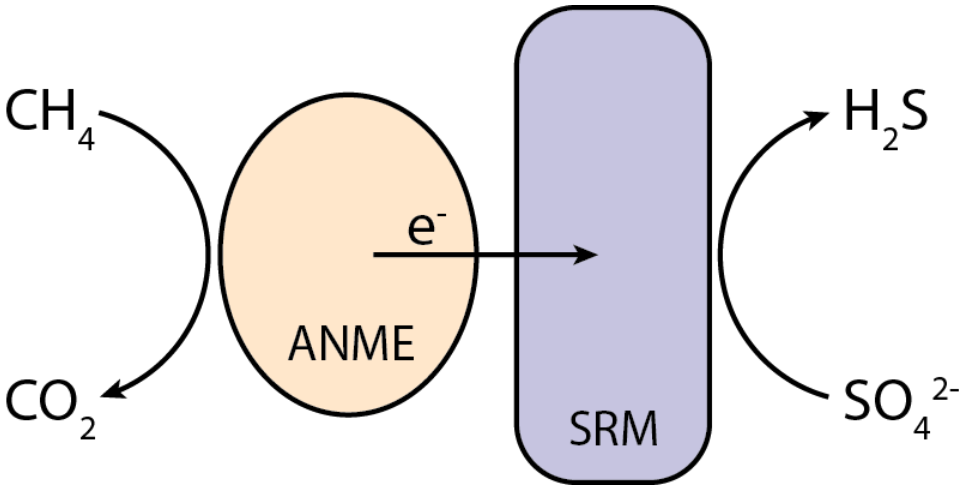


Figure **7.4**: Conceptual model of interspecies electron transfer between anaerobic methanotrophs (ANME) and sulfate reducing microorganisms (SRM). This figure is based on figure 3 of Lovley (2017)
https://commons.wikimedia.org/wiki/File:Electroactive_microbiology.png

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7.7: Concept Check Questions

1. How do cells use carbon, nitrogen, and phosphorus? Where do they get those nutrients?
2. What nutrients are necessary for an organism to make the amino acid cysteine?
3. What role do extracellular enzymes play in carbon cycling?
4. What is nutrient stoichiometry and how can it influence microbial communities?
5. Where is chemotrophy possible? Where is phototrophy possible?
6. Explain how transport and/or environmental change can play a role in delivering energy sources to lithotrophs.
7. What are some potential electron donors that are derived from mantle outgassing? How do these electron donors reach the land surface or seafloor?
8. Where do serpentinites form and how can their formation fuel microbial communities?
9. Explain how fermentation in fine-grained sediments can be linked to respiration in adjacent coarse-grained sediments.
10. What are some examples of microbial activity fueled by atmospheric trace gases? Where might atmospheric trace gases have the potential to contribute a significant portion of the energy to microorganisms?

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CHAPTER OVERVIEW

8: Thermodynamic Controls

> *"The concept of a thermodynamic ladder has over the past three decades almost indelibly colored the environmental scientist's view of the distribution of microbial activity in groundwater flows."*
>
> *— Bethke et al. (2011)*

Cells use energy for life functions, including growth and cell maintenance (Russell, 2007; Russell and Cook, 1995; von Stockar et al., 2006). Growth requires energy to drive anabolic reactions that synthesize biological molecules (Russell, 2007). Maintenance requires energy for at least three functions: motility, turnover of biological molecules, and re-establishment of proton gradients across the cell membrane (Russell, 2007). These functions make up much of the work carried out by cells.

To supply energy for these needs, chemotrophs catalyze chemical reactions that release energy. We can assess the net energy yield of a chemical reaction using Gibbs free energy calculations. Thus, Gibbs free energy calculations can tell us which redox reactions within an environment might be useful as sources of energy for microorganisms. Moreover, the free energy yield of a reaction also has the potential to influence rates of microbial reactions. In this chapter, we primarily focus on describing how to carry out Gibbs free energy calculations and how we can use these relationships to construct a framework for evaluating what microbial reactions are occurring in an environment. In Chapter 9, we consider microbial reaction kinetics, including the link to reaction thermodynamics.

8.1: Mass action
8.2: Gibbs free energy
8.3: Impacts of changes in product and reactant activities
8.4: Available, captured, and usable energy
8.5: Redox zonation
8.6: Characterizing redox processes in aqueous systems
8.7: Answers to practice problems
8.8: Concept Check Questions
8.9: References

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8.1: Mass action

There is a lot of misleading information in the scientific literature about how to quantify the amount of energy released by a microorganism's catabolic reaction (Amend and LaRowe, 2019). To help you avoid mistakes, we will start with the basics and first consider the concept of mass action before moving on to free energy calculations.

At equilibrium, the forward rate of a reaction equals the reverse reaction rate, so there is no net change in the reaction mixture. We can describe the equilibrium point of a reaction using the mass action equation. Consider the following generic reaction:

$$a\ \mathrm{A} + b\ \mathrm{B} \longleftrightarrow c\ \mathrm{C} + d\ \mathrm{D} \tag{8.1.1}$$

where A, B, C, and D represent reactants and products and a, b, c, and d represent their respective stoichiometric coefficients. For this reaction, we can define a reaction quotient (Q) as follows:

$$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \tag{8.1.2}$$

Here and throughout this book, brackets [ ] indicate chemical activity for aqueous species and fugacity for gases, following Faure (1991). For a brief review of the concepts of activity and fugacity, see Box 8.1. Also, when formulating the reaction quotient, we can often exclude pure solids and liquids if they are present in a reaction. The activity of pure solids and liquids is 1 and the activity of dilute aqueous solutions is also nearly 1.

When a reaction mixture is in equilibrium, the value of Q is equal to K, the equilibrium constant for the reaction. Specifically, regardless of what values of activity and/or fugacity are inserted for each product and reactant, if the reaction mixture is at equilibrium, then the value of the quotient is constant at a given temperature and pressure and equal to K. This relationship is referred to as the law of mass action. If Q is less than K, then the reaction needs to move forward to reach equilibrium. If the value of Q is greater than K, then the reaction needs to go backward to reach equilibrium.

As an example, we will calculate the value of Q for the following reaction, which describes microbial reduction of iron in hematite ($\mathrm{Fe_2O_3}$) coupled with dihydrogen oxidation:

$$\mathrm{H_2}\ (aq) + \mathrm{Fe_2O_3}\ (s) + 4\ \mathrm{H^+} \longleftrightarrow 3\ \mathrm{H_2O}\ (l) + 2\ \mathrm{Fe^{2+}} \tag{8.1.3}$$

Using an activity of 1 for water and hematite, the reaction quotient is:

$$Q = \frac{\left[\mathrm{Fe^{2+}}\right]^2}{\left[\mathrm{H_2}\right]\left[\mathrm{H^+}\right]^4} \tag{8.1.4}$$

It is acceptable to calculate Q as formulated in equation 8.1.4. However, by putting the quotient in log form, we can make the calculation more convenient by removing exponents:

$$\log Q = 2\log\left[\mathrm{Fe^{2+}}\right] - \log\left[\mathrm{H_2}\right] - 4\log\left[\mathrm{H^+}\right] \tag{8.1.5}$$

If the environment where the reaction is occurring has a composition consistent with that in Table 8.1, the $\log Q$ value is 23.68. The $\log K$ at the temperature of the environment (25°C) is equal to 29.18 (Appendix A). Thus, the value of Q is less than K and we conclude that the reaction needs to move forward to reach equilibrium.

Table 8.1: Hypothetical Conditions used for Example and Practice Calculations

Parameter	Concentration/Value	Activity*	Log activity
$H_2\ (aq)$	10 nM	9.89×10^{-9}	−8.005
CH_3COO^-	50 μM	4.51×10^{-5}	−4.3654
$O_2\ (aq)$	100 μM	9.89×10^{-5}	−4.005
NO_3^-	200 μM	1.83×10^{4}	−3.7376
SO_4^{2-}	1 mM	6.69×10^{-4}	−3.1746
$N_2\ (aq)$	0.5 mM	4.94×10^{-4}	−3.3065
NH_4^+	100 μM	9.13×10^{-5}	−4.0394
Fe^{2+}	100 μM	7.29×10^{-5}	−4.1633
$H_2S\ (aq)$	5 μM	4.41×10^{-6}	−5.3559
$CH_4\ (aq)$	100 μM	9.89×10^{-5}	−4.005
HCO_3^-	2 mM	5.80×10^{-4}	−3.2369
H^+	pH 6.00	1.00×10^{-6}	−6

*Activities are calculated using The Geochemist's Workbench program SpecE8 with temperature at 25°C and solution ionic strength at 4.2 mmolal.

Practice 8.1.1

Calculate the value of the reaction quotient for the following reactions under the hypothetical conditions listed in Table 8.1.

$$CH_3COO^- + H^+ + SO_4^{2-} \longleftrightarrow 2\ HCO_3^- + H_2S\ (aq)$$
$$CH_3COO^- + 8\ FeOOH\ (s) + 15\ H^+ \longleftrightarrow 2\ HCO_3^- + 12\ H_2O\ (l) + 8\ Fe^{2+}$$

Use an activity of 1 for solids and liquids. Answers are provided at the end of the chapter (Practice 8.1.1).

Box 8.1: Activity and Fugacity

The **activity** of an aqueous chemical species can be thought of as an effective concentration. In very dilute solutions, activity is numerically equivalent to concentration in molality (Bethke, 2008). However, as the concentrations of solutes increases in a solution, the difference between activity and concentration grows.

Activity differs from concentration in response to electrostatic interactions within solutions. Ions and polar molecules with like charges repulse one another whereas those with opposite charges attract. These interactions increase order within the solution by creating a loose structure. Some of the system's energy is consumed in creating that order and the amount consumed is proportional to the extent of electrostatic interactions. In other words, as solute concentrations increase, electrostatic interactions increase and cause the difference between activity and concentration to grow. To account for these effects in our thermodynamic calculations, we use activities rather than concentrations.

Several approaches have been developed to calculate activities. Many are based on the Debye-Hückel equation, which calculates an activity coefficient (γ) that is used to calculate the activity (a) of chemical species (i) as:

$$a_i = \gamma_i C_i$$

where C is the concentration in molal units (mol solute/kg solvent) and activity and the activity coefficient are unitless. In an ideal solution, the activity coefficient is one and therefore activity and concentration are equal.

Fugacity is conceptually similar to activity except it is applied to gases rather than aqueous chemical species. Specifically, we can think of **fugacity** as the effective partial pressure of a gas. For gases at low partial pressures, fugacity is numerically

equivalent to partial pressure, but as partial pressure increases, the difference between fugacity and partial pressure grows to account for greater deviation from ideal gas behavior. Fugacity (f) for a gas species (i) is related to partial pressure (P) in bars according to the following equation:

$$f_i = \gamma_i P_i$$

where γ is the fugacity coefficient, and fugacity and the fugacity coefficient are unitless.

For most parameters, analytical laboratories do not report results in terms of activity and fugacity. Therefore, in order to calculate the free energy change of a microbial reaction, we first need to calculate the activities and fugacities of all chemical species found in the reaction. These are the values that should typically be inserted into the reaction quotient, not concentrations and partial pressures. A convenient way to accomplish this task is with geochemical modeling software. Numerous geochemical modeling programs have been developed. Two commonly used options include The Geochemist's Workbench (GWB) (Bethke, 2018) and PHREEQC (Parkhurst, 1995). Among other capabilities, these programs calculate chemical speciation and the activity or fugacity of those species within a given geochemical system. An example of how to carry out a speciation calculation with one of the GWB programs is available online (Bethke and Farrell, 2016).

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8.2: Gibbs free energy

As described above, the difference between the reaction quotient (Q) and the equilibrium constant (K) tells us about the extent to which a reaction is out of equilibrium. By calculating the Gibbs free energy change of a reaction (ΔG_r), we take this a step further and convert the extent of disequilibrium into an amount of energy.

For a reaction at equilibrium, $Q = K$ and the free energy change is zero ($\Delta G_r = 0$). Exergonic reactions are those that need to move forward to reach equilibrium ($Q < K$) and in doing so, they release energy and thus have a negative free energy change ($\Delta G_r < 0$) (Fig. 8.1). Endergonic reactions are those that need to move backward to reach equilibrium ($Q > K$). For an endergonic reaction to move forward, energy would need to be added to the reaction mixture ($\Delta G_r > 0$). Microorganisms catalyze both types of reactions as part of their metabolisms, but only exergonic reactions can supply chemotrophs with energy.

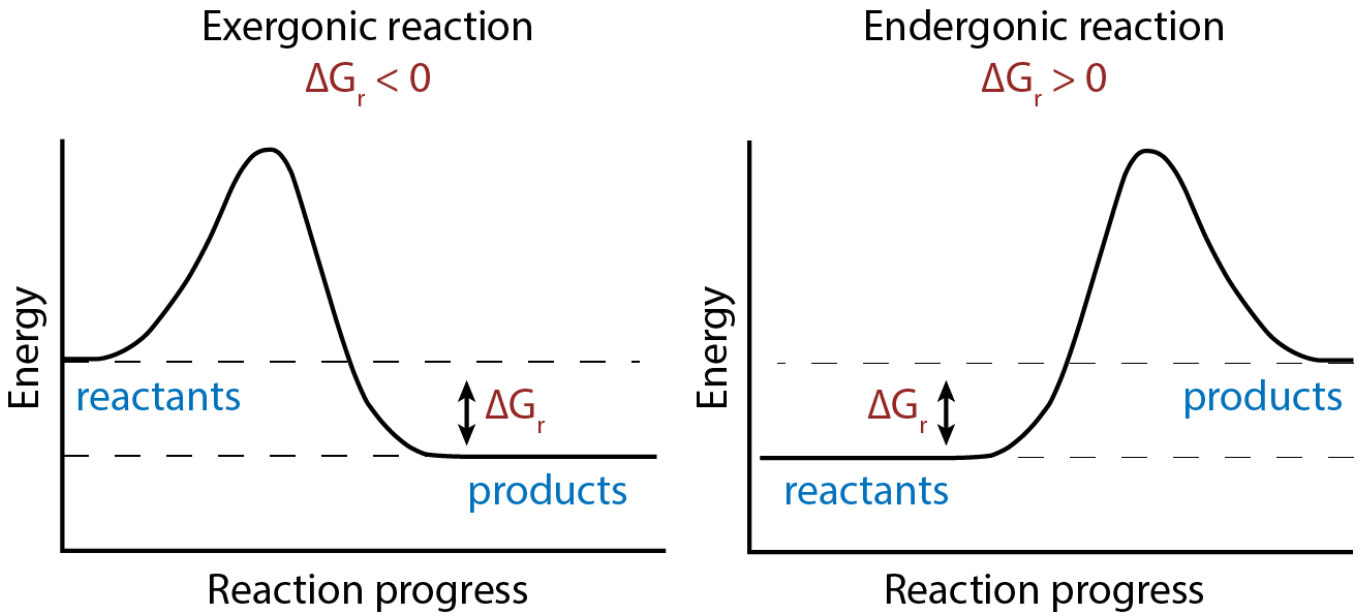


Figure 8.1: Variation in free energy during an exergonic and endergonic reaction according to transition-state theory. https://commons.wikimedia.org/wiki/File:Gibbs_free_energy_changes.png

There are multiple ways to calculate the free energy change of a reaction. Here, we will calculate free energy changes by correcting the standard state free energy change of the reaction (ΔG_r°) for the conditions of the environment:

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q \tag{8.2.1}$$

where R is the gas constant ($0.008314\ \text{kJ mol}^{-1}\text{K}^{-1}$), T is temperature (in Kelvin (K)), and Q is the reaction quotient. We can also write the equation in terms of log base 10:

$$\Delta G_r = \Delta G_r^\circ + 2.303RT \log Q \tag{8.2.2}$$

The value of Q reflects the activities of reactants and products of microbial reactions within an environment. T accounts for the temperature of the environment of interest. Thus, we can see that changes in the composition and temperature of an environment can alter the energy yields of microbial reactions.

Before we can carry out this calculation, we also need the standard state free energy change for the reaction. We can calculate one based on equation (8.2.2). As noted above, when $Q = K$, a reaction is at equilibrium and $\Delta G_r = 0$. Inserting these values into equation (8.2.2), we get

$$0 = \Delta G_r^\circ + 2.303RT \log K \tag{8.2.3}$$

Solving for the standard state free energy change gives the following:

$$\Delta G_r^\circ = -2.303RT \log K \tag{8.2.4}$$

Therefore, given values of $\log K$ at the temperature of interest, we can calculate standard state free energy changes for a reaction at that temperature. Equilibrium constant values for select microbial reactions are provided in Appendix A. The values listed are only appropriate for environments with temperatures of $25°C$ $(298.15\ K)$. However, the appendix also includes polynomial equations that can be used to estimate the log value of the equilibrium constants at different temperatures.

For an example calculation, let's reconsider the reaction from our example reaction quotient calculation (reaction $(8.1.3)$). Using equation $(8.2.4)$ and a $\log K$ value for the reaction at $25°C$ (29.1806), the standard state free energy change of the reaction is:

$$\Delta G_r^\circ = -2.303\left(0.008314\ \frac{\text{kJ}}{\text{mol K}}\right)(298.15\ \text{K})(29.1806) = -166.58\ \text{kJ/mol} \tag{8.2.5}$$

Assuming conditions consistent with our hypothetical environment (Table 8.1) the log of the reaction quotient is 23.68. Inserting this value and the standard state free energy into equation $(8.2.2)$, we get:

$$\Delta G_r = \left(-166.58\ \frac{\text{kJ}}{\text{mol}}\right) + 2.303\left(0.008314\ \frac{\text{kJ}}{\text{mol K}}\right)(298.15\ \text{K})(23.68) \tag{8.2.6}$$

which gives a Gibbs free energy change of $-31.4\ \text{kJ/mol}$. Under these conditions, therefore, the reaction is thermodynamically favorable $(\Delta G_r < 0)$ and has the potential to serve as an energy source for iron-reducing microorganisms.

Practice 8.2.1

Based on reaction quotient values calculated for parts A and B of Practice $8.1.1$, what are the free energy yields of those reactions? Use Appendix A to obtain $\log K$ values for the reactions at $25°C$.

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8.3: Impacts of changes in product and reactant activities

As noted above, changes in the chemical composition of an environment can alter the free energy yield of microbial reactions. We can illustrate this relationship by extending the example calculation above to consider environments with different pH values and activities of ferrous iron. For convenience, the microbial reaction we are considering is repeated here:

$$H_2\ (aq) + Fe_2O_3\ (s) + 4\ H^+ \leftrightarrow 3\ H_2O\ (l) + 2\ Fe^{2+} \tag{8.3.1}$$

First, let's consider the impact of variation in pH. As we do, we will assume concentrations identical to those in Table 8.1, except allow pH to increase from 6 to 8. As that happens, the Gibb's free energy yield of the reaction changes from -31.4 to $14.0\ kJ/mol$ (Figure 8.2A). Thus, as pH increases, the reaction becomes endergonic and not useful as a source of energy for chemotrophs.

We can anticipate this change in reaction energy yield based on the reaction itself, which includes a large number of hydrogen ions as reactants. As we increase pH, or in other words, decrease the activity of hydrogen ions, we are removing a reactant from the system and thus making it less favorable for the reaction to move forward.

Next, we will consider the impact of variation in ferrous iron activity. Holding pH at 6, if ferrous iron concentration increases from $100\ \mu M$ to $1\ mM$, the Gibb's free energy yield of the reaction changes from -31.4 to $-20.1\ kJ/mol$ (Figure 8.2B). Thus, as ferrous iron activity increases, the reaction becomes less thermodynamically favorable. However, it remains exergonic and thus has the potential to continue to serve as an energy source across the range of ferrous iron activities considered.

Again, the impact of increasing ferrous iron activity can be anticipated based on the reaction, which includes ferrous iron as a product. Accumulation of a product causes a reaction to become less thermodynamically favorable. Taken together with our observations about pH above, we can generally say that reactant removal and product accumulation can cause reactions to become less thermodynamically favorable, whereas reactant addition and product removal cause reactions to become more favorable.

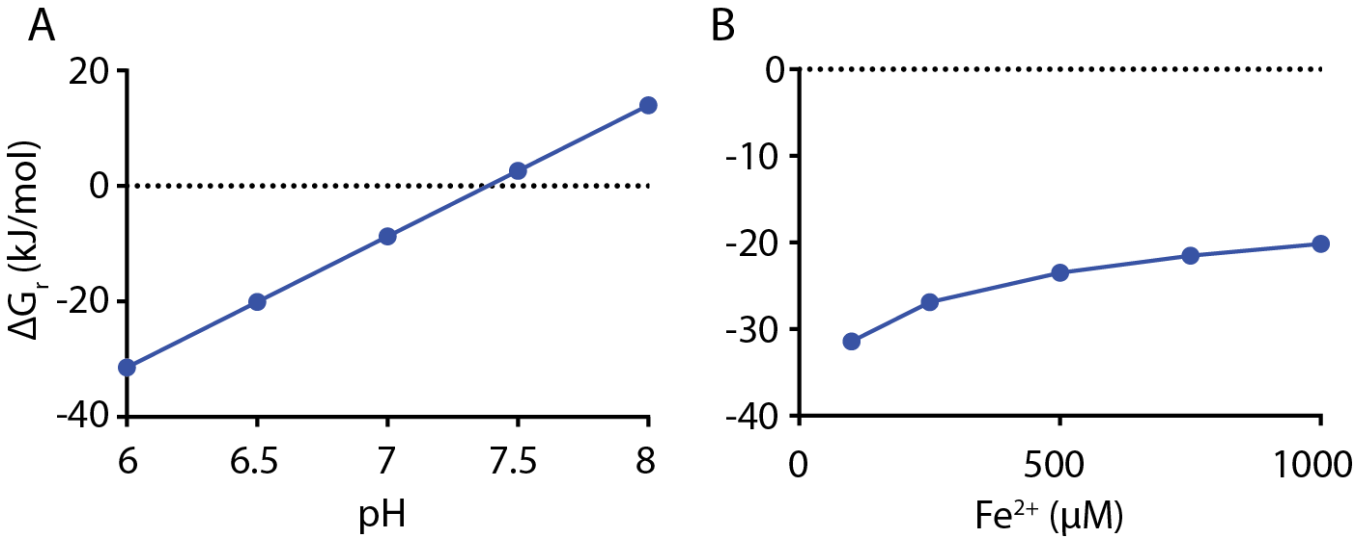


Figure 8.2: Variation in the Gibbs free energy yield of hematite reduction in response to variation in (A) pH and (B) ferrous iron concentration. Note that (B) plots ferrous iron concentration but the free energy calculation was carried out with ferrous iron activities corresponding to those concentrations.
https://commons.wikimedia.org/wiki/File:Energy_yield_of_iron_reduction.png

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8.4: Available, captured, and usable energy

Previously, we noted that chemotrophs can only obtain energy from reactions that are exergonic, but there is a little more to the story than that. First, even if a reaction is exergonic, it may not release enough energy to be useful for a cell. There appears to be an energy threshold that must be cleared before a reaction can be useful for catabolism. Secondly, there are limits to how much energy a cell can capture from a reaction. If a reaction releases significantly more than that amount, changes in the reaction's free energy yield may have little impact on its use by the microbial community.

The analysis of Bethke et al. (2011) offers one approach to quantifying these relationships. For their analysis, they characterized the amount of energy available in the environment for a reaction as the negative of that reaction's free energy yield:

$$\Delta G_A = -\Delta G_r \tag{8.4.1}$$

Here, positive values of energy available (ΔG_A) indicate that a reaction is thermodynamically favorable. They characterized the energy captured by the cell (ΔG_C) as:

$$\Delta G_C = m\Delta G_P \tag{8.4.2}$$

where m is the number of ATPs produced per turnover of the net reaction and ΔG_P is the free energy change of ATP synthesis ($\mathbf{kJ \cdot mol^{-1}}$). The value of ΔG_P is commonly assumed to be $\mathbf{45\ kJ/mol}$ but its value would vary with conditions within the cell. Putting these concepts together, Bethke et al. then defined usable energy (ΔG_U) as the difference between the amount of energy available in an environment and the amount captured by the cell:

$$\Delta G_U = \Delta G_A - \Delta G_C \tag{8.4.3}$$

Based on their analysis and previous studies, useable energy provides the thermodynamic drive for a cell's catabolism (Bethke et al., 2011; Jin and Bethke, 2002; von Stockar et al., 2006). As the amount of energy available decreases and approaches the amount captured by the cell, usable energy dwindles and reactions slow and eventually stop. Thus, we can think of the amount of energy captured as the energy threshold that needs to be cleared for a reaction to be useful. Conversely, where energy availability in an environment far exceeds the amount a cell can capture, further increases in energy availability would not necessarily benefit the cell. As such, we may not see a direct correlation between the energy yield of a microbial reaction and the extent to which a microbial community is using that reaction.

Practice 8.4.1

Picking up the results from Practice **8.2.1**, calculate the amount of usable energy for each reaction. Assume that the cells require $\mathbf{45\ kJ/mol}$ for ATP synthesis and that sulfate reducers produce 1 ATP per turnover of their net reaction whereas iron reducers produce 1.25. These values are from Bethke et al. (2011).

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8.5: Redox zonation

Patterns in the redox chemistry of many environments indicate that the electron acceptors used by chemotrophic respiration tend to be depleted sequentially in order of decreasing energy yield (Fig. **8.3**). Oxygen is typically more thermodynamically favorable as an electron acceptor than nitrate. Therefore, microbial communities tend to consume oxygen before nitrate. Where oxygen is depleted, the community may primarily respire nitrate if it is available, and where nitrate is depleted, respiring microorganisms may move on to less favorable electron acceptors such as ferric iron minerals, sulfate, and carbon dioxide. Patterns in chemistry consistent with this redox zonation have been observed in aquifers, soils, marine sediments, microbial biofilms, and more (Champ et al., 1979; Froelich et al., 1979; Patrick Jr. and Henderson, 1981; Stewart and Franklin, 2008).

Zonation in electron acceptor use has been interpreted to reflect competition between microbes for electron donors (Chapelle and Lovley, 1992; Hoehler et al., 1998; Lovley and Phillips, 1987). Microorganisms that can capture more energy from their reactions can have competitive advantages over those that capture less, including more energy for growth and maintenance and faster reactions (Jin, 2012; Jin and Bethke, 2007; Lovley and Goodwin, 1988; Roden and Jin, 2011). As such, the microbial community uses more energetically favorable reactions preferentially to less favorable reactions. In other words, the community works its way along the thermodynamic ladder from most to least favorable reactions.

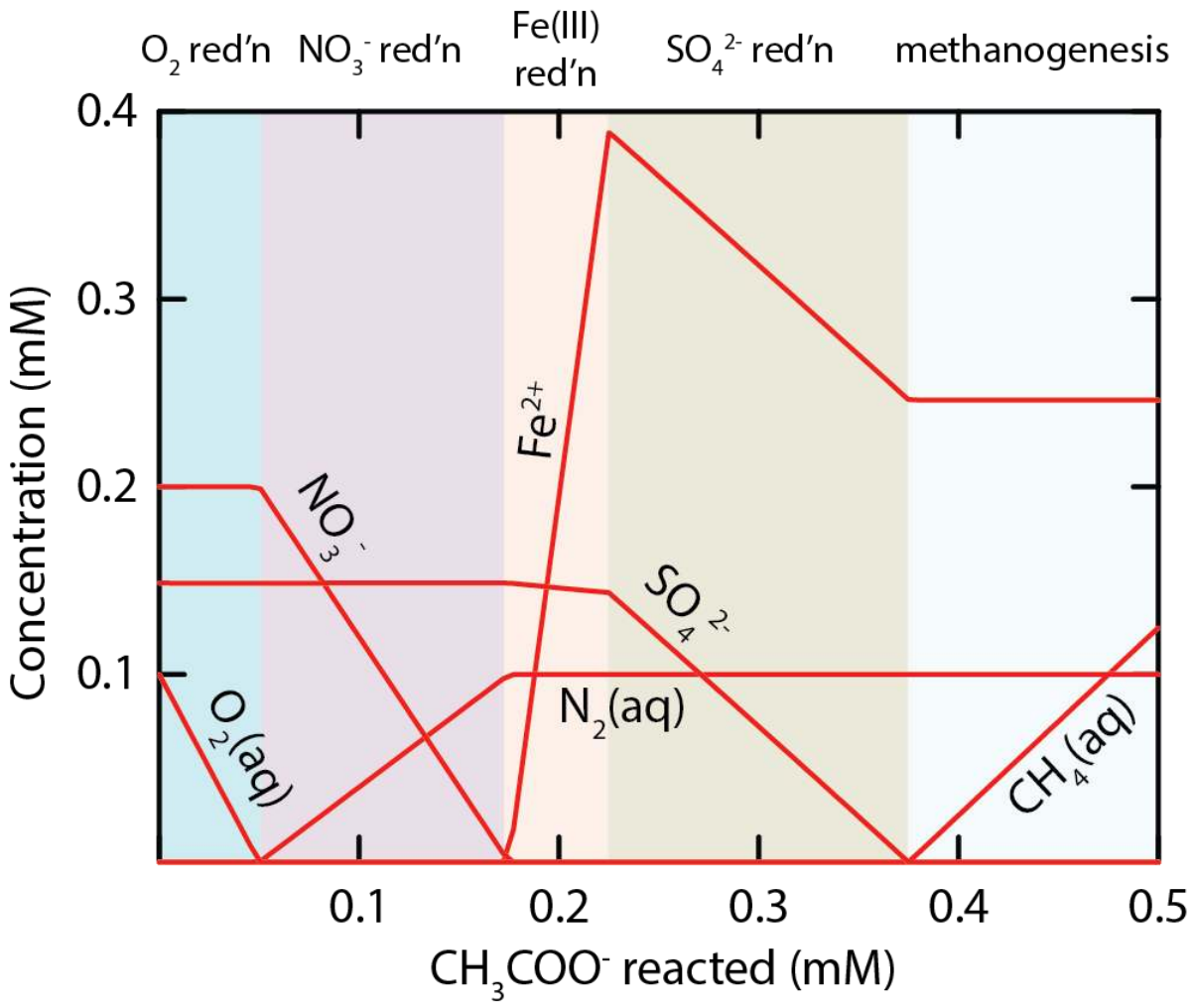


Figure **8.3**: Redox zonation illustrated using reaction path modeling. The model simulates titration of a closed system with acetate. The system initially contains oxygen, nitrate, ferrihydrite ($Fe(OH)_3$), and sulfate as potential acceptors of electrons liberated by acetate oxidation. As acetate is added, electron acceptors are depleted in order of decreasing free energy yield. Specifically, oxygen is depleted first, followed by nitrate, and so forth. Once sulfate is depleted, acetate is consumed by acetoclastic methanogenesis. Dinitrogen, ferrous iron, and methane concentrations increase in response to nitrate reduction, iron reduction, and methanogenesis, respectively. In the iron-reducing zone, free sulfate concentration decreases slightly in response to formation of an aqueous iron-sulfate complex ($FeSO_4$ (*aq*)). In the sulfate-reducing zone, mackinawite (FeS) precipitation lowers ferrous iron concentration and prevents significant accumulation of dissolved sulfide (not shown). Initial conditions in the model system are consistent with those listed in Table **8.1**, except sulfate concentration is 150 µM, 400 µM of ferrihydrite is included, and dinitrogen is not present. The model was calculated with the React module of The Geochemist's Workbench software. The calculation assumes that reactions reach equilibrium at each step along the reaction path.
https://commons.wikimedia.org/wiki/File:Redox_zonation.png

This model can allow us to define an overall framework for predicting microbial processes based on redox chemistry, which we do later in this chapter. However, it is also recognized that this redox zonation model is an oversimplification (Bethke et al., 2011; Konhauser, 2007), and it is important to understand some of the reasons why that is the case if we are to use such a framework effectively.

First, free energy yields of microbial reactions vary with environmental conditions. As a result, a ranking of reactions in terms of energy yield can differ from one environment to the next. Moreover, energy yields of different reactions can overlap, obscuring any thermodynamic hierarchy that might exist otherwise. As an example, pH affects the amount of energy released by reduction of ferric iron in (oxyhydr)oxide minerals, as shown in Figure **8.2A**. As pH increases, the reaction becomes less favorable. Because of this relationship, iron reduction can be more favorable than sulfate reduction and methanogenesis if the pH of the environment is acidic. However, where pH is neutral or basic, sulfate reduction and methanogenesis can release as much or more energy than iron

reduction (Bethke et al., 2011; Jin and Kirk, 2018; Kirk et al., 2013; Marquart et al., 2019; Paper et al., 2021; Postma and Jakobsen, 1996).

Secondly, microbial environments are typically heterogenous in chemical and physical properties. The properties of microbial environments can change significantly on scales that are small relative to human perception but enormous to a microbe. We recall from Chapter 3 that microorganisms are very small. If you lined up 10,000 cells each with a length of 1 μm, the line of cells would only extend for 1 cm. However, properties of many microbial environments can change significantly within a centimeter. Therefore, the likelihood that more than one form of microbial respiration is present in a microbial habitat increases quickly with the scale of observation.

As an example, we can consider the existence of anoxic microenvironments with upland soils. In terms of bulk chemical properties, upland soils are often considered to be well aerated and dominated by aerobic microbial respiration. However, anoxic microenvironments can exist within upland soils and play an important role in organic carbon storage (Keiluweit et al., 2017, 2016). In upland soils, macropores ($> 50\ \mu m$) surround aggregates and soil peds. Gas and water flow can advectively transport oxygen through the macroporesm, but transport into the interior of an aggregate or ped may be limited to diffusion. If demand for electron acceptors exceeds oxygen supply in the aggregate or ped interior, then anoxic conditions can develop there, and anaerobic microorganisms may be active. Thus, structural and compositional heterogeneity within upland soils can create complex patterns of redox chemistry.

A third source of complexity stems from the fact that the redox state of an environment is not necessarily constant over time. As such, the spatial distribution of redox zones can vary. As an example, variation in water saturation in soil can decrease oxygen supply relative to electron acceptor demand, causing development of anoxic conditions, as discussed in Chapter 6. Therefore, where water saturation varies over time, the redox state of the soil can also be temporally variable (Fig. 6.3B).

Fourth, it is critical to recognize that thermodynamics is not the only thing that controls the distribution of microbial reactions. Properties of the environment such as temperature, salinity, and the form and abundance of electron donors influence microbial populations. Competition between different groups of microorganisms for electron donors has the potential to be influenced not only by thermodynamics but also kinetics (Bethke et al., 2008). Moreover, interactions between microbial groups extend beyond competition, as discussed in Chapter 10. Some groups coexist and can even cooperate with one another, for example, which influences their ability to grow within an environment. Such complexity is not well captured by a framework primarily based on the thermodynamic ladder.

Practice 8.5.1

Calculate the free energy change (ΔG_r) for the following reactions. Assume environmental conditions consistent with those listed in Table 8.1 and an activity of 1 for water. Obtain $\log K$ values for each reaction in Appendix A. Which of these reactions has the potential to give microorganisms the biggest advantage in terms of energy?

$$CH_3COO^- + 2\ O_2 \longleftrightarrow 2\ HCO_3^- + H^+$$
$$CH_3COO^- + 0.6\ H^+ + 1.6\ NO_3^- \longleftrightarrow 2\ HCO_3^- + 0.8\ N_2\ (aq) + 0.8\ H_2O$$
$$CH_3COO^- + H_2O \longleftrightarrow HCO_3^- + CH_4\ (aq)$$

Practice 8.5.2

How does the source of ferric iron affect the energy available for microbial iron reduction? To find out, calculate the free energy change (ΔG_r) for the following reactions. Assume environmental conditions consistent with those listed in Table 8.1 and an activity of 1 for water. Obtain $\log K$ values for each reaction in Appendix A. Which of these reactions has the potential to give microorganisms the biggest advantage in terms of energy?

$$CH_3COO^- + 15\ H^+ + 8\ Fe(OH)_3 \longleftrightarrow 2\ HCO_3^- + 20\ H_2O + 8\ Fe^{2+}$$
$$CH_3COO^- + 15\ H^+ + 8\ \text{Goethite} \longleftrightarrow 2\ HCO_3^- + 0.8\ N_2\ (aq) + 0.8\ H_2O$$
$$CH_3COO^- + 15H^+ + 4\ \text{Hematite} \longleftrightarrow 2\ HCO_3^- + 8\ H_2O + 8\ Fe^{2+}$$

Practice 8.5.3

Repeat the calculation for Practice **8.5.2** with all parameters the same except increase the pH from 6 to pH 8. Are all three ferric iron sources still potentially useful for dissimilatory metabolism? What do the results suggest about the pattern of redox zonation in systems with pH 8?

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8.6: Characterizing redox processes in aqueous systems

We can make rough estimates of the redox processes in aqueous environments using routinely collected water chemistry data. Results of such an analysis can improve our understanding of controls on concentrations of natural and anthropogenic contaminants. We can gain insight into production and consumption of greenhouse gases, including carbon dioxide, nitrous oxide, and methane. We can also improve our ability to predict how the chemistry and microbiology of a system will respond to changes in conditions. Thus, such an analysis can have many applications, whether it is used by itself or alongside a direct analysis of microbial community composition.

The flowchart provided in Figure **8.4** provides criteria that we can use to assess the dominant redox process where a water sample is collected. It assumes electron acceptors will be used in an order of preference consistent with the thermodynamic ladder and is modified from the criteria described by McMahon and Chapelle (2008). Concentration thresholds for oxygen, nitrate, and ferrous iron are taken directly from McMahon and Chapelle. The threshold indicated for sulfate concentration (3 mg/L) is based on a kinetic modeling analysis (Lovley and Klug, 1986) and results of a field study (Flynn et al., 2013). Also, sulfate reduction and methanogenesis are indicated as potential reactions that can occur alongside iron reduction. Based on results from Marquart et al. (2019) and Paper et al. (2021), iron reduction is more likely to occur alongside either sulfate reduction or methanogenesis if the pH of the environment is basic rather than acidic.

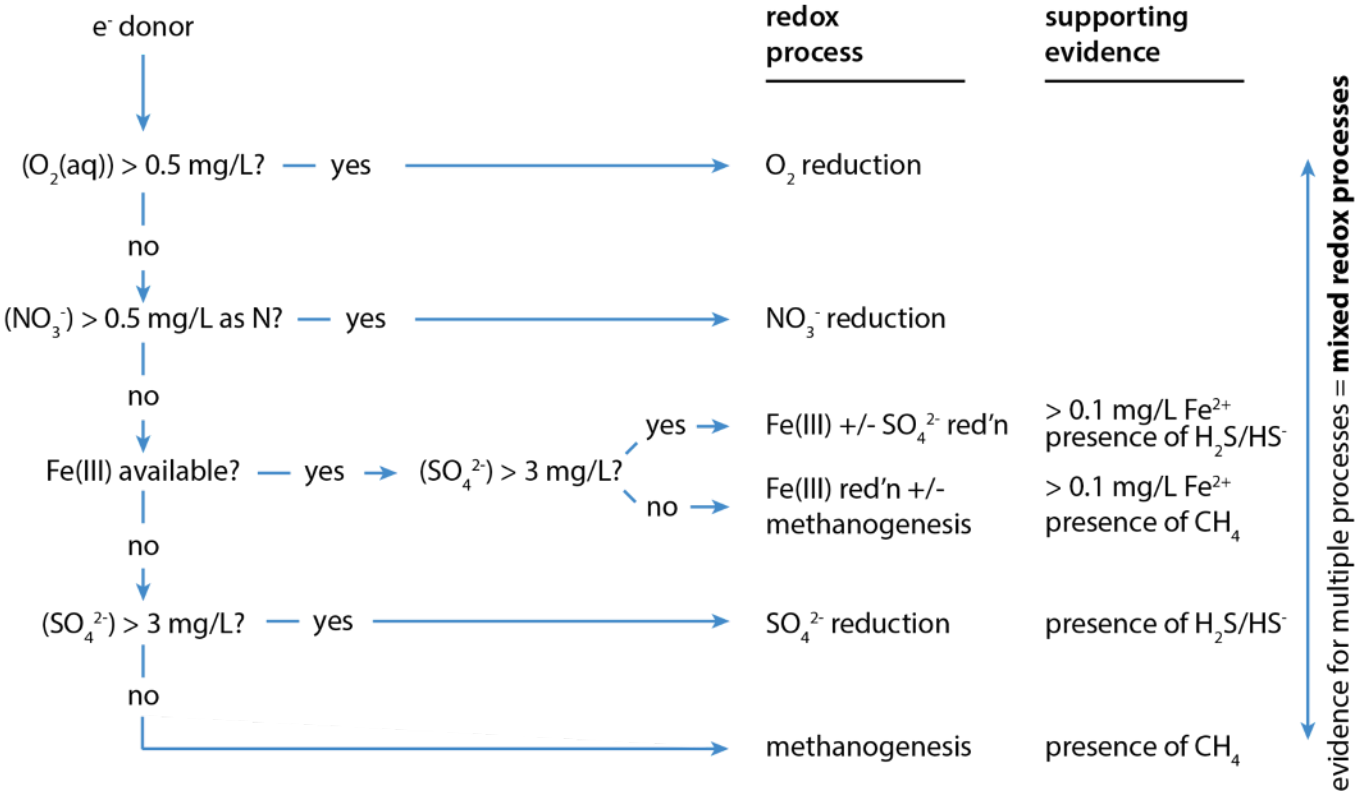


Figure **8.4**: Flowchart for evaluating the dominant redox process in an aqueous system using water chemistry data. As described in the text, this framework is modified from that presented in McMahon and Chapelle (2008).
https://commons.wikimedia.org/wiki/File:Redox_framework.png

When applying this framework, it is important to recognize the shortcomings of the redox zonation model, as previously noted in Section 8.5. This flowchart can help us get a sense of the main redox process that is occurring. However, other redox processes may also be occurring, even if few clues are preserved in the bulk chemistry of water samples. Products of microbial reactions can be removed from solution by subsequent reactions. For example, where iron reduction and sulfate reduction occur simultaneously, sulfide may be held to low concentrations by precipitation with ferrous iron, and thus of no help in identifying sulfate-reducing activity. As a second example, imagine that methanogenesis is occurring within an anoxic microenvironment within an aquifer. If the methane diffuses out of the microenvironment and is then exposed to sulfate, ferric iron, nitrate, or oxygen, it can then be oxidized and removed from the solution.

To provide an example application, we consider the groundwater geochemistry data in Table 8.2. The groundwater samples described in the table were collected from the Mahomet glacial aquifer in Illinois, USA. Based on the criteria in Figure 8.4, an interpretation of the redox process for each sample is as follows:

- Sample 1: the composition is consistent with iron reduction and possibly also sulfate reduction. Oxygen and nitrate reduction may also occur, although the low concentrations of oxygen and nitrate suggests that they are not dominant processes.
- Sample 2: elevated oxygen concentration suggests that aerobic respiration is dominant.
- Sample 3: elevated iron and methane concentrations and low oxygen, nitrate, and sulfate concentrations suggest that iron reduction and methanogenesis are dominant.
- Sample 4: elevated iron and sulfate concentrations and low concentrations of oxygen, nitrate, and methane are consistent with iron reduction and possibly also sulfate reduction.
- Sample 5: like sample 3, elevated iron and methane concentrations and low oxygen, nitrate, and sulfate suggest iron reduction and methanogenesis are dominant.

These interpretations are based on groundwater chemistry, but the results are consistent with findings from a study that directly examined the microbial community in the aquifer with sequencing analysis. Flynn et al. (2013) examined microbial samples from wells producing water with low concentrations of oxygen and nitrate. Sequences related to species associated with iron reduction were common in all of their samples. Samples with sulfate concentrations above 3 mg/L also contained sequences related to sulfate reducers whereas those with sulfate concentration below 3 mg/L contained methanogens. Thus, sulfate availability appears to be a major control on the function of the microbial community in the aquifer.

Table 8.2: Composition of select groundwater samples collected from the Mahomet glacial aquifer*

Sample	pH	O_2 (aq)	Fe (aq)	NO_3-N	SO_4^{2-}	CH_4 (aq)
		mg/L	mg/L	mg/L as N	mg/L	µM
1	7.41	0.33	1.6	0.41	3.8	n/a**
2	7.24	8.65	< 0.1	17	42	n/a
3	6.62	< 0.27	3.5	< 0.06	< 0.25	627.4
4	6.95	< 0.36	1.2	< 0.06	61	0.9
5	7.07	0.4	2.8	< 0.06	< 0.25	520.8

*Data sources: methane data are from Kirk et al. (2004) and the rest of the data are from Holm et al. (2004)

** n/a indicates that the concentration of the parameter was not analyzed and < indicates that the concentration is below the detection limit.

Practice 8.6.1

Use the framework provided in Figure 8.4 to identify the major redox process or processes for each groundwater sample in the table below. Assume that the dissolved iron is ferrous iron. At the pH of the samples, ferric iron has low solubility. The samples were collected from the High Plains aquifer. The data source is the USGS National Water Information System (USGS, 2016).

Table 8.3: Groundwater Sample Data for Practice 8.6.1

Sample	pH	O_2 (*aq*)	NO_3-N		SO_4^{2-}	Fe (*aq*)	
	field	mg/L	r*	mg/L	mg/L	r	µg/L
1	7.7	0.2		0.455	93.1	<	3
2	7.3	6.5		8.23	286	<	3.2
3	7.3	0.1		13.5	61.6	<	10
4	7.6	7.5		10.8	146	<	3.2
5	6.6	0.2	E	3.41	57		655
6	7.5	8.3		0.983	13.6	<	3.2
7	7.3	0.1	<	0.06	52.4	E	5.5
8	6.6	0.1	*E*	3.56	57.3		1810
9	7.4	0.2		0.497	19.7	<	6
10	7.6	0.2	<	0.06	31.8		8.4
11	7.6	5.3		8.7	220	<	3.2
12	7.3	0.3		4.94	430	<	10
13	7.4	0.1	<	0.06	104		491
14	7.2	0.1		0.824	75		22.1
15	7.2	0.1	<	0.05	44.7		1260
16	7.7	0.1	<	0.05	0.1		18

*Remark codes (r): < indicates concentration is below detection limit and value reported is detection limit; E indicates estimated value

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8.7: Answers to practice problems

Practice 8.1.1

A. $Q = \dfrac{[H_2S\ (aq)]\,[HCO_3^-]^2}{[CH_3COO^-]\,[H^+]\,[SO_4^{2-}]} = 51.32$

Or in log form:

$\log Q = \log [H_2S\ (aq)] + 2\log [HCO_3^-] - \log [CH_3COO^-] - \log [H^+] - \log [SO_4^{2-}] = 1.71$

B. $Q = \dfrac{[Fe^{2+}]^8\,[HCO_3^-]^2}{[CH_3COO^-]\,[H^+]^{15}} = 3.84 \times 10^{54}$

Or in log form:

$\log Q = 8\log [Fe^{2+}] + 2\log [HCO_3^-] - \log [CH_3COO^-] - 15\log [H^+]^{15} = 54.59$

Practice 8.2.1

A. $\log K = 15.3544; \Delta G_r = -77.9\ \frac{kJ}{mol}$

B. $\log K = 82.8455; \Delta G_r = -161.3 \frac{kJ}{mol}$

Practice 8.4.1

A. $\Delta G_u = 32.9\ \frac{kJ}{mol}$

B. $\Delta G_u = 105.1\ \frac{kJ}{mol}$

Practice 8.5.1

A. O_2 reduction: $\log K = 146.7487;\ \Delta G_r = -838.3\ \frac{kJ}{mol};$ most energetically favorable

B. NO_3^- reduction: $\log K = 140.5573;\ \Delta G_r = -774.8\ \frac{kJ}{mol}$

C. Methanogenesis: $\log K = 2.6407;\ \Delta G_4 = -31.5\ \frac{kJ}{mol}$

Practice 8.5.2

System with pH 6

A. $Fe(OH)_3$ reduction: $\log K = 117.9583;\ \Delta G_r = -361.4\ \frac{kJ}{mol}$

B. Goethite reduction: $\log K = 82.8455;\ \Delta G_r = -161.3\ \frac{kJ}{mol}$

C. Hematite reduction: $\log K = 79.0195;\ \Delta G_r = -138.5\ \frac{kJ}{mol}$

All reactions are thermodynamically favorable (i.e., exergonic) and thus have the potential to be used as energy sources by iron-reducing microorganisms. Of these reactions, $Fe(OH)_3$ reduction is the most thermodynamically favorable.

Practice 8.5.3

A. $Fe(OH)_3$ reduction: $\Delta G_r = -190.4\ \frac{kJ}{mol}$

B. Goethite reduction: $\Delta G_r = 9.9\ \frac{kJ}{mol}$

C. Hematite reduction: $\Delta G_r = 31.2\ \frac{kJ}{mol}$

Only $Fe(OH)_3$ reduction remains potentially useful as an energy source for dissimilatory iron reduction. The result suggests that an iron-reducing zone might not appear in a system with pH 8 unless poorly crystalline ferric iron sources such as $Fe(OH)_3$

are available, or if some other reduction mechanism besides dissimilatory iron reduction were active.

Practice 8.6.1

1. Sulfate reduction or possibly a mixture of nitrate and sulfate reduction
2. Oxygen reduction
3. Nitrate reduction
4. Oxygen reduction
5. Mixed: evidence for nitrate and iron reduction
6. Oxygen reduction
7. Sulfate reduction
8. Mixed: evidence for nitrate and iron reduction
9. Sulfate reduction or possibly a mixture of nitrate and sulfate reduction
10. Sulfate reduction
11. Oxygen reduction
12. Nitrate reduction

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8.8: Concept Check Questions

1. Consider the relationships plotted in Figure 8.2. Is the energy yield of the reaction more sensitive to changes in pH or ferrous iron activity? Can you explain why, based on the reaction stoichiometry?
2. Imagine that iron reduction is occurring within a clay lens in an alluvial aquifer. How might evidence for that reaction be obscured if the groundwater adjacent to the clay lens contains oxygen or nitrate?
3. Why would you expect aerobic respiration in an environment with more than 0.5 mg/L O_2? If other electron acceptors are also available, would they be used alongside oxygen?
4. In terms of aqueous chemistry, how would you describe an environment where nitrate reduction is likely occurring? What oxygen concentration would you expect and what sorts of products might be accumulating?
5. How would the presence of sulfate reduction affect dissolved ferrous iron accumulation during iron reduction?
6. In terms of aqueous chemistry, how would you describe an environment where methanogenesis is likely occurring?

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CHAPTER OVERVIEW

9: Kinetic Controls

> *"Chemotrophic metabolism involves catalysis of energetically possible, but kinetically hindered redox reactions."*
>
> *—Banfield and Welch (2000)*

Thermodynamics determine which reactions have the potential to be useful as a source of energy for microorganisms. If those reactions proceed rapidly on their own, without any microbial catalysis, then microbial populations may not be able to capture any energy from them. However, if those reactions occur slowly without catalysis, then the opportunity exists for microorganisms to catalyze the reaction and capture energy for growth.

Microorganisms can make a living from such a reaction, avoiding a population decline, if the reaction allows them to grow new cells faster than the cells are removed from the environment. Viable cells are effectively removed when they die or when they are transported away by, for example, flowing water. The rate of biomass production is tied to the kinetics of the group's catabolic reaction and the efficiency with which they use nutrients and energy resources. Species that can grow faster generate more biomass and are thus more likely to avoid decline. The kinetic properties of different species, even some using the same catabolic reaction, can vary widely. These properties, together with the physical and chemical conditions of the environment, help determine the proportions of species within microbial communities.

This chapter examines how microorganisms speed up redox reactions using enzymes. We will briefly consider factors that influence rates of enzymatic reactions and then examine a kinetic rate law for microbial reactions, which can quantify links between the kinetic impacts of substrate concentrations, enzyme properties, and reaction free energy yields.

9.1: Role of enzymes
9.2: Influence of pH and temperature on enzyme activity
9.3: Influence of substrate concentrations
9.4: Kinetic rate laws
9.5: Thermodynamic constraints on rates
9.6: Kinetic constraints on competition between sulfate reducers and methanogens
9.7: External controls on microbial reaction rates
9.8: Answers to practice problems
9.9: Concept Check Questions
9.10: References

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9.1: Role of enzymes

Enzymes help make life possible by speeding up (i.e., catalyzing) many biological reactions. They are usually composed of protein although some RNA-based enzymes are known to exist. Enzymes speed reactions by providing a reaction pathway with a lower activation energy (E_A), the energy barrier that exists between reactants and products in a chemical reaction (Fig. 9.1).

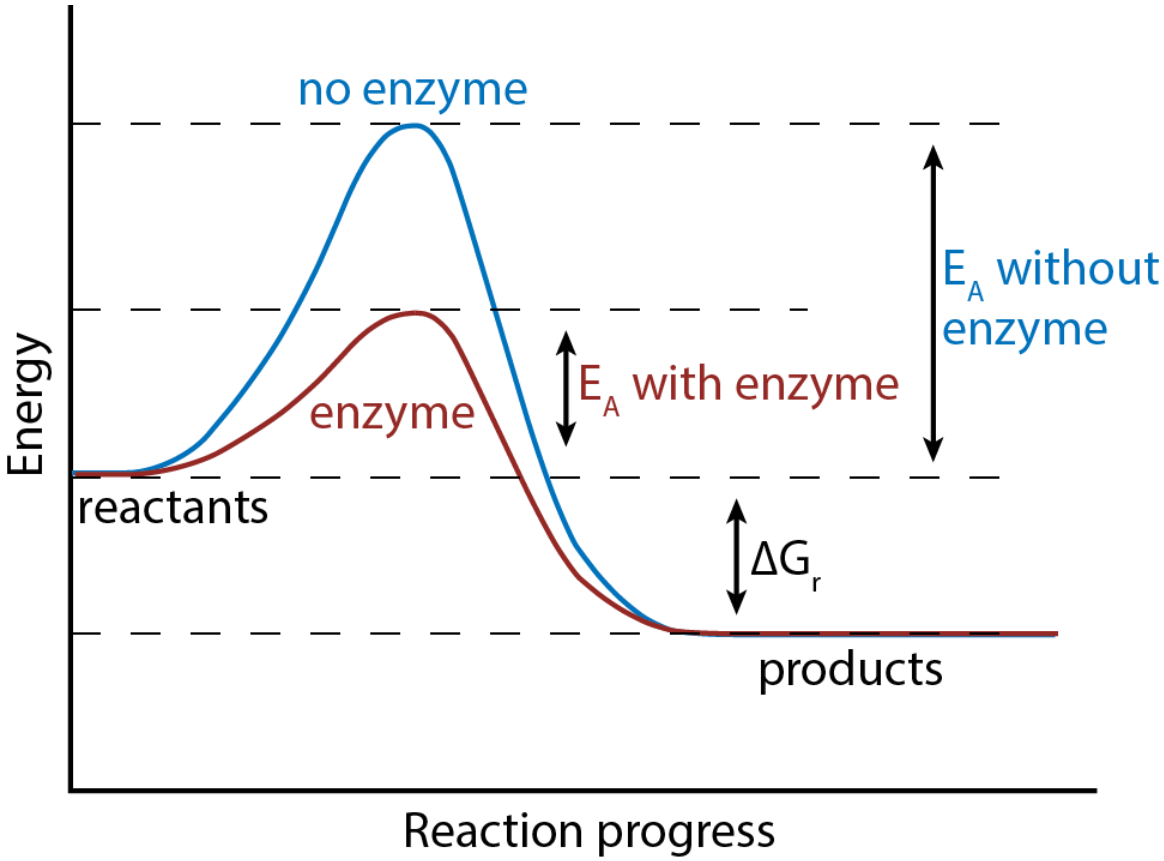


Figure 9.1: Activation energy (E_A) of a biological reaction with and without enzymatic catalysis. ΔG_r is the Gibbs free energy change of the reaction. Figure based on figure 14.1 of Garrett and Grisham (1999).
https://commons.wikimedia.org/wiki/File:Enzymatic_reactions.png

During an enzymatic reaction, reactant molecules bind with an enzyme to form a transitional state and ultimately reaction products. Molecules that can bind with an enzyme are referred to as substrates. The site on an enzyme where a substrate binds and catalysis can occur is known as the active site. The structure of an enzyme affects which molecules can bind to its active site, and thus determines which specific reaction the enzyme catalyzes. Figure 9.2 illustrates this aspect of enzymes based on an early conceptual model known as the lock and key model.

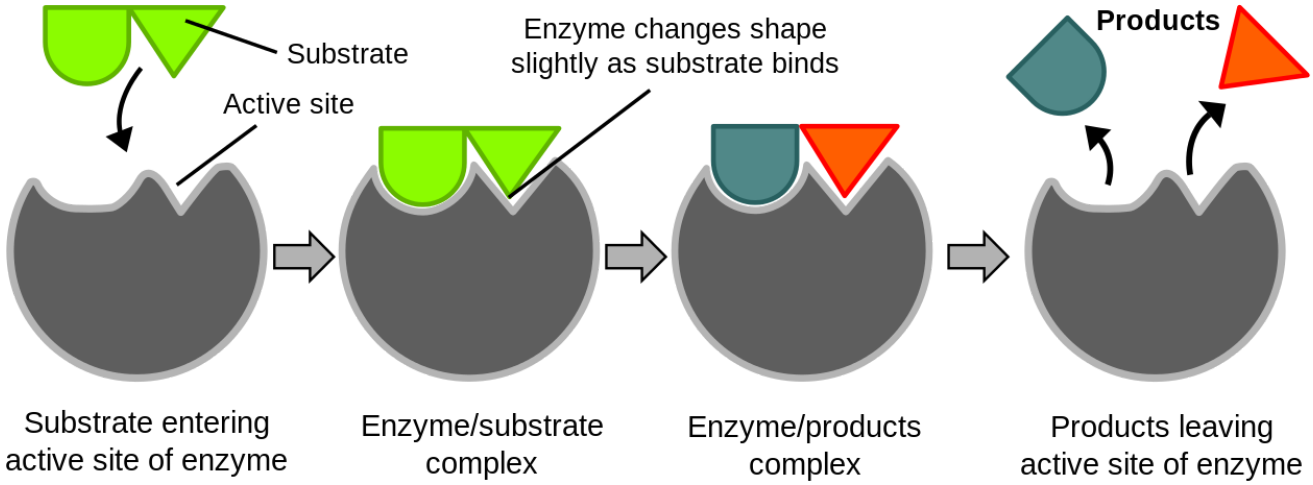


Figure **9.2**: Schematic illustration of the lock and key model. Substrates enter the active site, form a transitional complex, which can then form reaction products. Image source: public domain.
https://commons.wikimedia.org/wiki/File:Induced_fit_diagram.svg

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9.2: Influence of pH and temperature on enzyme activity

The activity of an enzyme is sensitive to temperature and pH, as discussed in Chapter 6. Variation in temperature and pH affect the structure of enzymes, which in turn affects their ability to bind substrates and catalyze reactions. As such, enzyme activity decreases outside of its optimal temperature and pH (Fig. **9.3**).

Enzyme properties help define temperature and pH preferences of individual microbial species, but microbial communities are generally composed of many species, which can vary in their enzyme properties. As a result, microbial activity does not necessarily cease because temperature and/or pH changes. Instead, changes in temperature and/or pH may alter who is growing and at what rates.

With regard to changes in temperature, rates of abiotic reactions tend to increase as temperature increases. The same can also be true of microbial enzymatic reactions. As an example, Craine et al. (2010) demonstrated that rates of microbial organic matter degradation in soil increase with warming, with the largest increases associated with organic matter pools that are difficult to degrade. Their findings imply that, as soils warm in response to climate change, organic matter stored within them can be more rapidly oxidized and returned to the atmosphere as carbon dioxide. Thus, this influence of temperature on degradation rates has the potential to serve as a positive feedback on climate change.

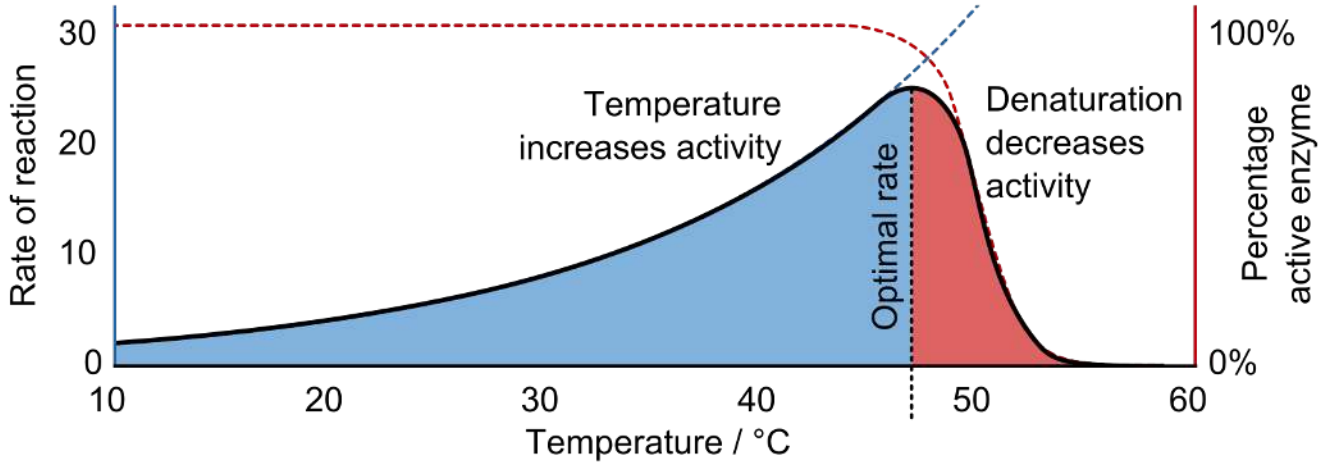


Figure **9.3**: Relationship between enzyme activity and temperature. As temperature increases and approaches the optimal temperature for an enzyme, activity increases. As temperature increases above the optimal temperature, however, enzyme activity decreases and eventually the enzyme can lose its structure (i.e., denature) and ability to function.
Image source: Thomas Shafee CC 4.0, https://commons.wikimedia.org/w/index.php?curid=47436421

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9.3: Influence of substrate concentrations

Rates of enzymatic reactions vary with the availability of substrates. As shown in Figure **9.4**, as substrate concentration increases, the rate of an enzymatic reaction increases and asymptotically approaches some maximum. In one of the best-known enzyme kinetic models, the Michaelis-Menton model, the maximum rate of the reaction is known as V_{max}. The model predicts that reaction rates become less sensitive to substrate concentration as V_{max} is approached because the enzyme starts to become saturated with substrate. Where saturated, addition of substrate will not result in additional substrate binding and reaction catalysis. Thus, the availability of active sites on enzymes sets an upper limit on the rate at which the enzymes can catalyze a reaction.

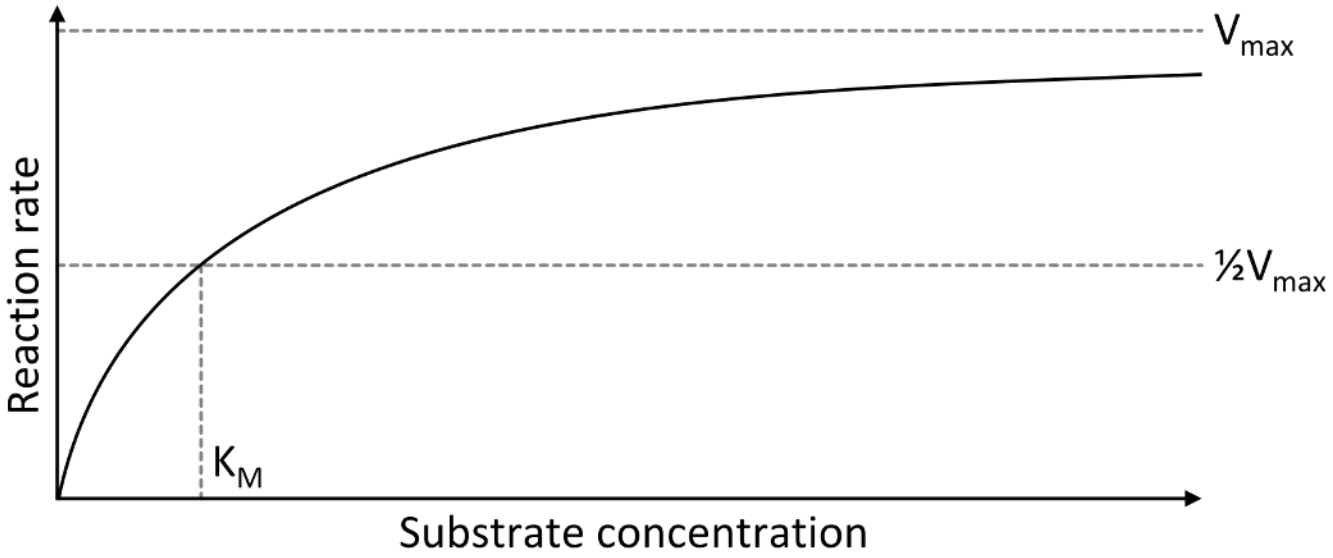


Figure **9.4**: Variation in reaction rate with substrate concentration in a hypothetical enzymatic reaction. V_{max} is the maximum reaction rate possible for the enzyme and K_M is the half-saturation constant for the enzyme.
Image source: Thomas Shafee, CC 4.0 International, https://commons.wikimedia.org/wiki/File:Michaelis_Menten_curve_2.svg

Reflecting differences in enzyme properties, some groups of microorganisms grow rapidly at low nutrient concentrations while others grow rapidly at high nutrient levels. As a result, the extent of nutrient loading in the environment can affect which group can grow the fastest and can thus account for a larger portion of the community (Button, 1985). Half-saturation constants (K_M) are used to characterize the nutrient or substrate concentration preferences of different microbial groups. K_M is the substrate concentration at which the reaction rate equals one-half the maximum rate (Fig. **9.4**) and can be taken as a measure of the affinity of an enzyme for substrate.

A range of half saturation constants exist in the literature for individual functional groups and species. Differences may reflect growth conditions used to measure parameters and/or differences in enzyme properties between species. Even within the same species, kinetic properties are not necessarily constant. Some microorganisms can alter their properties to better take advantage of the conditions of their environment. For example, *Desulfobacterium autotrophicum* HRM2 can switch between low and high apparent half-saturation constants depending on what sulfate concentration is present within their environment (Tarpgaard et al., 2017).

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9.4: Kinetic rate laws

We can organize our thoughts on the kinetics of microbial reactions by considering rate laws for microbial growth. One of the best known rate laws is the Monod equation defined by Monod (1949). The equation relates the rate of growth of a microbial population to the concentration of a limiting resource. If the limiting nutrient is an electron donor, we can write:

$$r = k_+[X]F_D \tag{9.4.1}$$

where k_+ is the rate constant for the forward reaction $\left(\text{mol (g biomass)}^{-1}\text{s}^{-1}\right)$, $[X]$ represents biomass concentration $\left(\text{(g biomass) (kg} \cdot \text{H}_2\text{O)}^{-1}\right)$, and F_D is a kinetic factor for electron donation. Biomass is included because the overall rate of a microbial reaction varies directly with the size of the microbial population that is actively catalyzing it. As the abundance of active cells increases, more enzymes can be produced, and more catalysis can occur.

F_D can be expanded as:

$$F_D = \frac{m_D}{m_D + K_D} \tag{9.4.2}$$

where m_D is the electron donor concentration (molal) and K_D is the half-saturation constant (molal) corresponding to the electron donor. Thus, the kinetic factor considers substrate availability and the kinetic properties of the microorganism's enzymes.

The dual-Monod equation is a slightly expanded version that accounts for not one but two limiting resources. For example, the following rate equation includes factors for the electron donor (F_D) and electron acceptor (F_A):

$$r = k_+[X]F_DF_A \tag{9.4.3}$$

Here F_A is defined in an equivalent manner as F_D (equation (9.4.2)), except the substrate considered is the electron acceptor rather than the electron donor:

$$F_A = \frac{m_A}{m_A + K_A} \tag{9.4.4}$$

where m_A is electron acceptor concentration (molal) and K_A is the half saturation constant for the electron acceptor (molal).

The Monod equation works well for resource-rich environments where only a small number of factors vary. However, in geochemical systems, resources are often limited and conditions can be spatially and temporally variable. In such systems, therefore it may be necessary to use rate expressions that also account for thermodynamic controls (Jin and Bethke, 2005). To that end, the Jin and Bethke model (2007, 2005, 2003, 2002) provides an example of a rate model that expands the Monod equation further by adding a thermodynamic potential factor (F_T):

$$r = k_+[X]F_DF_AF_T \tag{9.4.5}$$

The thermodynamic potential factor (F_T) is unitless and defined as follows:

$$F_T = 1 - \exp\left(-\frac{\Delta G_A - m\Delta G_P}{\chi RT}\right) \tag{9.4.6}$$

where ΔG_A is energy available in the environment for the microbial reaction as described in Section 8.4 and repeated here for convenience:

$$\Delta G_A = -\Delta G_r \tag{9.4.7}$$

m is the number of ATPs produced (unitless), ΔG_P is the free energy change of ATP synthesis $\left(\text{kJ mol}^{-1}\right)$, χ is the average number of times the rate determining step occurs (unitless), R is the gas constant $\left(\text{kJ mol}^{-1}\text{K}^{-1}\right)$, and T is temperature (K). As also discussed in Section 8.4, $m\Delta G_P$ quantifies energy captured by the cell (ΔG_C) and thus the numerator in equation 9.4.6 is usable energy (ΔG_U). Thus, thermodynamic potential factor equation can also be written as:

$$F_T = 1 - \exp\left(-\frac{\Delta G_U}{\chi RT}\right) \tag{9.4.8}$$

For each of these rate laws, reaction rates can then be related to change in biomass concentration according to:

$$\frac{d[X]}{dt} = Yr - D[X] \tag{9.4.9}$$

where Y is the amount of biomass growth relative to the amount of substrate consumed $\left(\text{(g biomass) (mol substrate)}^{-1}\right)$, which is known as growth yield, and D is the biomass decay constant (s^{-1}), which accounts for the rate at which cells die.

By these rate laws, F_D and F_A approach values of one as substrate concentrations increase. Similarly, if the amount of energy available (ΔG_A) is much greater than the amount captured by the cell $(m\Delta G_P)$, the exponential term in equation **9.4.6** approaches zero and the overall value of F_T approaches one. If the value of any of these factors, F_D, F_A, or F_T, is one, then that factor does not affect the rate of the reaction. Thus, if the values of all three factors is 1, all three factors have no influence on the reaction rate. In this case, the rate is simply equal to the product of the rate constant and biomass concentration $(k_+[X])$, which is the maximum rate of the reaction (V_{max}) (Jin and Bethke, 2002).

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9.5: Thermodynamic constraints on rates

One simple application of the Jin and Bethke rate law uses the thermodynamic potential factor to extend our analysis of thermodynamic controls on microbial reactions beyond that considered in Chapter 8. Imagine that we compare energy available for iron reduction coupled with acetate oxidation (Practice **8.1.1B**) in two environments. In environment A, the reaction releases **100 kJ/mol** and in environment B, it releases **60 kJ/mol**. If we assume a value of **1.25** for the ATP number (m) and **45 kJ/mol** for ATP synthesis (ΔG_P) (Bethke et al., 2011), then the amount of energy that could be captured from the reaction in both environments is **56.25 kJ/mol**:

$$\Delta G_C = (1.25)\left(45\ \frac{\text{kJ}}{\text{mol}}\right) = 56.25\ \frac{\text{kJ}}{\text{mol}} \tag{9.5.1}$$

Subtracting this value from the amounts of energy available indicates that the usable energy for the reaction (ΔG_U) would be **43.75 kJ/mol** in A and **3.75 kJ/mol** in B.

$$\textbf{Environment A:} \qquad \Delta G_U = 100\ \frac{\text{kJ}}{\text{mol}} - 56.25\ \frac{\text{kJ}}{\text{mol}} = 43.75\ \frac{\text{kJ}}{\text{mol}} \tag{9.5.2}$$

$$\textbf{Environment B:} \qquad \Delta G_U = 60\ \frac{\text{kJ}}{\text{mol}} - 56.25\ \frac{\text{kJ}}{\text{mol}} = 3.75\ \frac{\text{kJ}}{\text{mol}} \tag{9.5.3}$$

If we then assume that the rate limiting step (χ) occurs eight times during reaction turnover (Bethke et al., 2011) and use values of **0.008314kJ/(mol K)** for the gas constant (R) and **298.15 K** for temperature (T), then the value of the thermodynamic potential factor (F_T) is **0.89** in A and **0.17** in B according to equation **9.4.8**:

$$\textbf{Environment A:} \qquad F_T = 1 - \exp\left(-\frac{43.75\ \frac{\text{kJ}}{\text{mol}}}{(8)\left(0.008314\ \frac{\text{kJ}}{\text{mol K}}\right)(298\ \text{K})}\right) = 0.89 \tag{9.5.4}$$

$$\textbf{Environment B:} \qquad F_T = 1 - \exp\left(-\frac{43.75\ \frac{\text{kJ}}{\text{mol}}}{(8)\left(0.008314\ \frac{\text{kJ}}{\text{mol K}}\right)(298\ \text{K})}\right) = 0.17 \tag{9.5.5}$$

These results indicate that, in response to thermodynamic controls, the reaction rate could be at most 89% of the maximum rate in environment A and 17% of the maximum rate in environment B. Thus, the analysis indicates that thermodynamic controls would have a much greater influence on the reaction rate in environment B than environment A.

Practice 9.5.1

In bioreactors analyzed by Kirk et al. (2013), about **60kJ/mol** was available for sulfate reduction coupled to acetate oxidation over the final half of the incubation. Calculate the thermodynamic potential factor for the reaction. Assume a value of **1.0** for the ATP number (m), **45 kJ/mol** for ATP synthesis (ΔG_P), and that the rate limiting step (χ) occurs six times during reaction turnover (Bethke et al., 2011). Use values of **0.008314kJ/mol K** for the gas constant (R) and **295.15 K** for temperature (T).

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9.6: Kinetic constraints on competition between sulfate reducers and methanogens

Sulfate reducers can typically outcompete methanogens for electron donors if sulfate is available, consistent with the flowchart provided in the last chapter (Section 8.6). You might assume that this relationship reflects thermodynamic controls, since methanogenesis generally does not yield a large amount of energy. However, previous studies indicate that the outcome of this competition mainly stems from differences in the growth yield (Y) and half-saturation constant for electron donation (K_D) of each group of microorganisms (Bethke et al., 2011, 2008; Lovley and Klug, 1986). Thus, competition between sulfate reducers and methanogens provides a useful example of how these factors can be influential.

Before getting into the details, we can first illustrate the relationship between sulfate reduction and methanogenesis by briefly considering the results from a kinetic reaction path model (Fig. 9.5). The model simulates rates of microbial sulfate reduction and methanogenesis in a flowing system at 25°C. The volume of water in the system is replaced 20 times over a 400-day simulation period, giving the water a residence time of 20 days. Water entering the system has neutral pH and contains 0.1 mM acetate, 0.2 mM sulfate, 0.5 mM bicarbonate, and 1 mM each of sodium and chloride. Kinetic parameters for sulfate reducers and methanogens are taken from Jin and Roden (2011). Both groups have the same initial cell abundance (0.001 mg cells/kg water), which is represented by parameter $[X]$ in the Jin and Bethke rate law (equation 9.5).

Model results show that the thermodynamic potential factor (F_T) is slightly higher for methanogens than sulfate reducers over the first 25 days (Fig. 9.5A). Thus, methanogens initially hold a small thermodynamic advantage over sulfate reducers, at least in terms of the thermodynamic potential factor. Despite this advantage, however, sulfate reducers grow a population much more rapidly than methanogens (Fig. 9.5B), allowing them to speed up their reaction more quickly than methanogens (Fig. 9.5C), and, by about 30 days, hold acetate at a low concentration for the remainder of the simulation (Fig. 9.5D). Sulfate reducers essentially take control of the electron donor supply before methanogens can establish a large population. As acetate concentration decreases, the thermodynamic potential factor for methanogenesis decreases and the population of methanogens begins to slowly decline.

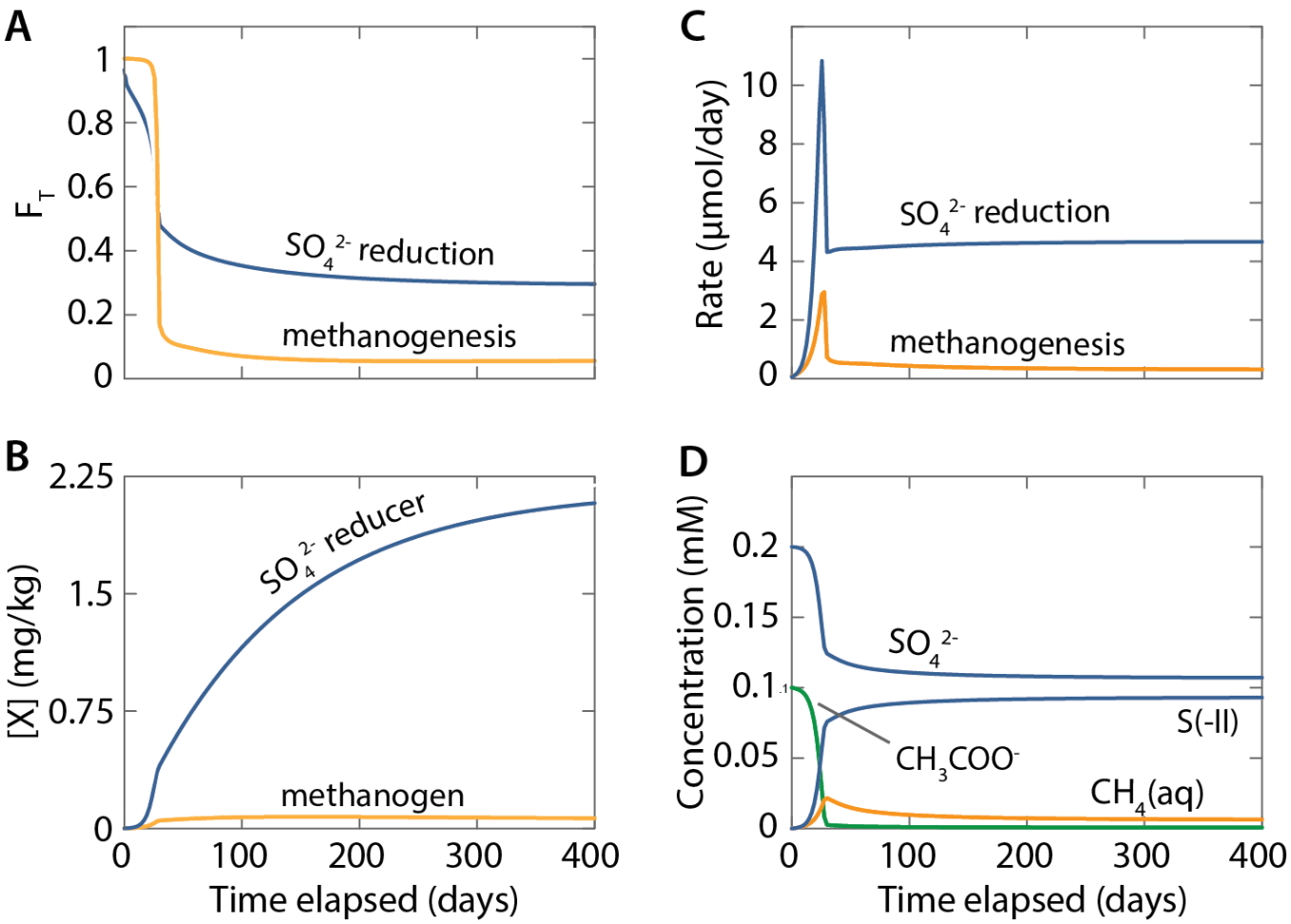


Figure 9.5: Results of a kinetic reaction path model of sulfate reduction and methanogenesis. Graphs show variation over time in (A) thermodynamic potential factors (F_T), (B) biomass abundances [X], (C) reaction rates, and (D) concentrations of sulfate (SO_4^{2-}), sulfide (S(-II)), acetate (CH_3CO^-), and methane (CH_4). Reaction rates and population dynamics were simulated according to the Jin and Bethke rate law (2007, 2005, 2003, 2002) using kinetic parameters from Jin and Roden (2011). The model was calculated using the flush configuration in the React module of The Geochemist's Workbench. Additional details about the model are provided in the main text.
https://commons.wikimedia.org/wiki/File:SRM_methanogen_model_results.png

To understand how kinetic factors can help create this outcome, we need to consider the substrate threshold concept. Substrate concentrations below which cells cannot grow are called threshold concentrations (Button, 1985). We can quantify threshold relationships using a kinetic rate law. To start with, consider equation 9.4.9 above, which shows the relationship between biomass concentration and reaction rate. If growth occurs, then it follows that the rate of change in biomass abundance must be positive:

$$\frac{d[X]}{dt} > 0 \tag{9.6.1}$$

This relationship therefore implies that the product of growth yield and reaction rate is greater than the product of the biomass decay constant and biomass abundance:

$$Yr = D[X] \tag{9.6.2}$$

which rearranges to

$$\frac{r}{[X]} > \frac{D}{Y} \tag{9.6.3}$$

Next, we can apply this relationship to a Monod function for a reaction consuming acetate (ac):

$$r = k_+[X]\frac{m_{ac}}{m_{ac} + K_D}F_T \tag{9.6.4}$$

Since environmental electron donor concentrations are often much smaller than half saturation constant values ($m_{ac} << K_D$), we can simplify equation **9.6.4** to

$$r = k_+[X]\frac{m_{ac}}{K_D}F_T \tag{9.6.5}$$

which rearranges to

$$\frac{r}{[X]} = k_+\frac{m_{ac}}{K_D}F_T \tag{9.6.6}$$

Combining equations **9.6.3** and **9.6.6** gives

$$k_+\frac{m_{ac}}{K_D}F_T > \frac{D}{Y} \tag{9.6.7}$$

which rearranges to

$$m_{ac} > \frac{D}{Y}\cdot\frac{K_D}{k_+F_T} \tag{9.6.8}$$

Thus, substrate concentration (m_{ac}) must exceed the value of the equation's right-hand side; otherwise, the organism will not be able to grow faster than it dies.

Returning to the example of sulfate reducers and methanogens, methanogens typically have a smaller growth yield and a larger half saturation constant than sulfate reducers (Table **9.1**). Both differences increase the value of the threshold for methanogens compared to sulfate reducers. As a result, even if methanogens hold a thermodynamic advantage over sulfate reducers, sulfate reducers may be able to grow rapidly and then hold electron donor concentration at a concentration that is sufficient for their own needs but too low for methanogens to avoid the extinction vortex (Bethke et al., 2011), consistent with the modeling results above (Fig. **9.5**).

Table **9.1**: Kinetic parameters for sulfate reduction and methanogenesis*

Reaction	K_D (molal)	Y (mg/mol)
SO_4^{2-} reduction	5×10^{-6}	4000
Methanogenesis	2.3×10^{-5}	1700
*Parameters from Jin and Roden (2011)		

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9.7: External controls on microbial reaction rates

The contents of this chapter have largely focused on the properties of microorganisms, but external factors can also play large roles in determining microbial reaction rates within an environment. Two such controls considered here are the rate of energy resource supply and the surface area of solid-phase reactants.

The rate at which energy resources are supplied often sets the upper limit on the rates at which microorganisms can be active in natural systems. As an example, Bernhardt et al. (2022) demonstrated the importance of light availability on gross primary productivity and ecosystem respiration using data collected from 222 U.S. rivers. Statistical modeling indicated that annual solar energy inputs, together with the stability of flows, were the primary drivers of gross primary production and ecosystem respiration. Thus, light availability sets a limit on organic matter production by phototrophs, which in turn constrains the amount of respiration that can occur.

As a second example, fermentation is generally considered to be the overall rate limiting step in anaerobic degradation of organic matter (Arndt et al., 2013; Postma and Jakobsen, 1996; Westrich and Berner, 1984). This assertion is supported by the short turn over times of fermentation products such as dihydrogen and acetate (Novelli et al., 1988) and the fact that fermentation products are generally maintained at very low concentrations by respiring microorganisms (Postma and Jakobsen, 1996). Fermentation products are not piling up. They are being used virtually as fast as they are supplied. Kinetic properties of individual groups of respiring microorganisms may determine rates of their specific respiration reactions. However, this conceptual model implies that the overall respiration is set by the fermenters.

To illustrate, consider again the model results shown in Figure 9.5. Kinetic factors associated with sulfate reducers and methanogens determined the outcome of their competition. However, the overall rate of acetate oxidation was set by the rate at which acetate was delivered to the system by inflowing water. In the model, acetate was simply included as a reactant in the inflowing water but in an actual anaerobic system, acetate typically originates as a fermentation product.

Lastly, for reactions that involve multiple phases (i.e., heterogeneous reactions), the surface area of the interface between the reactions is a constraint on the reaction rate. The reaction must occur through the interface surface area and thus, the size of the interface places an upper limit on the amount of reaction that can occur within a given time. This relationship applies to both abiotic and biotic reactions. As an example, where microorganisms use solid-phase ferric iron as an electron acceptor, they must be able to transfer electrons to the solid phase from the aqueous phase (Fig. 9.6). Therefore, ferric iron crystals with larger surface areas can support more rapid iron reduction. In fact, based on findings from laboratory studies, Roden and others concluded that the surface area of ferric iron minerals was more important than their mineralogical and thermodynamic properties as a control on the rate of microbial iron reduction (Roden, 2006, 2003; Roden and Zachara, 1996).

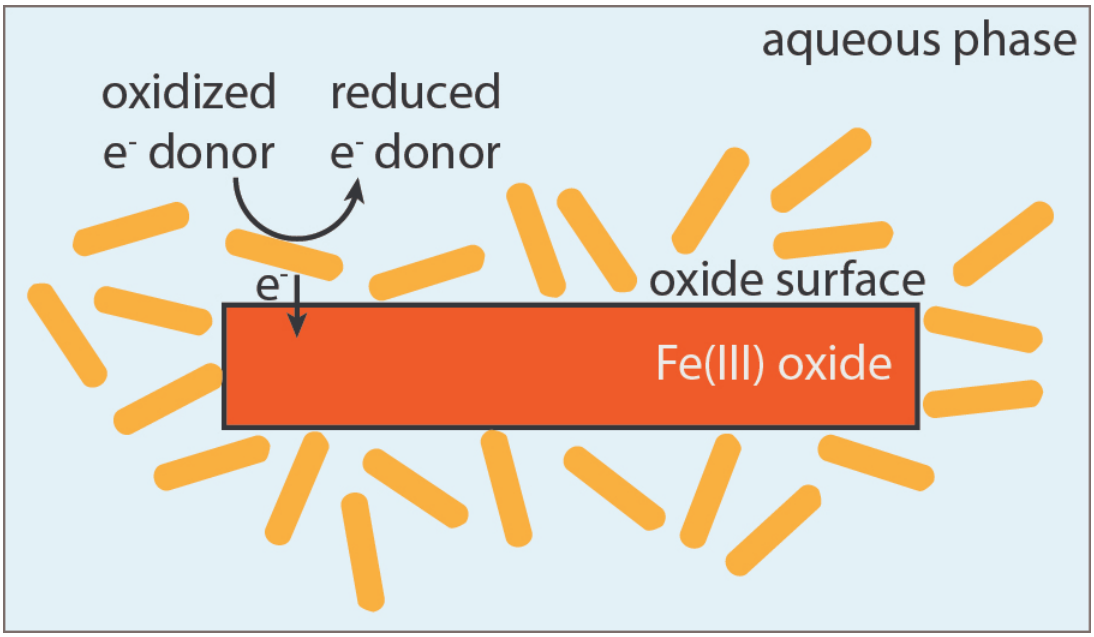


Figure **9.6**: Schematic illustration of microbial reduction of crystalline ferric iron. The microorganisms exist within the aqueous phase and possibly attached to the surface of the oxide mineral. They can transfer the electrons to solid-phase ferric iron using a variety of strategies, as described in Chapter 5. Unless they cause the mineral to dissolve, the electrons must pass through the interface between the solid and aqueous phases. The size of that interface varies with the surface area of the oxide crystal. Thus, oxide surface area can influence the rate of the reaction.
https://commons.wikimedia.org/wiki/File:Heterogeneous_microbial_reaction.jpg

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9.8: Answers to practice problems

Practice 9.5.1

$$F_T = 1 - exp\left(-\frac{60\ \frac{\text{kJ}}{\text{mol}} - (1)\left(45\ \frac{\text{kJ}}{\text{mol}}\right)}{6\left(0.008314\ \frac{\text{kJ}}{\text{mol K}}\right)(295.15\ \text{K})}\right) = 0.64$$

Thus, the rate of the reaction could be at most 64% of the maximum rate possible as a result of thermodynamic controls.

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9.9: Concept Check Questions

1. How does the shape of an enzyme affect its ability to function? Why does variation in pH and temperature affect enzyme shape?
2. What is a substrate and what is the half-saturation constant?
3. How would an increase in the concentration of a substrate affect the rate of an enzymatic reaction?
4. Explain why it may be an advantage for a microorganism to have a large growth yield.
5. Surface areas of (oxyhydr)oxide minerals influence the rate of iron reduction. Why?
6. Fermenting organisms generate dihydrogen, which can then be consumed by respiring microbes. If the rate of fermentation controlled the rate of respiration, would you expect fermentation products to be found at high concentrations? Why or why not?
7. Why might a small half-saturation constant provide a competitive advantage?
8. Are the parameters for rate laws fixed quantities? Why might they vary even for an individual species?

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CHAPTER OVERVIEW

10: Biological Environment

> *"Pure or single population cultures are almost always the creations of microbiologists."*
>
> *—Fredrickson and Stephanopoulos (1981)*

Microbial communities are multi-species assemblages in which organisms live together and interact (Konopka, 2009). As we have discussed in the previous chapters, abiotic factors such as the chemistry and stability of an environment influence who exists within a community and the reactions that the community carries out (i.e., their function). Coupled with those abiotic controls are biotic interactions such as predation, competition, and mutualism, which can also affect who can grow within a community, as well as their sensitivity to environmental conditions (García et al., 2023). Therefore, we can think of the composition of a microbial community itself as an environmental control on the function and make-up of the community.

In fact, many species cannot grow at all without their partner organisms. As an example, microbiology studies in the past often involved isolation of pure cultures (i.e., those consisting of just one strain of microorganisms). However, with the development of molecular techniques, microbiologists realized that the strains they could grow represented only a tiny fraction of microbial life. Most of microbial life is considered to be uncultivable. One of the factors that can make a species difficult to grow is their dependence on other microbes (Garcia et al., 2015). Cultures are often designed to selectively grow microorganisms with specific capabilities, but such conditions may limit or prevent growth of necessary partner microorganisms.

This chapter describes some of the interactions that occur within microbial communities and then considers a few examples of those interactions. There are many well-documented examples of the interactions between groups of microorganisms and between microorganisms and macroorganisms. An extensive review of such examples is beyond the scope of this book. However, it is useful to examine a few examples to help illustrate the roles of interactions in shaping microbial communities.

10.1: Microbial interactions

10.2: Example interactions

- 10.2.1: Viral predation/parasitism of bacteria
- 10.2.2: Mutualisms between plants and soil microorganisms
- 10.2.3: Interactions of anammox microorganisms with other nitrogen cycles
- 10.2.4: Interactions among iron and sulfur cycling microorganisms
- 10.2.5: Interactions among iron reducers, methanogens, and methanotrophs

10.3: Spatial scales of interactions

10.4: Concept Check Questions

10.5: References

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10.1: Microbial interactions

Interactions appear to be a fundamental characteristic of life and can take many forms (Moënne-Loccoz et al., 2014). Organisms can interact without any positive or negative response to those interactions. This type of interaction is known as neutralism (Fig. 10.1). However, most types of interactions do involve a positive or negative response. The paragraphs below consider some interactions defined by conflict, in which at least one of the microorganisms involved is negatively affected by the interactions. Also considered are beneficial interactions, in which neither microorganism is negatively affected and at least one has a positive response to the interaction. As you read about each interaction, it is important to note that interactions between organisms are not necessarily fixed but can change with circumstances, including the conditions of the environment and the development of the organisms.

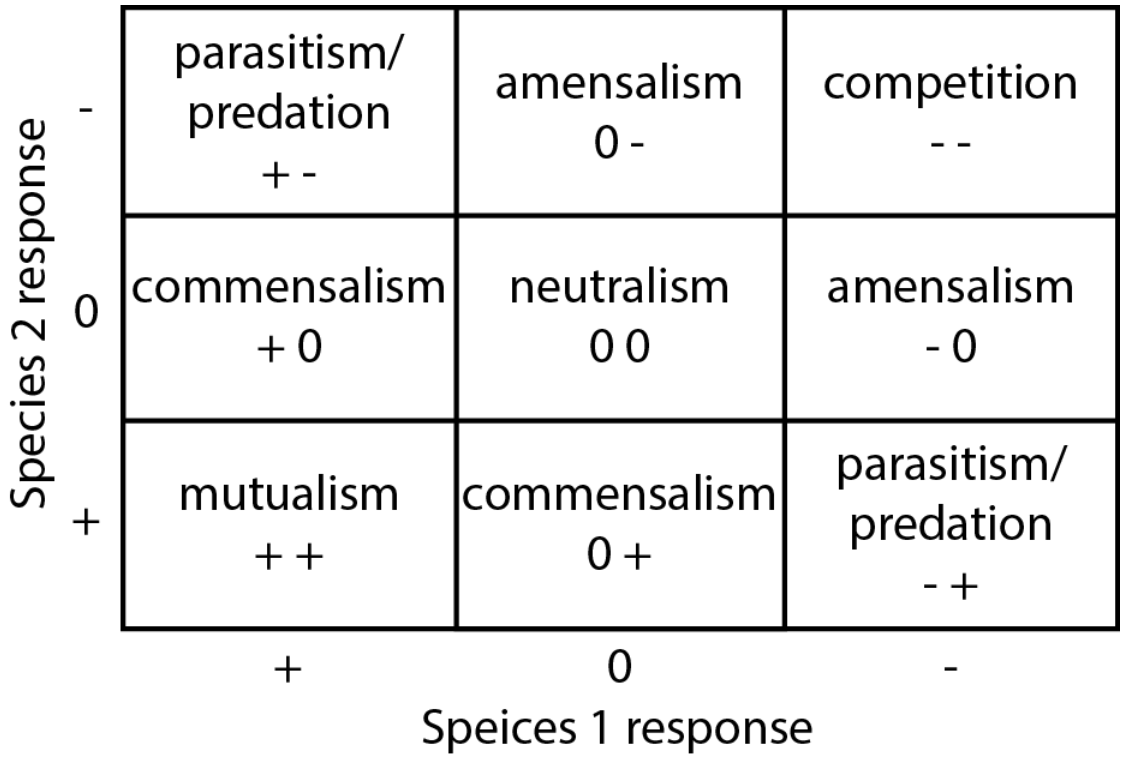


Figure 10.1: Types of interactions between two hypothetical species (1 and 2). This figure is a modified version of figure 1 in Johnson et al. (1997). Along each axis, species responses are characterized as positive (+), negative (-), or neutral (0). https://commons.wikimedia.org/wiki/File:Biological_interactions.png

Predation is characterized as a short-term interaction in which one organism, the predator, kills and eats another organism, the prey. Microbial predators impact microbial communities and their ecosystems in diverse ways, including by helping turn over resources, influencing the abundance and diversity of prey species, and helping induce the evolution of community traits (Nair et al., 2019; Velicer and Mendes-Soares, 2009).

Parasitism occurs when one organism, the parasite, lives on or in another organism, the host, and causes it harm (e.g., feeding on the host). Viruses can be parasites or predators (Chen and Williams, 2012). The thing that differs between the two interactions is the time scale of interaction. Parasites feed off of the host for extended periods of time whereas predators rapidly kill their prey (Chen and Williams, 2012). Viral parasitism has similar impacts to the ecosystem and community as predation (Chen and Williams, 2012; Fernandez et al., 2018).

Competition occurs when multiple organisms require the same resource and the use of that resource lowers growth rates of one or both populations involved (Fredrickson and Stephanopoulos, 1981). Competition can be considered as a natural selection towards the most efficient microbial strategies (González-Cabaleiro et al., 2015). Scramble competition occurs when competitors take up the limiting resource as quickly as they can without directly interacting, whereas contest competition (i.e., interference competition) involves direct antagonistic interactions between competitors, with the winner getting the rewards (Hibbing et al., 2010). For example, a species may restrict their competitor's access to a resource or excrete substances that inhibit their competitor (Hibbing

et al., 2010). Competition can ultimately result in the loss of a species or functional group from a habitat, a phenomenon known as competitive exclusion (Hibbing et al., 2010). However, competitors often coexist (Fredrickson and Stephanopoulos, 1981).

Mutualism occurs when two different organisms interact and both benefit from the interaction (Orphan, 2009). Syntrophy is a form of mutualism involving nutrition in which one microorganism consumes the metabolic products of another (Morris et al., 2013). In a syntrophic interaction, one microorganism benefits by obtaining energy resources whereas the other benefits from limited product accumulation. Kehe et al. (2021) note that positive interactions have often been described as rare but may be much more common within microbial communities than previously recognized. Some members of the community play key roles and if they are lost, the function of the community can be significantly altered (Garcia et al., 2015). Thus, positive interactions have the potential to shape community composition as well as function.

Commensalism is similar to mutualism except one organism benefits while the other is unaffected. For example, the activity of one microorganism may alter the composition of an environment in such a way that growth of another microorganism becomes more favorable. In this case, the microorganism altering the environment has no clear gain from the interaction, but the other microorganism gains a better habitat.

In contrast to commensalism, amensalism is an interaction that negatively affects one of the organisms involved while the other organism is unaffected (Moënne-Loccoz et al., 2014). Thus, we can think of amensalism as the opposite of commensalism. Microorganisms interacting through amensalism are not competing with one another for a resource. Instead, the negative affect of one microorganism on the other occurs because one of the microbes alters the chemical and/or physical properties in the environment in such a way that it inhibits the ability of the other microorganism to grow. Often, this negative affect occurs through the release of toxic compounds (Moënne-Loccoz et al., 2014).

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10.2: Example interactions

See the following subsections for examples of different types of microbial interactions.

10.2.1: Viral predation/parasitism of bacteria

10.2.2: Mutualism between plants and soil microorganisms

10.2.3: Interactions of anammox microorganisms with other nitrogen cyclers

10.2.4: Interactions among iron and sulfur cycling microorganisms

10.2.5: Interactions among iron reducers, methanogens, and methanotrophs

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10.2.1: Viral predation/parasitism of bacteria

Everywhere cellular microorganisms exist, viruses also exist. Viruses can kill cellular microorganisms, and thus influence the death rate of a population. Some species within a community may be more susceptible to infection from a particular virus than others. Therefore, viral predation/parasitism can alter proportions of species within an overall microbial community (Danczak et al., 2020; Orsi, 2018).

Previous studies show that bacteriophages, or viruses that prey on bacteria, play a major role in the evolution of microbial communities (Fernandez et al., 2018). Phage genetic information can be incorporated into bacterial genomes and phages introduce selection pressure for community traits. Responses to viral predation are complex and depend on factors that include the identity of the bacterial host and virus and the extent of infection (Fernandez et al., 2018).

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10.2.2: Mutualisms between plants and soil microorganisms

There are numerous examples of both positive and negative interactions between plants and soil microorganisms. Here, we will briefly consider the well-established mutualistic interactions of plants with mycorrhizal fungi and nitrogen fixers.

Mycorrhizal fungi are a diverse group of fungi that connect with the roots of most plants on Earth (Van Der Heijden et al., 2008). Partnerships between plants and specific mycorrhizal fungi reflect the traits of the mycorrhizal fungi and the plants' nutrient needs (Averill et al., 2019). The fungi can boost plant productivity by helping supply the plant with resistance to disease and drought and several nutrients, including phosphorous, nitrogen, copper, iron, and zinc (Van Der Heijden et al., 2008). In fact, mycorrhizal fungi supply up to 75% of the phosphorus obtained by plants each year (Van Der Heijden et al., 2008). In exchange, the plant benefits the fungi by providing sugars produced by photosynthesis. The relationship is often mutualistic, but can become parasitic if the cost of the exchange exceeds the benefits for the plant (Johnson et al., 1997).

Similarly, nitrogen-fixing microorganisms can also form mutualistic relationships with plants. As described in Section 5.2.1, some nitrogen fixers live within root nodules formed by their partner plants, whereas others are free-living (Smercina et al., 2019). Both types can benefit plants by providing reactive nitrogen, one of the main nutrients that limits plant productivity (Chapin, 1980). In exchange, the nitrogen fixers receive sugars produced by photosynthesis.

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10.2.3: Interactions of anammox microorganisms with other nitrogen cycles

Anaerobic ammonia oxidation (anammox) is thought to be responsible for consuming a large portion of the fixed nitrogen in a wide range of environments, as discussed in Section 5.2.4. The reaction combines oxidation of ammonia with reduction of nitrite:

$$\mathrm{NH_4^- + NO_2^- \longleftrightarrow N_2 + 2\ H_2O} \qquad (10.2.3.1)$$

Therefore, anammox microorganisms can only drive the reaction forward where ammonium and nitrite are simultaneously available.

Multiple groups of nitrogen cyclers influence the availability of ammonium and nitrate, creating opportunities for interactions with microorganisms that catalyze anammox. Nitrifying microorganisms can supply nitrite for anammox, but nitrifiers also consume nitrite as well as ammonium (Fig. **10.2**). Similarly, denitrifying microorganisms can also supply and consume nitrite. Microbes that catalyze dissimilatory nitrate reduction to ammonia (DNRA) can supply ammonia, but they also produce and consume nitrite, like denitrifiers and nitrifiers. Lastly, numerous groups of microorganisms also consume and produce ammonium and other reactive nitrogen compounds in assimilation and ammonification reactions. Thus, several groups of nitrogen-cycling microorganisms can have both mutualistic and competitive interactions with microorganisms that catalyze anammox (Kuenen, 2020).

One of the main environmental factors that influences the outcome of these interactions is oxygen availability. Anammox often occurs at the interface of oxic and anoxic conditions (Kuenen, 2020). Near the interface, where oxygen concentration are low, nitrifiers may form a positive relationship with anammox microorganisms by oxidizing only part of the available ammonium to nitrite (Yan et al., 2012). Moreover, on the anoxic side of the interface, anaerobic nitrate reduction via denitrification and DNRA can occur, which collectively have the potential supply both nitrite and ammonia for anammox.

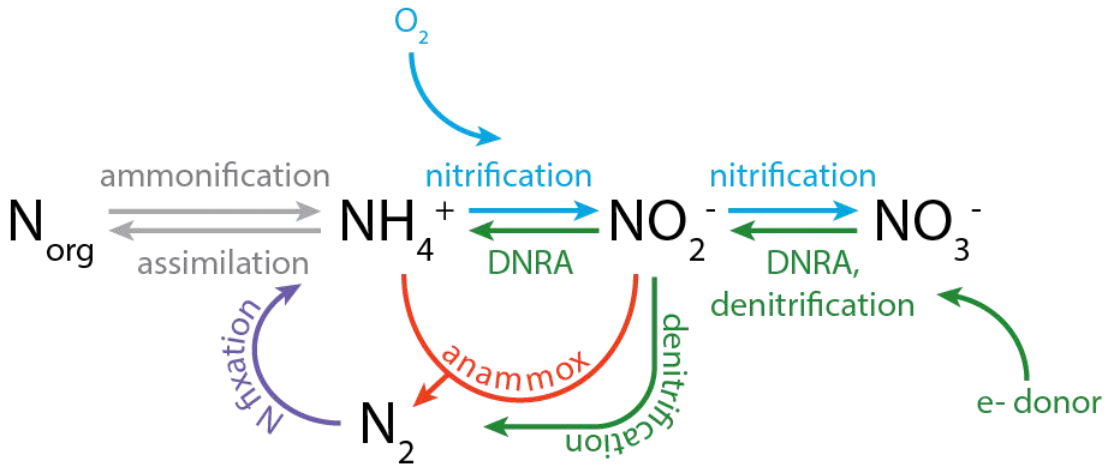


Figure **10.2**: Conceptual model of potential interactions among nitrogen cycling microorganisms. This figure is based on figure 5 of Kuenen (2020) and represents a linear version of the nitrogen cycle figure in Chapter 5 (Fig. 5.3).
https://commons.wikimedia.org/wiki/File:N_cyclers_and_anammox.png

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10.2.4: Interactions among iron and sulfur cycling microorganisms

The simultaneous occurrence of iron reduction and sulfate reduction can lead to a variety of microbial interactions. Microbes that catalyze iron reduction and sulfate reduction often appear to compete with one another. However, abiotic reactions may provide a basis for mutualistic interactions between iron reducers and sulfate reducers and create opportunities for growth of microorganisms that can catabolize intermediate sulfur compounds.

As discussed in Section 5.3.1, dissimilatory iron reduction occurs when microorganisms catalyze iron reduction directly and use the reaction as a source of energy. Ferric iron can also be reduced abiotically by reacting with the sulfide produced by sulfate-reducing microorganisms (Fig. **10.3**). Where that is the case, the products of the reaction will include ferrous iron and sulfur compounds with intermediate oxidation states. Those sulfur compounds can then fuel microorganisms that grow using sulfur disproportionation reactions. They can also fuel microorganisms that reduce intermediate sulfur compounds back to sulfide. Thus, sulfate reducers create the opportunity for growth of other sulfur-cycling microorganisms where the sulfide they produce abiotically reduces ferric iron.

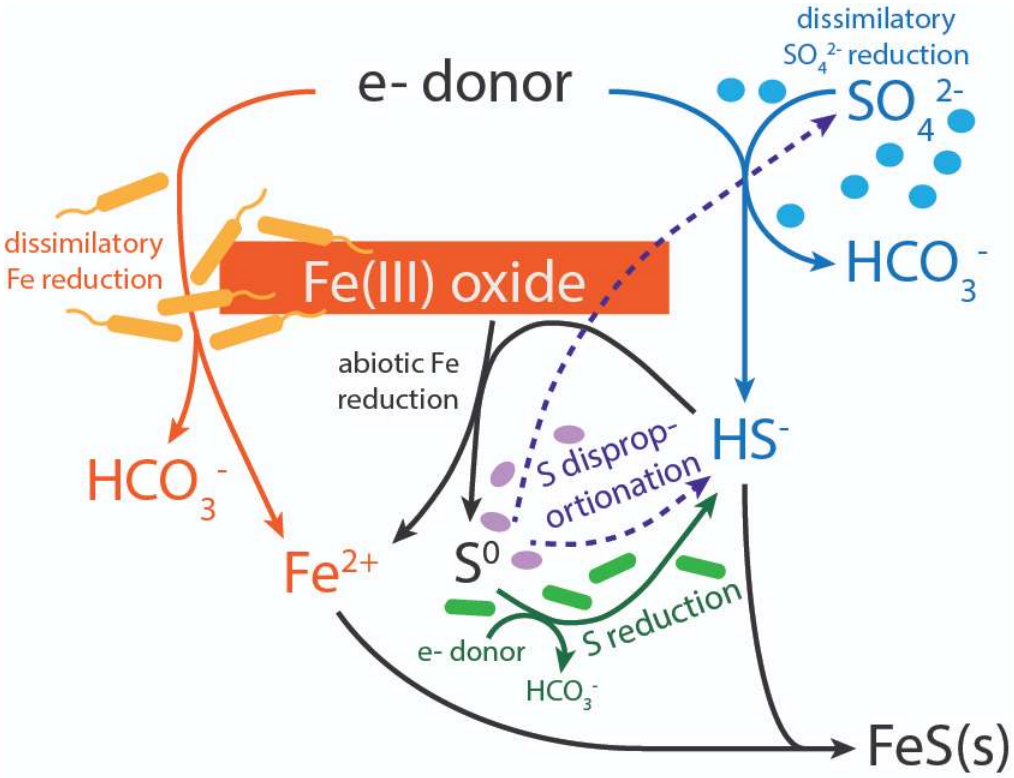


Figure **10.3**: Conceptual model of potential interactions between iron reducers and microorganisms associated with the sulfur cycle. Elemental sulfur (S^0) represents one of several possible intermediate sulfur compounds, some of which can be disproportionated to sulfate and sulfide or used as an electron acceptor and reduced to sulfide.
https://commons.wikimedia.org/wiki/File:Iron%2Bsulfate_reduction.jpg

Where iron reduction by sulfide oxidation occurs, the relationship between sulfate reducers and other sulfur cyclers may be a form of commensalism. Specifically, microbes that reduce or disproportionate sulfur can exist because sulfate reduction and abiotic iron reduction create chemically favorable conditions for their growth. However, that characterization may be an oversimplification. For one reason, there may be overlap in the groups that use some of these reactions. Specifically, some microorganisms that can reduce sulfur or use sulfur disproportionation for energy can also use sulfate reduction. Secondly, if different species are involved, microorganisms using sulfur reduction may compete with sulfate reducers for electron donors.

Regardless of how ferric iron is reduced (abiotic or biotic), where iron reduction and sulfate reduction both occur, mackinawite (**FeS**) can precipitate:

$$\mathbf{Fe^{2+} + HS^- \leftrightarrow FeS\ (s) + H^+} \qquad (10.2.4.1)$$

Bethke et al. (2011, 2008) hypothesized that mackinawite precipitation can provide a basis for mutualism between iron reducers and sulfate reducers because it limits the accumulation of their metabolic products, ferrous iron and sulfide. Thus, both groups can benefit from mackinawite precipitation where their activities coexist. Consistent with this possibility, multiple studies have observed iron reduction and sulfate reduction falling into a $1:1$ molar ratio ($Fe:S$), matching the stoichiometry of mackinawite (Bethke et al., 2011; Kirk et al., 2013; Paper et al., 2021). More details about mackinawite precipitation are provided in Chapter 11.

It remains unclear what factors determine whether iron reduction is a dissimilatory reaction or abiotic. Paper et al. (2021) hypothesized that the pH of the environment is one of the major controls based on results from laboratory experiments. Recall from Section 8.3 that the energy yield of iron reduction decreases as pH increases. At acidic pH, where energy available for iron reduction is often high, Paper et al. hypothesized that interactions between iron reducers and sulfate reducers is mainly competitive. However, at basic pH, where energy available for iron reduction can be low, iron reducers may become increasingly reliant on the benefits of mackinawite precipitation, thus encouraging mutualistic interactions with sulfate reducers. Alternatively, at basic pH, iron reduction may become increasingly driven abiotically by sulfur cycling. Additional research is needed to fully test these hypotheses.

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10.2.5: Interactions among iron reducers, methanogens, and methanotrophs

In addition to sulfate reducers, microorganisms capable of iron reduction can also interact with methanogenic microorganisms. They can compete with one another for electron donors (Fig. **10.4**), with their reactions segregated in to distinct zones (Achtnich et al., 1995; Lovley and Goodwin, 1988) or occurring simultaneously within the same zone (Flynn et al., 2013; Herndon et al., 2015; Jakobsen and Postma, 1999; Küsel et al., 2008; Marquart et al., 2019; Metje and Frenzel, 2007; Paul et al., 2006). They can also interact syntrophically through interspecies electron transfer (IET). During this interaction, ironreducing microorganisms can consume electron donors and then transfer electrons to methanogens who use them to reduce carbon dioxide to methane (Rotaru et al., 2014b, 2014a), as described in Chapter 5.

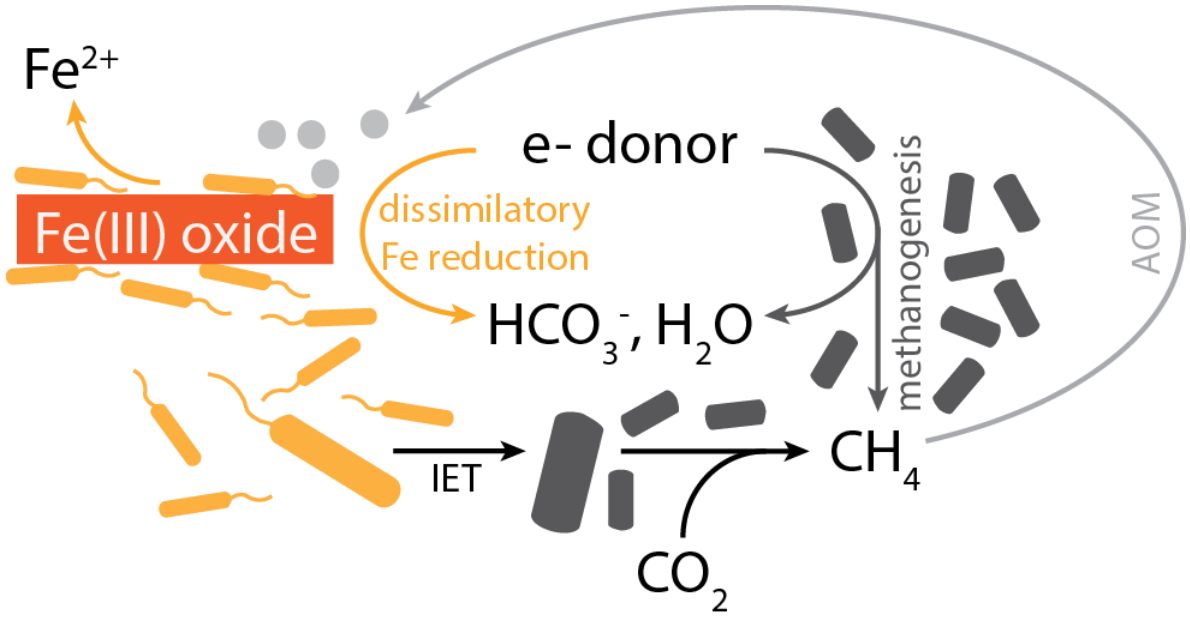


Figure **10.4**: Conceptual model of potential interactions between iron reducers, methanogens, and anaerobic methanotrophic (ANME) archaea. The iron (Fe) reducers can compete with methanogens or interact syntrophically via interspecies electron transfer (IET). Where ferric iron and methane are available, it provides a potential opportunity for anaerobic oxidation of methane (AOM) by anaerobic methanotrophic (ANME) archaea.
https://commons.wikimedia.org/wiki/File:Methanogens_and_Fe_reducers.png

Where iron reduction and methanogenesis are both occurring, methane and ferric iron must be available, which has the potential to support anaerobic oxidation of methane (AOM) by anaerobic methanotrophic (ANME) archaea (Fig. **10.4**). If the methanogen benefits from consumption of methane by the ANME archaea, then their interaction would be syntrophic. However, if there is no gain for the methanogen, then the interaction is a form of commensalism.

Similarly to the work of Paper et al. (2021), Marquart et al. (2019) hypothesized that pH may also influence interactions of iron reducers with methanogens based on data from laboratory experiments. At low pH, where energy available for iron reduction is often high, they interpreted that the interactions between each group were primarily defined by competition for electron donors. However, at basic pH, where energy available for iron reduction can be low, Marquart et al. hypothesized that iron reducers increasingly transfer electrons to methanogens rather than ferric minerals and thus interact syntrophically. As with the hypotheses defined by Paper et al. (2021), additional research is needed to fully test this hypothesis.

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10.3: Spatial scales of interactions

Microbial interactions can occur over scales that are much larger than microbial cells themselves. As described in Chapter 3, cellular microorganisms exist on the scale of microns. As such, direct interactions between them may often occur on the micron scale. However, microorganisms can directly interact over longer distances through filamentous structures. For example, most fungi exist within hyphae, which are only a few microns in diameter but can extend over the scale of meters and serve multiple functions, including nutrient absorption and transport. Cable bacteria, as a second example, construct filamentous structures over centimeter distances and use them to transfer electrons across redox zones (Marzocchi et al., 2014; Nielsen et al., 2010; Pfeffer et al., 2012).

In addition to direct interactions, microorganisms can also interact indirectly by altering the chemistry of an environment (Konopka, 2009). For example, aerobic respiration in recharge areas of aquifers can create downgradient anoxic zones that host the activity of anaerobic microorganisms (Bethke et al., 2008). By lowering oxygen concentrations, the aerobes create conditions that are favorable for the anaerobes, which is arguably consistent with commensalism. Indirect interactions are not necessarily as strong as direct interactions, but they have the potential to span larger distances.

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10.4: Concept Check Questions

1. If a bacteriophage quickly kills a bacterium it has infected, it is an example of parasitism or predation and why?
2. What is a microbial community? How could bacteriophages alter the composition of a bacterial community?
3. If use of a critical resource by one group of microbes cuts off the supply of that resource to another, what is the name of the interaction?
4. How is syntrophy distinct from mutualism?
5. Is oxygen depletion by nitrifiers beneficial to anammox microorganisms?
6. How can abiotic iron reduction by sulfide oxidation lead to growth of other sulfur cyclers?
7. Imagine two environments, A and B. In environment A, iron reducers transfer electrons to ferric minerals. In environment B, iron reducers share electrons with methanogens through interspecies electron transfer. How would you expect the chemistry of the environments to differ?

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CHAPTER OVERVIEW

11: Mechanisms of Microbial Impacts

In the first two parts of this book, we consider properties of microorganisms and how environments influence their activities. For the final third of this book, we shift our perspective and consider how microorganisms impact their environments. These impacts are crucial for earth scientists to understand because microorganisms are collectively one of the most powerful forces shaping the planet, from the makeup of sediment being deposited in the oceans to the abundance of greenhouse gases in the atmosphere. Microorganisms make life possible in all higher trophic levels (Cavicchioli et al., 2019), and we cannot paint a complete picture of earth system processes if we leave them out. Moreover, we can combine our understanding of these impacts with our knowledge of the environmental controls on microbial populations to develop solutions for environmental challenges.

None of the major parts of the earth system are immune from microbial impacts. The chapters ahead (12–14) provide examples of impacts to the lithosphere, atmosphere, and hydrosphere. In this chapter, we focus on the coupled mechanisms by which impacts occur, which are divided into four categories: (1) catalyzing reactions, (2) generating biomass, (3) forming minerals, and (4) dissolving minerals.

- 11.1: Catalyzing reactions
  - 11.1.1: Direct impacts
  - 11.1.2: Indirect impacts
  - 11.1.3: Practice
- 11.2: Generating biomass
- 11.3: Forming minerals
- 11.4: Dissolving minerals
  - 11.4.1: Redox mechanism
  - 11.4.2: Acid mechanism
  - 11.4.3: Chelation mechanism
- 11.5: Answers to practice problems
- 11.6: Concept Check Questions
- 11.7: References

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11.1: Catalyzing reactions

Subsections:

11.1.1: Direct impacts

11.1.2: Indirect impacts

11.1.3: Practice

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11.1.1: Direct impacts

Microorganisms impact the chemistry of their environments by driving their reactions forward. This mechanism is obvious, but important to confront here because it is a fundamental part of the interactions between microorganisms and their environments. Microbial reactions can increase concentrations of reaction products and decrease concentrations of reactants. For example, consider the following overall reaction for nitrification:

$$\mathrm{NH_4^+ + 2\ O_2 \longleftrightarrow 2\ H^+ + NO_3^- + H_2O} \tag{11.1.1.1}$$

The reaction produces nitrate and hydrogen ions and therefore can cause nitrate concentration to increase and pH to decrease where it occurs. In contrast, the reaction consumes ammonium and molecular oxygen and can cause their concentrations to decrease.

We can take advantage of these effects to calculate rates of microbial reactions. For example, imagine that you wanted to know how rapidly ammonium was being consumed in a culture of nitrifying microorganisms. If the initial ammonium concentration was $\mathbf{1\ mM}$ and the concentration after four days was $\mathbf{0.1\ mM}$, then overall rate of ammonium oxidation during that time is calculated as:

$$rate = \frac{(\mathrm{NH_4^+})^{initial} - (\mathrm{NH_4^+})^{final}}{time} = \frac{1.00\ \mathrm{mM} - 0.10\ \mathrm{mM}}{4\ \mathrm{days}} = 0.23\ \frac{\mathrm{mM}}{\mathrm{day}} \tag{11.1.1.2}$$

This simple calculation can be helpful, but it has its limitations. The value calculated represents an overall rate for the time period between measurements. The instantaneous rate could vary considerably during that time. Also, the microbial reaction of interest may not be the only control on reactant and product concentrations. If so, it would be necessary to assess the contributions of those other controls in order to accurately quantify the reaction rate.

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11.1.2: Indirect impacts

Microbes catalyze reactions directly to obtain energy and nutrients. But those reactions can in turn drive other reactions. In this way, microbes mediate many reactions indirectly. For example, consider the following glucose fermentation reaction:

$$\text{glucose} \longleftrightarrow \frac{4}{3}\ \text{propionate} + \frac{2}{3}\ \text{acetate} + \frac{2}{3}\ CO_2 + 2\ H^+ + \frac{2}{3}\ H_2O \tag{11.1.2.1}$$

The reaction produces carbon dioxide and hydrogen ions, which would both work to lower the pH of the environment. The hydrogen ions do so directly, and the carbon dioxide can lower pH by forming carbonic acid:

$$CO_2\ (aq) + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \tag{11.1.2.2}$$

By lowering the pH of the environment through acid production, these reactions would have a broad range of consequences. The pH of a solution is a major control on the chemical speciation of its solutes as well as the mineral surfaces it contacts. Both tend to become increasingly protonated as acid is added to a solution and pH decreases. Moreover, the acid can drive mineral dissolution reactions, which we discuss in the section on microbial weathering below. Carbon dioxide generated by organic matter degradation and plant respiration (i.e., root respiration) is a major driver of mineral weathering in soils and the subsurface (Chorover et al., 2020; Olshansky et al., 2019; Sanchez-Canete et al., 2018).

The bottom line is that microbes directly or indirectly mediate many of the chemical reactions that occur at Earth's surface and in the upper 5 km of the subsurface. These reactions significantly affect the compositions of our soil, sediment, rocks, water, and atmosphere.

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11.1.3: Practice

During a 7 day incubation, the sulfate concentration in a culture of sulfate-reducing microorganisms decreased from 1.50 to $0.80\ \mathrm{mM}$. Use this result to answer the following questions:

A. What is the overall rate of sulfate reduction during that time period?

B. If the sulfate reducers used dihydrogen as their electron donor, what is the overall rate of dihydrogen oxidation? For this calculation, you need to consider the stoichiometry of the reaction: $4\ \mathrm{H_2}\ (aq) + 2\ \mathrm{H^+} + \mathrm{SO_4^{2-}} \longleftrightarrow 4\ \mathrm{H_2O} + \mathrm{H_2S}\ (aq)$

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11.2: Generating biomass

Microorganisms can live freely in solutions, but they often exist within biofilms, which include the cells themselves as well as extracellular polymeric substances (EPS) (Section 3.5). Biofilms can facilitate mineral precipitation, as discussed in the next section (Section 11.3). They can also alter an environment by filling open space and altering surfaces, which we consider here.

As biofilm fills open spaces in porous media, such as soils, sediments, and rocks, it reduces their porosity, which is the percentage of void space in the medium. If the growth occurs in places that affect fluid flow through the porous media, such as pore throats and fracture openings, then it can also lower the permeability of the porous media (Gerlach and Cunningham, 2010). Indeed, studies have demonstrated that biofilms can lower the permeability of the porous media by multiple orders of magnitude (Gerlach and Cunningham, 2010). As such, stimulating biofilm growth has been investigated as a way to strategically alter permeability for subsurface technologies, such as geological carbon storage (Mitchell et al., 2009) and enhanced oil recovery (Nikolova and Gutierrez, 2020).

Images collected from experiments by Kirk et al. (2012) illustrate the effect of biofilm growth in porous media (Fig. **11.1**). They show growth of microbial biofilm within capillary tubes containing glass beads. In the images, the black spheres are glass beads, the red areas show water with rhodamine dye, and the green regions are biofilms formed by *Pseudomonas fluorescens*. The strain of *P. fluorescens* that was used in the experiments produced a green fluorescent protein, allowing its biofilm to be easily visualized with fluorescence microscopy. Some of the biofilm growth occurred within pore throats, the narrow regions between the glass beads. As a result, the permeability of the tube decreased significantly as growth progressed.

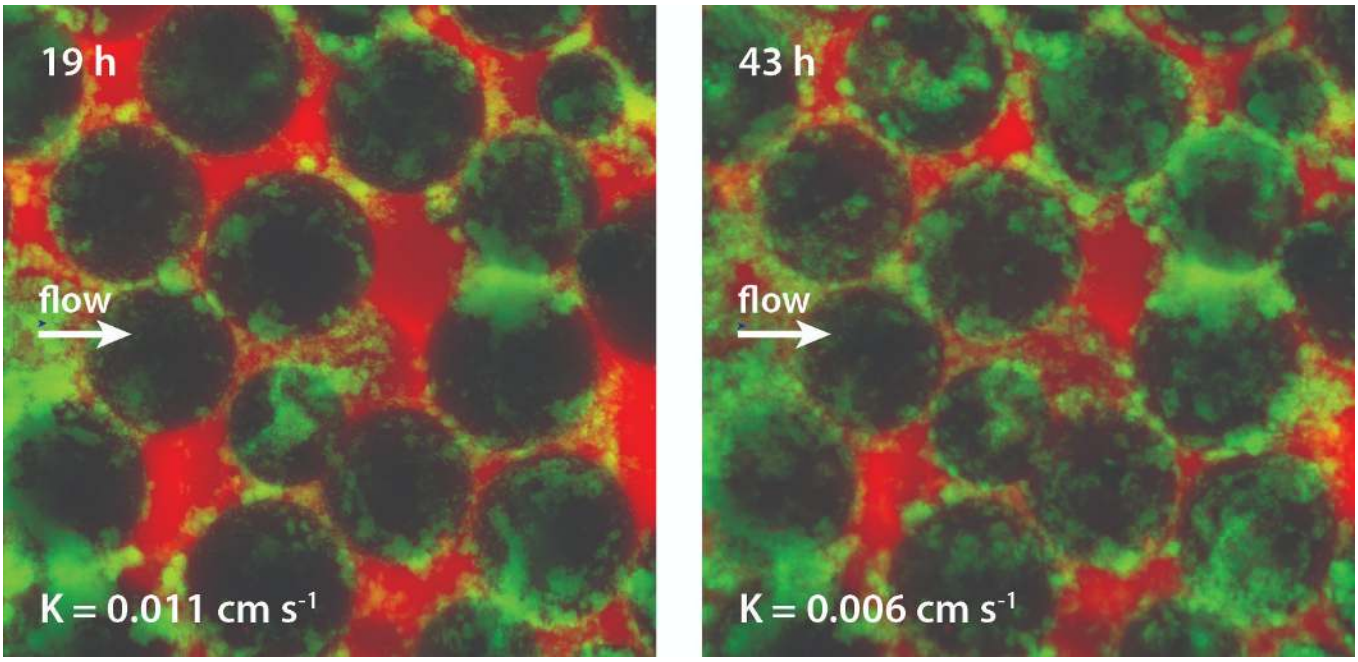


Figure **11.1**: Confocal microscopic image showing growth of *Pseudomonas fluroescens* biofilm (green) in a capillary tube filled with glass beads (black) and water (red). These images were collected from laboratory experiments described by Kirk et al. (2012). The image on the left was collected 19 hours after cells were added to the capillary tube and the image on the right, 43 hours after cells were added. Hydraulic conductivity (K) at each time point is indicated in the bottom left of each image. Hydraulic conductivity describes the ease with which a fluid can pass through a porous media. It includes permeability as well as properties of the fluid.
https://commons.wikimedia.org/wiki/File:Bioclogging.jpg

Regarding surface alteration, formation of biofilms on mineral surfaces can create a microenvironment capable of inhibiting dissolution under some conditions and enhancing dissolution under others (Douglas, 2005; Welch et al., 1999). The composition of the microenvironment can differ from the bulk chemistry of the adjacent solution in terms of pH, redox state, and solute concentrations (Welch et al., 1999). Where that is the case, the reactivity of the mineral may disagree with what would be expected based on the composition of the bulk solution. Moreover, microbial biofilms can help retain water at the mineral surface, which can extend available time for chemical and microbial reactions as a system dries (Chenu and Roberson, 1996).

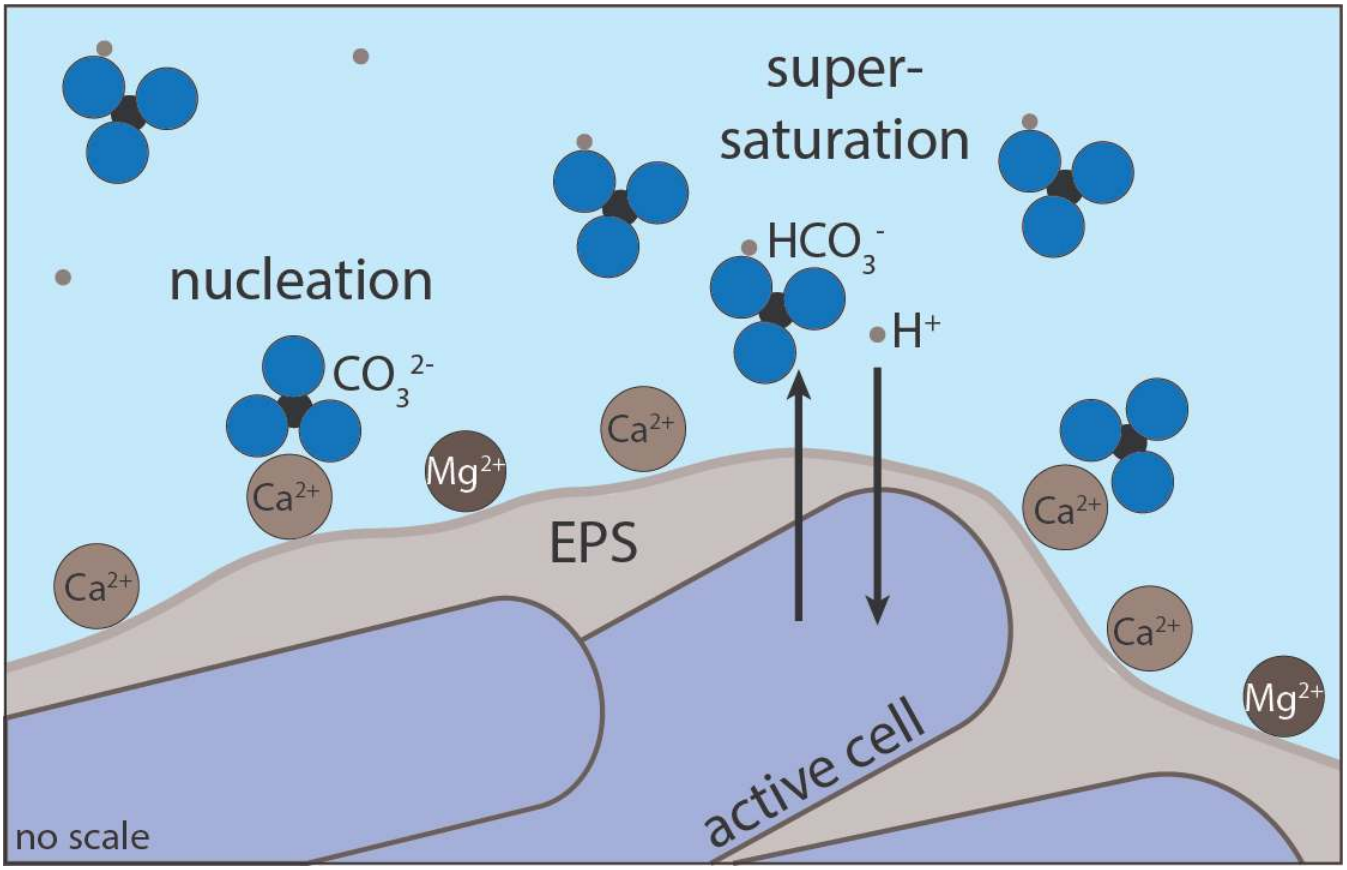
As an example, Gray and Engel (2013) studied microbial communities attached to carbonate bedrock in the Edwards aquifer, a major aquifer in central Texas, USA. Groundwater samples they collected were all supersaturated with respect to calcite, meaning that precipitation rather than dissolution of calcite was thermodynamically favored based on the composition of the bulk solutions (see Box 11.1). Despite this result, some dissolution occurred on calcite chips incubated within the aquifer when the chips were colonized by microbes. The researchers concluded that surface colonization by active microbial cells promoted mineral dissolution by creating local disequilibria between the groundwater and mineral surfaces.

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11.3: Forming minerals

Biomineralization is the process by which living organisms cause minerals to form (Benzerara et al., 2011). Biomineralization impacts the composition of the environment, by affecting the distribution of elements among different phases in geochemical systems. Biomineralization, like biofilm formation, also impacts the physical properties of environments, but creating solid phases that fill voids.

There are two main mechanisms by which microorganisms cause minerals to form (Fig. **11.2**). Microorganisms can provide surfaces that help nucleate minerals. They can also alter the chemistry of the environment in such a way that mineral precipitation becomes thermodynamically favorable. In other words, their activities can alter the saturation state of a mineral and can cause it to become supersaturated (Box 11.1).



][

Figure **11.2**: Schematic illustration of biomineralization mechanisms. Microorganisms can cause a mineral to form by changing the chemistry of a solution such that the mineral become supersaturated (see Box **11.1**) and by forming biomass that provides nucleation surfaces. As an example, microorganisms can promote carbonate precipitation by producing bicarbonate and consuming hydrogen ions, which would help drive the minerals to supersaturation, and by producing biomass that complexes metals such as calcium and magnesium, which then serve as nucleation sites. That biomass can include extracellular polymeric substances (EPS), as depicted, as well as the cells themselves. Note that the figure is not to scale and that the relative size of ions is greatly exaggerated.
https://commons.wikimedia.org/wiki/File:Biomineralization.jpg

Nucleation, in the context of this discussion, is the formation of a new solid phase and a basic requirement for mineral formation. Homogenous nucleation occurs when a nucleus forms from a bulk solution whereas heterogeneous nucleation occurs when a nucleus forms in contact with a surface (Drever, 1997). Microbial biomass, including cells and extracellular polymeric substances (EPS), can provide surfaces for heterogenous mineral nucleation. Specifically, the reactive functional groups on biomass such as carboxyl, phosphate, and amino groups can form complexes with ions from an adjacent solution (Fig. **11.2**). Once an ion has complexed, it can then serve as a nucleation site for mineral growth (Beveridge, 1989; Schultze-Lam et al., 1996). This reaction

pathway can enhance precipitation by helping overcome some of the factors that can inhibit precipitation directly from solution, such as ion pairing and the presence of hydration spheres (Braissant et al., 2007).

Supersaturation is also a basic requirement for mineral growth. A solution becomes supersaturated if ingredients needed to form the mineral have higher concentrations than they would if they mineral were in equilibrium with the solution. Microbes can cause this situation to occur by generating those ingredients or otherwise changing the chemistry of the environment in such a way that precipitation becomes more thermodynamically favorable (Fig. **11.2**).

As an example, microbial iron reduction can create conditions that are more thermodynamically favorable for precipitation of the mineral siderite ($\mathbf{FeCO_3}$) (Fredrickson et al., 1998). Siderite precipitation consumes ferrous iron and bicarbonate and releases a hydrogen ion:

$$\mathbf{Fe^{2+} + HCO_3^- \longleftrightarrow FeCO_3\ (s) + H^+} \tag{11.3.1}$$

Therefore, the reaction becomes more thermodynamically favorable as ferrous iron and bicarbonate activities increase and hydrogen ion activity decreases (or in other words pH increases). Microbial iron reduction can cause all three of these changes to occur, as shown in the following example reaction with acetate as the electron acceptor and goethite ($\mathbf{FeOOH}$) as the source of ferric iron:

$$\mathbf{CH_3COO^- + 15\ H^+ + 8\ FeOOH \longleftrightarrow 2\ HCO_3^- + 12\ H_2O + 8\ Fe^{2+}} \tag{11.3.2}$$

The reaction consumes a large number of hydrogen ions, which works to increase pH. It also produces ferrous iron and bicarbonate, and thus can cause concentrations of those ions to increase.

Regardless of how, why would they do it? In many cases, microorganisms are not intentionally causing minerals to form. We refer to this scenario as biologically induced mineralization (Lowenstam, 1981). They may, for example, just happen to produce ingredients needed for the mineral or provide a favorable surface for precipitation, which generally occurs outside of the cell. In contrast, some microorganisms intentionally precipitate minerals for some physiological purpose (Konhauser, 2007). We refer to this scenario as biologically controlled mineralization. During controlled mineralization, microorganisms often produce vesicles for mineral growth. Supersaturation may be induced in some cases through active accumulation of an ingredient. Often, a template for mineral growth is provided by the cell and as a consequence, the morphology of the mineral product is not random.

Box 11.1: Saturation Index

The saturation index of a mineral tells us whether a solution is in equilibrium with a mineral phase and if not, whether dissolution or precipitation of the mineral is thermodynamically favorable. We calculate the saturation index of a mineral in a solution based on the reaction quotient (Q) for the mineral's dissolution reaction and the equilibrium constant for the reaction (K). Consider the following reaction, which describes dissolution of the mineral siderite ($\mathbf{FeCO_3}$):

$$\mathbf{FeCO_3\ (s) + H^+ \longleftrightarrow Fe^{2+} + HCO_3^-}$$

This reaction is simply reaction **11.3.1** written as a mineral dissolution reaction (i.e., the mineral dissolves as the reaction moves forward). The quotient for this reaction calculated as:

$$Q = \frac{[\mathbf{Fe^{2+}}]\,[\mathbf{HCO_3^-}]}{[\mathbf{H^+}]\,[\mathbf{FeCO_3\ (s)}]}$$

Assuming an activity of one for siderite, the equation simplifies to

$$Q = \frac{[\mathbf{Fe^{2+}}]\,[\mathbf{HCO_3^-}]}{[\mathbf{H^+}]}$$

Putting the equation into log form, we get:

$$\log Q = \log [\mathbf{Fe^{2+}}] + \log [\mathbf{HCO_3^-}] - \log [\mathbf{H^+}]$$

This is the same as

$$\log Q = \log [\mathbf{Fe^{2+}}] + \log [\mathbf{HCO_3^-}] - pH$$

To calculate the saturation index (SI) for siderite, we subtract the $\log K$ of the mineral dissolution reaction from $\log Q$:

$$SI = \log Q - \log K$$

If the result is zero, the solution is equilibrated with the mineral, or in other words, the solution is saturated with respect to the mineral. If the result is a negative number ($\log Q - \log K < 0$), the solution is undersaturated and dissolution of the mineral is possible. If the result is positive ($\log Q - \log K > 0$), then the solution is supersaturated, and mineral precipitation is possible. Be aware that the interpretation of these results will differ if the mineral reaction is not written in terms of dissolution (mineral on the reactant side of the reaction) and if the reaction quotient and equilibrium constants are not in log form.

For an example calculation, imagine that a solution has a temperature of 15°C and composition equal to that of Solution A in the table below. What is the saturation index for siderite in the solution? First, calculate the reaction quotient value:

$$\log Q = (-3.812) + (-2.888) + 6 = -0.700 \tag{11.3.3}$$

Next, calculate the saturation index, given that the $\log K$ value for siderite dissolution is −0.0339 at 15°C:

$$SI = (-0.700) - (-0.0339) = -0.666 \tag{11.3.4}$$

This result indicates that it is not thermodynamically favorable for siderite to precipitate from the solution. In other words, siderite is undersaturated. Note, this calculation should typically be carried out using chemical activities rather than concentrations. Refer to Chapter 8, Box 8.1, for more information on chemical activities and how to calculate them with geochemical modeling software.

Box 11.1.1 Practice

Repeat the saturation index calculation but increase the pH and log activities of ferrous iron and bicarbonate, as indicated for Solution B in the table below, to simulate impacts of microbial iron reduction.

Table 11.1: Hypothetical solutions used for Box 11.1.1 example and practice calculations

	Solution A		Solution B	
Parameter	Concentration/value	Log activity*	Concentration/value	Log activity*
Fe^{2+}	200 μM	−3.812	1 mM	−3.16
HCO_3^-	5 mM	−2.888	6 mM	−2.523
H^+	pH 6.00	−6.00	pH 6.50	−6.50
Na^+	2 mM	−2.732	2 mM	−2.741
Cl^-	1 mM	−3.032	1 mM	−3.042
T	15°C		15°C	

*Activities are calculated using The Geochemist's Workbench program SpecE8.

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11.4: Dissolving minerals

Mineral weathering occurs when minerals are broken down by physical and/or chemical mechanisms. Weathering reactions can increase the porosity of porous media (McMahon et al., 1992). They are one of the major controls on the abundance of carbon dioxide in the atmosphere (Berner, 2003). They generate dissolved ions that affect the composition of groundwater and surface water and ultimately the oceans (Banfield et al., 1999). Mineral weathering reactions produce secondary minerals such as clays that help form sediments and soils (Banfield et al., 1999). They help buffer soils against acidification (van Schöll et al., 2008). Moreover, mineral weathering by soil microorganisms helps supplying nutrients to plants (Ribeiro et al., 2020; van Schöll et al., 2008). Thus, microbial mineral weathering has diverse impacts that collectively help determine our planet's habitability.

Why do microorganisms drive mineral weathering reactions? Like biomineralization, microbial mineral weathering can be induced or controlled. Microorganisms can induce mineral weathering if they just happen to produce products such as acid that can cause weathering to occur. Microorganisms may intentionally drive weathering to obtain nutrients or energy resources. For example, numerous studies have demonstrated that microorganisms can liberate phosphate for assimilation by producing acids and chelators that accelerate dissolution of phosphate minerals such as apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) (Banfield and Welch, 2000; Welch et al., 2002).

Many different microbial groups can drive weathering reactions. In soils, fungi have been found to contribute to as much as 50% of the mineral weathering (van Schöll et al., 2008), although many several microbial groups have been reported to have mineral weathering abilities (Uroz et al., 2009). How do they do it? Microorganisms help drive chemical weathering by catalyzing redox reactions, by producing acids and chelators, or by some combination of these mechanisms (Uroz et al., 2009). In the subsections below, we consider each of these mechanisms individually.

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11.4.1: Redox mechanism

Microorganisms can weather minerals by altering the redox state of a mineral component. The microbial reaction can reduce the mineral component, causing reductive dissolution of the mineral, or they can oxidize it, causing oxidative dissolution.

As an example of reductive dissolution, microbial reduction of oxidized manganese can cause dissolution of manganese oxides, as illustrated by the following example reaction, which includes the mineral pyrolusite ($\mathbf{MnO_2}$) as the source of oxidized manganese and acetate as the source of electrons:

$$\mathbf{CH_3COO^- + 7\ H^+ + 4\ MnO_2 \leftrightarrow 2\ HCO_3^- + 4\ Mn^{2+} + 4\ H_2O} \tag{11.4.1.1}$$

As an example of oxidative dissolution, microbial oxidation of reduced iron and sulfur in pyrite can cause the mineral to dissolve. Although mechanisms vary with conditions (Baker and Banfield, 2003; Chen et al., 2014), the overall reaction of pyrite weathering can be represented by the following reaction:

$$\mathbf{FeS_2 + 3.5\ O_2 + H_2O \leftrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+} \tag{11.4.1.2}$$

Pyrite weathering causes significant impacts to water quality, which are discussed in more detail in Section 14.4.3. Among the impacts, a substantial amount of acid can be generated by pyrite oxidation, which in turn can react with other minerals and cause their dissolution. We consider this acid mechanism in the next section.

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11.4.2: Acid mechanism

Mineral dissolution caused by microbial acid production is widespread. Microbial reactions that directly cause or induce acid generation are broadly distributed in natural environments. Moreover, the stability of many common rock-forming minerals, including aluminosilicates and carbonates, is sensitive to pH, reflecting the fact that they are salts composed of strong base cations and weak acid anions (Faure, 1991). As acid is produced, the weak acid anions of the minerals can protonate, which in turn can help push mineral dissolution reactions forward.

As an example, calcite ($\mathbf{CaCO_3}$) dissolution can be written as:

$$\mathbf{CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{2-}} \tag{11.4.2.1}$$

Carbonate ($\mathbf{CO_3^{2-}}$) is an anion of carbonic acid ($\mathbf{H_2CO_3}$), which is a weak acid and only starts to completely dissociate as a solution's pH rises above 8. Most natural waters have near-neutral pH (e.g., pH 6 – 8), and under those conditions the carbonate ion largely protonates and forms bicarbonate:

$$\mathbf{CO_3^{2-} + H^+ \longleftrightarrow HCO_3^-} \tag{11.4.2.2}$$

Combining reactions **11.4.2.1** and **11.4.2.2** gives the following overall reaction:

$$\mathbf{CaCO_3 + H^+ \longleftrightarrow Ca^{2+} + HCO_3^-} \tag{11.4.2.3}$$

Because hydrogen ions are included as a reactant in reaction **11.4.2.3**, acid produced by microorganisms can push the reaction forward and cause mineral dissolution.

Many different microbial reactions generate acid. Major microbial sources of acid include carbonic acid and organic acids generated by organic matter degradation, nitric and nitrous acid produced by nitrifying microorganisms, and sulfuric acid produced by sulfur oxidizers. Furthermore, iron-oxidizing microorganisms can induce acid generation where the ferric iron they produce then participates in hydrolysis reactions (Section 12.1.3).

To place these reactions within an environmental context, we consider microbial acid generation in a soil linked with subsurface mineral weathering, as shown in Figure **11.3**. In the conceptual diagram, products of soil respiration include carbon dioxide generated by plant respiration and microbial degradation of organic matter. Some portion of that carbon dioxide can be emitted to the atmosphere, and some can dissolve into water, forming carbonic acid (Reaction **11.1.2.2**), and then migrate into the subsurface with infiltrating water. A recent study at the Santa Catalina Mountains-Jemez River Basin Critical Zone Observatory, for example, found that two-thirds of the carbon dioxide from soil respiration was transported into the subsurface, where it drove mineral weathering reactions (Sanchez-Canete et al., 2018). Lastly, in addition to carbonic acid, organic matter degradation also generates organic acids such as oxalic, fumaric, and succinic acids, which also help drive mineral weathering.

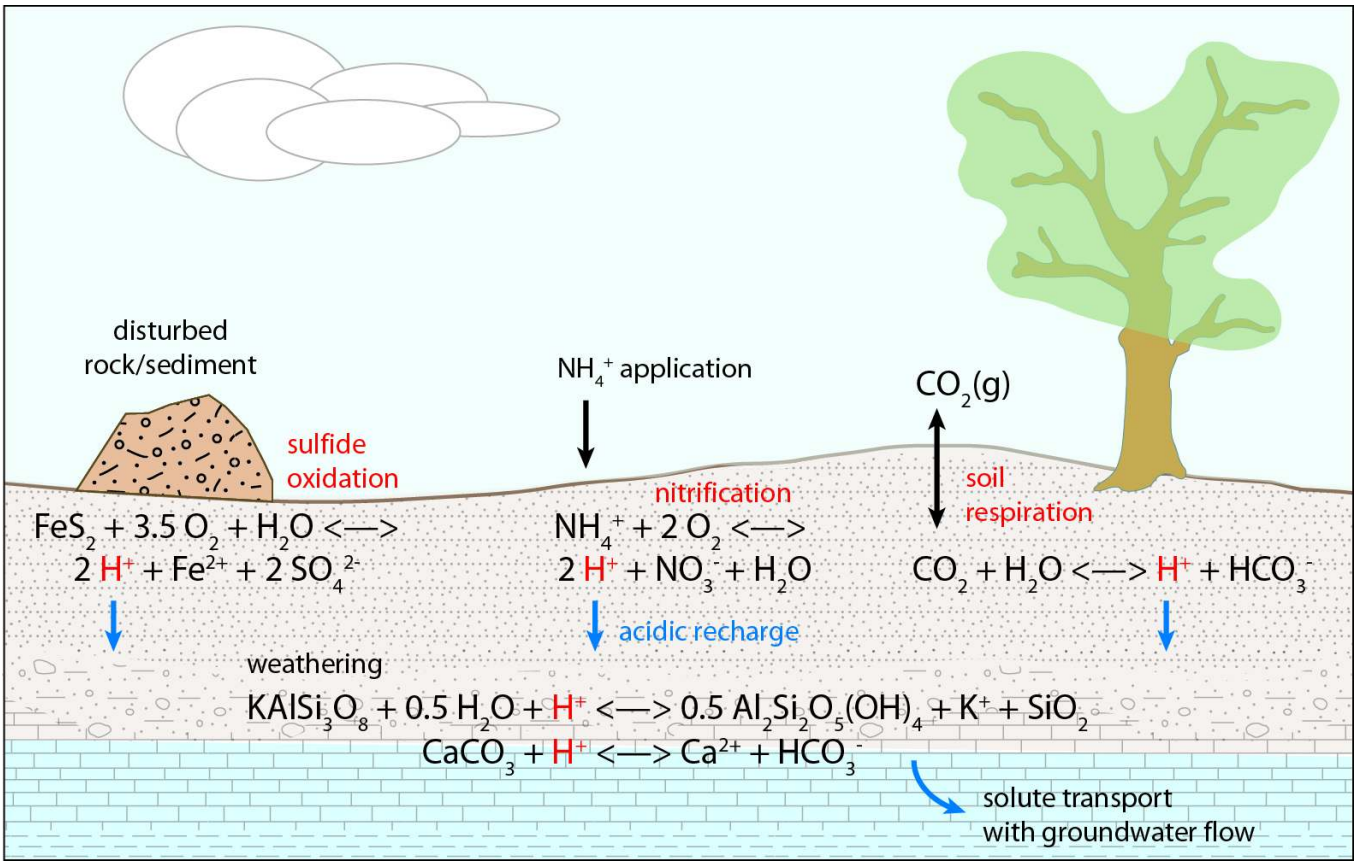


Figure **11.3**: Conceptual diagram of weathering in the subsurface driven by acid production in an overlying soil. Some of the acid generated in soil may be neutralized by mineral weathering reactions in the soil and unsaturated zone. The acid that is not neutralized there may react with the aquifer matrix. Two example weathering reactions are shown, one in which potassium feldspar ($KAlSi_3O_8$) reacts with acid to produce kaolinite ($Al_2Si_2O_5(OH)_4$) and aqueous potassium and silica, and the other in which calcium carbonate ($CaCO_3$) reacts with acid to produce aqueous calcium and bicarbonate. Solutes generated by these reactions can be transported by groundwater flow to nearby surface water bodies or into the deep subsurface.
https://commons.wikimedia.org/wiki/File:Weathering.jpg

Acid production by nitrification appears to be growing in significance as a result of human activities that add ammonium to the environment. Major anthropogenic sources of ammonium include sewage, livestock waste, and nitrogen fertilizer. Nitrogen fertilizer can take multiple forms, but commonly, ammonium-based fertilizers are applied to crop soils where microorganisms then convert the ammonium to nitrate via nitrification (Böhlke, 2002). Enormous amounts of nitrogen fertilizers are applied to crop soils globally each year to increase food production (Gruber and Galloway, 2008; Liu et al., 2010). One of the consequences is acidification of crop soils and the water passing through them into the subsurface (i.e., groundwater recharge) (Böhlke, 2002). As an example, Guo et al. (2010) demonstrated that the pH of crop soils across China have decreased significantly since the 1980's. Acid produced by nitrification stimulates weathering in soils and the shallow subsurface and has been found to cause concentrations of numerous solutes to increase in groundwater and streams (Böhlke, 2002; Perrin et al., 2008).

Dissolved sulfide and sulfide minerals can be stable under anoxic conditions, but where they are exposed to oxygen or nitrate, then microorganisms can oxidize them and generate acid in the process, as noted previously (Section 11.4.1). Such exposure can be natural, but it is common in mining areas, where rocks and sediment are disturbed and those not containing sufficient densities of ore may be left exposed to oxidative weathering (Newsome and Falagán, 2021; Nordstrom et al., 2015). Sulfide within subsurface rocks and sediment can also be exposed to oxygen introduced through boreholes or water level fluctuations (Schreiber et al., 2000). Moreover, nitrogen fertilizer use can also stimulate weathering of subsurface sulfide by increasing fluxes of nitrate into anoxic zones of the subsurface (Xu et al., 2021).

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11.4.3: Chelation mechanism

Chelation involves formation of a complex between a ligand and a metal cation. Ligands are often organic molecules, and some can be produced and released into natural environments by microorganisms. Microorganisms can secrete chelators to increase the mobility of specific nutrients. If that nutrient is a structural component of a mineral, then removal from the mineral by the chelator can ultimately cause the mineral to dissolve. Chelators can complex many different metals, suggesting that they can play a role in accelerating dissolution of a wide range of minerals (Konhauser, 2007).

As an example, many microorganisms secrete siderophores, which are organic compounds that form strong complexes with ferric iron (Sandy and Butler, 2009). In most natural waters, ferric iron solubility is low, as discussed in Section 12.1.3. Under such conditions, ferric iron commonly exists within an (oxyhydr)oxide mineral rather than a dissolved ion, making it difficult to import into a cell. However, by releasing siderophore into the environment, microorganisms can mobilize the iron and more easily import it. As a consequence, the (oxyhydr)oxide at least partially dissolves.

Page and Huyer (1984) demonstrated that siderophore production directly relates to iron bioavailability and microbial growth. They examined siderophore production in culture experiments containing *Azotobacter vinelandii*, a nitrogen-fixing microbe. Recall from earlier sections (5.2.1, 7.3) that iron is an essential ingredient needed to make nitrogenase, the enzyme used to fix nitrogen. In their experiments, the types and amounts of siderophores secreted by *A. vinelandii* depended on the mineralogical forms of iron that were present and the overall iron abundance. Thus, the mineralogy of an environment appears to influence not only the types of chelators being secreted by a microbial community but also the overall significance of chelation weathering.

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11.5: Answers to practice problems

Practice 11.1.3

Reaction rate calculations:

A. $0.1\ \text{mM day}^{-1}$

B. $0.4\ \text{mM day}^{-1}$

Box 11.1.1 Practice

Siderite saturation index = 0.851.

The mineral is supersaturated and thus precipitation may occur.

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11.6: Concept Check Questions

1. Given a microbial reaction, could you explain in general terms how it might affect the chemical composition of an aqueous system?
2. What is a biofilm and when does biofilm growth impact the permeability of a porous medium?
3. What is the saturation index of a mineral? How might microorganisms cause a mineral to form by altering its saturation index?
4. How could a biofilm help cause mineral precipitation?
5. Can you explain the difference between biologically induced and biologically controlled precipitation?
6. What are the three microbial mechanisms that can cause mineral weathering?
7. Why might microorganisms purposefully cause mineral weathering to occur?

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CHAPTER OVERVIEW

12: Impacts to the Lithosphere

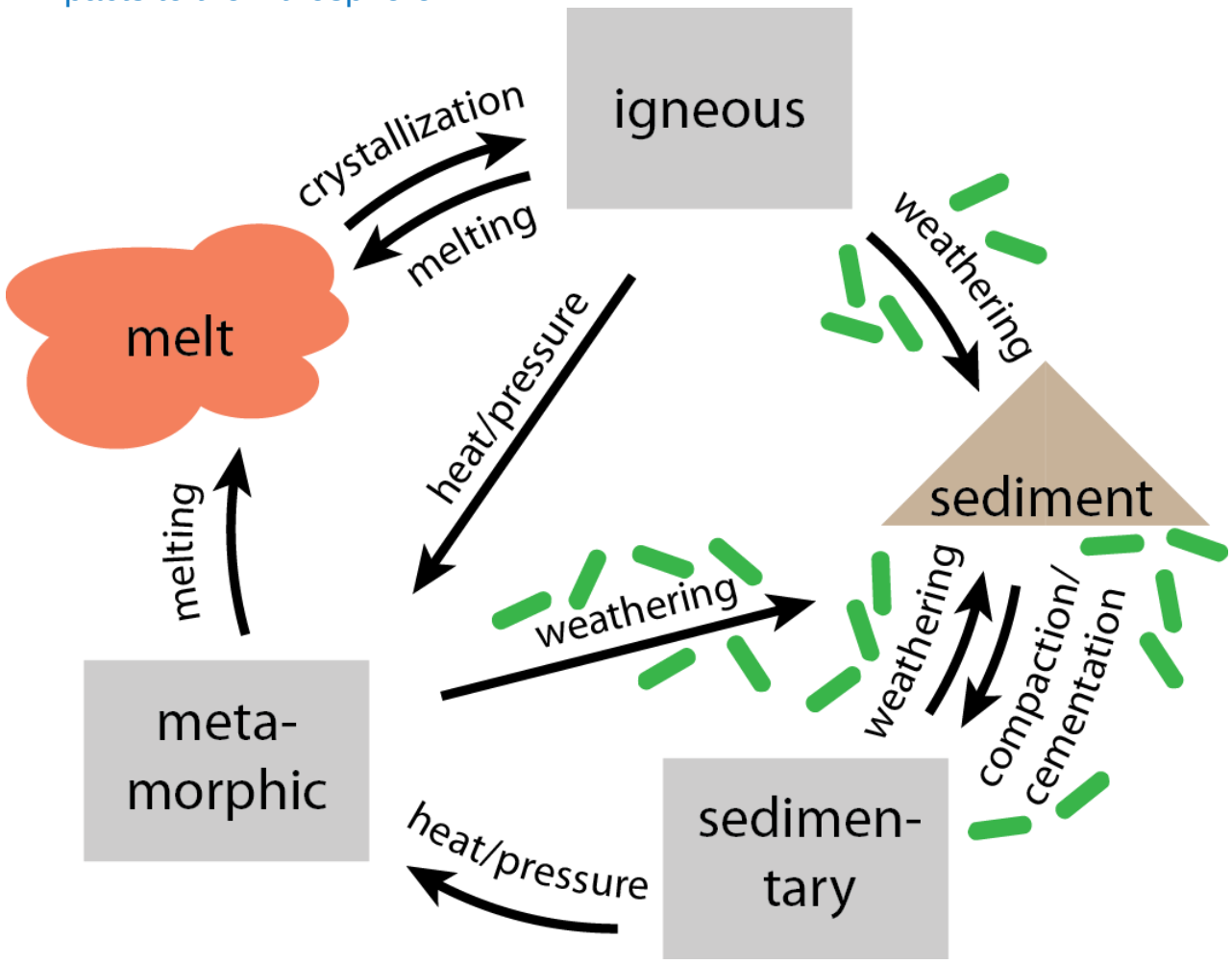


Figure 12.1: Copy and Paste Caption here. (Copyright; author via source)

Plate tectonics and the hydrologic cycle are well-recognized drivers of Earth's rock cycle, but contributions from microorganisms and other life forms are also significant (Fig. 12.1). Microorganisms push mineral weathering forward and thus help accelerate the transformation of rocks into sediments. Microbial reactions produce directly or indirectly many of the minerals that accumulate in depositional environments, some of which would not form in purely inorganic systems. Microbial reactions help convert sediments to sedimentary rocks during diagenesis. Moreover, by helping to drive weathering and determine the properties of sedimentary rocks, microorganisms even influence tectonic activity. Thus, microorganisms impact the lithosphere, the solid outermost rocky shell of the Earth, in diverse and significant ways.

In this chapter, we will consider these impacts in more detail. We will examine some of the major groups of microbial biominerals and the roles microorganisms play in forming them. We discuss how microbial activity affects the composition of sediments that are deposited in the oceans. We will also discuss how microbial activities have affected tectonic activity and the evolution of Earth's mineralogy over time.

12.1: Examples of biomineralization
12.1.1: Carbonates
12.1.2: Amorphous silica
12.1.3: Iron (oxyhydr)oxides

12.1.4: Sulfides
12.1.5: Clay minerals
12.2: Microbial influence on marine sediments
12.3: Microbial influences on tectonic activity
12.4: Mineral evolution
12.5: Concept Check Questions
12.6: 12.6 References

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12.1: Examples of biomineralization

Microorganisms can form a wide variety of minerals. To illustrate the significance of biominerals and mechanisms of their formation, this section provides a brief summary of microbial contributions to five mineral groups: carbonates, amorphous silica, iron (oxyhydr)oxides, sulfides, and clays. These phases have widespread occurrence and play important roles in geochemical systems, as discussed below. As you read, recognize that this section is not intended as a comprehensive review of these mineral groups and all of the ways the minerals within them form. Instead, we focus on areas where microbiology plays a significant role.

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12.1.1: Carbonates

Carbonates are a group of minerals that include the carbonate ion (CO_3^{2-}) as an essential structural unit (Deer et al., 1992). Among the most common are calcite $(CaCO_3)$, aragonite $(CaCO_3)$, magnesite $(MgCO_3)$, dolomite $(CaMg(CO_3)_2)$, siderite $(FeCO_3)$, rhodochrosite $(MnCO_3)$, strontionite $(SrCO_3)$, and witherite $(BaCO_3)$ (Deer et al., 1992). These minerals function as important pH buffers in geochemical systems and major carbon reservoirs in the global carbon cycle. They function as cements for sedimentary rocks. Carbonate biominerals also serve as a marker for the emergence of life on Earth. Specifically, stromatolites are among the earliest evidence of life in the rock record and their layered structures form by sediment trapping and carbonate biomineralization on microbial mats (Grotzinger and Knoll, 1999) (Fig. **12.2A, B**).

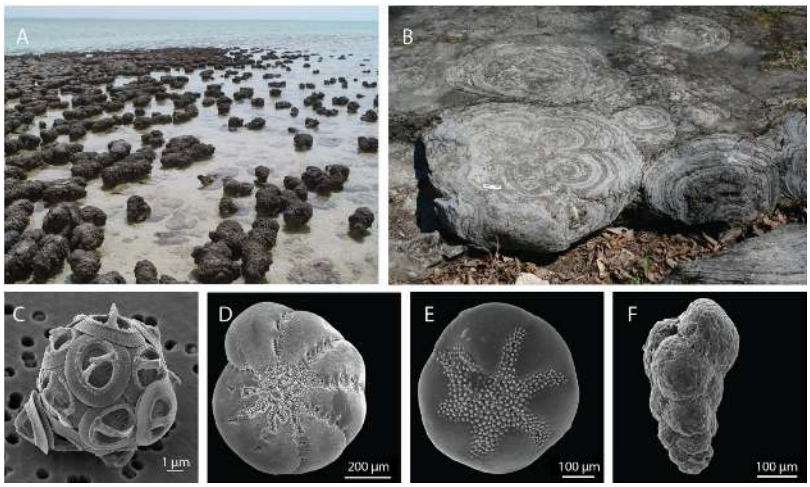


Figure **12.2**: Examples of carbonate biomineralization. Image (A) shows modern marine stromatolites in Shark Bay, Western Australia, (B) shows ancient stromatolites in the Cambrian Hoyt Limestone, exposed at Lester Park, near Saratoga Springs, New York, (C) a coccolith was formed by *Gephyrocapsa oceanica*, and (D - F) benthic foraminifera collected from Long Island Sound. Image sources: (A) Paul Harrison, https://commons.wikimedia.org/w/index.php?curid=714512; (B) Michael C. Rygel, https://commons.wikimedia.org/wiki/File:Stromatolites_hoyt_mcr1.JPG; (C), https://commons.wikimedia.org/wiki/File:Gephyrocapsa_oceanica.jpg; (D - F) Thomas et al. (2000)

Microorganisms can help form carbonate minerals by generating surfaces that promote nucleation (Fig. 11.2). In the microbial mats of modern carbonate stromatolites, for example, extracellular polymeric substances (EPS) produced by cyanobacteria and other microorganisms can serve as sites for mineral nucleation. Negatively charged functional groups on the EPS can strongly bind calcium and other cations from the seawater. This binding of calcium ions can actually inhibit precipitation by decreasing the availability of calcium for precipitation. However, if the EPS becomes saturated with calcium or if the EPS is altered and reorganized, it can then serve as a template for carbonate precipitation (Dupraz and Visscher, 2005).

Coupled with these nucleation effects, microorganisms can also induce carbonate mineralization by altering the chemistry of their environment in ways that cause carbonate minerals to become supersaturated. They may, for example, cause supersaturation by producing bicarbonate or consuming hydrogen ions (i.e., increasing pH) (Fig. **12.3**), as discussed in Section 11.3. In addition, microbial reactions can also help supply cations that precipitate in carbonate minerals. For example, microorganisms can supply divalent metal cations by reducing (oxyhydr)oxide minerals and by degrading EPS that has inhibited carbonate precipitation by sequestering calcium and magnesium ions (Dupraz and Visscher, 2005).

Many microbial reactions include hydrogen ions, either as a reactant or product. Recall from Chapter 4 that we often add hydrogen ions when we balance redox reactions. Moreover, many microorganisms generate bicarbonate by oxidizing organic carbon, and most are thought to live within biofilms (Costerton et al., 1995; Flemming and Wuertz, 2019). Taken together, these observations indicate that the ability to induce carbonate mineralization is widespread across microbial life. Indeed, this possibility has been recognized for many years based on observations from cultures (Boquet et al., 1973). In addition to induced carbonate mineralization, some microorganisms intentionally form calcium carbonate phases. Notable examples of biologically controlled carbonate mineralization include coccolithophores and foraminifera, groups that commonly construct their shells (or tests) out of calcium

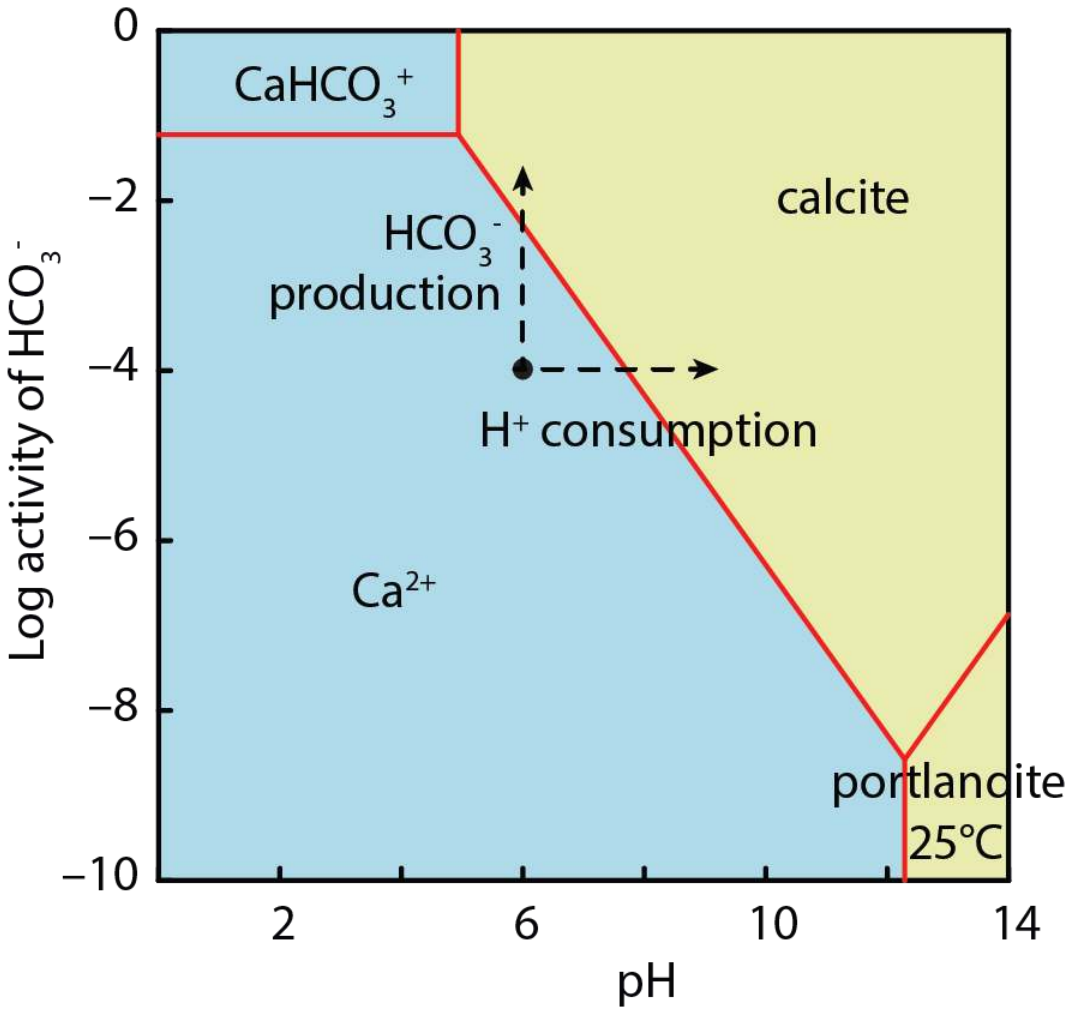


Figure **12.3**: Variation in calcium speciation with bicarbonate activity and pH. Calcium is thermodynamically favored to exist as dissolved ions in the regions shaded blue and within minerals in the regions shaded yellow. The scatter point and dashed lines illustrate how bicarbonate production and hydrogen ion consumption by microbial reactions can cause calcite to become supersaturated in a solution with a temperature of 25°C. At the scatter point, the solution has a pH of 6 and contains **−2** and **−4** log activities of calcium and bicarbonate, respectively. From there, microbial reactions can cause calcite to saturate by increasing pH to just under 7 or by increasing the log activity of bicarbonate to just under **−2**. Many microbial reactions can cause both changes, creating a diagonal reaction path to saturation. Further increases in bicarbonate activity and/or pH would work to progressively supersaturate calcite, increasing the likelihood of precipitation. This activity diagram was calculated with The Geochemist's Workbench software (Bethke, 2018).
https://commons.wikimedia.org/wiki/File:Calcium_speciation.png

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12.1.2: Amorphous silica

Amorphous silica ($SiO_2 \cdot n\ H_2O$) is also referred to as amorphous opal (opal-A). Amorphous silica forms in a variety of settings as dissolved silica molecules ($SiO_2\ (aq)$) combine (i.e., polymerize) and precipitate. During diagenesis, amorphous silica precipitates can gradually transform into more stable silica polymorphs and ultimately the mineral quartz (Kastner et al., 1977; Mizutani, 1977).

Dissolved silica necessary to form amorphous silica originates from dissolution of silicate minerals where those minerals are undersaturated. If those solutions eventually become supersaturated with respect to amorphous silica, microorganisms can help precipitation occur by providing nucleation surfaces.

As an example, numerous studies have investigated potential roles of microorganisms in the formation of siliceous hot-spring deposits known as sinters (Campbell et al., 2015). In these systems, high temperature water dissolves silicate minerals in the subsurface. Following discharge at the surface, the hot spring water cools, decreasing the amount of dissolved silica that it can hold and ultimately causing amorphous silica to become supersaturated (Guidry and Chafetz, 2002) (Fig. **12.4; 12.5A**). Thus, abiotic processes drive precipitation of amorphous silica from hot springs (Campbell et al., 2015). However, laboratory and field studies indicate that biomass generated by hot spring microorganisms helps nucleate amorphous silica precipitates and also affects the structure of the sinter deposits (Campbell et al., 2015; Konhauser et al., 2004). Similar roles of microorganisms have also been observed in non-hydrothermal settings (Sauro et al., 2018).

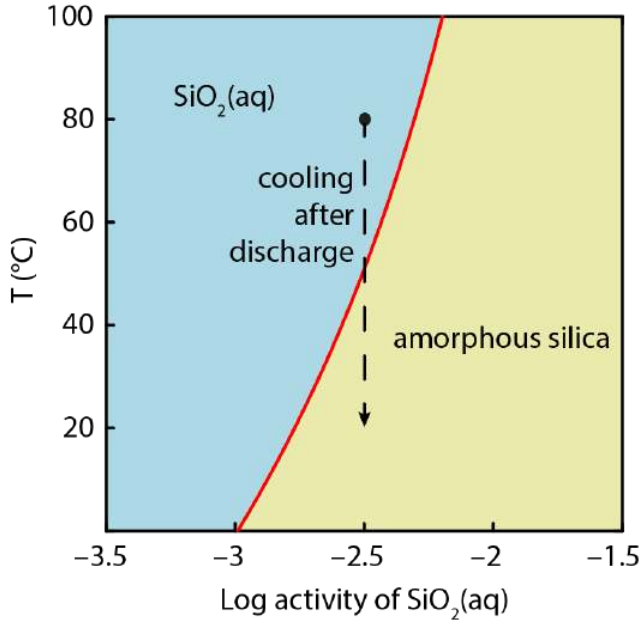


Figure **12.4**: Variation in amorphous silica stability with temperature and dissolved silica activity. Amorphous silica is undersaturated in the region shaded blue and supersaturated in the region shaded yellow. The scatter point and dashed line illustrate how cooling of hot spring water with **−2.5** log activity of dissolved silica (~200 mg/L) can cause amorphous silica to become supersaturated. At the scatter point, the water has a temperature of 80°C. From that point, cooling to about 55°C causes amorphous silica to saturate. Further cooling causes amorphous silica to become increasingly supersaturated. In addition to cooling, other drivers of silica supersaturation in hot spring systems can include evaporation, changes in pH, and other factors (Guidry and Chafetz, 2002). This temperature-activity diagram was calculated with The Geochemist's Workbench software (Bethke, 2018).
https://commons.wikimedia.org/wiki/File:Silica_speciation.png

In addition to this passive role, amorphous silica precipitation can also be biologically controlled. Some microorganisms actively take up dissolved silica and use it to form structures composed of amorphous silica. Examples include diatoms and radiolarians (Fig. **12.5B, C**) as well as some bacteria and fungi (Baines et al., 2012; Ehrlich and Newman, 2009).

Diatoms are a group of algae that live in fresh and marine systems and silicify their cell walls to form structures known as frustules. Diatoms are considered to be the most important silicifiers in modern marine environments (Hendry et al., 2018). Diatoms lower silica concentrations in shallow ocean water and transport it along with other nutrients into the deep ocean as they settle (Buesseler, 1998). Diatom growth also influences the flux of silica from terrestrial environments to the oceans (Ehrlich and Newman, 2009). In the Amazon River estuary, for example, Milliman and Boyle (1975) estimated that diatoms remove 25% of the dissolved silica

from the river water, which is then deposited landward into the river system rather than into the adjacent ocean sediment. Silica supersaturation in the external environment is not necessary for frustule formation because diatoms can induce supersaturation internally. They do this by actively pumping dissolved silica from the external environment into a membrane bound vesicle where amorphous silica can become supersaturated and precipitate (Hildebrand et al., 2018).



Figure **12.5**: Examples of amorphous silica precipitation (A) in a hot spring and by (B) diatoms and a (C) radiolarian. The sinter deposits are forming from hot spring water near Shoshone Lake in Yellowstone National Park, USA. The diatoms were filtered from water collected in 2004 from the Thermaic Gulf in the Aegean Sea. The radiolarian is identified as *Cladococcus abeitinus* and was collected in 2018 from a deep-water sample in the northwestern Mediterranean Sea.
Image sources: (A) Jake Lowenstern, https://www.usgs.gov/media/images/silica-sinter-amorphous-form-silicon-dioxide-forms ; (B) Kostas Tsobanoglou, https://commons.wikimedia.org/wiki/File:Diatoms-HCMR.jpg ; (C) https://en.Wikipedia.org/wiki/Radiolaria#/media/File:Cladococcus_abietinus.jpg

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12.1.3: Iron (oxyhydr)oxides

Ferric iron commonly exists as hydroxide, oxide, and oxyhydroxide phases, which are collectively referred to as (oxyhydr)oxide minerals in this book, as noted in Section 5.3.1. These phases are widespread in nature, reflecting the fact that iron is the fourth most abundant element in Earth's crust. They serve as a sink for electrons liberated by microbial carbon oxidation in anoxic environments, they act as powerful sorbents that influence the mobility of numerous solutes (Dzombak and Morel, 1990), they help stabilize organic matter in soils and sediment (Keil et al., 1994; Longman et al., 2022; Torn et al., 1997), and more. Some common iron (oxyhydr)oxide minerals are listed in Table **12.1**, although many more are known to exist. A more complete review of (oxhydr)oxide minerals is available in Cornell and Schwertmann (2003).

Microorganisms can induce (oxyhydr)oxide formation by catalyzing ferrous iron oxidation. Some chemotrophic microorganisms obtain energy by coupling ferrous iron oxidation with reduction of oxygen or nitrate (Section 5.3.2). In addition, some anoxygenic phototrophs oxidize ferrous iron and use the electrons for carbon fixation (Section 4.5). The ferric iron produced by these reactions complexes more strongly than ferrous iron with other chemical species (Langmuir, 1997), including water molecules, which can complex and deprotonate in hydrolysis reactions:

$$Fe^{3+} + 6\ H_2O \longleftrightarrow Fe\left(H_2O\right)_6^{3+} \tag{12.1.3.1}$$

$$Fe\left(H_2O\right)_6^{3+} \longleftrightarrow Fe(OH)\left(H_2O\right)_5^{2+} + H^+ \tag{12.1.3.2}$$

$$Fe(OH)\left(H_2O\right)_5^{2+} \longleftrightarrow Fe(OH)_2\left(H_2O\right)_4^{+} + H^+ \tag{12.1.3.3}$$

$$Fe(OH)_2\left(H_2O\right)_4^{+} \longleftrightarrow Fe(OH)_3\left(H_2O\right)_3^{0} + H^+ \tag{12.1.3.4}$$

In environments with low pH, hydrolysis is incomplete, and ferric iron can remain dissolved. However, most natural waters have near neutral pH. Where that is the case, the reactions can produce $Fe(OH)_3\left(H_2O\right)_3^0$ (or for simplicity $Fe(OH)_3$), which lacks an overall charge and can precipitate from solution (Fig. **12.6A**). This initial precipitate formed by rapid hydrolysis is metastable and transforms into more stable (oxhydr)oxide phases, such as those listed in Table **12.1**. Timescales of crystallization vary with conditions and tend to be more rapid in solutions with greater iron concentrations (Langmuir and Whittemore, 1971).

Alongside these metabolic effects, iron-oxidizing microorganisms can also help (oxyhydr)oxides form by providing biomass that facilitates nucleation (Figures **12.6B-D**). Precipitation of (oxyhydr)oxides within cells or on their surface has the potential to damage cells. For example, Figures **12.6C** and **12.6D** show encrusted *Acidovorax* sp. cells grown in cultures by Miot et al. (2015), who found that the metabolic activity of cells in their cultures varied with the extent of encrustation. In response to this limitation, some iron oxidizers have evolved strategies to direct precipitation away from the cells (Bird et al., 2011; Cosmidis and Benzerara, 2022). For example, a species of the phototroph *Thiodictyon* has been observed to create a low pH microenvironment around the cell to limit ferric iron sorption to the cell surface (Hegler et al., 2010). As a second example, many chemotrophic iron oxidizers create extracellular stalks that nucleate (oxhydr)oxides as they age (Chan et al., 2011, 2009, 2004; Hallbeck and Pedersen, 1995). Twisted stalks of organic matter and mineral composites, such as those shown in Figure **12.6B**, have been recognized since the early eighteenth century (Koeksoy et al., 2021).

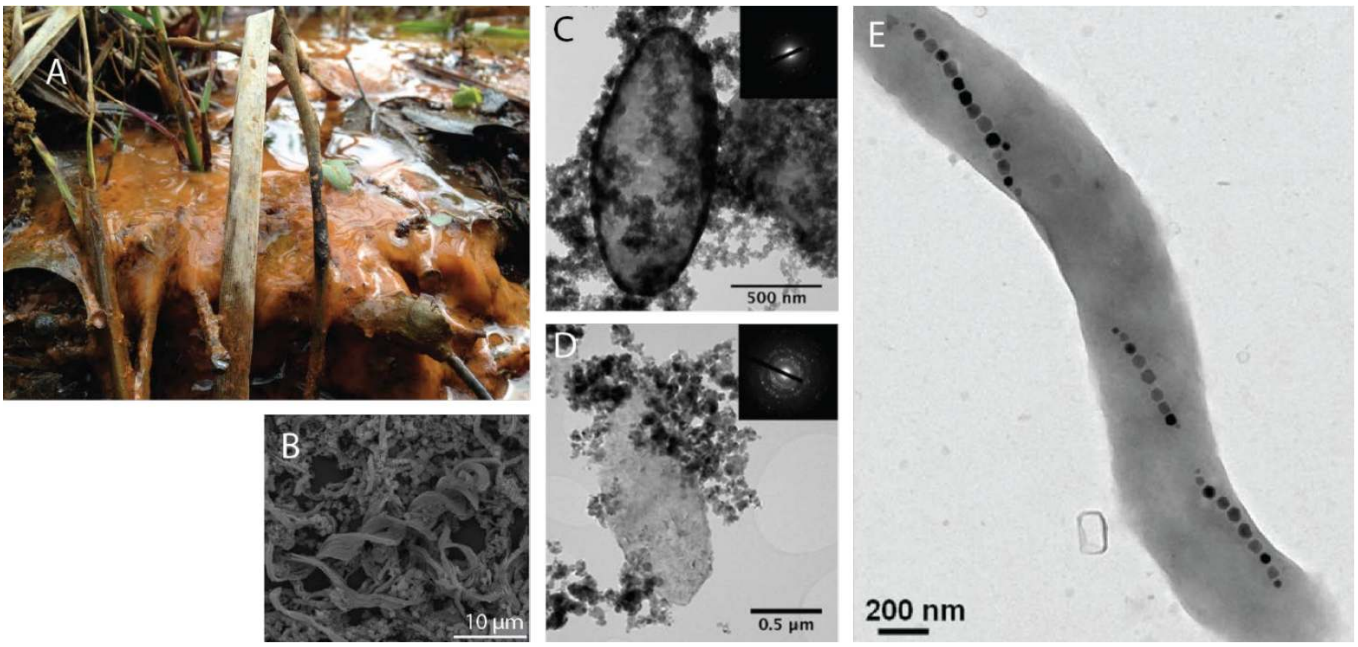


Figure 12.6: Examples of iron (oxyhydr)oxide biominerals: (A) unidentified (oxyhydr)oxides forming on biofilm (B) cell-stalk aggregates, (C) lepidocrocite and (D) magnetite (induced) encrustations on cells, and (E) magnetite magnetosomes (controlled) within a magnetotactic bacterium. The iron oxidizing biofilm shown in (A) exists at a location where groundwater discharges at the surface adjacent to a dam. Anoxic groundwater likely accumulates some ferrous iron along flow through the subsurface and, upon discharge at the surface, the ferrous iron is exposed to oxygen and can serve as an energy source for iron oxidizers. The twisted stalk visible in (B) formed in cultures of *Mariprofundus* sp. DIS-1. The (oxyhydr)oxides in (C) and (D) formed in cultures of the nitrate-reducing iron oxidizer *Acidovorax* sp. strain BoFeN1. Cells were grown under different conditions to promote development of different (oxyhydr)oxide phases. The small inset boxes show electron diffraction patterns used to identify the minerals.
Image sources: (A) https://commons.wikimedia.org/wiki/File:Iron_oxyhydroxides.jpg; (B) Koeksoy et al. (2021); (C) and (D) Miot et al. (2015); (E) Alphandéry (2014).

In addition to iron-oxidizing microorganisms, iron-reducing microorganisms can also induce (oxhydr)oxide formation through their metabolic activity. Specifically, when iron reducers use ferrihydrite as their electron acceptor, some portion of the ferrous iron they produce can react with the ferrihydrite and form magnetite, goethite, and green rusts (Bell et al., 1987; Fredrickson et al., 1998; Hansel et al., 2003). As described by Hansel et al. (2003), the ferrous iron excreted by the iron reducer sorbs onto ferrihydrite and then forms secondary (oxyhydr)oxides through solid-state conversions. In the experiments by Hansel et al., formation of the minerals occurred on the surface of the ferrihydrite, which they interpreted to be consistent with induced mineralization.

Lastly, microorganisms can also form (oxyhydr)oxide crystals through biologically controlled pathways. Specifically, magnetotactic bacteria actively form intercellular chains of magnetite (Fe_3O_4) or greigite (Fe_3S_4) crystals (Blakemore, 1975; Mann et al., 1990) (Fig. 12.6E), which both have relatively strong magnetic properties (Roberts, 1995). Greigite is an iron-sulfide mineral that will be discussed more in the next section below. The crystals formed by magnetotactic bacteria are known as magnetosomes. The properties of magnetosomes vary among species but they tend to range in size from about 30 to 120 nm and have uniform elongated, cubo-octahedral, or bullet-shaped morphologies (Schüler, 2008). Magnetosome properties contrast with induced magnetite (Fig. 12.6D), which is extracellular, not aligned in chains, not uniform in morphology, and has crystal sizes ranging from 10 to 50 nm (Konhauser, 2007).

Creating magnetosomes consumes some of the cell's resources, including a large amount of adenosine triphosphate (ATP) (Yang et al., 2013). This cost suggests that the cells gain some advantage by forming magnetosomes. So why do they do it? Magnetotactic bacteria are motile and are thought to use their magnetosomes as a compass needle to help guide their movements (Bazylinski and Williams, 2007). They appear to use this capability to position themselves within preferred conditions along redox gradients (Bazylinski and Williams, 2007).

Table 12.1: Iron (oxyhydr)oxide minerals

Oxyhydroxides and hydroxides		Oxides	
Goethite	α-FeOOH*	Hematite	α-Fe_2O_3
Akaganéite	β-FeOOH	Maghemite	γ-Fe_2O_3
Lepidocrocite	γ-FeOOH	Magnetite	$Fe^{(II)}Fe^{(III)}{}_2O_4$
Ferrihydrite	$Fe_5HO_8 \cdots 4\,(H_2O)$**		
Green rusts	$Fe^{(III)}{}_x Fe^{(II)}{}_y (OH)_{3x+2y-z} (A^-)_z$ ***		
Schwertmannite	$Fe_{16}O_{16}(OH)_y\,(SO_4)_z \cdot n\,(H_2O)$		

*α indicates hexagonal close packing of anions in the mineral structure, β represents body-centered cubic packing, and γ indicates cubic close packing.

**Ferrihydrite composition is sometimes approximated as $Fe(OH)_3$ in scientific literature. The formula listed in this table is described as preliminary by Cornell and Schwertmann (2003), who also note that the composition of ferrihydrite seems to be variable.

***The formula for green rusts is from Cornell and Schwertmann (2003). A^- represents a variety of anions that can occur within the mineral, including chloride and sulfate.

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12.1.4: Sulfides

Sulfides are a group of minerals that include the sulfide ion (S^{2-}) as an essential structural unit (Deer et al., 1992). Sulfide minerals can impact water quality by serving as a source of acid where they are oxidatively weathering (Rice and Herman, 2012) and by helping regulate the mobility of numerous trace elements (Dellwig et al., 2002; Kirk et al., 2010; Raiswell and Plant, 1980). They are a large reservoir of sulfur in the global sulfur cycle and one of the links between the sulfur and iron cycles. Moreover, their burial in sediments is a major control on both the oxygen levels of the atmosphere (Berner, 1989) and the concentration of sulfate in seawater (Holland, 1978) over geological time scales.

Most of the sulfide precipitation on Earth is driven by microbial activity in low-temperature anoxic environments (Picard et al., 2016). Microorganisms can induce formation of sulfide minerals by catalyzing sulfate reduction and causing the minerals to become supersaturated. Numerous microbial groups can use sulfate as their electron acceptor in dissimilatory metabolism (Section 5.4.1). The sulfide produced by sulfate reduction can react with several divalent cations and precipitate. Examples of sulfide minerals that have been observed in microbial systems include mackinawite (FeS), greigite (Fe_3S_4), pyrite (FeS_2), cinnabar (HgS), rambergite (MnS), orpiment (As_2S_3), and sphalerite (ZnS) (Duverger et al., 2020; Labrenz et al., 2000; Lee et al., 2011; Mann et al., 1990; Newman et al., 1997; Thiel et al., 2019). Other groups of microorganisms can contribute by supplying those divalent cations. For example, microbial iron reduction can supply ferrous iron ($Fe(II)$), which can react with sulfide to form mackinawite. Ferrous iron can also be supplied by abiotic reaction of sulfide with iron (oxyhydr)oxide minerals (Sections 5.3.1 and 10.2.4).

Like each of the other three groups of minerals discussed above in this section, microorganisms also appear to provide nucleation surfaces for sulfide mineralization. Labrenz et al. (2000), for example, observed micron-scale sphalerite aggregates forming on biofilms dominated by sulfate-reducing bacteria of the family *Desulfobacteriaceae*. Picard et al. (2018), as a second example, examined sulfide minerals precipitated in the presence and absence of *Desulfovibrio hydrothermalis* AM13 cells. Their results demonstrated that the surfaces of cells and extracellular polymeric substances (EPS) provided templates for mackinawite nucleation. Moreover, the presence of live cells also influenced the morphology of the minerals and whether greigite could also form during the incubations.

Among the iron-sulfide minerals that form in near-surface environments, pyrite is the most thermodynamically stable and abundant (Rickard and Luther, 2007). Pyrite is unlikely to directly precipitate from a simple precipitation reaction because the sulfur in pyrite (S_2^{-2}) is not stable as a dissolved ion in low-temperature aqueous solutions (Kamyshny et al., 2004). Instead, pyrite is thought to form through multi-step reaction paths that begin with mackinawite.

Mackinawite is typically the first precipitate to form during sulfate reduction in iron-bearing systems (Berner, 1970) (Fig. **12.7A**). Mackinawite has low solubility in water with near-neutral pH (Benning et al., 2000). Under such conditions, extensive sulfate reduction is not necessary cause the mineral to supersaturate even if ferrous iron concentrations are relatively low (Kirk et al., 2010). Moreover, mackinawite can rapidly nucleate (Schoonen and Barnes, 1991). Mackinawite was previously thought to initially precipitate as an amorphous iron-sulfide phase (e.g., amorphous FeS) and then crystalize over time. However, a detailed analysis by Michel et al. (2005) indicates that the initial precipitates are nanoscale mackinawite crystallites, not amorphous solids.

Pyrite forms from mackinawite through the intermediate phase greigite (Hunger and Benning, 2007) (Fig. **12.7B** and **12.7C**). One pathway by which these reactions occur is referred to as the polysulfide pathway (Berner, 1970). Through this pathway, mackinawite forms greigite by reacting with zerovalent sulfur (S^0) dissolved as polysulfide molecules:

$$3\ FeS + S^0 \longleftrightarrow Fe_3S_4 \qquad (12.1.4.1)$$

Polysulfides are chains of sulfur atoms that can form as a result of sulfide oxidation (Kamyshny et al., 2004; Steudel, 1996). The greigite produced from reaction **12.1.4.1** can then react with additional sulfur to form pyrite:

$$Fe_3S_4 + 2\ S^0 \longleftrightarrow 3\ FeS_2 \qquad (12.1.4.2)$$

A second potential pathway of pyrite formation is known as the H_2S pathway (Rickard, 1997, 1975). Reactions describing this pathway follow, again with greigite as an intermediate between mackinawite and pyrite:

$$3\ FeS + H_2S \longleftrightarrow Fe_3S_4 + H_2 \qquad (12.1.4.3)$$
$$Fe_3S_4 + 2\ H_2S \longleftrightarrow FeS_2 + 2\ H_2 \qquad (12.1.4.4)$$

Sulfate reducers and potentially iron reducers can feed both of these pathways by supplying mackinawite, as discussed above. Sulfur-oxidizing microorganisms have the potential to contribute to the polysulfide pathway by supplying zerovalent sulfur. Moreover, hydrogenotrophic microorganisms can help facilitate the H_2S pathway by consuming dihydrogen (Thiel et al., 2019). Beyond those contributions, the reactions that form pyrite may be largely abiotic. However, the boundaries between biotic and abiotic processes in these pathways are not clear (Picard et al., 2016).

Lastly, as noted above in the discussion of iron (oxyhydr)oxides, magnetotactic bacteria sometimes form greigite magnetosomes as an alternative to magnetite. At least one bacterium can produce both magnetite and greigite, but most strains of magnetotactic bacteria produce one or the other (Bazylinski and Frankel, 2004). Iron-sulfide minerals other than greigite have been observed in magnetotactic bacteria, including mackinawite (tetragonal FeS) and cubic FeS. However, they are thought to be precursors to greigite (Bazylinski and Frankel, 2004).

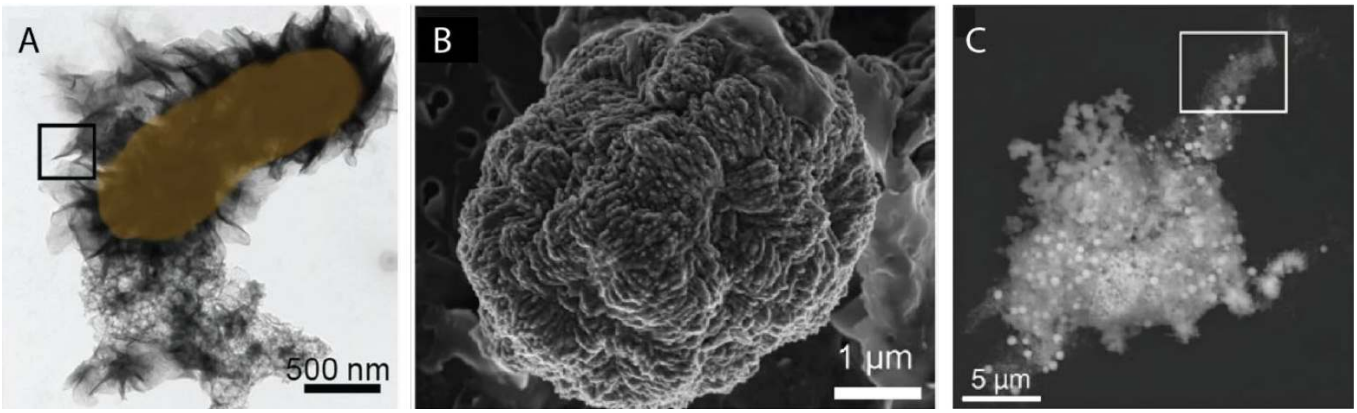


Figure 12.7: Examples of sulfide biominerals: (A) mackinawite encrusting a microbial cell, (B) pyrite spherule, and (C) pyrite spherules within a mackinawite aggregate. Minerals in (A) and (B) formed in cultures containing *Desulfovibrio* and *Sulfurospirillum* species from lake water. The minerals in (C) formed in cultures of *Desulfovibrio desulfuricans*. Boxes in (A) and (C) were used for purposes in the original publications and are not relevant here.
Image sources: (A) and (B) Berg et al. (2020), (C) Duverger et al. (2020).

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12.1.5: Clay minerals

Clay minerals are a diverse group of fine-grained ($\leq 2\ \mu m$ particles) hydrous aluminum phyllosilicates. They help form soils and sediment deposits in terrestrial and marine environments. As such, they are major components of mudstones and shales, which comprise about 70% of the sedimentary rock record (Blatt et al., 1980). They also help control the chemistry of natural waters through ion exchange and sorption reactions.

Clay minerals can form through a variety of pathways, some of which involve microorganisms. Microbial biomass can induce clay mineralization nucleation and growth (Konhauser and Urrutia, 1999). We can consider clays that form by this pathway to be biominerals. Microorganisms also contribute to formation of clays through weathering and diagenesis. Clays formed by these pathways are not considered to be biominerals, although the microbial contributions to their formation are significant. In the paragraphs below, we discuss each of these clay sources and the ways microorganisms contribute.

Microbial biomass can form clay biominerals by providing a surface where iron (oxyhydr)oxides can accumulate and react with aluminum and silica. As described by Konhauser and Urrutia (1999), first, ferric (oxyhydr)oxides form on biomass, including cells and extracellular polymeric substances (EPS). Then, the (oxyhydr)oxides react with silica and aluminum, which can be dissolved or present in small ($\leq 1\ \mu m$) particles known as colloids. Eventually the reactions produce amorphous clay-like phases, which can dehydrate and convert to more stable crystalline phases. Formation of these phases is likely common in lakes and rivers and may play an important role in facilitating transfer of metals into bottom sediment and as a control on aqueous chemistry (Konhauser and Urrutia, 1999).

Silicate weathering is considered to be the primary way that clay minerals form at the Earth's surface today (Foley, 1999). Climate and the identity of the minerals being weathered are among major factors that determine which clays form during silicate weathering. In general, however, kaolinite is found in most weathered profiles, montmorillonites are common in lower parts of soil profiles near bedrock, and complex mixed-layered clays such as illite-smectites are commonly formed by weathering of micabearing rocks (Foley, 1999). Weathering involves both abiotic and biotic processes, but certainly microorganisms play a major role by producing acid and chelators and by catalyzing oxidative or reductive dissolution reactions (Section 11.4).

Lastly, microorganisms help generate phases that react to produce early diagenetic clay minerals in marine sediments. Specifically, within centimeters of the sediment-water interface, authigenic clay minerals begin to form from reactive components such as amorphous silica, degraded aluminosilicates, and aluminum and iron (oxyhydr)oxides (Aplin, 2000). Microorganisms induce or biologically control production of some of these reactive phases, as discussed previously in Section 12.1. Several different clay minerals can form but most are smectites (Aplin, 2000).

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12.2: Microbial influence on marine sediments

Microorganisms can significantly influence the composition of sediments accumulating in depositional environments. To provide an example, this section considers how microorganisms affect the composition of marine sediments. Major sources of sediments to the Earth's oceans include detrital inputs from terrestrial environments, biogenic material that forms in the water column, hydrogenous precipitates, and authigenic phases that form within sediment following deposition. Microorganisms play significant roles in generating these sediment phases and transforming them following deposition, as discussed in the paragraphs below. Content presented here draws heavily from Aplin (2000), which offers a wider and more detailed discussion of the mineralogy of modern marine sediments.

Detrital material is generated by weathering in terrestrial environments and transported to the oceans by water (including ice), wind, and gravity. Any mineral can be supplied to the oceans as detritus but the most common are clay minerals and quartz (Aplin, 2000). Organic detritus also enters the oceans from terrestrial areas, and consists mostly of living biomass, plant litter, and highly-degraded soil organic matter (Burdige, 2007). Most river sediment is deposited in nearshore environments but fine-grained detritus reaches the open ocean (Aplin, 2000). Some detrital phases persist beyond early diagenesis and become deeply buried, whereas others are consumed as reactants in diagenetic reactions. Microorganisms help supply these sediments by driving weathering reactions in terrestrial environments (Section 11.4). Moreover, microorganisms also induce formation of some of the clay minerals in freshwater systems (Konhauser and Urrutia, 1999) (Section 12.1.5).

Biogenic material that forms in the marine water column is mostly skeletal biominerals and organic matter from planktonic microorganisms (Berner, 1979; Honjo et al., 1982). Regarding biominerals, the main phases are carbonates formed by foraminifera and coccolithophorids as well as amorphous silica produced by radiolarians and diatoms. The abundance of these biogenic mineral inputs in marine sediment reflects the balance between biological productivity in the water column, the amount of dissolution that occurs between the water column and sediment-water interface, and the extent to which they are diluted by non-biogenic phases (e.g., detritus) (Aplin, 2000). Some portion of these phases dissolve as they settle because seawater is undersaturated with respect to amorphous silica and, except in surface waters, undersaturated with respect to calcite (Aplin, 2000). Roles of microorganisms in generating these sediments are obvious, given that their production is biologically controlled by eukaryotic microorganisms (Sections 12.1.1 and 12.1.2).

Regarding organic biogenic material from the water column, most is considered to be phytoplankton debris (Burdige, 2007). Phytoplankton are also known as microalgae. They are phototrophic microorganisms, and major groups include dinoflagellates, diatoms, coccoliths, and cyanobacteria. Organic matter inputs to the ocean, both terrestrial organics and that produced by phytoplankton, are mostly degraded before they can be buried in sediment. Specifically, less than 0.2% of marine primary production and less than 20% of terrestrial inputs are preserved in marine sediments (Hedges, 1992). Factors that influence what proportion of organic matter is preserved include rates of primary production, the composition of the organic matter, and the speed with which it can be buried and shielded from aerobic degradation (Berner, 1979; Hedges, 1992).

Hydrogenous components of marine sediments are those that precipitate from dissolved reactants in the water column. The most common examples of hydrogenous sediments are iron and manganese (oxyhydr)oxides (Aplin, 2000). They can form where metal-rich anoxic hydrothermal waters discharge and mix with oxic seawater. Discharge of reduced hydrothermal waters into oxic seawater provides a rich energy source for chemolithotrophic microorganisms (Jannasch and Mottl, 1985) (Section 7.5.3). Oxidation of reduced metals within those solutions can produce (oxyhydr)oxide phases that settle onto the seafloor. Metal (oxyhydr)oxides also form in response to upward diffusion of dissolved iron and manganese produced by metal reduction in marine sediment. For both pathways, microorganisms can help drive (oxyhydr)oxide production by catalyzing the associated redox reactions.

Authigenic phases form within the sediment as products of reactions between mineral inputs, organic matter, and pore water. Authigenic clays are generated by reactions involving sediment inputs of amorphous silica, degraded aluminosilicates, and metal (oxyhydr)oxides (Aplin, 2000), as noted above (Section 12.1.5). Other minerals form in response to organic matter degradation. Specifically, microbes couple oxidation of organic matter within the sediments with reduction of available electron acceptors. Oxygen can be depleted from pore water within centimeters of the sediment-water interface, followed by zones where microorganisms reduce nitrate, manganese(IV), iron(III), sulfate, and carbon dioxide as they work their way along the thermodynamic ladder (Section 8.5). Section 12.1 includes descriptions of how such microbial reactions can lead to formation of

sulfide and carbonate minerals (12.1.1 and 12.1.4). Among other possibilities, phosphate minerals may also form. Microbial reactions can induce supersaturation of carbonate fluorapatite ($Ca_{10}(PO_4)_{5.74}(CO_3)_{0.26}F_{2.26}$) by increasing the phosphate and alkalinity content of pore water (Aplin, 2000). Phosphate necessary to form the mineral is supplied from breakdown of organic matter and reductive dissolution of metal (oxyhydr)oxide, which contain sorbed phosphorus. Microbial reactions can also help increase alkalinity by consuming hydrogen ions and producing bicarbonate.

Taken together this section illustrates that microorganism play major roles marine depositional environments, as suppliers of reactive inputs, drivers of redox reactions, and contributors to terrestrial weathering. It should be emphasized here that not all geochemical reactions are microbial, and many major sedimentary processes do not involve microorganisms. Nonetheless, the contributions of microorganisms are clearly enormous. Microorganisms play significant roles in the supply of each major category of marine sediment and in the transformation of that sediment following deposition.

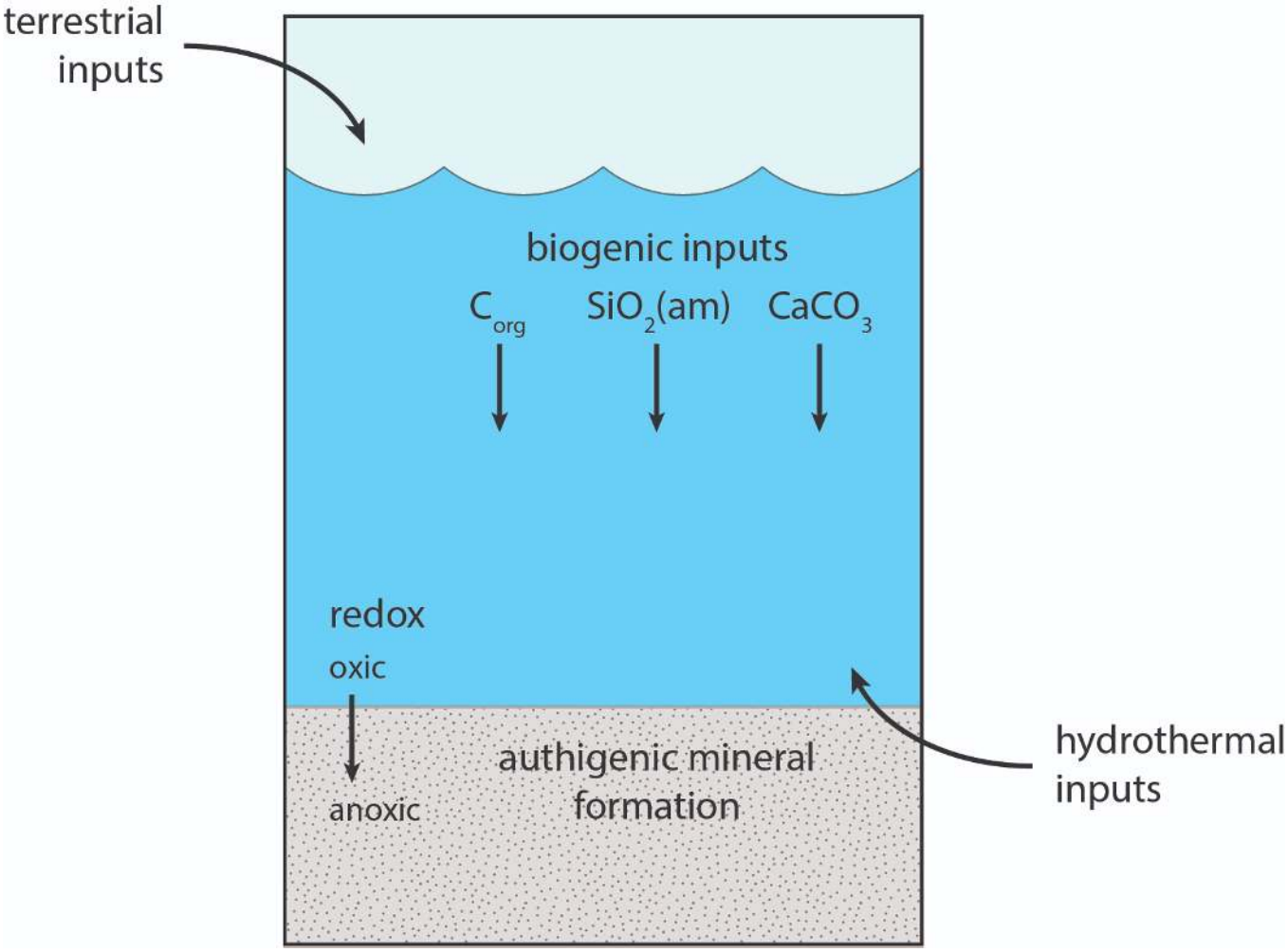


Figure 12.8: Schematic illustration of major inputs and reactions that guide marine sediment composition. Terrestrial sediment inputs include dust and river sediment. Hydrothermal inputs are fluids with reduced elements that can serve as energy sources for vent microbial communities. Redox zones develop in marine sediment as microorganisms couple oxidation of organic matter with available electron acceptors. Authigenic minerals form in response to those redox reactions and reactions between reactive sediment inputs, including organic matter (C_{org}), amorphous silica (SiO_2 (am)), and calcium carbonate ($CaCO_3$).
https://commons.wikimedia.org/wiki/File:Marine_sediment.jpg

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12.3: Microbial influences on tectonic activity

Tectonic plates move in response to ridge push and slab pull forces, with contributions from mantle convection fueled by Earth's internal heat. Given the immense scale of tectonic activity and magnitude of forces involved, what role could microorganisms possibly play?

Microorganisms certainly do not cause tectonics to occur, but multiple studies point to evidence that they help determine the outcomes. By affecting the composition of sediments, as discussed in the previous section, microorganisms affect the compositions of sedimentary rocks. In turn, the composition of a sedimentary rock influences its mechanical properties and thus how it, or any metamorphic rock formed from it, would respond to tectonic stress. Secondly, biological productivity in the oceans influences the abundances of sediments on subducting slabs of oceanic crust, which in turn can influence rates of slab subduction (Behr and Becker, 2018) and fluxes of carbon dioxide from arc volcanoes (Aiuppa et al., 2017). And third, microbial activity helps redistribute mass at the Earth's surface through its contribution to weathering. As mass is removed from regions of continental crust, the crust responds by essentially floating higher on the underlying asthenosphere, consistent with the principle of isostacy. Thus, an implication of microbial weathering reactions is that they help drive uplift over time.

To illustrate these relationships further, we consider the research of Parnell and Brolly (2021), who examined evidence from 20 orogens and found that anomalously high carbon burial about 2 billion years ago helped trigger mountain building events. After the Great Oxidation Event (2.5 to 2.3 billion years ago; Section 13.1), growth of marine cyanobacteria greatly increased, causing increased burial of organic carbon in the crust. Potential factors contributing to rapid cyanobacterial growth include increased availability of oxygen and changes in nutrient inputs (Bekker and Holland, 2012; Canfield, 2021; Kamennaya et al., 2018; Martin et al., 2015). Regardless of why, the sediment that was deposited had high carbon content, which in turn affected the mechanical properties of the rocks that formed from the sediments. Rocks rich in carbon create zones of weakness that can reduce friction along fault planes or in other words lubricate them (Craw and Upton, 2014; Lyu et al., 2020; Oohashi et al., 2013; Rutter et al., 2013). Where tectonic plates collide and form mountains, such low frictional strength layers can increase thrust stacking and therefore crustal thickening (Cooper et al., 2006; Mouthereau et al., 2013).

These observations suggest that the high carbon burial after the Great Oxidation Event created a setting ripe for collisional orogenesis and indeed, multiple lines of evidence indicate that was the case (Parnell and Brolly, 2021). A large number of orogens date back to a peak in orogenesis about 2 billion years ago. Parnell and Brolly selected 20 orogens distributed worldwide and showed that within each, deformation is focused in pelitic/graphitic metasediments. Isotopic compositions of the carbon in each orogen indicate it is biotic in origin rather than abiotic. Moreover, they showed that the time lag between deposition of organic-rich sediments and deformation was less than 200 million years for all of the orogens they examined, which agrees well with the time lag of oceanic lithosphere consumption today. Taken together, their analysis provides compelling evidence that the increased burial of marine cyanobacteria biomass after the Great Oxidation Event triggered widespread mountain building.

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12.4: Mineral evolution

In a last example of the ways microorganisms have impacted Earth's lithosphere, we circle back to their impacts on mineralogy. The mineralogy of terrestrial planets evolves over time as they form and differentiate. Initially on Earth, mineral evolution was driven entirely by physical and chemical processes. These processes are estimated to have produced about 1500 different mineral species (Hazen et al., 2008).

However, by the Eoarchean Era (4 to 3.6 billion years ago), microbial activities also began to contribute to Earth's mineral evolution. The number of mineral species on Earth increased considerably after life appeared and now stands at about 4,300 different species (Hazen et al., 2008). Three categories of mechanisms have driven this evolution of Earth's mineralogy (Hazen et al., 2008): (1) the separation and concentration of elements as the Earth's mass accreted and differentiated, (2) an expansion in range of intensive properties such as pressure, temperature, and the activities of water, carbon dioxide, and oxygen, and (3) creation of far-from-equilibrium conditions through the metabolic activity of living organisms. Of these, life, and especially microbial life, has contributed significantly to the second and third categories.

One of the biggest jumps in mineral diversity occurred as a result of the Great Oxidation Event (roughly 2.5 to 2.3 billion years ago). During that time, oxygen started to accumulate in the atmosphere, changing the redox state of Earth's surface from anoxic to oxic. This redox shift alone led to the emergence of more than 2,000 new (oxyhydr)oxide minerals (Hazen et al., 2008). Subsequent increases also occurred with development of biomineralization and biologically driven mineral weathering. Oxygenic phototrophic microorganisms produced the oxygen that acclimated during the Great Oxidation event, and they continue to generate much of the oxygen that enters the modern atmosphere (Section 13.1). Moreover, microorganisms are major contributors to biomineralization and mineral weathering, as discussed above in this chapter and in Chapter 11. Thus, much of the mineral evolution of Earth has been driven by microorganisms.

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12.5: Concept Check Questions

1. Which portions of the rock cycle do microorganisms impact?
2. Can you explain mechanistically how microorganisms can help form carbonates, amorphous silica, iron (oxyhydr)oxides, sulfides, and clays?
3. How can biofilm EPS help or hinder precipitation of carbonate minerals?
4. What are the two magnetic minerals that magnetotatic bacteria produce?
5. What microbial reactions can induce formation of iron (oxyhydr)oxides?
6. Do microorganisms cause amorphous silica to form by causing the phase to become supersaturated?
7. How can microbial activity help supply terrestrial sediment to the oceans?
8. Why would more rapid settling and burial help preserve organic matter in marine sediment?
9. How do high levels of organic carbon burial ultimately affect the mechanical properties of the sedimentary and metamorphic bedrock?

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12.6: 12.6 References

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CHAPTER OVERVIEW

13: Impacts to the Atmosphere

> *"… the impact of climate change will depend heavily on responses of microorganisms"*
>
> *—Cavicchioli et al. (2019)*

Earth's atmosphere consists of layers of gases which we call 'air' that surround the planet. By volume, dry air contains 78.09% dinitrogen, 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide, varying amounts of water vapor, and trace amounts of several other gases. Levels of these gases reflect the rates at which they are added and removed from the atmosphere, which depend on numerous physical, chemical, and biological processes.

In this chapter, we focus our attention on examples of ways that microorganisms impact atmospheric concentrations of oxygen (O_2) and three greenhouse gases: carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Atmospheric oxygen levels affect surficial redox processes and have been a major influence on the evolution of Earth's organisms (Reinhard et al., 2016) and minerals (Hazen et al., 2008). Greenhouse gas levels are a major control on Earth's climate. Some can also impact ozone levels. Methane helps form hazardous tropospheric ozone (i.e., smog), whereas nitrous oxide is destructive to beneficial stratospheric ozone. Thus, microbial impacts to levels of these gases in the atmosphere help determine the habitability of our planet for humans and other organisms.

One important detail to note as you read this chapter is that microorganisms help determine greenhouse gas levels, but there are many controls. For a comprehensive quantitative analysis of atmospheric gas budgets, the reader is referred to Friedlingstein et al. (2022) for carbon dioxide, Saunois et al. (2020) for methane, and Tian et al. (2020) for nitrous oxide. Moreover, additional details about all three greenhouse gases and climate change research in general are available from the United Nations Intergovernmental Panel on Climate Change (IPCC) reports (e.g., IPCC, 2021).

13.1: Oxygen
13.2: Trends in greenhouse gases
13.3: Carbon dioxide
13.4: Methane
13.5: Nitrous oxide
13.6: Responses of microorganisms to climate change
13.7: Managing greenhouse gas emissions
13.8: Answers to practice problems
13.9: Concept Check Questions
13.10: References

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13.1: Oxygen

Oxygen is produced primarily by oxygenic photosynthesis (Section 4.5). Reactions that can consume oxygen include aerobic respiration, oxidative mineral weathering reactions (Section 11.4.1), and abiotic oxidation of other reduced chemical species, including some of the gases emitted from volcanoes and reduced compounds in aqueous systems. Processes that change the balance between these reactions have the potential to alter the oxygen content of the atmosphere.

In the modern world, we easily recognize plants as producers of oxygen, but phototrophic microorganisms are also major contributors. For example, at least half of the oxygen inputs to the atmosphere each year come from marine phytoplankton, the vast majority of which are microorganisms. In fact, a single genus of marine cyanobacteria, *Prochlorococcus* (Chisholm et al., 1988), is thought to be the most abundant photosynthesizer on the planet (Partensky et al., 1999) and is estimated to be responsible for producing about 20% of the oxygen in the atmosphere (Morsink, 2017).

Although oxygen is abundant in the modern atmosphere, early Earth's atmosphere contained very little. Oxygen levels began to increase during the 'Great Oxidation Event', which occurred roughly 2.5 to 2.3 billion years ago (Fig. **13.1**). This increase does not coincide with the emergence of land plants, which appears to have occurred about 500 million years ago (Morris et al., 2018). This event also does not coincide with the emergence of oxygenic phototrophic microorganisms, though they were involved. Oxygenic phototrophs were present on Earth hundreds of millions of years before the Great Oxidation Event based on multiple lines of evidence (Garvin et al., 2009; Godfrey and Falkowski, 2009; Planavsky et al., 2014; Satkoski et al., 2015; Schirrmeister et al., 2015; Stüeken and Buick, 2018). So, what triggered it?

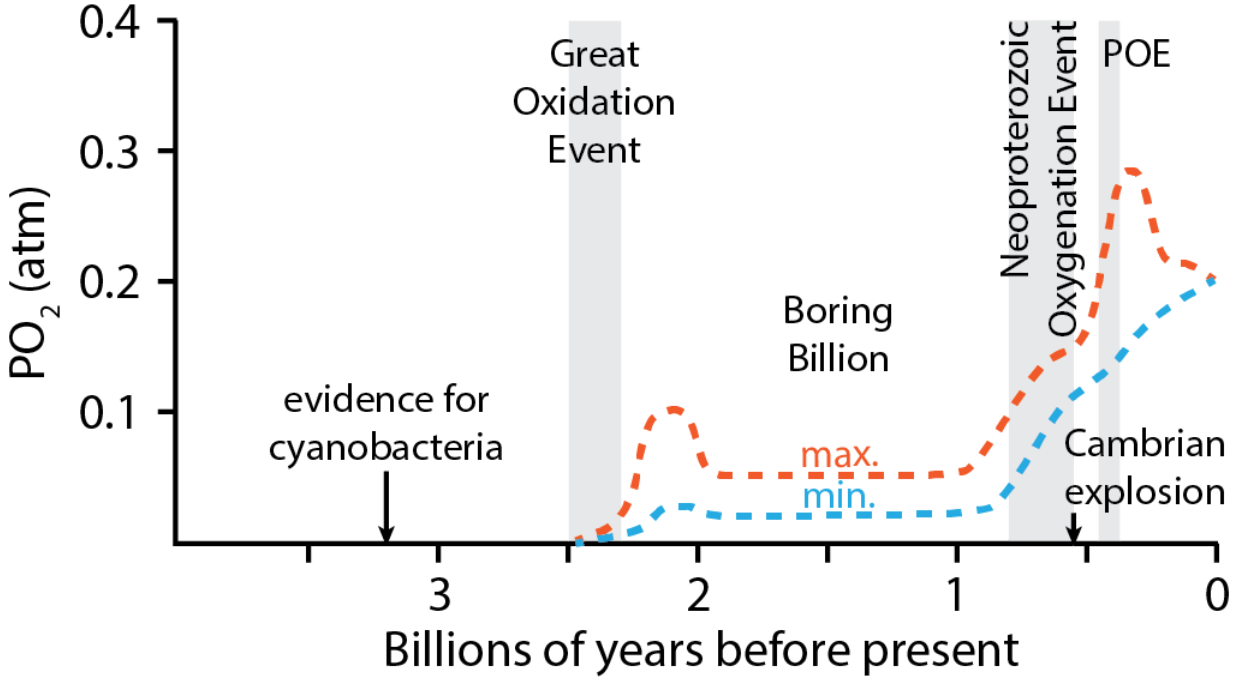


Figure **13.1**: Estimated variation in the partial pressure of oxygen in the atmosphere over the past four billion years. Oxygen levels are reproduced from Bekker and Holland (2012). Research by Satkoski et al. (2015) indicates cyanobacteria were active by at least 3.2 billion years ago. The Great Oxidation Event is shown in the figure to have occurred from 2.5 to 2.3 billion years, although the literature varies on the specific time range. POE refers to the Paleozoic Oxygenation Event. A recent reconstruction by Mills et al. (2023) provides a more detailed look at variation in atmospheric oxygen levels during the Phanerozoic.
Image: https://commons.wikimedia.org/wiki/File:Oxygen_vs_time.png

The exact cause of the Great Oxidation Event is unknown, though hypotheses from several previous studies invoke shifts in the balance between oxygen production and consumption (Kadoya et al., 2020). Prior to the event, atmospheric inputs of reduced gases exceeded microbial inputs of oxygen, causing the atmosphere to have a 'weakly reduced' redox state (Kasting, 2014, 1993). Volcanic emissions, such as dihydrogen, carbon monoxide, hydrogen sulfide, sulfur dioxide, and methane, can react with oxygen relatively quickly and thus limit its accumulation. Sediment and water at the surface also contained reduced compounds that could

react with oxygen. One vivid example is ferrous iron ($Fe(II)$) in seawater, which formed banded iron formations (BIFs) when it oxidized (Fig. **13.2**). But then something happened that allowed rates of oxygen production to exceed rates of oxygen consumption.



Figure **13.2**: Sample of 2-billion-year-old banded iron formation (BIF) from the Upper Peninsula of Michigan, USA. Commonly, the dark layers in BIFs are rich in magnetite or hematite whereas the reddish layers are primarily silicates such as clay and chert. For scale, individual bands of the BIF pictured are roughly on the order of a centimeter in thickness. The rock resides outside of the Department of Earth and Environmental Sciences at the Michigan State University. More details about its history are available here: https://ees.natsci.msu.edu/alumni-and-friends/bif/dedication/.
Image: https://commons.wikimedia.org/wiki/File:BIF_boulder.jpg

One possible explanation for this redox shift is that microbial populations expanded and started generating more oxygen. Productivity may have increased, for example, as a result of changes in ocean nutrient availability (Eguchi et al., 2020) or changes in Earth's rotation that affected daylength (Klatt et al., 2021). Alternatively, emissions of reduced gases may have also decreased. Recent research by Kadoya et al. (2020), for example, indicates that Earth's mantle started to become more oxidized, which caused a decrease in the flux of reduced gases from the solid earth to the atmosphere.

Regardless of why, once this tipping point was reached, oxygen generated by oxygenic phototrophic microorganisms began to accumulate and the atmosphere transitioned from a reduced to oxidized redox state. From about 1.8 to 0.8 billion years ago, a time period sometimes referred to as the 'Boring Billion', oxygen stabilized near levels that were roughly 10 to 20% of modern levels (Fig. **13.1**). Oxygen levels then began to increase again during the Neoproterozoic Oxygenation Event, which occurred from about 800 to 540 million years ago and coincided with the first oxygenation of the deep oceans (Och and Shields-Zhou, 2012; Poulton et al., 2004). Finally, oxygen levels increased yet again during the Paleozoic Oxygenation Event, which occurred roughly around 450 to 400 million years ago (Alcott et al., 2019).

Consequences of the rise in oxygen levels on Earth are enormous. As discussed in Chapter 12 (Section 12.4), oxygen accumulation in the atmosphere transformed the redox state at Earth's surface and caused a large increase in Earth's mineral inventory. Perhaps more importantly, from our perspective as multicellular aerobic eukaryotes, is that elevated oxygen levels paved the way for the evolution of aerobic respiration. Oxygen is a powerful electron acceptor (see Chapter 8) and greater energy availability allowed greater cellular complexity (Reinhard et al., 2016). During the Boring Billion, Eukaryotes appeared (Katz, 2012) and started to diversify (Javaux et al., 2003). These events helped lay the groundwork for the 'Cambrian Explosion' (Fig. **13.1**), the name given to the time period around 540 million years ago when nearly all major animal phyla started appearing in the fossil record. Increased oxygen levels are unlikely to be the only driver of these evolutionary events (Mukherjee et al., 2018), though they appear to be a key part of the equation.

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13.2: Trends in greenhouse gases

Concentrations of greenhouse gases in the atmosphere affect Earth's climate by determining the strength of the greenhouse effect. Briefly, some of the radiation from the sun is absorbed at Earth's surface and radiated as infrared radiation, which we feel as heat. Some of this infrared radiation is lost to space but much of it is absorbed by greenhouse gases in the atmosphere and re-radiated in all directions, including back to Earth's surface. This re-radiation of infrared radiation by greenhouse gases constitutes the greenhouse effect. Global average temperature is about 33°C warmer than it would be without this effect. As concentrations of greenhouse gases increase, the Earth system warms, affecting patterns of energy transfer through the atmosphere and oceans that define climate.

There are several greenhouse gases in the atmosphere. This chapter focuses on three of the most influential: carbon dioxide, methane, and nitrous oxide. Concentrations of all three of these gases follow an overall increasing trend as a result of human activities (Fig. **13.3**). Relative to atmospheric levels in 1750, near the beginning of the Industrial Revolution, concentrations measured in 2019 were higher by 47% for carbon dioxide, 156% for methane, and 23% for nitrous oxide (IPCC, 2021).

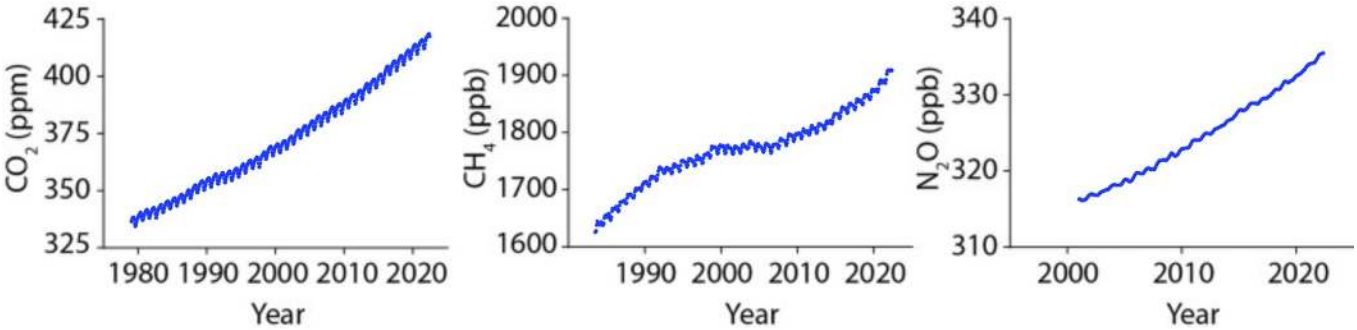


Figure **13.3**: 3 Variation with time in the abundance of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) in the atmosphere. Values are globally-averaged monthly means determined from marine surface sites. Units are mole fractions expressed as parts per million (ppm) for carbon dioxide and parts per billion (ppb) for methane and nitrous oxide. Note that x-axes differ in scale for each graph. Data plotted are available from the U.S. National Oceanic and Atmospheric Administration (https://gml.noaa.gov/ccgg/). Image: https://commons.wikimedia.org/wiki/File:Greenhouse_gas_trends.jpg

As these increases have occurred, the Earth has warmed. The United Nations Intergovernmental Panel on Climate Change (IPCC) recently concluded that the likely range of total human-caused warming is 0.8 to 1.3°C from 1850-1900 to 2010-2019 (IPCC, 2021). Most of this warming is from the increased concentration of carbon dioxide, which has by far the highest rate of emissions among greenhouse gases emitted from human activities. However, warming from the other gases is still significant because they are more potent as greenhouse gases than carbon dioxide. The 100-year warming potentials of methane and nitrous oxide are, respectively, about 27-30 times and 273 times that of carbon dioxide (US EPA, 2022).

Various human activities are causing these increases. The biggest source of carbon dioxide is fossil fuel use, followed by cement production and land use effects such as agricultural activity and deforestation (Friedlingstein et al., 2022; IPCC, 2021). Drivers of increased methane levels are not as well understood as those for carbon dioxide, but likely contributors include expansion of oil and gas production, gas distribution systems, and rising emissions from landfills, livestock herds, and wetlands, including those used for rice cultivation (Plant et al., 2022; Turner et al., 2019). Lastly, increases in nitrous oxide levels are thought to be driven primarily by increased applications of nitrogen fertilizer for food production (Park et al., 2012; Tian et al., 2020) though other sources include industrial emissions and combustion of fossil fuels.

Human impacts to greenhouse gases are coupled with natural biogeochemical cycles and the microbial activities within those cycles. For example, nitrous oxide production from fertilizer primarily occurs via nitrification and denitrification, which are catalyzed by microorganisms. Humans are effectively setting the table for growth in the populations of these microorganisms by adding nitrogen fertilizers to crop soils over broad regions. In other words, we are providing more nourishment for nitrous oxide-producing microbes, and as a result nitrous oxide levels in the atmosphere are increasing. More details about the roles of microorganisms are included below for each greenhouse gas.

Lastly, within the overall increasing trends, you may have noticed that concentrations of each greenhouse follow a repeating pattern of increasing and decreasing each year (Fig. **13.4**). These patterns reflect seasonal variation in the proportions of gas production and

consumption. For carbon dioxide, global atmospheric levels decrease during spring and summer in the Northern Hemisphere, when carbon dioxide uptake by plants is high relative to carbon dioxide emissions from respiration and other sources. However, during cool months in the Northern Hemisphere, carbon dioxide uptake by plants decreases and the trend reverses. For methane, the cycle reflects seasonality in its destruction by photochemical reactions (Dlugokencky et al., 1994). For nitrous oxide, the seasonal cycle is relatively weak and reflects mixing of air in the atmosphere and seasonality in nitrous oxide production (Jiang et al., 2007).

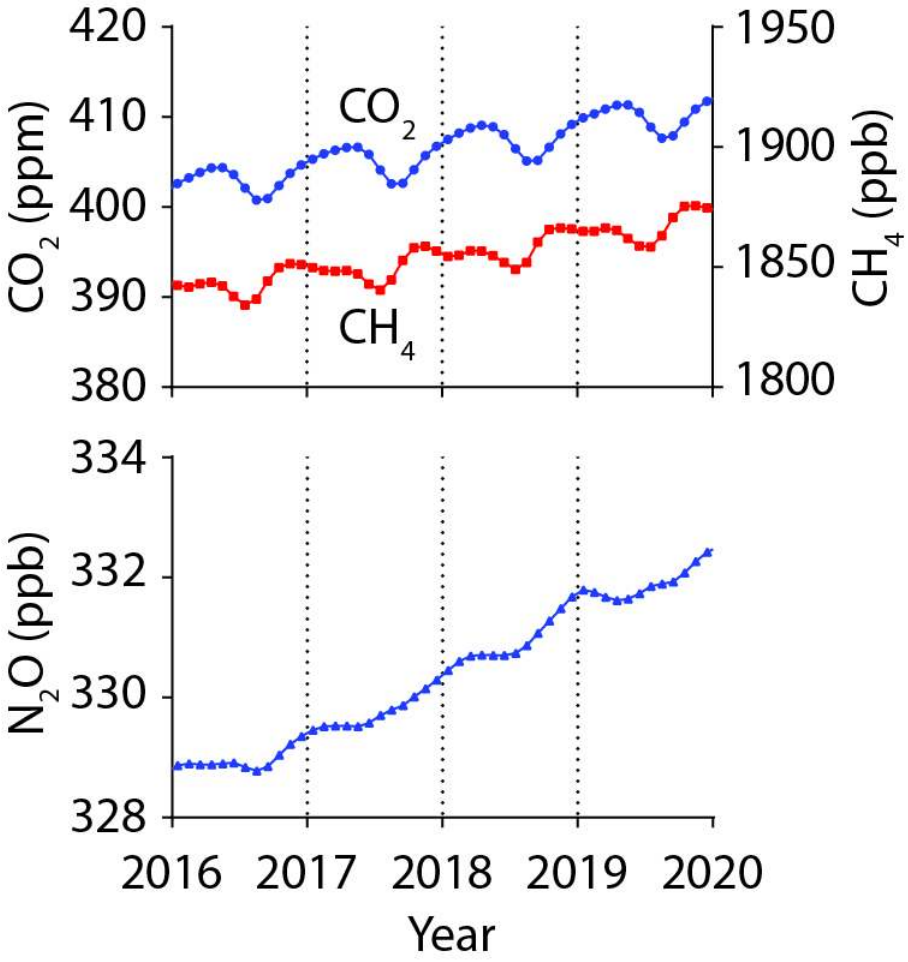


Figure **13.4**: Variation in atmospheric concentrations of the abundance of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) from 2016 to 2020. Dotted vertical lines coinciding with January 1 each year are included to highlight the seasonality of trends in concentrations of each gas. Scatter points are globally-averaged monthly means determined for marine surface sites. Units are mole fractions expressed as parts per million (ppm) for carbon dioxide and parts per billion (ppb) for methane and nitrous oxide. Data plotted are available from the U.S. National Oceanic and Atmospheric Administration (https://gml.noaa.gov/ccgg/).
Image: https://commons.wikimedia.org/wiki/File:Greenhouse_gases_seasonal_cycles.jpg

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13.3: Carbon dioxide

Microorganisms can produce and consume carbon dioxide and thus help determine carbon dioxide concentrations within their environments. Microorganisms that can help lower carbon dioxide levels include autotrophs, which form organic carbon from carbon dioxide in biosynthesis reactions (Section 4.3), as well as acetogens and methanogens that use carbon dioxide as an electron acceptor (Section 5.1.3 and 5.1.4). Note that methanogens also produce methane, which is itself a potent greenhouse gas. In contrast, microorganisms that can cause carbon dioxide levels to increase in their environments include chemoorganotrophs, which oxidize organic carbon and can produce carbon dioxide (Section 4.3).

In addition to these direct impacts on carbon dioxide levels, microorganisms also influence carbon dioxide concentrations in water indirectly by affecting pH (Kirk et al., 2013). Specifically, as illustrated by Figure **13.5**, microbial reactions that consume hydrogen ions can help drive the following reactions forward, converting dissolved carbon dioxide into bicarbonate and then carbonate:

$$\mathrm{CO_2\ (aq) + H_2O \leftrightarrow H^+ + HCO_3^-} \quad (13.3.1)$$

$$\mathrm{HCO_3^- \leftrightarrow H^+ + CO_3^{2-}} \quad (13.3.2)$$

In pushing the reactions forward, microorganisms help store inorganic carbon in aqueous solutions as bicarbonate and carbonate, which do not partition into a gas phase like carbon dioxide. Moreover, bicarbonate and carbonate can also react with other ions and precipitate as carbonate minerals, thus sequestering inorganic carbon as a solid. Conversely, microbial reactions that produce hydrogen ions can cause carbonate minerals to dissolve and push the reactions above in the opposite direction, increasing carbon dioxide concentrations.

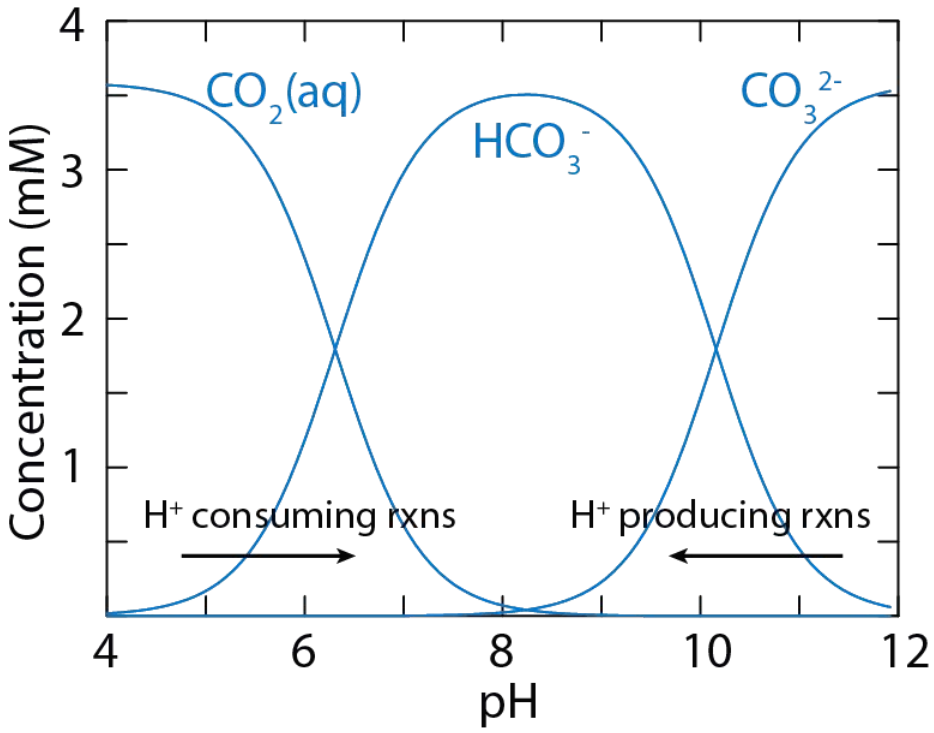


Figure **13.5**: Variation with pH in the proportions of dissolved inorganic carbon species. Reactions that consume hydrogen ions lower hydrogen ion activity and thus increase pH. As such, they work to transform dissolved carbon dioxide $(\mathrm{CO_2})$ (aq) into bicarbonate $(\mathrm{HCO_3^-})$and carbonate $(\mathrm{CO_3^{2-}})$. Reactions that produce hydrogen ions do the opposite. Species distributions shown in this figure were calculated using the React module of The Geochemist's Workbench software for a solution with an ionic strength of 20 mmolal and an initial carbon dioxide gas fugacity of 0.1.
Image: https://commons.wikimedia.org/wiki/File:DIC_speciation.png

By affecting the carbon dioxide content of their environments, microorganisms can influence how much carbon dioxide is taken up or lost to the atmosphere. This impact is a possibility even if the environment hosting the microbes is not physically connected to the atmosphere because transport can bridge the gap between the microbe's environment and the atmosphere. This relationship also applies to the other gases considered in this chapter.

To place these relationships in an environmental context, we first consider the fate of carbon dioxide generated in soils. Large amounts of carbon dioxide are produced in soils by plant respiration and microbial degradation of organic matter, which we can collectively refer to as soil respiration. The carbon dioxide that is produced can diffuse out of soil aggregates into macropores that connect to the atmosphere. Partial pressures of carbon dioxide in soil gas are often 10 to 100 times higher than the atmosphere (Brook et al., 1983; Macpherson, 2009). As such, it is commonly favorable for them to emit carbon dioxide to the atmosphere. Much of the carbon dioxide produced in soils can also be transported into the subsurface during groundwater recharge (Fig. **13.6**). A recent study at the Santa Catalina Mountains-Jemez River Basin Critical Zone Observatory, for example, found that two-thirds of the carbon dioxide from soil respiration was transported into the subsurface (Sanchez-Canete et al., 2018).

As carbon dioxide from soil makes its way through the subsurface, a portion is consumed by chemical and microbial reactions. Some is typically consumed by mineral weathering (Section 11.4.2). Significant quantities can also be fixed by autotrophs. A recent study by Overholt et al., (2022), for example, concluded that carbon fixation rates by microorganisms in carbonate aquifers are similar to those measured in low-nutrient marine surface waters. In addition to carbon fixation, microorganisms can also affect carbon dioxide concentration by using it as an electron acceptor (e.g., methanogenesis, acetogenesis) and by catalyzing reactions that produce or consume hydrogen ions and thus affect dissolved inorganic carbon speciation (reactions **13.3.1** and **13.3.2**).

If the groundwater eventually discharges into a stream or some other surface water body, some of the remaining soil carbon dioxide that is moving with it may then be lost to the atmosphere. Alternatively, surficial aquatic habitats can also take in carbon dioxide from the atmosphere. Major factors that determine whether it is favorable for an aquatic habitat to be a source or a sink for carbon dioxide include the concentration of dissolved carbon dioxide ($CO_2\ (aq)$) in the water, the partial pressure of carbon dioxide in the gas phase in contact with the water ($CO_2\ (g)$), and the temperature of the water (see Box 13.1 for more on gas solubility). If the water contains a higher dissolved carbon dioxide concentration than it would if it were in equilibrium with the gas phase, then it is favorable for the water to emit carbon dioxide gas. In other words, we can say that the water is supersaturated with carbon dioxide relative to the atmosphere. Indeed, water in many streams and rivers is supersaturated with carbon dioxide relative to atmospheric levels (Butman and Raymond, 2011), with groundwater inputs, instream metabolism, and riparian wetlands serving as major carbon dioxide sources (Kirk and Cohen, 2023).

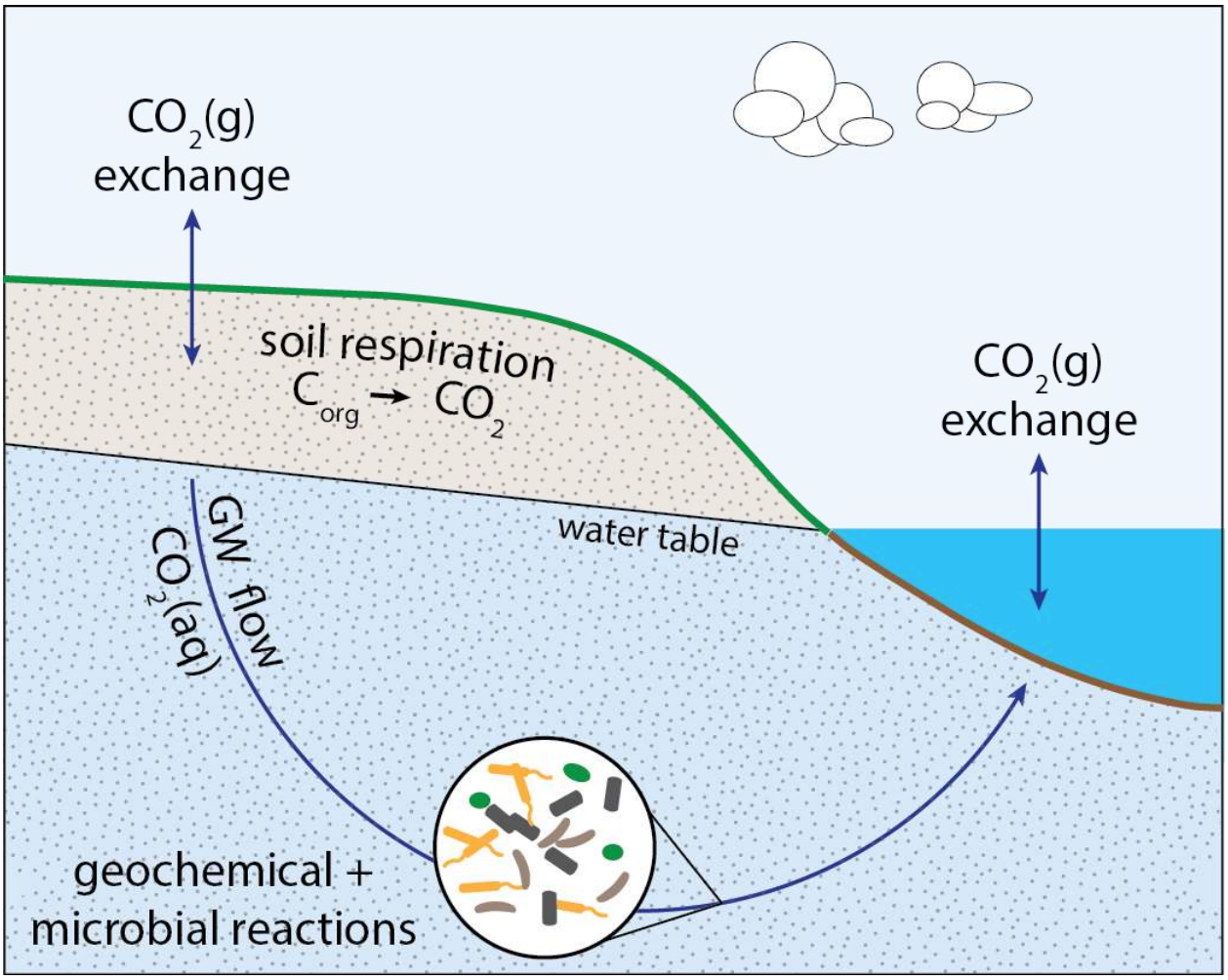


Figure **13.6**: Schematic illustration of potentials fates of carbon dioxide produced by organic matter oxidation (C_{org}) during soil respiration. Carbon dioxide produced by soil respiration can reach the atmosphere directly from the soil. It may also be transported by groundwater flow to adjacent surface water bodies, where it can then be emitted.
Image: https://commons.wikimedia.org/wiki/File:Fates_of_soil_CO2.png

The example above considers the fate of carbon dioxide that is produced near the surface, but what about carbon dioxide emanating from deep within the Earth? Microorganisms appear to also play a significant role in affecting the fate of that carbon dioxide as well, effectively forming a biological filter that decreases how much carbon dioxide is able to reach the surface.

As an example, we briefly consider recent studies by Fullerton et al. (2021) and Rodgers et al. (2022) along the Costa Rican convergent margin. There, the Cocos plate is actively subducting beneath the Caribbean plate. As the Cocos plate subducts, large fluxes of carbon dioxide and other volatiles are released into the overlying Caribbean plate, where they make their way upward toward the surface and atmosphere. The researchers considered how these fluids impact the subsurface biosphere by examining the microbiology and geochemistry of hot springs near the convergent margin. Their findings indicate that subsurface chemolithotrophic microorganisms fix large quantities, as much as $\mathbf{1.4 \times 10^9}$ mol per year, of slab-derived carbon dioxide in the subsurface, and thus significantly alter fluxes of carbon at the plate margin. This microbial carbon sink operates alongside other sinks at the plate margin, including calcite precipitation, formation of dissolved inorganic carbon species such as bicarbonate and carbonate, and production of dissolved organic carbon (Barry et al., 2019; de Moor et al., 2017).

Box 13.1: Henry's Law

Henry's Law states that the amount of dissolved gas in a solution is proportional to its partial pressure above the solution. Thus, we can use this relationship to understand how much gas will dissolve into water if the water and an adjacent gas phase are allowed to equilibrate. For water that is in contact with the atmosphere, this relationship can tell us whether the water would be a source or sink for atmospheric gases.

For an example calculation, consider the following reaction, which describes dissolution of carbon dioxide in water:

$$CO_2\ (g) \leftrightarrow CO_2\ (aq)$$

The equilibrium constant (K) for this reaction, like all reactions, is temperature dependent. The log value of K at $15°C$ is -1.3240 (see Appendix A). The mass action equation for the reaction at $15°C$ is as follows:

$$-1.3240 = -\log\left[CO_2(g)\right] + \log\left[CO_2(aq)\right]$$

Note that brackets indicate activity for dissolved species and fugacity for gases. For a review of these concepts and mass action, please see Chapter 8. If we assume that activity and fugacity are equivalent to molar concentration and partial pressure in atmospheres, respectively, and insert a value for carbon dioxide gas consistent with atmospheric levels (~ 0.0004 atm), then the equation becomes:

$$-1.3240 = -\log(0.0004) + \log\left(CO_2(aq)\right)$$

Solving for dissolved carbon dioxide concentration gives

$$\log\left(CO_2(aq)\right) = -1.3240 + \log(0.0004) = -4.722$$

The antilog value of this result gives a dissolve carbon dioxide concentration of 1.9×10^{-5} M or $19\ \mu$M. Thus, if water at $15°C$ has a concentration of carbon dioxide that exceeds this level, then the water is supersaturated with carbon dioxide and it is favorable for the water to lose carbon dioxide to the atmosphere. Alternatively, if a water at $15°C$ has a concentration below this level, then it is undersaturated with carbon dioxide and favorable for the solution to dissolve more from the atmosphere.

Box 13.2: Practice Henry's Law

Practice 13.1. For more practice, recalculate the dissolved carbon dioxide concentration that would exist in a solution equilibrated with the atmosphere at $5°C$ ($\log K = -1.2000$) and $25°C$ ($\log K = -1.4524$). How does the equilibrium dissolved carbon dioxide concentration change with temperature? Answers are provided at the end of this chapter.

Practice 13.2. How do the solubilities of carbon dioxide and methane compare? Assume a water at $15°C$ is in equilibrium with a gas phase that contains 0.0001 atm of each gas. What are the dissolved concentrations of each gas in the water? Which gas is more soluble? For the calculation, assume activity equals concentration in molar units and fugacity equals partial pressure in atmospheres. Gas dissolution reactions and information needed to calculate $\log K$ values at various temperatures are available in Appendix A.

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13.4: Methane

Like carbon dioxide, microorganisms can both make and consume methane. Microorganisms that produce methane as a major product of their catabolism are known as methanogens, whereas those that consume it as an electron donor are known as methanotrophs. In addition to these groups, there are also microorganisms that produce methane as a byproduct of their metabolism. Some key information for each of these groups is briefly summarized below and more details are available in the discussion of the carbon cycle in Chapter 5 (sections 5.1.4 and 5.1.6).

Methanogens are all members of domain Archaea and are considered to be obligate anaerobes, meaning they are only able to survive under anoxic conditions. Moreover, their activity also tends to be limited where nitrate and sulfate are available and in some cases where ferric (oxyhydr)oxides are available (Marquart et al., 2019) (Sections 8.5, 9.3, and 10.2.5). Anoxic conditions with low nitrate and sulfate availability often occur in wetland soils, lake and river sediments, and animal intestines. Zones hosting active methanogens are also found in the subsurface, especially in organic-rich layers such as coalbeds and black shales, where electron acceptors needed for alternative microbial metabolisms are often in low supply.

Recent studies have shined a bright light on methane production by microbial groups not considered to be methanogens. These microorganisms can form methane as a byproduct when they cleave methyl groups from organic matter as they scavenge for nutrients (Repeta et al., 2016; Yao Mengyin et al., 2016) or through the reaction of some nitrogenases and nitrogenase-like enzymes (North Justin A. et al., 2020; Zheng et al., 2018). Recent research also shows that cyanobacteria can produce methane at significant rates under both oxic and anoxic conditions (Bižić M. et al., 2020). Although methanogenic Archaea deserve much attention as methane producers, these alternative pathways can also be significant. Thottathil et al. (2022) demonstrated that oxic methane production accounted for up to 76% of the methane in the five small lakes they studied.

Methanotrophs can couple oxidation of methane to reduction of oxygen, nitrate, ferric iron, and sulfate, in some cases with assistance from partner microorganisms (Section 5.1.6). Thus, they can be active in both oxic and anoxic environments. A recent review of published studies indicated that methane oxidation is primarily carried out by anaerobes in the oceans, where it mostly occurs within sediments (Gao et al., 2022). In contrast, the study found that aerobic methanotrophs typically consume more methane than anaerobic methanotrophs in wetlands, rice paddies, lakes, and rivers (Gao et al., 2022). Collectively, aerobic and anaerobic methanotrophs play a major role in helping limit atmospheric methane levels. For example, annual methane formation in ocean sediment is estimated to be $85\text{-}300 Tg/yr$. Most (>90%) is consumed by methanotrophs before it can reach the atmosphere (Knittel and Boetius, 2009). In general, the amount of methane emitted from an ecosystem ultimately reflects the balance between methane production and methane oxidation (Bridgham et al., 2013).

As first example of these reactions in an environmental context, we consider microbial methane production in wetlands. Wetlands are the single largest natural source of methane and estimated to account for about a third of global emissions (Bridgham et al., 2013). Water saturation within wetlands can create anoxic conditions that are conducive to methanogen growth. Specifically, when soil pores are filled with water, oxygen transport within them becomes limited. If the rate of electron acceptor use exceeds that rate at which oxygen can be supplied, anoxic conditions can develop that may be suitable for methanogens, depending on the availability of nitrate, sulfate, and ferric iron. Food sources for methanogens in wetlands typically include degradation of organic matter as well as organic substrates delivered by plants through root exudates (Bridgham et al., 2013).

Soils that are largely oxic in wetlands may also host methanogens within anoxic microenvironments. For example, Angle et al. (2017) examined methanogenesis in soils beneath three wetland land coverage types: areas covered with plants, periodically exposed mudflats, and continuously submerged soils. They observed similar oxygen depth profiles at all three sites. Depths shallower than 10 cm were always oxic and those deeper than 25 cm were always anoxic. Net methane production occurred at all three land-use types during their sampling seasons, and the largest methane generation occurred in oxygenated layers. An analysis of the microbial community demonstrated that the microorganisms forming the methane were methanogenic Archaea, not those that produce it as a byproduct. There was also no evidence that the methanogens had oxygen tolerance genes, leading the researchers to suggest that methanogen activity occurred in anoxic microenvironments within oxic zones of the wetland soils.

Methane can leave a wetland by diffusion, bubble release (i.e., ebullition), and plant-mediated transport (Bridgham et al., 2013). The extent to which methane is exposed to methanotrophy likely differs between these pathways. Ebullition and transport through plants may allow methane to bypass zones of aerobic methanotrophy (Bridgham et al., 2013). In contrast, relatively slow transport

by diffusion may provide greater opportunity for methanotrophs to consume the methane before it escapes to the atmosphere. Thus, differences in methane transport may contribute to differences in the balance between methanotrophy and methanogenesis between systems or over time with an individual system.

As a second example, we briefly consider the recent study by D'Ambrosio and Harrison (2021), who studied methane sources and sinks in lake sediments. Data collected from 60 different lakes and reservoirs showed that methane was more likely to escape oxidation by methanotrophs if methane was being rapidly produced. In other words, methanotrophy was less efficient as a microbial filter for methane removal where methane production was high. Furthermore, they observed a strong positive correlation between methane production rate and the availability of nutrients. Eutrophic lakes, those rich in nutrients and biological productivity, tend to have high methane emissions. Taken together, these observations imply, therefore, that lower methane oxidation efficiencies contribute to greater methane emissions in such systems.

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13.5: Nitrous oxide

Like carbon dioxide and methane, microorganisms can produce and consume nitrous oxide (N_2O), also known as laughing gas. The main pathways by which microorganisms produce nitrous oxide are denitrification and nitrification. Microorganisms can consume nitrous oxide by catalyzing the terminal step of denitrification. This chapter summarizes some information about these microbial reactions, though additional details are provided in Chapter 5 (Sections 5.2.5 and 5.2.3).

During nitrification, ammonium (NH_4^+) is oxidized to hydroxylamine (NH_2OH) and then to nitrite (NO_2) and nitrate (NO_3^-) (see Fig. 5.3). As described by Glass and Orphan (2012), nitrous oxide is produced from two offshoots of nitrification: nitrifier denitrification and hydroxylamine oxidation. Nitrifier denitrification is a somewhat confusing term. Essentially, some nitrifiers can not only nitrify but also denitrify as well (Ritchie and Nicholas, 1972), which is referred to as nitrifier denitrification (Wrage et al., 2001). Through this pathway, nitrite is reduced to nitric oxide (NO) and then to nitrous oxide or dinitrogen (N_2) instead of being oxidized to nitrate (Glass and Orphan, 2012). In the hydroxylamine pathway, hydroxylamine is oxidized to nitric oxide and then reduced to nitrous oxide (Glass and Orphan, 2012). For both pathways, ammonium is aerobically oxidized, and thus nitrification produces nitrous oxide in oxic environments.

During denitrification, nitrate is reduced to nitrite, and then nitric oxide, nitrous oxide, and ultimately dinitrogen under favorable conditions (see Fig. 5.3). However, the process is leaky and some intermediates, including nitrous oxide, are typically released as well, with proportions of nitrous oxide generation sensitive to pH and oxygen concentration (Glass and Orphan, 2012). Denitrification is thought to primarily occur in anoxic environments. However, some bacteria can use the reaction in oxic environments (Ji et al., 2015).

In terms of a microbial nitrous oxide sink, the terminal step of denitrification, oxidation of nitrous oxide to dinitrogen, appears to be the main pathway. Intracellular nitrous oxide as well as nitrite can exchange with external pools, creating the possibility that they take in more than they produce and thus serve as a net sink for nitrous oxide (Bourbonnais et al., 2017; Sun et al., 2021).

To place these microbial activities in an environmental context, we first consider nitrous oxide production in soil. Significant emissions of nitrous oxide occur from terrestrial environments and the oceans, but the largest source overall is terrestrial soils (Gruber and Galloway, 2008; Tian et al., 2016). As an example study, Davidson and Swank (1986) and Davidson et al. (1986) examined gaseous nitrogen losses from nitrification and denitrification in soils collected from two forested watersheds. They found nitrous oxide generation by nitrification was most important in well-drained sites of a disturbed watershed where nitrate concentrations were relatively high (Fig. 13.7). In contrast, denitrification was most important in poorly drained sites within the riparian zones of the streams in each study watershed. At those locations, the soils were wetter than they were upslope and also richer in organic matter, increasing the likelihood of oxygen depletion. Similar relationships between soil moisture and denitrification have also been observed in agricultural soils (e.g., Ryden, 1983; Tiedje et al., 1984). Taken together, these results illustrate how the moisture content of soils can impact oxygen levels and ultimately the pathway of nitrous oxide production.

One thing to bear in mind for these results is that nitrous oxide is not necessarily produced by one pathway or the other at a particular location within an environment. In fact, both nitrification and denitrification can occur even within the same soil aggregate (Stevens et al., 1997). Environmental controls that determine the rate and pathway of nitrous oxide production include soil moisture content, oxygen concentration, temperature, pH, and substrate availability (Butterbach-Bahl et al., 2013). The status of these controls can vary significantly over short distances in soils.

As a second example, we consider a study by Beaulieu et al. (2014), who examined nitrous oxide generation in the hypolimnion of a thermally stratified reservoir in a watershed dominated by agricultural land use. The hypolimnion is the lower layer of water in a stratified lake or reservoir, which is cooler and often contains lower oxygen concentrations than water near the lake surface. Their findings indicate that denitrification was a consistent sink for nitrate and source of dinitrogen gas while the lake was stratified. However, whether it was a source or sink of nitrous oxide varied over time. Production of nitrous oxide relative to dinitrogen ranged from -3.4% (net N_2O sink) to 19.5% (net N_2O source) during the study period. Their results suggest that this variation was not caused by changes in denitrification rates, but rather changes in the extent to which denitrification was able to complete its final step, oxidation of nitrous oxide to dinitrogen. The authors concluded that the mechanisms responsible for the observed variation include variation in environmental controls on the activity of nitrous oxide reductase, the enzyme that catalyzes the final step of denitrification.

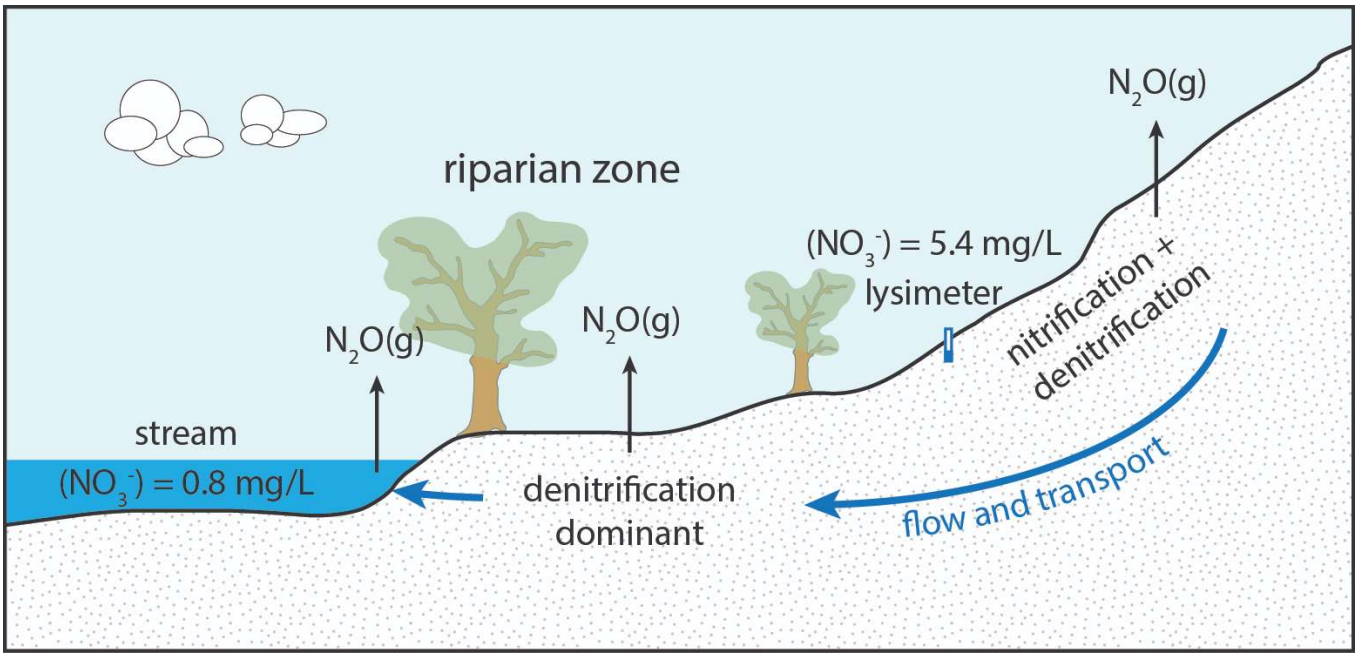


Figure **13.7**: Schematic illustration of the distribution of nitrous oxide (N_2O) sources in one of the watersheds studied by Davidson and Swank (1986) and Davidson et al. (1986). Both nitrification and denitrification occurred in the soils at the study area, but nitrification was most important in well-drained upslope areas and denitrification was most important in poorly drained areas in the riparian zone, the interface between the terrestrial and aquatic ecosystems. Concentrations of nitrate measured in the stream and in soil water collected from a lysimeter are shown. The difference in nitrate concentrations between those sampling locations is consistent with nitrate removal by denitrification as subsurface water (groundwater and soil water) flows toward the stream. This figure is based on figure 5 of Davidson and Swank (1986).
Image source: https://commons.wikimedia.org/wiki/File:Nitrous_oxide_sources.jpg

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13.6: Responses of microorganisms to climate change

The quote at the beginning of this chapter notes that the impact of climate change will depend heavily on the response of microorganisms. Why is that?

Ultimately, the answer comes down to two things. First, climate change will directly alter many of the environmental controls on the activity of microorganisms, including the temperature and pH of their environments, plant productivity, water availability, redox conditions, and the intensity and frequency of disturbances. These environmental controls will also vary with changes to land use, as human populations adapt to changing climate. Secondly, microorganisms play enormous roles in shaping our planet, as discussed throughout the third part of this book. Because those roles include serving as consumers and producers of greenhouse gases, their response can feedback on climate change in both positive and negative ways. Microbes could lessen climate change if their response decreases net greenhouse gas production, representing a negative feedback on climate change. Alternatively, microbes could amplify warming if they increase net greenhouse gas production, representing a positive feedback. Thus, the full extent of climate change will depend on these responses.

As an example, we consider some of the research on soils and climate change. Soils are major carbon reservoirs. They contain about 2,000 billion tons of organic carbon, which exceeds the mass of carbon in the atmosphere and vegetation combined (Singh et al., 2010). A positive feedback on climate change could occur if degradation of that organic matter increases relative to uptake of new carbon, causing net soil carbon emissions to increase (Davidson and Janssens, 2006; Jenkinson et al., 1991). Alternatively, a negative feedback would occur if plant inputs of organic carbon increase relative to carbon export by degradation.

Previous research has shown that climate change can alter organic matter degradation rates by warming soils and modifying their water content. Warming can increase rates of degradation because, like most reactions, rates of microbial enzymatic reactions generally increase with warming (Craine et al., 2010). Warming is also causing permafrost to thaw, making its dense stocks of organic carbon available for degradation. Permafrost contains about 30% of global soil carbon, and 28% to 53% of permafrost globally is expected to thaw with 1.5 to $2°C$ of warming relative to global mean surface temperature in 1850-1900 (Cavicchioli et al., 2019; IPCC, 2018). Water content may change in some soils because climate change is altering precipitation patterns (IPCC, 2021). Changes in soil water content can affect soil carbon emissions by affecting respiration rates and the extent to which their organic carbon is exposed to aerobic degradation, as discussed in detail in Sections 6.3 and 6.4.

Consistent with these possibilities, worldwide soil respiration measurements indicate that soil respiration rates have been increasing as soils have warmed (Bond-Lamberty and Thomson, 2010). There is also evidence that soil organic carbon stocks are degrading more rapidly as they warm (Craine et al., 2010; Crowther et al., 2016; Karhu et al., 2014). If there are no major changes to our production of greenhouse gases, Crowther et al. (2016) estimated that, by 2050, climate change will drive carbon losses from upper soil horizons that are equivalent to 12 to 17% of the expected for anthropogenic emissions over the same time period. They noted that, although there is a large amount of uncertainty in their estimates, net carbon soil losses were consistently predicted across all scenarios. Thus, their analysis indicates soil carbon emissions will be a positive feedback on climate change.

There are many other examples in the scientific literature that illustrate microbial responses to climate change. For further reading, the list below includes example studies that are available by open access and relevant to greenhouse gases.

- Bizic (2021) examined methane production by phytoplankton and includes a discussion of potential climate change feedbacks.
- Canarini et al. (2021) examined impacts on soil microbial communities of droughts, which are changing in frequency and severity as a consequence of climate change.
- Cavicchioli et al. (2019) documented the central role and importance of microorganisms in climate change biology and considered marine and terrestrial environments, including agricultural systems.
- Guo et al. (2020) examined methane emissions from boreal lakes in Finland and considered impacts of warming water and sediment and shorter lake ice coverage as a result of climate change.
- Paranaíba et al. (2020) evaluated consequences of sediment drying-rewetting cycles for greenhouse gas emissions, nutrient and trace element release, and water contaminants in freshwater sediments.
- Poeplau et al. (2020) examined the net loss of organic carbon as a consequence of warming in subarctic forest and grassland soils.

- Rees et al. (2022) considered how the rapid pace of environmental change in the Arctic Ocean will affect emissions of nitrous oxide and methane.
- Röβger et al. (2022) documented rising methane emissions from thawing permafrost in the Arctic.
- Weldeab et al. (2022) examined destabilization of methane hydrates in ocean sediment during a warming period 126,000 to 125,000 years ago and discusses these findings in the context of modern warming.
- Zhang et al. (2017) investigated methane emissions from global wetlands as a feedback on climate change.
- Zhao et al. (2021) examined soil organic carbon loss in response to warming and drying in a watershed on the Chinese Loess Plateau.

Aside from impacts to greenhouse gas levels, microbial responses to climate change will affect many other things about our planet, including impacts that affect crop production and water resources. Readers are encouraged to explore further to deepen their knowledge of this important topic.

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13.7: Managing greenhouse gas emissions

By learning more about environmental controls on microbial greenhouse gas emissions, we will be better able to predict how emissions will change in the future in response to climate and land use changes. In addition, this knowledge can be used to develop strategies that alter microbial activity in some environments to decrease the extent to which they produce greenhouses gases.

To develop such a strategy, we can adopt the same thought process that this book recommends for developing strategies that employ microorganisms to remediate water resource contaminants (Section 14.5). Specifically, we can consider the two-way interactions between microorganisms and their environments. We must first consider what change(s) in microbial activity would decrease greenhouse gas production. Then, we need to consider the how we can alter the environment to bring about those change(s).

As an example, previous research has tested the ability of ferric iron amendments to decrease methane production in wetland soils. Microbial iron reduction can have thermodynamic and kinetic advantages over methanogenesis. Where fresh supplies of ferric iron minerals are available, therefore, iron-reducing microorganisms have the potential to outcompete methanogens for electron donors and thereby limit methane generation (Lueders and Friedrich, 2002; Roden, 2003; Roden and Wetzel, 2003).

To test this strategy, Roden (2003) added ferric iron minerals to organic carbon-limited cultures that contained wetland sediment microorganisms and slightly acidic water (initial pH 6.5 to 6.7). Ferric iron sources they tested were hydrous ferric oxide (HFO; a poorly crystalline ferric iron source), two different goethite phases, and hematite. Results showed that methane production was significantly lower in cultures that received ferric iron compared to unamended control cultures. Moreover, methane production was inhibited just as strongly by goethite and hematite as HFO when quantities of the mineral amendments were nearly equivalent in terms of mineral surface areas.

A main conclusion from the laboratory study is that ferric (oxyhydr)oxide amendments can be an effective strategy for suppressing methane production in wetland soils, but that the surface area of those phases is important to consider when determining how much mineral to add. Recall from Section 9.7 that (oxyhydr)oxide surface area influences the rate at which iron can be reduced. As such, surface area has the potential to influence the extent to which iron-reducing microorganisms can outcompete methanogens for electron donors.

In addition to surface area, pH will likely also be important to consider. Results from Marquart et al. (2019) indicate that iron reduction decreases relative to methanogenesis as pH increases in many systems, potentially in response to the decreasing free energy yield of iron reduction with increasing pH (Sections 8.3, 10.2.5). As a result, the strategy of amending soils with ferric iron to decrease methane generation may become less effective at basic pH, at least for highly crystalline amendments such as goethite and hematite, which are less thermodynamically favorable as electron acceptors than poorly crystalline phases (Postma and Jakobsen, 1996).

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13.8: Answers to practice problems

Practice 13.1

$25\ \mu M\ CO_2\ (aq)$ at $5°C$ and $14\ \mu M\ CO_2\ (aq)$ at $25°C$; gas solubility generally decreases as temperature increases.

Practice 13.2

$\log K$ for CO_2 reaction at $15°C = 1.3240$

$\log K$ for CH_4 reaction at $15°C = 2.7526$

$(CO_2(aq)) = 4.74\ \mu M$; $(CH_4(aq)) = 0.18\ \mu M$

CO_2 is more soluble than methane in the hypothetical solution.

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13.9: Concept Check Questions

1. What role did plants play in the Great Oxidation Event?
2. How would burial of pyrite in a sedimentary basin influence oxygen accumulation in the atmosphere?
3. What is causing atmospheric levels of carbon dioxide, methane, and nitrous oxide to increase?
4. Why does plant growth specifically in the Northern Hemisphere seem to have such a big impact on global carbon dioxide levels in the atmosphere?
5. Could you apply Henry's Law to determine whether a dissolved gas was supersaturated or undersaturated with respect to the atmosphere?
6. How would iron reduction and sulfate reduction affect dissolved inorganic carbon speciation in water? Based on the stoichiometry of the reactions, which has the potential to have a bigger impact and why?
7. What is soil respiration?
8. What groups of microorganisms are capable of producing methane?
9. Does methanotrophy occur in anoxic environments? If so, how?
10. How might nitrous oxide be generated differently in an anoxic microenvironment with a soil compared to an oxygenated zone?
11. If soil becomes increasingly saturated as a result of changing precipitation patterns, how would you expect the rate of organic matter degradation within the soil to change?

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CHAPTER OVERVIEW

14: Impacts to the Hydrosphere

Water is an essential resource that influences where microorganisms and other life forms can be active and to what extent. In turn, however, microorganisms significantly impact the movement and composition of water. By forming biofilms in soils and the subsurface and by causing minerals to dissolve and precipitate (Chapter 11), microorganisms help define the permeability distribution underground and its evolution over time (Gerlach and Cunningham, 2010; McMahon et al., 1992). By impacting water composition, microorganisms affect water quality, which is the focus of this chapter.

Water quality is a measure of the suitability of water for a particular use. Suitability can be assessed based on chemical characteristics (e.g., concentrations of hazardous solutes), physical properties (e.g., turbidity), and biological characteristics (e.g., pathogen abundance). Desired levels of chemical, physical, and biological properties depend on the intended use of the water. For example, water that may not be suitable for humans to use as drinking water may be acceptable for irrigation or livestock.

Microorganisms can impact water quality in many ways. What may come to mind first is the fact that the presence of some microorganisms, such as pathogens and some algal blooms, can make water unsafe for humans to drink. In addition, microorganisms impact water quality simply by driving chemical reactions forward, including reactions that affect the pH and major ion chemistry of water but also those that affect specific contaminants. This chapter considers these types of impacts to water quality as well as applications of microbiology to improve water quality.

14.1: Pathogens
14.2: Groundwater quality
14.2.1: Chemical evolution of groundwater
14.2.2: Middendorf aquifer
14.3: Surface water quality
14.3.1: Connections to groundwater
14.3.2: Algal blooms
14.4: Examples of microbial impacts to chemical contaminants
14.4.1: Nitrate
14.4.2: Arsenic
14.4.3: Acid mine drainage
14.4.4: Chlorinated solvents
14.4.5: Petroleum hydrocarbons
14.5: Applying microbiology to remediate contaminated water
14.6: Concept Check Questions
14.7: References

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14.1: Pathogens

Microorganisms that can cause disease are known as pathogens. They can be bacteria, viruses, and eukaryotes. Most microbial pathogens are enteric, meaning that they originate from the gastrointestinal tracts of warm-blooded animals. Therefore, they are found in large quantities in feces and can contaminate a water supply when the water contacts untreated animal waste. Consumption of contaminated water can cause diseases such as diarrhea, cholera, dysentery, typhoid, and polio (World Health Organization, 2022). Globally, at least two billion people are thought to use drinking water sources contaminated with feces (World Health Organization, 2022).

The abundance of *Escherichia coli* and coliform bacteria are commonly used as indicators of the sanitary quality of water and foods. *E. coli* are gram-negative bacteria that are commonly found in the lower intestines of warm-blooded animals. Coliform bacteria are rod-shaped gram-negative bacteria that can ferment lactose. Coliform bacteria do not typically cause human illness themselves, but rather, their presence is taken as an indication that gastrointestinal pathogens are present.

Because animal waste is primarily generated at the surface, groundwater is typically less vulnerable to pathogen contamination than surface water. Nonetheless, pathogen contamination does still occur in groundwater. A long-term study by scientists at the US Geological Survey (USGS), for example, found *E. coli* contamination in groundwater from 8% of the 1,400 wells that they tested for pathogens (DeSimone et al., 2014). Compared to other lithologies, the study found that carbonate or crystalline rock aquifers were more frequently contaminated, reflecting the high rates of flow that are possible through enlarged cracks and fissures in such aquifers (Hartmann et al., 2021). The USGS study also detected *E. coli* most frequently in samples from areas overlain by agricultural land use, likely in response to livestock operations and application of manure as fertilizer. Thus, the study highlights land use and aquifer hydrologic properties as influential factors determining vulnerability to pathogen contamination.

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14.2: Groundwater quality

14.2.1: Chemical evolution of groundwater

14.2.2: Middendorf aquifer

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14.2.1: Chemical evolution of groundwater

Microorganisms play a major role in determining concentrations of several groundwater contaminants, as we will discuss in the sections below. However, even if groundwater is not contaminated, microorganisms have generally had a significant influence on its chemical composition.

Groundwater ultimately starts out as meteoric water, which is largely distilled water that contains some dust and dissolved gases. Fresh meteoric water is not in equilibrium with the minerals and other phases found in soils and the subsurface so it can react with everything as it goes belowground. Its pH tends to be slightly acidic because atmospheric carbon dioxide dissolves into the water and forms carbonic acid (Fig. **14.1**). As the water passes through soils, it tends to become even more acidic because soils contain high levels of carbon dioxide produced by plant and microbial respiration. In addition, other potential sources of acidity include organic acids generated by organic matter degradation and acid produced by microbial nitrification and sulfide oxidation (Sections 11.4.2 and 13.3). As the water moves through the subsurface, over time it typically becomes less acidic, more reduced (e.g., lower dissolved oxygen concentration), and more concentrated in solutes. These changes in chemistry are often largely due to microbial activity and mineral reactions.

Mineral dissolution reactions that consume hydrogen ions cause the pH of water to increase. They also increase solute concentrations by releasing mineral components as products (Fig. 11.3). Carbonate minerals react relatively quickly with acid and cause increases in concentrations of bicarbonate and metals such as calcium and magnesium. Silicate minerals tend to react more slowly than carbonate minerals but can contribute significantly to pH buffering over time scales relevant to the groundwater residence times. Solutes generated by silicate weathering can include metals and silica. Secondary clay minerals can also form as primary silicates dissolve (Section 12.1.5).

In addition to mineral reactions, microorganisms can cause the pH of water to increase by consuming hydrogen ions in their metabolic reactions. As an example, microbial iron reduction and sulfate reduction consume hydrogen ions and can cause pH to increase significantly (Chapter 1, Box 1.1). Thus, some microorganisms help generate the acid, but others can help neutralize it. In terms of redox state, groundwater tends to become more reduced along flow because groundwater is isolated from the atmosphere and thus, oxygen that is consumed by subsurface aerobes cannot be resupplied. Where the supply of oxygen is largely depleted, aquifer microorganisms instead respire alternative electron acceptors, potentially creating redox zones as they move along the thermodynamic ladder (see Sections 8.5 and 8.6). These reactions can be fueled by organic compounds and dihydrogen supplied by degradation of organic matter at the surface and within the subsurface, as shown in Figure **14.1**, but there are many other potential energy sources as well (see Chapter 7).

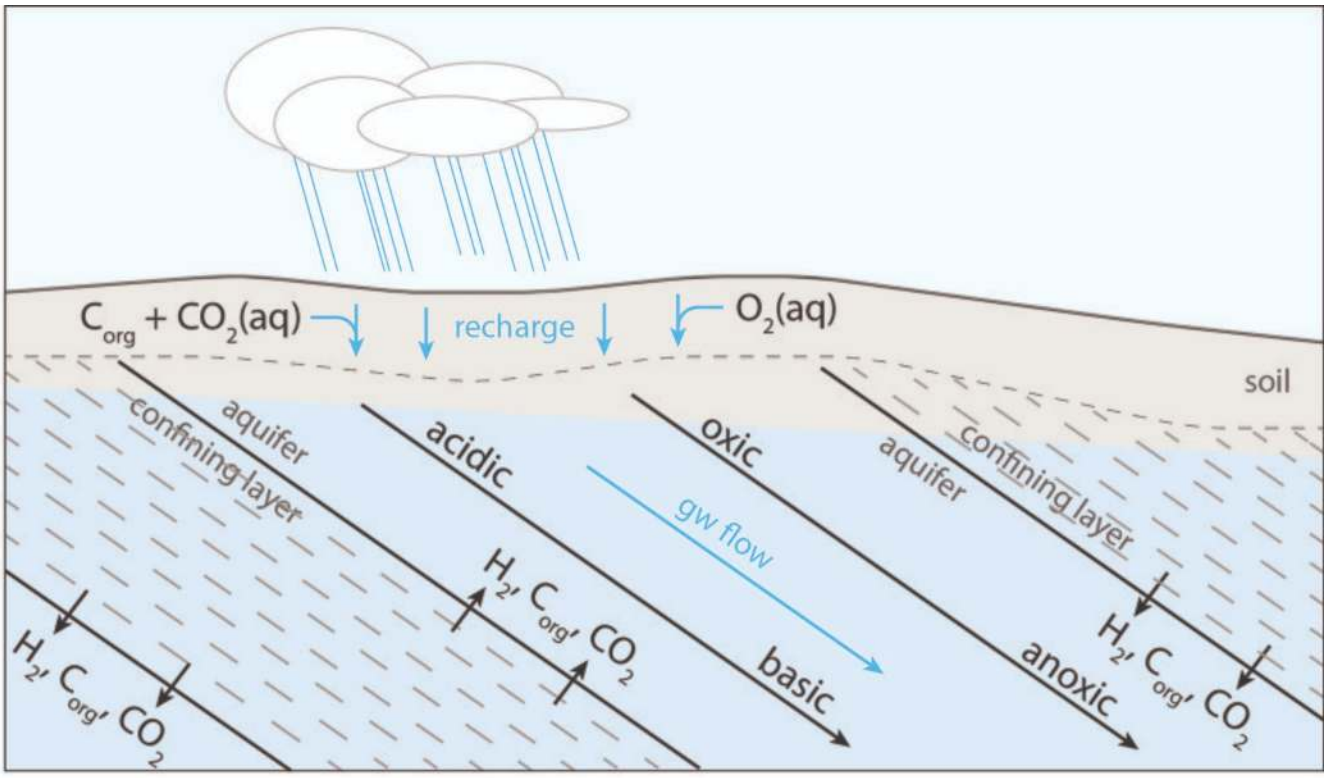


Figure 14.1: General trends in groundwater (gw) chemistry along flow. This simple conceptual model is based on trends observed in coastal plain aquifers in South Carolina, USA (Chapelle and Lovley, 1992; Lovley and Goodwin, 1988; McMahon and Chapelle, 1991; Park et al., 2009, 2006). According to the model, organic matter degradation is concentrated in the overlying soil and within fine-grained confining layers in the subsurface. These reactions help supply acid and potential electron donors to the groundwater by producing carbon dioxide $(CO_2)\,(aq)$, dissolved organic compounds (C_{org}), and dihydrogen (H_2). As the groundwater flows away from the recharge area, its pH evolves from acidic to basic because, within the aquifer, microbial reactions and mineral buffering reactions occur that consume hydrogen ions. The groundwater also tends to become increasingly anoxic, as aquifer aerobes deplete the groundwater's initial supply of oxygen and groups of anaerobes become active. https://commons.wikimedia.org/wiki/File:Evolution_of_groundwater_chemistry.jpg

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14.2.2: Middendorf aquifer

As an example, we consider trends in geochemistry in the Middendorf coastal plain aquifer in South Carolina, USA. Groundwater recharges the aquifer where its sediment outcrops along the Atlantic Seaboard Fall Line, and from there flows southeast toward the Atlantic Ocean (Chapelle and Lovley, 1992). Along its flow, the groundwater passes through a series of redox zones that are consistent with the general trends described previously in Fig. **14.1** of Section 14.2.1, and in Chapter 8 (Section 8.5). Near the recharge area, dissolved oxygen is present in the groundwater (Fig. **14.2**) and aerobic microorganisms are interpreted to dominate. As groundwater flows away from the recharge area, oxygen concentration decreases and then the groundwater passes through a zone with relatively high ferrous iron concentrations and then a zone with low iron concentrations (Fig. **14.2**). These zones are interpreted to host iron- and sulfate-reducing microorganisms, with changes in the proportions of their activities causing the observed variation in iron levels (Park et al., 2006). Specifically, iron reduction appears to decrease relative to sulfate reduction with distance along flow.

A major factor that helps cause changes in the proportions of iron reduction and sulfate reduction along flow is variation in ferric iron availability. Sediment in the upgradient portion of the aquifer was deposited in an upper delta plain environment and its ferric iron content is greater than that for the sediment in the downgradient portion, which consists of lower delta plain and marine sediment (Chapelle and Lovley, 1992). Thus, the capacity of the aquifer to support iron-reducing microorganisms decreases along flow.

In addition, increasing groundwater pH along flow may contribute to shifts in the proportions of iron reduction and sulfate reduction. Along the nearly 100 km-long flowpath Park et al. (2006) sampled, groundwater pH increased from 4.9 to 8.5 (Fig. **14.2**). Microbial reduction of ferric iron in (oxhydr)oxides consumes a large number of hydrogen ions, and as a result, this increase in pH can sharply decrease the amount of energy available for iron reduction (see Section 8.3). In contrast, sulfate reduction consumes relatively few hydrogen ions and energy available for the reaction is much less sensitive to pH (Bethke et al., 2011; Postma and Jakobsen, 1996). Reflecting these relationships, previous studies have demonstrated that increasing pH can allow greater amounts of sulfate reduction relative to iron reduction in aquifers (Bethke et al., 2011; Kirk et al., 2016, 2013; Paper et al., 2021; Postma and Jakobsen, 1996).

In contrast to iron, concentrations of sulfate and sulfide are fairly stable throughout much of the aquifer (Fig. **14.2**). No sulfate sources are known to exist within the aquifer or recharge area. As such, previous researchers have suggested that sulfate is added to the groundwater as it flows through the aquifer from the adjacent confining layers or by cross-formational flow (Chapelle and Lovley, 1990). This sulfate input helps to prevent sulfate depletion from the groundwater even though sulfate reducers are active. Lastly, sulfide concentrations remain stable and relatively low despite sulfate-reducing activity likely because the sulfide that is produced reacts with ferrous iron to precipitate as mackinawite rather than accumulate in the groundwater (Park et al., 2006).

Changes in pH and major ion concentrations along the groundwater flowpath sampled by Park et al. (2006) are also consistent with the general trends described in Section 14.2.1. Near the recharge area, the groundwater is acidic because it contains a relatively high amount of carbon dioxide (~ 0.6 mM), which is almost entirely added from soil respiration (Park et al., 2006). Nearly as much carbon dioxide is also added to the groundwater by subsurface organic matter degradation, particularly in the adjacent confining layers (Fig. **14.1**) (Park et al., 2009). Despite these additions of acid, pH increases along flow because iron reduction, sulfate reduction, and mineral reactions consume hydrogen ions at a greater rate than they are added. Minerals reactions expected to contribute to pH buffering in the aquifer included weathering of albite, anorthite, and illite (Park et al., 2009). Their dissolution helped increase pH and also the concentrations of sodium, calcium, potassium, magnesium, and silica.

Taken as a whole, these findings illustrate the strong influence of microorganisms on the composition of groundwater in the Middendorf aquifer. Microorganisms are major contributors to acid production in the recharge area and subsurface sediments. This acid drives mineral weathering reactions that increase pH and concentrations of major ions. Groundwater pH and concentrations of oxygen and ferrous iron also evolve along flow as microorganisms work their way along the thermodynamic ladder, pushing the groundwater into a more reduced state.

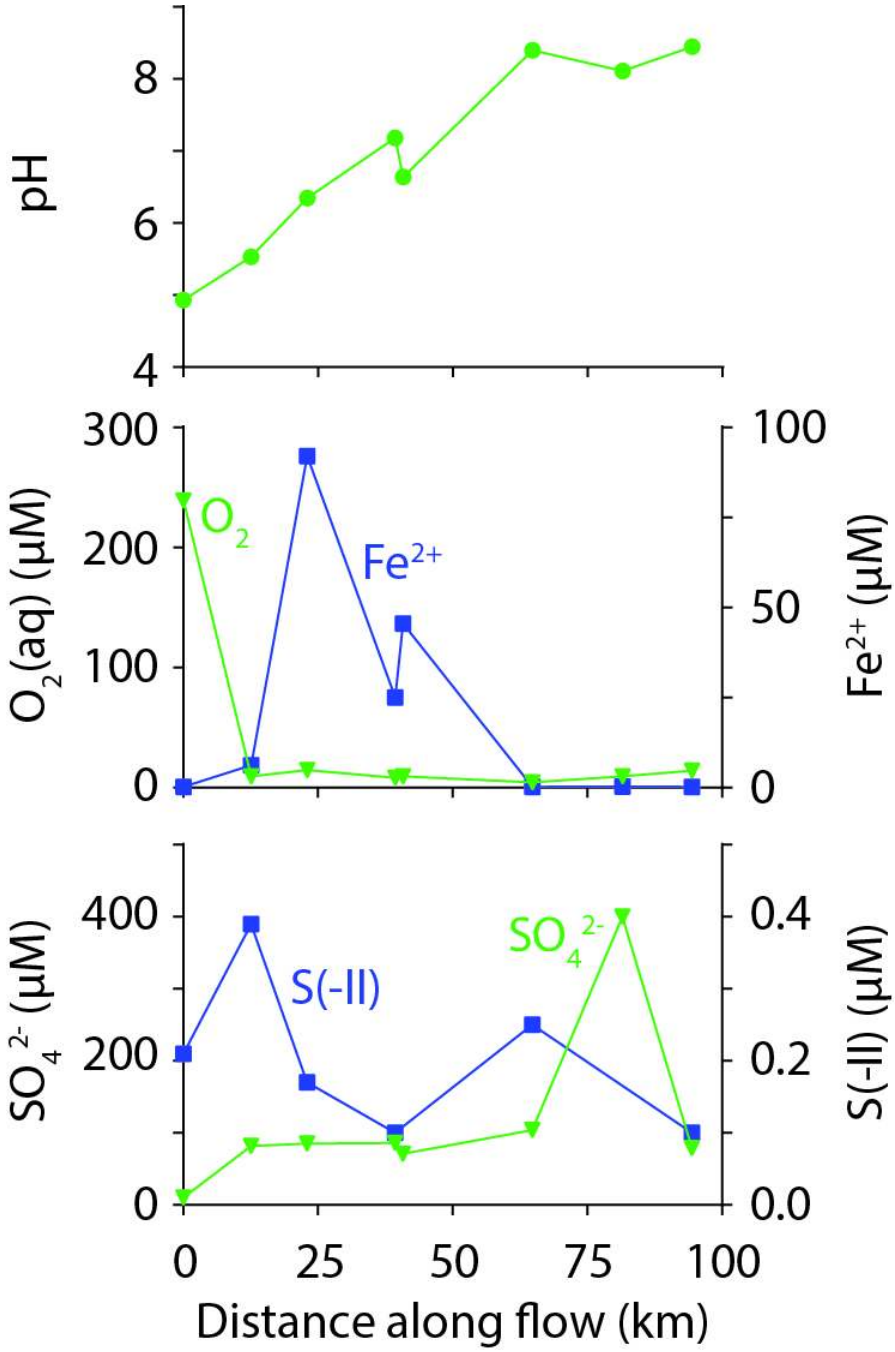


Figure **14.2**: Variation along flow in groundwater pH and concentrations of oxygen (O_2), ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and sulfide (S(-II)) in the Middendorf aquifer as measured by Park et al. (2006). Concentrations were below their detection limit for ferrous iron (0.2 μM) and sulfide (0.1 μM) for three and two samples, respectively. For those samples, detection limit concentrations are plotted. In addition, sulfide concentration was not determined for two samples, for which no scatter points are shown.
https://commons.wikimedia.org/wiki/File:Middendorf_groundwater_chemistry_from_Park_et_al._(2006)_chemical_geology.jpg

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14.3: Surface water quality

14.3.1: Connections to groundwater

14.3.2: Algal blooms

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14.3.1: Connections to groundwater

Surface water is hydrologically connected to groundwater in most landscapes (Winter, 1999; Winter et al., 1998) (Fig. **14.3**). Groundwater can discharge into surface water bodies, implying that microbial processes that impact groundwater quality also affect surface water quality. Alternatively, surface water can recharge the subsurface and become groundwater, in which case microbial impacts on surface waters help determine groundwater quality. Interactions can also go both ways, with the direction of interactions varying spatially, along a stream for example, or temporally, depending on factors such as climatic conditions, groundwater pumping, and so forth. Thus, we can think of groundwater and surface water as two conditions of one resource, with considerable overlap in the microbial impacts on water quality within each.

Some constraints on microbial activity differ between surface waters and groundwater. The presence of sunlight at the surface makes it possible for phototrophs to grow, and indeed annual solar inputs are one of the major drivers of metabolism in surface waters (Bernhardt et al., 2022). Oxygenic phototrophs can generate oxygen directly within the surface waters, and oxygen and other gases can also exchange with the atmosphere. As such, dissolved oxygen concentration is generally higher within the water column of surface waters compared to groundwater. Microbial populations in surface waters also experience more dynamic conditions than their subsurface counterparts, with variation at the surface contributed by daily cycles of light and darkness, seasonal cycles, precipitation events, floods, droughts, and more. Lastly, residence times of water within surface water bodies are often shorter than that of groundwater in the subsurface, affecting the time available for microbial reactions to alter water chemistry (Zeglin et al., 2019).

Where groundwater and surface water mix, a region known as the hyporheic zone, microorganisms are often particularly active (Boulton et al., 2003; Dahm et al., 1998; Krause et al., 2011) (Fig. **14.3**). Naegeli and Uehlinger (1997), for example, found that the hyporheic respiration contributed between 76% and 96% of the ecosystem respiration in the gravel-bed river they studied. Mixing within hyporheic zones can stimulate microbial activity by providing resource mixtures that are not available to microorganisms living in the stream or deeper in the subsurface (Stegen et al., 2018, 2016). For example, groundwater and surface water can both supply organic compounds to the hyporheic zone, but the composition of those compounds and their concentrations may differ between each water source. Where that is the case, the mixture provides a wider the range of opportunities available to hyporheic zone chemoorganotrophs (Stegen et al., 2018). As a second example, groundwater with reduced solutes can mix with oxic surface waters in the hyporheic zone, creating opportunities for chemolithotrophic microorganisms, including those that oxidize sulfide, ferrous iron ($Fe(II)$), and ammonium (Dahm et al., 1998).

In terms of water quality impacts, hyporheic zone microbial activity serves as an important control on nutrient fluxes (Dahm et al., 1998). Hyporheic zones can be a source of nitrate or a sink for nitrate, depending on the proportions of nitrification and denitrification within them. One of the factors that determines that proportion is the residence time of water within the hyporheic zone, with longer residence times favoring greater denitrification (Zarnetske et al., 2011). Hyporheic zones can also be an important control point for transport of some hazardous trace elements, like arsenic. For example, oxidation of reduced metals within the hyporheic zone can cause (oxyhydr)oxide minerals to form, which can sorb arsenic and numerous other solutes (Bone et al., 2006; Charette and Sholkovitz, 2002; Datta et al., 2009; Kirk et al., 2009). The impacts of these microbial reactions on water quality are not just important for the streams where they occur but also for any downstream water bodies that the streams feed.

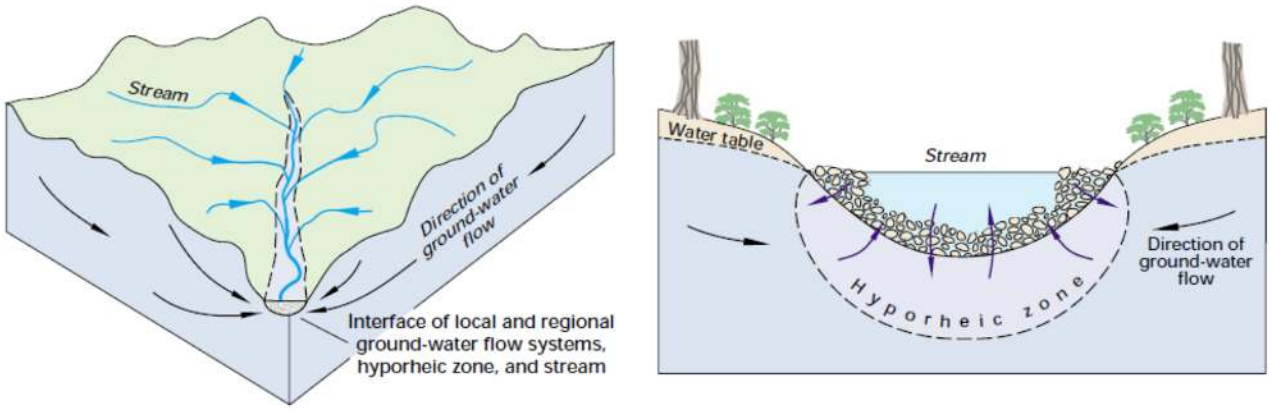


Figure **14.3**: Schematic illustration of groundwater and surface waters coming together within streambeds from Winter et al. (Winter et al., 1998). Exchanges between surface water and groundwater are temporally and spatially variable and can be driven by stream meandering, abrupt changes in streambed slope, changes in the elevation of the water table, and variation in the height of water within the stream channel (i.e., stage).
Image source: https://pubs.er.usgs.gov/publication/cir1139

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14.3.2: Algal blooms

As a final consideration for surface waters, we highlight the growing importance of algal blooms as a control on water quality. An algal bloom is the rapid increase in the population of algae in a surface water body. The term ‘algae’ encompasses multiple groups of oxygenic phototrophic organisms and some animal-like protozoans that do not have the availability to photosynthesize on their own (Anderson et al., 2002). They can be unicellular or multicellular and most live in water, where they can be free-floating (i.e., planktonic) or attached to surfaces (i.e., sessile). Eukaryotic algae include microalgae such as coccolithophores, diatoms, and dinoflagellates as well as large multicellular algae commonly known as ‘seaweed’. Among bacteria, many authors consider *Cyanobacteria* to be algae because they often share the same habitats as eukaryotic algae and have a similar lifestyle (Friedl et al., 2011).

Algae play large roles globally as cyclers of nutrients and producers of organic matter and oxygen, but dense algal growth can have significant negative impacts. Degradation of dead algal biomass can deplete oxygen from water, creating zones where fish, shellfish, and other aerobic organisms cannot live. These zones are known as dead zones. Moreover, some algae release toxins that are harmful to humans and other animals. Blooms of these toxin-producing algae are known as harmful algal blooms (HABs) (Fig. **14.4**). These negative impacts are costly. In the US alone, freshwater algal blooms are estimated to have resulted in economic losses of more than four billion US dollars annually (Ho et al., 2019).

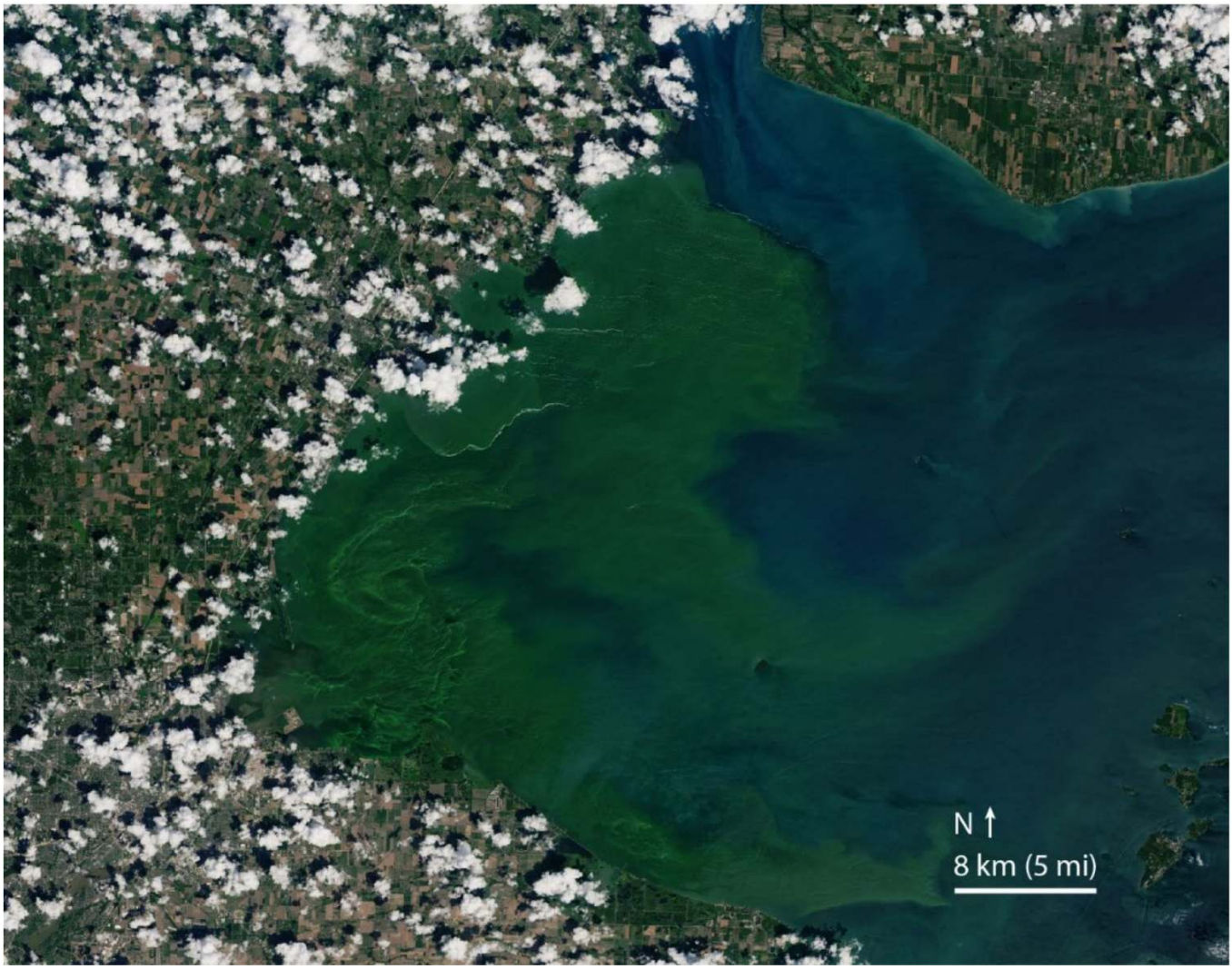


Figure **14.4**: Landsat 8 satellite image of a harmful algal bloom in the western end of Lake Erie during summer 2019. The dominant organism in the bloom was a cyanobacterium that produces the toxin microcystin, which can cause liver damage, numbness, dizziness, and vomiting. This image was captured on July 30, 2019. By August 13 of 2019, the algae had spread across 1606 km^2 (620 mi^2) of the lake surface.
Image source: https://earthobservatory.nasa.gov/images/145453/eerie-blooms-in-lake-erie

The occurrence of HABs is not a new phenomenon, but there is a perception that nutrient pollution and climate change may be increasing their occurrence. That perception may reflect intensified monitoring efforts and increased aquaculture production (Hallegraeff et al., 2021). Based on a statistical analysis of HAB occurrence in marine waters from 1985 to 2018, Hallegraeff et al. (2021) concluded that there was no uniform global trend in bloom occurrence or distribution. In contrast, in terrestrial waters, Ho et al. (2019) observed evidence for a global increase in the occurrence and intensity of blooms in large lakes. Moreover, several other studies have documented that HABs are occurring more frequently in new and different places and over longer durations (Glibert, 2020). Thus, evidence exists for increasing trends in some regions, even if the picture remains less clear for overall global trends.

Nutrients such as nitrate and phosphate contaminate groundwater and surface water in many watersheds used for agricultural activities. Nutrients can also be delivered to surface waters via discharge of treated wastewater and atmospheric deposition, particularly in areas downwind from major cities (Duce et al., 2008; Galloway et al., 2008). The extent to which these nutrients impact algal growth depends on the amounts delivered but also their forms and proportions. Changes in the composition of nutrient loads, for example, have been found to correlate with shifts in algal community composition (Anderson et al., 2002; Glibert, 2020), which in turn can impact levels of toxicity.

Example climate change impacts that can affect algal blooms include changes to water temperature and composition (Glibert, 2020). Water temperature helps determine which species grow within a bloom because different species have different temperature

optima (see Section 6.2.1). Increasing temperature is expected to favor greater growth of cyanobacteria and green algae relative to diatoms and dinoflagellates (O'Neil et al., 2012; Visser et al., 2016). Increasing water temperature can also increase thermal stratification in surface waters and thereby improve water column stability, which has been found to favor growth of some toxic cyanobacterial species (Dale et al., 2006; O'Neil et al., 2012; Visser et al., 2016). Lastly, algal community composition is also sensitive to water chemistry, which is changing in response to increasing atmospheric carbon dioxide levels, variation in precipitation patterns, and other impacts associated with climate change (Glibert, 2020).

As an example of climate and nutrient influences on algal blooms, we consider findings of LaRoche et al. (1997), who examined controls on harmful 'brown tides' caused by intense blooms of *Aureococcos anophagefferens* in coastal waters along Long Island in the eastern United States. *A. anophagefferens* blooms have occurred periodically since the mid-1980s. Study findings indicate that their occurrence is controlled by variation in the proportions of dissolved organic and inorganic nitrogen, which in turn varied with the amount of groundwater discharge along the coast. Groundwater was interpreted to be the main source of inorganic nitrogen. Thus, when groundwater discharge was relatively high, inorganic nitrogen availability increased relative to organic nitrogen, which promoted growth of mixed algal assemblages. However, when groundwater discharge was relatively low, organic nitrogen availability increased relative to inorganic nitrogen, which favored growth of *A. anophagefferens*.

This study highlights how interactions between climate, human activities, and biogeochemical cycling can impact algal blooms and water quality. Use of fertilizers and urbanization increased nitrogen loadings in the study system over the past several decades, which increased its capacity to support algal growth. Relative proportions of inorganic and organic nitrogen in turn varied with microbial cycling and climatological controls on groundwater discharge. By identifying these relationships for the study area, the research improves the ability to predict when HABs are likely to occur (LaRoche et al., 1997).

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14.4: Examples of microbial impacts to chemical contaminants

Microbial activity can alter concentrations of a wide range of contaminants and ultimately cause water quality to degrade or improve. The subsections below provide examples for some common contaminants and the ways that they are influenced by microorganisms. This information is critical to developing strategies that use microorganisms to help clean contaminated water, which is the subject of the next section (Section 14.5).

14.4.1: Nitrate

14.4.2: Arsenic

14.4.3: Acid mine drainage

14.4.4: Chlorinated solvents

14.4.5: Petroleum hydrocarbons

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14.4.1: Nitrate

Nitrate contamination occurs in both surface water and groundwater and commonly originates from human activities, although natural accumulations of nitrate are also known (e.g., Walvoord et al., 2003). Point sources of nitrate, those originating from a single location, include nitrate-rich water discharged from wastewater treatment facilities and septic systems. 'Non-point' sources, those that are more diffuse, include application of nitrogen fertilizer on fields used to grow crops in rural areas. Nitrogen fertilizer can take multiple forms, but most often, it is applied as ammonium, which is then converted to nitrate by nitrifying bacteria (Böhlke, 2002).

The maximum contaminant level for nitrate in drinking water is $10\ \mathrm{mg/L}$ as nitrogen, as applied by the US Environmental Protection Agency (EPA). The World Health Organization (WHO) recommends a similar level at $50\ \mathrm{mg/L}$ as nitrate, which is equal to $11.3\ \mathrm{mg/L}$ as nitrogen. High levels are particularly hazardous for young children, because they can cause infant methemoglobinemia (i.e., blue baby syndrome), a condition in which the blood has a decreased oxygen-carrying capacity. It may also cause increased risks of some cancers and birth defects (Ward et al., 2018).

Contamination with hazardous levels of nitrate is common and has been document in water bodies all around the world (Bijay-Singh and Craswell, 2021). In the US, results of long-term monitoring of principal aquifers by scientists at the US Geological Survey found that nitrate concentrations exceed the US EPA maximum contaminant level in 4.4% of the 2,132 wells sampled (DeSimone et al., 2014). The researchers concluded that nitrate was the most common anthropogenic contaminant they detected.

Nitrate contamination often coexists with other contaminants (Böhlke, 2002; Mencio et al., 2016). In addition to fertilizer, herbicides and pesticides are often also applied to fields used to grow crops and can accumulate alongside nitrate in water. Production of hydrogen ions by nitrification causes water percolating through soils to become more acidic (Böhlke, 2002; Guo et al., 2010). Fluxes of water can also be altered in crop soils as a result of irrigation and/or disturbance of soil structure. In turn, altered acidity and water flux can increase mineral weathering and groundwater solute concentrations (Böhlke, 2002). Addition of nitrate to groundwater can also cause oxidation of minerals that house hazardous trace elements, including uranium and selenium, causing their concentrations to increase (Bailey et al., 2014; Gates et al., 2009; Nolan and Weber, 2015). Moreover, nitrate contamination can also help stimulate blooms of algae in surface waters, as noted previously (Section 14.3.2)

Microorganisms transform nitrogen among various forms, as detailed in Section 5.2. As a result, they can affect the extent to which nitrate can accumulate in water. Potential microbial pathways of nitrate removal include assimilation by plants and microorganisms, denitrification, dissimilatory nitrate reduction to ammonia (DNRA), and anaerobic ammonium oxidation (anammox) (Burgin and Hamilton, 2007). A disadvantage of DNRA is that the reaction produces ammonium, and thus reactive nitrogen remains present, which could transform back to nitrate if suitable electron acceptors become available. Denitrification avoids this disadvantage, but it can generate significant quantities of the potent greenhouse gas nitrous oxide (Section 13.5). Anammox removes reactive nitrogen without nitrous oxide production, and thus avoids both of these complications. The activity of anammox microorganisms is sensitive to interactions with other nitrogen cyclers (Section 10.2.3), but recent research suggests it may play a larger role in nitrate removal than previously recognized (Mosley et al., 2022). These microbial pathways are all anaerobic, though they can occur within anoxic microenvironments of otherwise oxic systems (Mosley et al., 2022; Zarnetske et al., 2012).

As an example study, we consider the results of Lane et al. (2020), who examined nitrate contamination in the Great Bend Prairie aquifer in south-central Kansas, USA. The aquifer is a water table aquifer that forms part of the High Plains aquifer. The study found that, over the past four decades, groundwater nitrate concentrations have increased considerably, with the largest increases in shallow portions of the aquifer beneath areas used to grow crops (Fig. **14.5**). Consistent with that result, nitrate isotope data demonstrated that the source of the nitrate is primarily nitrogen fertilizer. These results indicate that changes in nitrate concentration in the aquifer largely reflect land use at the surface. Beyond this source control, however, redox conditions help set the stage for nitrate accumulation.

Microbial nitrate removal pathways are all anaerobic, as noted above. In contrast, nearly all of the groundwater sampled by Lane et al. contained significant amounts of dissolved oxygen (avg. $141\ \mu\mathrm{M}$). Although oxygen levels are often lower in groundwater than surface water (Section 14.2.1), the groundwater in the Great Bend Prairie aquifer recharges relatively quickly through sandy soils that contain low dissolved organic carbon content, a potential electron donor source for microorganisms in the soil and subsurface.

Thus, the low supply of electron donors together with rapid inputs of oxic recharge prevent oxygen depletion from the groundwater and limit the extent of microbial nitrate removal. Taken together, the findings show the importance of redox state in determining the vulnerability of an aqueous system for nitrate contamination. Systems that are largely oxic with low supplies of electron donors are generally more vulnerable to nitrate accumulation than anoxic systems with more abundant electron donor supplies.

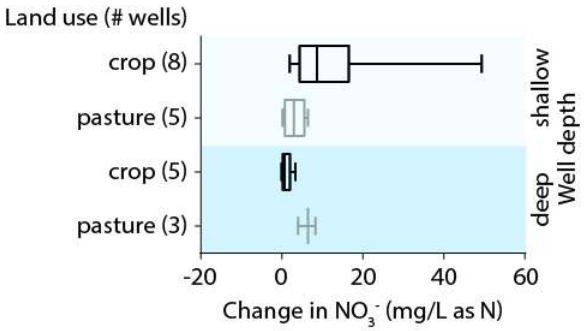


Figure **14.5**: Box plot showing changes in nitrate concentration between the 1970s and 2016 based on data from Lane et al. (2020). Boxes show the quartiles and whiskers show the range of values. Shallow wells have an average depth of 22 meters and are screened just below the water table in aquifer. Deep wells have an average depth of 41 meters and are screened near the aquifer base. Wells were sampled in areas used for crops and pastures, with the number of wells in each land use and depth category listed in parentheses.
https://commons.wikimedia.org/wiki/File:Changes_in_nitrate_concentration_measured_by_Lane_et_al._(2020)_Hydrogeol_J.jpg

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14.4.2: Arsenic

Like nitrate, arsenic is also a widespread contaminant that can occur in both surface water and groundwater. Unlike nitrate, however, arsenic contamination is usually caused by natural processes, with microorganisms playing central roles as discussed below. The maximum contaminant level for arsenic in drinking water is 10 µg/L as applied by the US EPA and recommended by the WHO. Consuming water with arsenic concentration above this level can cause disorders of the skin and vascular and nervous systems in addition to cancer (Hughes, 2002; Smith et al., 2000). Consumption of drinking water with high arsenic content is the main pathway of arsenic exposure, though exposure can also occur via ingestion of food (Podgorski and Berg, 2020).

Recent research estimates that 94 million to 220 million people worldwide are potentially exposed to hazardous arsenic levels through consumption of groundwater (Podgorski and Berg, 2020). Elevated arsenic concentrations have been identified all around the world, including Argentina, Bangladesh, Cambodia, China, India, Mexico, Pakistan, the US, and Vietnam (Podgorski and Berg, 2020). In the US, groundwater arsenic concentrations exceeded the 10 µg/L US EPA maximum contaminant level in 6.7% of all wells sampled during long term groundwater monitoring by the USGS (DeSimone et al., 2014).

Microorganisms can cause arsenic concentrations to increase or decrease by catalyzing parts of the iron cycle. One of the main mechanisms by which microorganisms can increase arsenic levels is by catalyzing iron reduction (Nickson et al., 2000). Recall that, when microorganisms reduce ferric iron (oxyhydr)oxides, they cause those minerals to dissolve (Section 11.4.1). Iron (oxyhydr)oxides have large surface areas that can strongly adsorb arsenic and other chemical components in aqueous systems and help hold arsenic to low levels (Smedley and Kinniburgh, 2002). Thus, when (oxyhydr)oxides dissolve during iron reduction, any arsenic and other solutes they contain can be released to the groundwater. Conversely, where microorganisms help form iron (oxyhydr)oxides by catalyzing ferrous iron oxidation (Section 12.1.3), arsenic can be sequestered by the freshly formed adsorption sites (Bone et al., 2006; Datta et al., 2009).

Similarly, microorganisms can increase or decrease arsenic concentrations by catalyzing parts of the sulfur cycle. Microorganisms can cause arsenic concentrations to increase by oxidizing sulfide minerals that contain arsenic (Schreiber et al., 2000). Conversely, where sulfate reduction is occurring, sulfide minerals can form that sequester arsenic and remove it from groundwater. Arsenic has the potential to precipitate as an arsenic sulfide phase such as orpiment (As_2S_3) and realgar (As_4S_4), or as an impurity within other metal sulfides, such as mackinawite, greigite, and pyrite (Burton et al., 2014; Huerta-Diaz and Morse, 1992; Kirk et al., 2010; Newman et al., 1997; Rittle et al., 1995).

In addition to these pathways, microorganisms can also affect arsenic concentrations via arsenic redox cycling and by arsenic methylation. Arsenic most commonly has either a $+3$ oxidation state (arsenite) or a $+5$ oxidation state (arsenate). Microorganisms catalyze transformations between the two oxidation states as a detoxification strategy or for energy capture (Oremland and Stolz, 2003). When microorganisms reduce arsenate to arsenite, they can decrease its ability to adsorb to (oxyhydr)oxide minerals, and cause dissolved arsenic concentration to increase (Burnol et al., 2007; Zobrist et al., 2000). Conversely, arsenite oxidation to arsenate increases arsenic removal by sorption if (oxyhydr)oxides are available to provide sorption sites (Karn et al., 2017).

Arsenic methylation occurs when microorganisms transfer methyl group(s) onto inorganic arsenic (Bentley and Chasteen, 2002). Methylation is thought to serve as a detoxification mechanism (Oremland and Stolz, 2003) and can allow arsenic to volatilize, thus affecting arsenic mobility. Although methylation was largely thought to be restricted to surface waters and soils, Maguffin et al. (2015) estimated that methylation in aquifers has the potential to transform 100 tons of inorganic arsenic to methylated forms globally, which falls within the range of values estimated for soils.

The most common cases of large-scale arsenic contamination occur in groundwater and particularly in aquifers composed of relatively young alluvial sediment (Podgorski and Berg, 2020). Within these aquifers, arsenic is thought to be mainly released from aquifer sediment to groundwater as a result of microbial iron reduction (Nickson et al., 2000) with potential contributions from arsenate reduction. Moreover, arsenic concentrations tend to be spatially variable, with potential causes including heterogeneity in the distributions of sulfate reduction (Buschmann and Berg, 2009; Kirk et al., 2004; Rowland et al., 2006), surface flooding (Connolly et al., 2022), aquifer sediment age and organic matter reactivity (Buschmann et al., 2007; Postma et al., 2012), floodplain geomorphic features (Papacostas et al., 2008), groundwater recharge sources (Nghiem et al., 2019), and other geochemical and hydrologic factors.

As an example study, we consider results from Kirk et al. (2004), who studied arsenic in the Mahomet glacial aquifer in Illinois, USA. Groundwater sampled for the study was anoxic with pH ranging from about 7 to 8 and nitrate concentrations that were mostly below detection ($0.25\ mg/L$ as N). Dissolved arsenic existed almost entirely as arsenite ($As(III)$). Based on results from Kirk et al. and subsequent studies by Flynn et al. (2013, 2008), iron reduction appears to occur throughout most of the aquifer. Moreover, sulfate reduction occurs where sulfate is available and methanogenesis where sulfate concentrations are low.

Because iron and arsenate reduction can mobilize arsenic, these findings imply that arsenic is being released from aquifer sediment throughout the aquifer. However, Kirk et al. (2004) only observed hazardous levels of arsenic in groundwater that contained little sulfate (Fig. 14.6). They interpreted that, under those conditions, arsenic can accumulate because sulfate reducers are not active and thus no sulfide minerals can form and remove arsenic from the groundwater.

In addition to arsenic, ferrous iron and methane concentrations were also higher on average in sulfate-limited zones (Fig. 14.6). Methane accumulation there was interpreted to occur because sulfate limitation prevented sulfate reducers from outcompeting methanogens for electron donors (Section 9.6). Higher iron concentrations likely also occurred there for the same reason as arsenic. Specifically, in the absence of sulfate reduction, no sulfide is available to precipitate iron as a sulfide mineral.

These findings highlight the importance of considering not only the sources of solutes to aqueous systems but also the sinks for those solutes, when considering controls on solute distributions. Although arsenic release from aquifer solids by iron and/or arsenate reduction is clearly a necessary step for arsenic contamination to develop, sulfate reduction can be the main factor that determines whether arsenic concentrations can increase to hazardous levels in an aquifer (Kirk et al., 2004).

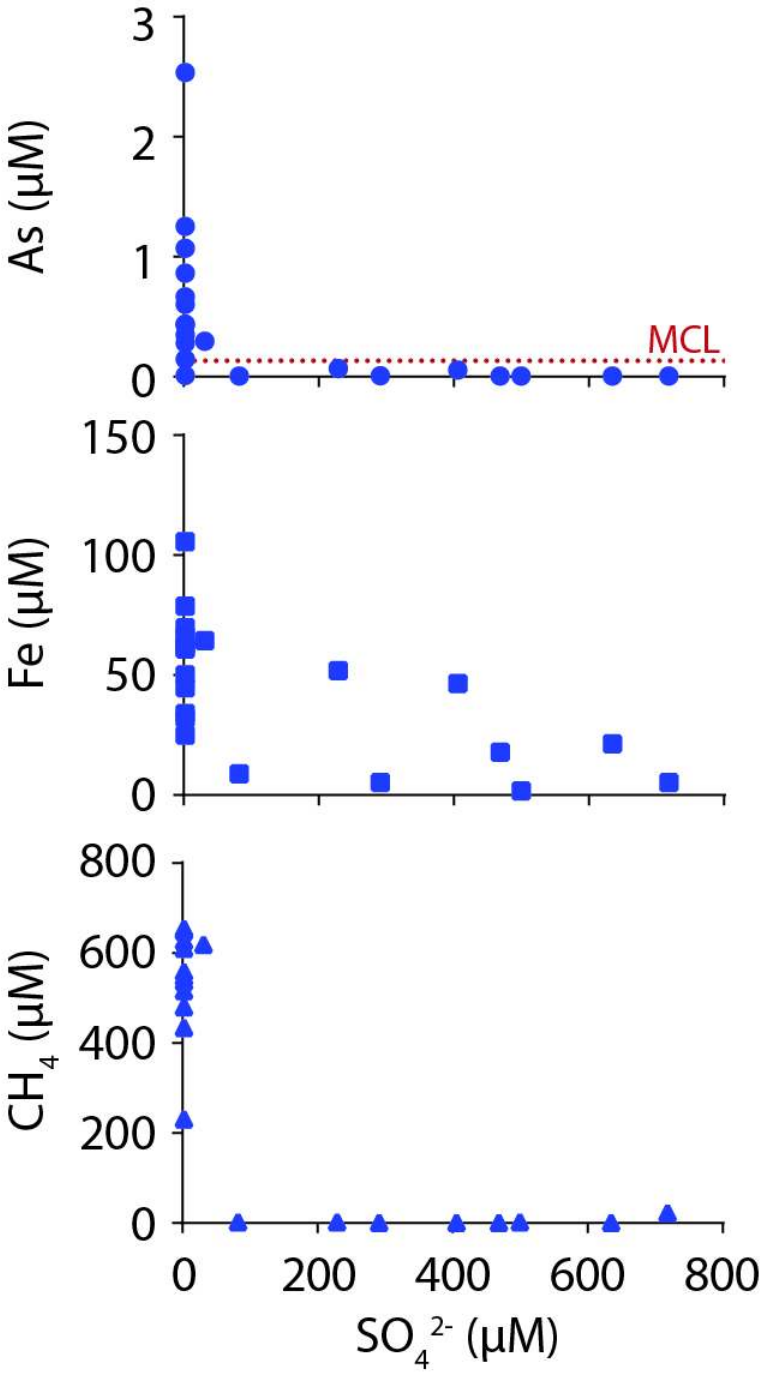


Figure **14.6**: Variation with sulfate concentration in total dissolved arsenic, iron, and methane concentrations in the Mahomet aquifer. Data plotted are from Kirk et al. (2004). Given the pH of the groundwater samples, dissolved iron is expected to be nearly entirely composed of ferrous iron because ferric iron has low solubility at near neutral pH. The plot with arsenic includes a dotted red horizontal line corresponding to the US EPA maximum contaminant level (MCL) for public drinking water supplies ($10\ \mu g/L = 0.133\ \mu M$). For samples with concentrations below the detection limits of the methods used for the study, detection limit values are plotted.
https://commons.wikimedia.org/wiki/File:Mahomet_aquifer_geochemistry_results.jpg

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14.4.3: Acid mine drainage

Acid mine drainage forms when water percolates through mining-impacted rock that contains sulfide minerals exposed to oxygen. Oxidation of those minerals produces hydrogen ions, which can drive the pH of the solution to acidic levels. In addition to acid, the water can also contain elevated concentrations of sulfate and numerous metals and metalloids, including arsenic, cadmium, cobalt, chromium, mercury, manganese, molybdenum, nickel, lead, and zinc (Newsome and Falagán, 2021; Nordstrom, 2011), creating a threat to the quality of nearby surface water and groundwater. Most acid mine drainage has pH between 2 and 6 (Nordstrom et al., 2015), although much lower values have been observed. In one of the most extreme cases, pH values as low as -2.5 have been measured in water with elevated concentrations of sulfate ($760,000\ mg/L$), iron ($111,000\ mg/L$), and several trace elements at the Richmond Mine at Iron Mountain, California, USA (Nordstrom, 2011; Nordstrom et al., 2000). Acid mine drainage exists within most countries worldwide and its source and toxicity has been recognized for thousands of years (Nordstrom, 2011).

Oxidation is thought to initiate with direct reaction between sulfide minerals and oxygen, which can be described with the following reaction in which sulfide minerals are represented by pyrite (FeS_2) (Nordstrom et al., 2015):

$$FeS_2 + 3.5\ O_2\ (aq) + H_2O \longleftrightarrow 2\ SO_4^{2-} + Fe^{2+} + 2\ H^+ \tag{14.4.3.1}$$

The ferrous iron ($Fe(II)$) produced by the reaction may subsequently oxidize to ferric iron ($Fe(III)$):

$$Fe^{2+} + H^+ + 0.25\ O_2\ (aq) \longleftrightarrow Fe^{3+} + 0.5\ H_2O \tag{14.4.3.2}$$

In a solution with near-neutral pH, ferrous iron oxidation can occur rapidly without the aid of microbial catalysis. The ferric iron produced can then form mixed (oxyhydr)oxide phases with variable stoichiometries including ferrihydrite ($Fe_5HO_8 \cdot 4\,(H_2O)$), goethite ($FeOOH$), schwertmannite ($Fe_{16}O_{16}(OH)_y\,(SO_4)_z \cdot n\,(H_2O)$), and jarosite ($KFe_3\,(SO_4)_2\,(OH)_6$) (Nordstrom and Southam, 1997). Such precipitates typically coat the beds of streams receiving mining impacted water, providing a vivid signal of the presence of acid mine drainage (Fig. 14.7).



Figure 14.7: Acid mine drainage flowing away from the collapsed entrance to the Davis Mine pyrite mine near Rowe, Massachusetts, USA. The mine was active from 1882 to 1911, after which the mine filled with water and began generating acidic drainage (Becerra et al., 2009). Near the mine entrance, drainage pH is near 2, and outside of the waste rock area, pH ranges from about 4.5 to 6 (Becerra et al., 2009).
Image source: https://commons.wikimedia.org/wiki/File:AMD_at_the_Davis_Mine.jpg

Combining reaction 14.4.3.1 with reactions for iron oxidation (reaction 14.4.3.2 and goethite precipitation gives the following overall net reaction (Nordstrom et al., 2015):

$$FeS_2 + 3.75\ O_2 + 2.5\ H_2O \longleftrightarrow 2\ SO_4^{2-} + FeOOH + 4\ H^+ \qquad (14.4.3.3)$$

Thus, the overall reaction generates four moles of hydrogen ions per mole of pyrite, which works to drive the pH of the environment downward to acidic levels.

Under acidic conditions, the pathway of sulfide mineral oxidation changes. Ferric iron solubility increases and dissolved ferric iron ions become more effective than oxygen as an oxidant for pyrite (Moses et al., 1987). In fact, in systems with pH below 3, ferric iron is the only important oxidizer of pyrite (Konhauser, 2007). An example net reaction can be written as follows:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \longleftrightarrow 2\ SO_4^{2-} + 15\ Fe^{2+} + 16\ H^+ \qquad (14.4.3.4)$$

In the reaction, ferric iron is reduced to ferrous iron. Thus, for the reaction to continue moving forward, ferric iron needs to be resupplied by ferrous iron oxidation (reaction 14.4.3.2). As such, oxygen remains an important ingredient because of its role in ferrous iron oxidation. Alternatively, ferrous iron oxidation could also be coupled with nitrate reduction if nitrate is available (Section 5.3.2).

As the reaction pathways shift with conditions, so do the contributions of microorganisms. Under near-neutral pH conditions, iron-oxidizing microorganisms may be involved (Percak-Dennett et al., 2017) although they are not thought to play a critical role because ferrous iron can rapidly oxidize without catalysis (Nordstrom et al., 2015). However, at acidic pH, ferrous iron oxidation is slow unless microbially catalyzed. Under these conditions, microorganisms can speed up the reaction by five orders of magnitude (Nordstrom et al., 2015). In doing so, they can resupply ferric iron and push pyrite oxidation forward (Fig. **14.8**). Without this push, pyrite oxidation would stop because ferrous iron oxidation is too slow at acidic pH (Nordstrom, 2011). Thus, iron-oxidizing microorganisms not only speed up pyrite oxidation but also help sustain it under acidic conditions.

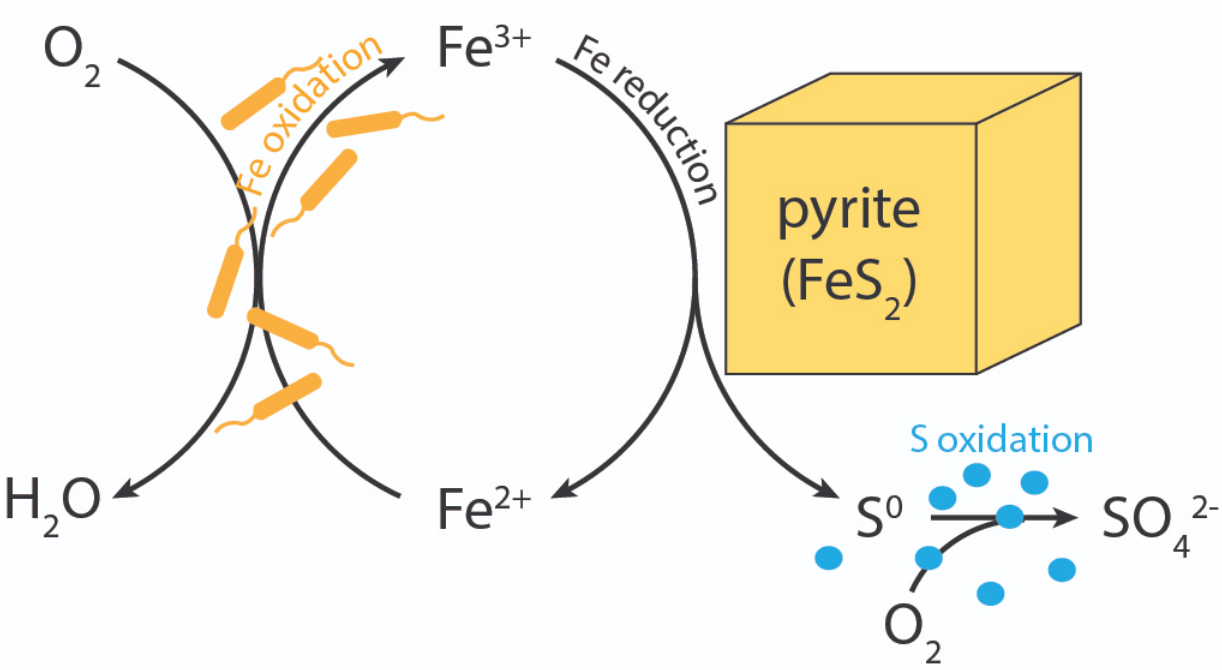


Figure **14.8**: Schematic illustration pyrite weathering under acidic conditions (e.g., below pH 4.5) by iron- and sulfur-oxidizing microorganisms. Elemental sulfur (S^0) represents one of multiple intermediate sulfur species that can be produced by sulfide oxidation. In addition to oxygen (O_2), iron-oxidizing microorganisms can also couple ferrous iron oxidation to nitrate reduction. This figure is based on figure 3 of Newsome and Falagán (2021).
Image source: https://commons.wikimedia.org/wiki/File:AMD_conceptual_model.jpg

In addition to iron oxidizers, sulfide oxidizers are also influential. In fact, pyrite oxidation has been found to be faster in experiments that contain iron- and sulfur-oxidizing microorganisms rather than just iron oxidizers (McGuire et al., 2001; Nordstrom and Southam, 1997). Intermediate reactions during sulfide mineral oxidation produce multiple sulfur species, including elemental sulfur (S^0), thiosulfate (S_2O_3), polythionates ($S_xO_6^{2-}$), and more. Sulfur oxidizers consume these intermediates and prevent their accumulation in solution and on mineral surfaces (McGuire et al., 2001) (Fig. **14.8**). Moreover, reactions catalyzed by sulfur oxidizers generate acid that benefits the acidophilic microorganisms that are responsible for driving sulfide mineral weathering forward (Banfield and Welch, 2000).

Although some microorganism help drive production of acid mine drainage, others can help clean up the contamination (Becerra et al., 2009; Coggon et al., 2012). Acid mine drainage is ultimately caused by oxidative weathering of sulfide minerals. Thus, the negative impacts of acidic drainage can be reversed by re-forming those minerals under conditions where they are not exposed to oxidation. Microorganisms can cause sulfide minerals to form where they catalyze reduction of ferric iron and sulfate (Section 12.1.4). The reactions consume hydrogen ions and thus help neutralize acid (Section 14.2.1). Moreover, the sulfide minerals that form sequester iron and sulfur, as well as hazardous trace elements (Fortin and Beveridge, 1997). Thus, microbial production of sulfide biominerals can lessen impacts of acid mine drainage in much the same way that it can lower arsenic concentrations in naturally contaminated aquifers (Section 14.4.2).

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14.4.4: Chlorinated solvents

Chlorinated solvents are relatively common contaminants that can cause significant adverse health effects. There are numerous compounds that fall within the category of chlorinated solvents. Here we focus on two of the most common, perchloroethylene (PCE) and trichloroethylen (TCE), as well as their degradation products (Table **14.1**). These solvents have numerous commercial and industrial uses, including use in dry cleaning and as degreasing agents and can be added to soil and groundwater from point sources, including improper disposals, accidental spills, and leaks from storage reservoirs (DeSimone et al., 2014). Groundwater contaminated with chlorinated solvents most commonly occurs at shallow depths under urban areas, reflecting their uses (DeSimone et al., 2014). Consumption of water contaminated with these solvents has been linked to liver, kidney, nervous system, and circulatory problems and increased risks of cancer. As such, US EPA maximum contaminant levels for these solvents are set to very low concentrations (see Table **14.1**).

Table **14.1**: Composition and maximum contaminant levels for some common chlorinated solvents

Chlorinated solvent	Acronym	Formula	MCL* ($\mu g/L$)
Tetrachloroethylene	PCE	C_2Cl_4	5
Trichloroethylene	TCE	C_2HCl_3	5
1,1-Dichloroethylene	1,1-DCE	$C_2H_2Cl_2$	7
cis-1,2-Dichloroethylene	cis-DCE	$C_2H_2Cl_2$	70
trans-1,2-Dichloroethylene	trans-DCE	$C_2H_2Cl_2$	100
Vinyl chloride	VC	C_2H_3Cl	2

*US EPA maximum contaminant levels (MCLs) for public water systems available at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Organic

Chlorinated solvents exist as dense non-aqueous phase liquids (DNAPLS) that sink through the subsurface until they encounter low-permeability sediment or bedrock (Fig. **14.9**). Dissolution of the DNAPL components into the adjacent groundwater creates an aqueous phase contaminant plume. Some of the DNAPL can also volatilize, forming a vapor plume in the unsaturated pore space overlying the water table.

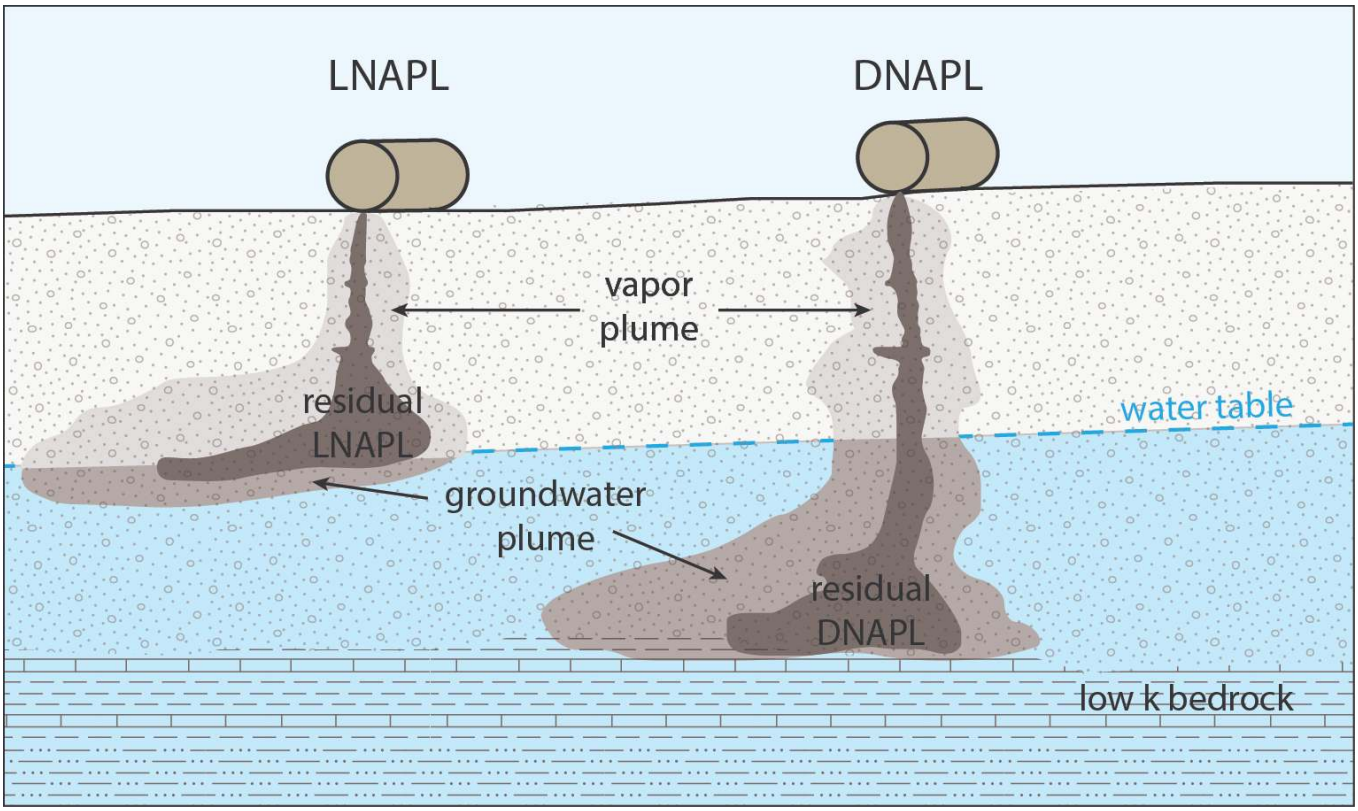


Figure **14.9**: Schematic illustration of the spreading of light non-aqueous phase liquid (LNAPL) and dense non-aqueous phase liquid (DNAPL) in the subsurface. LNAPLs are less dense than water and thus can accumulate at the water table. In contrast, DNAPLs are denser than water and thus can sink below the water table until they encounter a low permeability (k) surface. Both LNAPLs and DNAPLs volatilize and dissolve, creating vapor and groundwater plumes, respectively.
https://commons.wikimedia.org/wiki/File:NAPLs.jpg

PCE and TCE are resistant to degradation under oxic conditions. Under anoxic conditions, However, microorganisms can degrade chlorinated solvents through what is referred to as organohalide respiration (Adrian and Löffler, 2016). Although we often think of organic compounds as potential electron donors, some can also serve as terminal electron acceptors, and that is the case for chlorinated solvents. Microorganisms can oxidize organic electron donors or dihydrogen and transfer the electrons to chlorinated solvents (Debruin et al., 1992). As an example, the following reaction describes dihydrogen oxidation coupled with reduction of PCE to TCE:

$$C_2Cl_4 + H_2 \longleftrightarrow C_2HCl_3 + H^+ + Cl^- \quad (14.4.4.1)$$

Under ideal conditions, microorganisms remove the chlorine atoms from organohalides in stepwise reactions that ultimately produce ethylene (C_2H_4), which is nontoxic (Lee et al., 1998) (Fig. **14.10**). However, the reactions can also stall at harmful intermediates such as cis-DCE or VC (Table **14.1**), allowing their concentrations to increase.

Organohalide respiring bacteria are widespread, possibly reflecting the fact that some organohalides occur naturally at low concentrations in diverse environments (Adrian and Löffler, 2016). However, bacterial genus *Dehalococcoides* is the only group known to contain species capable of completing the final steps of degradation, that is reduction of cis-DCE to VC and then to ethylene (Atashgahi et al., 2016). Thus, factors that influence growth of members of this genus can in turn determine the extent of degradation. Among those factors, the availability of dihydrogen seems to be particularly important, given that all isolated obligate organohalide reducers and many facultative organohalide reducers use dihydrogen as an electron donor (Richardson, 2016). Moreover, acetate availability is also important because it is required as a carbon source by some organohalide reducers including *Dehalococcoides* (Richardson, 2016). Both dihydrogen and acetate are produced by fermenting microorganisms in anoxic environments, and thus their roles in organohalide degradation are essential.



Figure **4.10**: Sequential removal of chlorine during organohalide respiration with dihydrogen as the electron donor. Acronyms are defined in Table **14.1**. At each step, two electrons from dihydrogen oxidation are added to the organohalide, reducing it and causing its chlorine atoms to be replaced by hydrogens.
https://commons.wikimedia.org/wiki/File:Organohalide_respiration.jpg

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14.4.5: Petroleum hydrocarbons

As a final contaminant example, we consider the fate of another class of organic contaminants: petroleum hydrocarbons. Substances composed of petroleum hydrocarbons include crude oil, gasoline, aviation fuel, and diesel fuel. Petroleum hydrocarbons that are particularly concerning for water quality are benzene, toluene, ethylbenzene, and xylenes, which are known collectively by the acronym BTEX (Table **14.2**). These compounds are among the most soluble fractions of crude oil and can cause several adverse health effects, including some cancers, as a result of long-term exposure (Nadim et al., 2000). Additional concerns include methyl tertiary-butyl ether (MTBE), which is a gasoline additive that was phased out in the early 2000s. There is no national drinking water standard in the US for MTBE, though it is regulated in the state of California, with a maximum contaminant level of **13** μ**g/L**.

Table **14.2**: Composition and maximum contaminant levels for BTEX

Compound	Formula	MCL* (μg/L)
Benzene	C_6H_6	5
Ethylbenzene	C_8H_{10}	700
Toluene	C_7H_8	1,000
Xylenes (total)	C_8H_{10}	10,000

**US EPA maximum contaminant levels (MCLs) for public water systems available at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Organic

Petroleum hydrocarbons generally enter soil and groundwater from point sources. Natural petroleum seeps can form where petroleum leaks from the deep subsurface into terrestrial and marine environments. One well known example is the La Brea Tar Pits in California, USA, where oil that formed within the Los Angeles Basin has been naturally discharging at the surface for thousands of years (Fig. **14.11**). Anthropogenic point sources include leakage from underground storage tanks and leaks or spills that occur during processing and transport (Nadim et al., 2000). Petroleum hydrocarbons have been used in a variety of settings over many years and thus sites contaminated by human activity are widespread. For example, brownfield sites are locations where contamination with hazardous substances restricts how the land can be used. Of the 450,000 brownfield sites recognized by the US EPA across the US, about one half are impacted by petroleum, and of those, most are contaminated by leaking underground storage tanks at old gas stations (US EPA, 2022).

Petroleum hydrocarbons are low density non-aqueous phase liquids (LNAPLs), allowing them to float on water. They can pool at the surface of aquatic habitats such as streams and lakes. Where they are added to unsaturated soils and sediments, they can sink into the subsurface until they hit the water table, where they can spread out (Fig. **14.9**). Like DNAPLs, they can also volatilize into gas phases and dissolve into water.

Numerous groups of chemotrophic microorganisms can degrade petroleum hydrocarbons by using them as electron donors (Mindorff et al., 2023). Degradation can occur under oxic or anoxic conditions. However, degradation is more rapid and complete where oxygen is available as an electron acceptor (Das and Chandran, 2011), consistent with the differences between aerobic and anaerobic organic matter degradation rates discussed in Section 7.5.1. Among other controls, the composition of the hydrocarbons themselves and their physical properties can also affect degradation rates (Leahy and Colwell, 1990). Microorganisms tend to preferentially degrade the less complex hydrocarbon molecules within a mixture, causing it to become heavier and more viscous over time (Head et al., 2003). In terms of physical properties, LNAPL surface area is a key factor in determining how much of an LNAPL mass is exposed to degradation (Leahy and Colwell, 1990).



Figure 14.11: Tar bubble in the La Brea Tar Pits in Los Angeles, California USA.
Image by Daniel Schwen: https://commons.wikimedia.org/wiki/File:USA_tar_bubble_la_brea_CA.jpg

To illustrate these relationships further, we consider some findings of past research at a site contaminated by crude oil near Bemidji, Minnesota, USA. As described by Essaid et al. (2009), the site was contaminated in 1979 when a high pressure crude oil pipeline burst and spilled about 1,700,000 liters of crude oil onto a glacial outwash deposit. Crude oil also sprayed onto a 6,500 m^2 area of soil, which is referred to as the spray zone. After the leakage occurred, some of the crude oil was recovered, but approximately 400,000 liters remained in the soil and subsurface, where it began percolating down toward the water table. Oil trapped in the unsaturated zone and floating on the water table has been a continuous source of hydrocarbon contamination ever since the leakage occurred (Essaid et al., 2009).

Since 1983, USGS scientists and collaborators from numerous institutions have used the Bemidji site to better understand the fate and natural attenuation of crude oil contamination. Findings show that the residual LNAPL has a complex distribution, reflecting variation in the dispersal of oil at the surface, the complexities of flow through porous media, and mass loss via microbial degradation over time. Some of the oil remains in the unsaturated zone though the highest densities occur near the water table, where it has migrated downgradient several tens of meters (Fig. 14.12).

Within groundwater adjacent to the residual LNAPL, five geochemical zones are recognized (Fig. 14.12) (Essaid et al., 2009):

- Zone 1 contains uncontaminated groundwater with high dissolved oxygen levels.
- Zone 2 is below the spray zone and is characterized by low dissolved oxygen levels and high concentrations of inorganic and organic carbon.
- Zone 3 is immediately beneath and downgradient of the floating oil and consists of anoxic groundwater with high levels of hydrocarbons, reduced manganese (Mn^{2+}) and iron (Fe^{2+}), and methane.
- Zone 4 is just outside of Zone 3 and contains intermediate oxygen levels and low concentrations of hydrocarbons.
- Zone 5 is just outside of Zone 4 and contains high dissolved oxygen levels and concentrations of hydrocarbons that are slightly higher than background levels.

Similarly, unsaturated zone gas adjacent to the residual LNAPL contains three geochemical zones (Fig. 14.12) (Essaid et al., 2009):

- Zone 6 gas contains about 20% oxygen, consistent with the atmosphere.
- Zone 7 represents a transitional zone with 10 to 20% oxygen, hydrocarbon gas concentrations below 1 part per million (ppm), and elevated carbon dioxide (0 to 10%) and methane (0 to 10%) concentrations.

- Zone 8 is anoxic gas immediately above the oil body that contains high levels of carbon dioxide (>10%), methane (>10%), and hydrocarbon gases (>1 ppm).

These geochemical zones are consistent with the redox zonation model discussed in Section 8.5. Microbial populations in the zone nearest the residual LNAPL (zones 3, 8), have had the greatest access to petroleum hydrocarbons, which serve as a rich source of electron donors. High amounts of electron donor consumption there over time has driven the microbial community the furthest along the thermodynamic ladder in their electron acceptor usage. The most favorable electron acceptor, oxygen, has been depleted and the microorganisms have turned to less favorable alternatives. Accumulations of reduced manganese and iron in zone 3 are caused by microbial (oxyhydr)oxide reduction. Methane accumulation occurs in response to microbial methanogenesis. Compared to zones 3 and 8, the supply of hydrocarbon electron donors has been lower in zones 2, 4, and 7. As a result, microbial populations within them have not moved as far along the thermodynamic ladder as they have in zones 3 and 8. Oxygen remains available to support aerobic degradation of hydrocarbons in zones 2, 4, and 7, though the oxygen concentrations are lower than they are in uncontaminated zones (zones 1, 6).

Spatial extents of these geochemical zones have been relatively stable over time, suggesting that plume degradation has reach an equilibrium between the rates at which hydrocarbons are supplied to groundwater and the rates at which they are being removed by microbial oxidation (Delin et al., 1998). However, the extent and composition of these zones will inevitably evolve in the future as supplies of residual LNAPL migrate and deplete and (oxyhydr)oxide coatings are reductively dissolved from outwash mineral grains (Essaid et al., 2009).

Taken together, the findings summarized above demonstrate that microorganisms can successfully attenuate crude oil contamination given sufficient time. They do this by coupling the oxidation of petroleum hydrocarbons with the reduction of available electron acceptors. The patterns in electron acceptor usage that emerge are consistent with environmental controls on microbial activity and the end result, low concentrations of petroleum hydrocarbons, is beneficial for water quality.

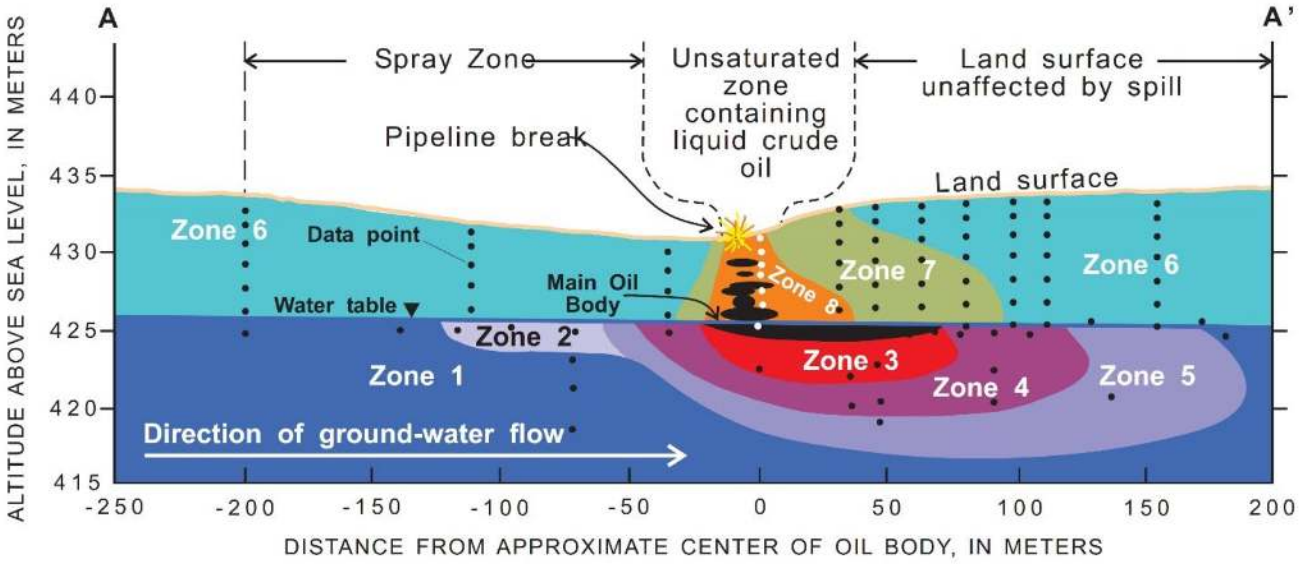


Figure **14.12**: Subsurface geochemical zones identified in groundwater and the unsaturated zone at the Bemidji north oil pool site. This figure was taken from USGS Fact Sheet 084-98 (Delin et al., 1998).

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14.5: Applying microbiology to remediate contaminated water

In this final section, we consider how we can use knowledge from this book to design strategies for remediating contaminants in aqueous systems. We focus our attention on the use of sulfate reduction as a strategy for remediating arsenic contamination. This example is just one of a virtually endless number of possibilities. However, it allows us to illustrate the basic approach to developing a microbial bioremediation strategy, which readers may then apply to other contaminants.

The basic premise of bioremediation is centered around the two-way interactions between microorganisms and their environments. We must first consider microbial impacts on their environments by asking: what change(s) in microbial activity would decrease the concentration of the contaminant? Then, we consider the ways environments control microbial activity by asking: what can we alter about the environment that can bring about those change(s) in microbial activity?

Regarding the first question, there may be multiple answers. Some microorganisms in a community may increase contaminant levels, in which case the desired change might involve decreasing their activities. Other microorganisms in a community may decrease contaminant levels, in which case the goal may be do increase their activities. A bioremediation strategy might leverage one of both of these possibilities, depending on the extents to which they are attainable.

Regarding the second question, it may be possible to do nothing, and simply let an indigenous microbial community clean up the contaminant over time, as is occurring at the Bemidji site. This approach is referred to as natural attenuation. Alternatively, we may want to speed up contaminant attenuation by increasing the activity of select groups. We can refer to this approach as enhanced bioremediation, which we may be able to achieve via biostimulation and/or bioaugmentation. Biostimulation enhances growth of select microbial populations by altering conditions, such as the availability of nutrients or energy resources. Bioaugmentation occurs when we add microorganisms to the environment to give added functional capabilities to a community. For example, bioaugmentation is used at some chlorinated solvent sites to increase the abundance and activity of *Dehalococcoides*, the only group of bacteria known to be able to complete the final steps of dechlorination (Section 14.4.4).

Applying these questions to arsenic contamination, we can see that multiple approaches may be possible. Iron-reducing microorganisms are the main group responsible for mobilizing arsenic. Thus, our strategy might involve decreasing their activity. Alternatively, iron oxidizers and sulfate reducers can reduce arsenic mobility by forming mineral phases that can sequester arsenic, so we might seek to increase their activities. Of these possibilities, stimulating sulfate reducers may be simplest and most cost effective. In many contaminated aquifers, arsenic levels are only elevated in zones where the microbial community has exhausted the supply of sulfate (Section 14.4.2). Thus, we may be able stimulate growth of sulfate reducers within these zones simply by dissolving a sulfate salt such as gypsum in water and then injecting it into the contaminated zones of an aquifer (Kirk et al., 2004).

Researchers recently tested this approach at an industrial site contaminated with arsenic-based herbicides in Florida, USA (Lee et al., 2019; Saunders et al., 2018). Previous attempts with conventional techniques stabilized the arsenic plume at the site but arsenic concentrations remained high, ranging from about 300 to 1,000 µg/L. Alongside these elevated arsenic concentrations, sulfate concentrations were low. Thus, the researchers aimed to stimulate sulfate-reducing activity by injecting sulfate into the aquifer. In addition to sulfate, the researchers also injected organic electron donors and iron to ensure the availability of key ingredients needed to rapidly generate sulfide biominerals. Within one week of the injection, significant growth of sulfate reducers began to occur, which persisted for at least two months following injection. In response to their growth, pyrite crystals began forming that contained 0.05 to 0.4 weight percent arsenic. Precipitation of these minerals lowered dissolved arsenic concentrations to below 50 µg/L for about six months, until untreated upgradient water displaced the treated groundwater being sampled at their monitoring wells. Overall, however, more than 90% of the dissolved arsenic was removed during the treatment period, demonstrating a strong potential of this strategy as an arsenic bioremediation technique.

Microbial bioremediation strategies such as that described here for arsenic are often more cost effective and sustainable than conventional treatment strategies. For example, a common approach for cleaning up a groundwater contaminant is known as pump-and-treat, in which groundwater is pumped out of a contamination plume, treated, and then discharged (Mackay and Cherry, 1989). This strategy can lower contamination levels, but it may require decades and enormous costs to reach safe levels. Alternatively, in situ microbial solutions may require less energy inputs and infrastructure development. They may even just take over on their own, as is the case with natural attenuation. By considering the two-way interactions between microorganisms and their environments, many such opportunities will be identified and used to achieve sustainable positive goals in the years to come.

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14.6: Concept Check Questions

1. Why does groundwater tend to become less acidic and more reduced as it flows away from recharge areas?
2. Where would you expect nitrate to be less likely to accumulate: an aquifer that contains oxygenated groundwater and hosts aerobic bacteria, or one that is anoxic and hosts iron reducers and sulfate reducers?
3. How would you expect the potential for nitrate contamination in groundwater to change if more organic carbon were added to an agricultural soil?
4. What is adsorption? How do microbes affect the ability of ions to sorb? Why could this negatively affect water quality?
5. How do microorganisms influence arsenic mobility in the Mahomet aquifer? Why are arsenic and methane concentrations elevated where sulfate concentrations are low in the aquifer? Why are arsenic and methane concentrations low where sulfate is available?
6. How do microorganisms enhance the rate of pyrite oxidation at acid mine drainage sites? Would their role be different initially, while pH is near neutral, compared to later on, after conditions become acidic?
7. Could sulfate-reducing microorganisms be useful in remediating acid mine drainage? Would you need to supply sulfate to stimulate their activity? If not, what other approaches might you take to achieve that goal?
8. How are chlorinated solvents degraded by microbes? How does this differ from degradation of crude oil? Are both primarily used as electron donors by microbes?
9. Imagine that a groundwater contaminant becomes less mobile when it is reduced by a microbial reaction. How might you take advantage of this relationship and stimulate microbial reduction of a contaminant within an aquifer?

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14.7: References

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CHAPTER OVERVIEW

15: Appendix A- Thermodynamic Data for Select Reactions

15.1: Redox Reactions

15.2: Gas Solubility Reactions

15.3: Mineral Reactions

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15.1: Redox Reactions

donor	acceptor	Reaction		as a function of temperature
$H_2\ (aq)$	O_2	$H_2(aq) + .5\ O_2(aq) = H_2O$	46.1129	$\log K = 50.49 - .1885T + .000563 - 1.194e - 6T^3 + 1.11e -$
$H_2\ (aq)$	NO_3^-	$H_2(aq) + .4\ H^+ + .4\ NO_3^- = 1.2\ H_2O + .2\ N_2(aq)$	44.565	$\log K = 48.71 - .1796T + .000592 - 1.329e - 6T^3 + 1.33e -$
$H_2\ (aq)$	NO_3^-	$H_2(aq) + NO_3^-(aq) = H_2O + NO_2^-$	30.7997	$\log K = 33.65 - .1224T + .000361 - 7.786e - 7T^3 + 7.78e -$
$H_2\ (aq)$	NO_2^-	$H_2(aq) + .6667\ H^+ + .6667\ NO_2^- = 1.333\ H_2O + .3333\ N_2(aq)$	53.7419	$\log K = 58.76 - .2177T + .000747 - 1.695e - 6T^3 + 1.698e$
$H_2\ (aq)$	NO_3^-	$H_2(aq) + .5\ NO_3^- + .5\ H^+ = .25\ N_2O + 1.25\ H_2O$	40.3459	$\log K = 44.06 - .1599T + .000468 - 8.663e - 7T^3 + 0T^4$
$H_2\ (aq)$	NO_2^-	$H_2(aq) + NO_2^- + H^+ = .5\ N_2O + 1.5\ H_2O$	49.8921	$\log K = 54.48 - .1974T + .000575 - 1.015e - 6T^3 + 0T^4$
$H_2\ (aq)$	NO_3^-	$H_2(aq) + .5\ H^+ + .25\ NO_3^- = .75\ H_2O + .25\ NH_4^+$	32.8798	$\log K = 35.94 - .1322T + .000413 - 8.769e - 7T^3 + 8.101e$
$H_2\ (aq)$	$Fe(OH)_3(s)$	$H_2(aq) + Fe(OH)_3(s) + 4\ H^+ = 6\ H_2O + 2\ Fe^{2+}$	38.9153	$\log K = 42.77 - .167T + .0005475 - 1.046e - 6T^3 + 6.45e -$
$H_2\ (aq)$	$FeOOH(s)$	$H_2(aq) + 2\ Goethite + 4\ H^+ = 4\ H_2O + 2\ Fe^{2+}$	30.1371	$\log K = 33.4 - .1412T + .0004465 - 8.129e - 7T^3 + 4.075e$
$H_2\ (aq)$	Fe_2O_3	$H_2(aq) + Hematite + 4\ H^+ = 3\ H_2O + 2\ Fe^{2+}$	29.1806	$\log K = 32.52 - .144T + .0004374 - 7.77e - 7T^3 + 3.669e -$
$H_2\ (aq)$	SO_4^{2-}	$H_2(aq) + .5\ H^+ + .25\ SO_4^{2-} = H_2O + .25\ H_2S(aq)$	13.2643	$\log K = 14.37 - .04823T + .00019 - 4.893e - 7T^3 + 5.265e$
$H_2\ (aq)$	CO_2	$H_2(aq) + .25\ CO_2 = .5\ H_2O + .25\ CH_4(aq)$	8.4944	$\log K = 9.387 - .03826T + 9.693e - 1.608e - 7T^3 + 7.808e$
CH_3COO^-	O_2	$CH_3COO^- + 2\ O_2(aq) = 2\ HCO_3^- + H^+$	146.7487	$\log K = 160.6 - .5958T + .001832 - 3.959e - 6T^3 + 3.773e$
CH_3COO^-	NO_3^-	$CH_3COO^- + .6\ H^+ + 1.6\ NO_3^- = 2\ HCO_3^- + .8\ N_2(aq) + .8\ H_2O$	140.5573	$\log K = 153.5 - .5601T + .001948 - 4.499e - 6T^3 + 4.654e$
CH_3COO^-	NO_3^-	$CH_3COO^- + 4\ NO_3^- = 2\ HCO_3^- + H^+ + 4\ NO_2^-$	85.4959	$\log K = 93.2 - .3313T + .001021T - 2.299e - 6T^3 + 2.445e$
CH_3COO^-	NO_2^-	$CH_3COO^- + 1.667\ H^+ + 2.667\ NO_2^- = 2\ HCO_3^-$	177.2648	$\log K = 193.6 - .7127T + .002566 - 5.966e - 6T^3 + 6.126e$

donor	acceptor	Reaction		as a function of temperature
		$+ 1.333\ N_2(aq)$ $+ 1.333\ H_2O$		
CH_3COO^-	NO_3^-	$CH_3COO^- + H^+$ $+ 2\ NO_3^- = N_2O(aq)$ $+ 2\ HCO_3^- + H_2O$	123.6807	$\log K = 134.9 - .4842T + .001503$ $- 2.917e - 6T^3 + 0T^4$
CH_3COO^-	NO_2^-	$CH_3COO^- + 4\ NO_2^-$ $+ 3\ H^+ = 2\ N_2O(aq)$ $+ 2\ HCO_3^- + 2\ H_2O$	161.8655	$\log K = 176.6 - .6343T + .00193$ $- 3.51e - 6T^3 + 0T^4$
CH_3COO^-	NO_3^-	$CH_3COO^- + H^+ + H_2O$ $+ NO_3^- = 2\ HCO_3^-$ $+ NH_4^+$	93.8161	$\log K = 102.4 - .3706T + .001232$ $- 2.692e - 6T^3 + 2.574e$
CH_3COO^-	$Fe(OH)_3(s)$	$CH_3COO^- + 15\ H^+$ $+ 8\ Fe(OH)_3(s)$ $= 2\ HCO_3^- + 20\ H_2O$ $+ 8\ Fe^{2+}$	117.9583	$\log K = 129.7 - .5098T + .001767$ $- 3.37e - 6T^3 + 1.913e -$
CH_3COO^-	$FeOOH(s)$	$CH_3COO^- + 15\ H^+$ $+ 8\ Goethite = 2\ HCO_3^-$ $+ 12\ H_2O + 8\ Fe^{2+}$	82.8455	$\log K = 92.23 - .4065T + .001363$ $- 2.436e - 6T^3 + 9.633e$
CH_3COO^-	$Fe_2O_3(s)$	$CH_3COO^- + 15\ H^+$ $+ 4\ Hematite = 2\ HCO_3^-$ $+ 8\ H_2O + 8\ Fe^{2+}$	79.0195	$\log K = 88.71 - .4179T + .001326$ $- 2.292e - 6T^3 + 8.009e$
CH_3COO^-	SO_4^{2-}	$CH_3COO^- + H^+ + SO_4^{2-}$ $= 2\ HCO_3^- + H_2S(aq)$	15.3544	$\log K = 16.11 - .03464T + .00035$ $- 1.141e - 6T^3 + 1.439e$
CH_3COO^-		$CH_3COO^- + H_2O$ $= HCO_3^- + CH_4(aq)$	2.6407	$\log K = 2.716 - .003792T + 6.667$ $- 1.036e - 7T^3 + 1.604e$
$HCOO^-$	O_2	$Formate + .5\ O_2(aq)$ $= HCO_3^-$	42.8054	$\log K = 46.92 - .1768T + .000542$ $- 1.183e - 6T^3 + 1.171e$
$HCOO^-$	NO_3^-	$Formate + .4\ H^+$ $+ .4\ NO_3^- = HCO_3^-$ $+ .2\ N_2(aq) + .2\ H_2O$	41.2575	$\log K = 45.14 - .1679T + .000571$ $- 1.318e - 6T^3 + 1.391e$
$HCOO^-$	NO_3^-	$Formate + NO_3^- = HCO_3^-$ $+ NO_2^-$	27.4922	$\log K = 30.07 - .1107T + .000339$ $- 7.675e - 7T^3 + 8.392e$
$HCOO^-$	NO_2^-	$Formate + .6667\ H^+$ $+ .6667\ NO_2^- =$ HCO_3^- $+ .3333\ N_2(aq)$ $+ .3333\ H_2O$	50.4344	$\log K = 55.19 - .2061T + .000725$ $- 1.684e - 6T^3 + 1.759e$
$HCOO^-$	NO_3^-	$Formate + .5\ NO_3^-$ $+ .5\ H^+ = .25\ N_2O(aq)$ $+ HCO_3^- + .25\ H_2O$	37.0384	$\log K = 40.5 - .1501T + .000489$ $- 1.079e - 6T^3 + 0T^4$
$HCOO^-$	NO_2^-	$Formate + NO_2^- + H^+$ $= .5\ N_2O(aq) + HCO_3^-$	46.5846	$\log K = 50.92 - .1876T + .000595$ $- 1.227e - 6T^3 + 0T^4$

donor	acceptor	Reaction		as a function of temperature
		$+ .5\ H_2O$		
$HCOO^-$	NO_3^-	$Formate + .25\ H_2O + .5\ H^+ + .25\ NO_3^- = HCO_3^- + .25\ NH_4^-$	29.5722	$\log K = 32.37 - .1205T + .000392 - 8.659e-7T^3 + 8.713e$
$HCOO^-$	$Fe(OH)_3(s)$	$Formate + 2\ Fe(OH)_3(s) + 4\ H^+ = HCO_3^- + 5\ H_2O + 2\ Fe^{2+}$	35.6078	$\log K = 39.2 - .1554T + .000526T - 1.035e-6T^3 + 7.062e$
$HCOO^-$	$FeOOH(s)$	$Formate + 2\ Goethite + 4\ H^+ = HCO_3^- + 3\ H_2O + 2\ Fe^{2+}$	26.8296	$\log K = 29.83 - .1295T + .000424 - 8.018e-7T^3 + 4.687e$
$HCOO^-$	$Fe_2O_3(s)$	$Formate + Hematite + 4\ H^+ = HCO_3^- + 2\ H_2O + 2\ Fe^{2+}$	25.8731	$\log K = 28.95 - .1324T + .000415 - 7.659e-7T^3 + 4.281e$
$HCOO^-$	SO_4^{2-}	$Formate + .5\ H^+ + .25\ SO_4^{2-} = HCO_3^- + .25\ H_2S(aq)$	9.9568	$\log K = 10.8 - .03656T + .000173 - 4.782e-7T^3 + 5.877e$
$HCOO^-$		$Formate + .25\ H_2O + .25\ H^+ = .75\ HCO_3^- + .25\ CH_4(aq)$	6.7784	$\log K = 7.453 - .02885T + .00010 - 2.188e-7T^3 + 2.283e$
$CH_3CH(OH)COO^-$	O_2	$Lactate + 3\ O_2(aq) = 2\ H^+ + 3\ HCO_3^-$	227.3625	$\log K = 248.7 - .9141T + .002658 - 5.509e-6T^3 + 5.093e$
$CH_3CH(OH)COO^-$	NO_3^-	$Lactate + .4\ H^+ + 2.4\ NO_3^- = 3\ HCO_3^- + 1.2\ H_2O + 1.2\ N_2(aq)$	218.0753	$\log K = 238 - .8606T + .00283T^2 - 6.318e-6T^3 + 6.414e$
$CH_3CH(OH)COO^-$	NO_3^-	$Lactate + 6\ NO_3^- = 2\ H^+ + 3\ HCO_3^- + 6\ NO_2^-$	135.4833	$\log K = 147.6 - .5174T + .00144T - 3.018e-6T^3 + 3.101e$
$CH_3CH(OH)COO^-$	NO_2^-	$Lactate + 2\ H^+ + 4\ NO_2^- = 3\ HCO_3^- + 2\ N_2(aq) + 2\ H_2O$	273.1367	$\log K = 298.3 - 1.089T + .003757 - 8.519e-6T^3 + 8.622e$
$CH_3CH(OH)COO^-$	NO_3^-	$Lactate + H^+ + 3\ NO_3^- = 1.5\ N_2O(aq) + 3\ HCO_3^- + 1.5\ H_2O$	192.7605	$\log K = 210.2 - .7483T + .002217 - 4.403e-6T^3 + 0T^4$
$CH_3CH(OH)COO^-$	NO_2^-	$Lactate + 6\ NO_2^- + 4\ H^+ = 3\ N_2O(aq) + 3\ HCO_3^- + 3\ H_2O$	250.0377	$\log K = 272.7 - .9734T + .002858 - 5.294e-6T^3 + 0T^4$
$CH_3CH(OH)COO^-$	NO_3^-	$Lactate + H^+ + 1.5\ H_2O + 1.5NO_3^- = 3\ HCO_3^- + 1.5\ NH_4^+$	147.9636	$\log K = 161.4 - .5763T + .001756 - 3.608e-6T^3 + 3.294e$
$CH_3CH(OH)COO^-$	$Fe(OH)_3(s)$	$Lactate + 22\ H^+ + 12\ Fe(OH)_3(s) = 3\ HCO_3^- + 30\ H_2O + 12\ Fe^{2+}$	184.1769	$\log K = 202.4 - .7852T + .002559 - 4.625e-6T^3 + 2.303e$

donor	acceptor	Reaction		as a function of temperature
$CH_3CH(OH)COO^-$	$FeOOH(s)$	$Lactate + 22\ H^+ + 12\ Goethite = 3\ HCO_3^- + 18\ H_2O + 12\ Fe^{2+}$	131.5077	$\log K = 146.2 - .6302T + .001953$ $- 3.224e - 6T^3 + 8.785e$
$CH_3CH(OH)COO^-$	$Fe_2O_3(s)$	$Lactate + 22\ H^+ + 6\ Hematite = 3\ HCO_3^- + 12\ H_2O + 12\ Fe^{2+}$	125.7687	$\log K = 140.9 - .6473T + .001899$ $- 3.008e - 6T^3 + 6.349e$
$CH_3CH(OH)COO^-$	SO_4^{2-}	$Lactate + H^+ + 1.5\ SO_4^{2-} = 3\ HCO_3^- + 1.5\ H_2S(aq)$	30.271	$\log K = 31.97 - .07238T + .00044$ $- 1.282e - 6T^3 + 1.592e$
$CH_3CH(OH)COO^-$		$Lactate = .5\ H^+ + 1.5\ CH_3COO^-$	7.2384	$\log K = 7.904 - .02817T + 6.867e$ $- 5T^2 - 1.268e - 7T^3 + 7$
$CH_3CH(OH)COO^-$		$Lactate + 6\ H_2O = 2\ H^+ + 3\ HCO_3^- + 6\ H_2(aq)$	-49.3149	$\log K = -54.26 + .217T - .00072$ $+ 1.653e - 6T^3 - 1.5673$
Fe^{2+}	O_2	$Fe^{2+} + 2.5\ H_2O + .25\ O_2(aq) = Fe(OH)_3(s) + 2\ H^+$	3.5988	$\log K = 3.862 - .01074T + 8.202e$ $- 7.366e - 8T^3 + 2.325e$
Fe^{2+}	NO_3^-	$Fe^{2+} + 2.4\ H_2O + .2\ NO_3^- = Fe(OH)_3(s) + 1.8\ H^+ + .1\ N_2(aq)$	2.8249	$\log K = 2.971 - .00629T + 2.26e -$ $- 1.411e - 7T^3 + 3.426e$
Fe^{2+}	NO_3^-	$Fe^{2+} + 2.625\ H_2O + .125\ NO_3^- = Fe(OH)_3(s) + 1.75\ H^+ + .125\ NH_4^+$	-3.0178	$\log K = -3.413 + .0174T - 6.691$ $+ 8.473e - 8T^3 + 8.257e$
H_2S	O_2	$H_2S(aq) + 2\ O_2(aq) = 2\ H^+ + SO_4^{2-}$	131.3943	$\log K = 144.5 - .5611T + .001475$ $- 2.818e - 6T^3 + 2.334e$
H_2S	NO_3^-	$H_2S(aq) + 1.6\ NO_3^- = .4\ H^+ + SO_4^{2-} + .8\ N_2(aq) + .8\ H_2O$	125.2029	$\log K = 137.4 - .5255T + .00159T$ $- 3.357e - 6T^3 + 3.214e$
H_2S	NO_3^-	$H_2S(aq) + H_2O + NO_3^- = SO_4^{2-} + NH_4^+$	78.4617	$\log K = 86.29 - .3359TT + .00087$ $- 1.551e - 6T^3 + 1.134e$
H_2S	$Fe(OH)_3(s)$	$H_2S(aq) + 14\ H^+ + 8\ Fe(OH)_3(s) = SO_4^{2-} + 20\ H_2O + 8\ Fe^{2+}$	102.6039	$\log K = 113.6 - .4752T + .001409$ $- 2.228e - 6T^3 + 4.739e$
H_2S	$FeOOH(s)$	$H_2S(aq) + 14\ H^+ + 8\ Goethite = SO_4^{2-} + 12\ H_2O + 8\ Fe^{2+}$	67.4911	$\log K = 76.12 - .3719T + .001005$ $- 1.294e - 6T^3 - 4.759e$
H_2S	$Fe_2O_3(s)$	$H_2S(aq) + 14\ H^+ + 4\ Goethite = SO_4^{2-} + 8\ H_2O + 8\ Fe^{2+}$	63.6651	$\log K = 72.6 - .3833T + .0009687$ $- 1.151e - 6T^3 - 6.383e$
CH_4	O_2	$CH_4(aq) + 2\ O_2(aq) = HCO_3^- + H^+ + H_2O$	144.108	$\log K = 157.9 - .592T + .001766T$ $- 3.856e - 6T^3 + 3.772e$
CH_4	NO_3^-	$CH_4(aq) + .6\ H^+$	137.9166	$\log K = 150.8 - .5563T + .001881$ $- 4.395e - 6T^3 + 4.652e$

e^- donor	e^- acceptor	Reaction	$\log K$ (25°C)	$\log K$ as a function of temperature
		$+ 1.6\ NO_3^- = HCO_3^-$ $+ .8\ N_2(aq) + 1.8\ H_2O$		
CH_4	$Fe(OH)_3(s)$	$CH_4(aq) + 15\ H^+$ $+ 8\ Fe(OH)_3(s) = HCO_3^-$ $+ 21\ H_2O + 8\ Fe^{2+}$	115.3176	$\log K = 127 - .506T + .0017T^2$ $- 3.266e - 6T^3 + 1.912e$
CH_4	$FeOOH(s)$	$CH_4(aq) + 15\ H^+$ $+ 8\ Goethite = 13\ H_2O$ $+ HCO_3^- + 8\ Fe^{2+}$	80.2048	Not available
CH_4	$Fe_2O_3(s)$	$CH_4(aq) + 15\ H^+$ $+ 4\ Hematite = 9\ H_2O$ $+ HCO_3^- + 8\ Fe^{2+}$	76.3788	$\log K = 85.99 - .4141T + .00126T$ $- 2.188e - 6T^3 + 7.993e$
CH_4	SO_4^{2-}	$CH_4(aq) + H^+ + SO_4^{2-}$ $= HCO_3^- + H_2S(aq)$ $+ H_2O$	12.7137	$\log K = 13.39 - .03084T + .00029$ $- 1.038e - 6T^3 + 1.438e$

*Most of the thermodynamic data were acquired from datasets available in The Geochemist's Workbench (GWB) software.

**The GWB program Rxn was used to obtain polynomial functions that can be used to estimate $\log K$ at various temperatures.

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15.2: Gas Solubility Reactions

Reaction	$\log K$ (25°C)	$\log K$ as a function of temperature**
$CO_2(aq) = CO_2(g)$	1.4524	$\log K = 1.134 + .01363T - 6.614e-5T^2 + 1.286e-7T^3 - 7.348e-11T^4$
$CH_4(aq) = CH_4(g)$	2.8202	$\log K = 2.657 + .007051T - 4.616e-5T^2 + 7.493e-8T^3 - 6.005e-11T^4$
$N_2O(aq) = N_2O(g)$	1.612	$\log K = 1.265 + .0151T - 5.16e-5T^2 + 1.152e-7T^3 + 0T^4$

*Most of the thermodynamic data were acquired from datasets available in The Geochemist's Workbench (GWB) software. In addition, data for reactions involving N_2O were provided by Dr. Robert Sanford.

**The GWB program Rxn was used to obtain polynomial functions that can be used to estimate $\log K$ at various temperatures.

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15.3: Mineral Reactions

Reaction	$\log K$ (25°C)	$\log K$ as a function of temperature**
$Mackinawite + 2\ H^+ = Fe^{2+} + H_2S(aq)$	3.1	Not available
$Sphalerite + 2\ H^+ = H_2S(aq) + Zn^{2+}$	−4.5135	$\log K = -4.448 - .002311T + .0001182T^2 - 4.113e-7T^3 + 4.104e-10T^4$
$Orpiment + 8\ H_2O = 3\ H_2S(aq) + 2\ H^+ + 2\ As(OH)_4^-$	−58.6085	$\log K = -63.3 + .2077T - .0004919T^2 + 5.21e-7T^3 - 9.242e-11T^4$
$Cinnabar + 2\ H^+ = H_2S(aq) + Hg^{2+}$	−32.0254	$\log K = -34.7 + .1156T - .0002475T^2 + 3.825e-7T^3 - 3.576e-10T^4$
$Siderite + H^+ = Fe^{2+} + HCO_3^-$	−0.2214	$\log K = .254 - .01936T + 9.481e-6T^2 + 1.171e-7T^3 - 4.124e-10T^4$
$Calcite + H^+ = Ca^{2+} + HCO_3^-$	1.713	$\log K = 2.069 - .01427T - 6.061e-6T^2 + 1.459e-7T^3 - 4.189e-10T^4$
$Amorphous\ silica = SiO_2(aq)$	−2.7136	$\log K = -2.991 + .01211T - 5.684e-5T^2 + 1.733e-7T^3 - 2.231e-10T^4$

*Most of the thermodynamic data were acquired from datasets available in The Geochemist's Workbench (GWB) software. In addition, mackinawite data are from Benning et al. (2000).

**The GWB program Rxn was used to obtain polynomial functions that can be used to estimate $\log K$ at various temperatures.

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    - 2.2: Evaluating phylogeny - *CC BY-SA 4.0*
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    - 2.4: Analyzing microbial populations using 16S rRNA genes - *CC BY-SA 4.0*
    - 2.5: Example analysis - *CC BY-SA 4.0*
    - 2.6: Viruses - *CC BY-SA 4.0*
    - 2.7: Concept Check Questions - *CC BY-SA 4.0*
    - 2.8: References - *CC BY-SA 4.0*
  - 3: Properties of Microorganisms - *CC BY-SA 4.0*
    - 3.1: Components of cells - *CC BY-SA 4.0*
    - 3.2: Cell morphology and size - *CC BY-SA 4.0*
    - 3.3: Gram-positive and gram-negative bacteria - *CC BY-SA 4.0*
    - 3.4: Bacterial sporulation - *CC BY-SA 4.0*
    - 3.5: Biofilms - *CC BY-SA 4.0*
    - 3.6: Cell growth - *CC BY-SA 4.0*
    - 3.7: Virions - *CC BY-SA 4.0*
    - 3.8: Concept Check Questions - *CC BY-SA 4.0*
    - 3.9: References - *CC BY-SA 4.0*
  - 4: Redox and Mechanism - *CC BY-SA 4.0*
    - 4.1: Redox basics - *CC BY-SA 4.0*
    - 4.2: Balancing redox reactions - *CC BY-SA 4.0*
    - 4.3: Metabolism - *CC BY-SA 4.0*
    - 4.4: Chemotrophy - *CC BY-SA 4.0*
    - 4.5: Phototrophy - *CC BY-SA 4.0*
    - 4.6: Answers to Practice Problems - *CC BY-SA 4.0*
    - 4.7: Concept Check Questions - *CC BY-SA 4.0*
    - 4.8: References - *CC BY-SA 4.0*
  - 5: Global Biogeochemical Cycles - *CC BY-SA 4.0*
    - 5.1: Carbon cycle - *CC BY-SA 4.0*
      - 5.1.1: Organic matter - *CC BY-SA 4.0*
      - 5.1.2: Aerobic and anaerobic respiration - *CC BY-SA 4.0*
      - 5.1.3: Fermentation and syntrophy - *CC BY-SA 4.0*
      - 5.1.4: Methanogenesis - *CC BY-SA 4.0*
      - 5.1.5: Acetogenesis - *CC BY-SA 4.0*
      - 5.1.6: Methanotrophy - *CC BY-SA 4.0*
    - 5.2: Nitrogen cycle - *CC BY-SA 4.0*
      - 5.2.1: Nitrogen fixation - *CC BY-SA 4.0*
      - 5.2.2: Ammonification - *CC BY-SA 4.0*
      - 5.2.3: Nitrification - *CC BY-SA 4.0*
      - 5.2.4: Anaerobic ammonia oxidation (anammox) - *CC BY-SA 4.0*
      - 5.2.5: Denitrification - *CC BY-SA 4.0*
      - 5.2.6: Dissimilatory nitrate reduction to ammonia (DNRA) - *CC BY-SA 4.0*
    - 5.3: Iron cycle - *CC BY-SA 4.0*
      - 5.3.1: Ferric iron reduction - *CC BY-SA 4.0*
      - 5.3.2: Ferrous iron oxidation - *CC BY-SA 4.0*
    - 5.4: Sulfur cycle - *CC BY-SA 4.0*
      - 5.4.1: Sulfate reduction - *CC BY-SA 4.0*
      - 5.4.2: Desulfurylation - *CC BY-SA 4.0*

- 5.4.3: Oxidation of sulfide and intermediate sulfur compounds - *CC BY-SA 4.0*
- 5.4.4: Reduction of intermediate sulfur compounds - *CC BY-SA 4.0*
- 5.4.5: Sulfur disproportionation - *CC BY-SA 4.0*
- 5.5: Concept Check Questions - *CC BY-SA 4.0*
- 5.6: References - *CC BY-SA 4.0*

6: Basic Environmental Controls - *CC BY-SA 4.0*
- 6.1: Categories of controls - *CC BY-SA 4.0*
- 6.2: Basic properties of the environment - *CC BY-SA 4.0*
  - 6.2.1: Temperature - *CC BY-SA 4.0*
  - 6.2.2: Pressure - *CC BY-SA 4.0*
  - 6.2.3: Oxygen - *CC BY-SA 4.0*
  - 6.2.4: pH - *CC BY-SA 4.0*
  - 6.2.5: Water availability - *CC BY-SA 4.0*
- 6.3: Transport processes - *CC BY-SA 4.0*
- 6.4: Environment stability - *CC BY-SA 4.0*
- 6.5: Dispersal mechanisms and barriers - *CC BY-SA 4.0*
- 6.6: Interactions between controls - *CC BY-SA 4.0*
- 6.7: Concept Check Questions - *CC BY-SA 4.0*
- 6.8: References - *CC BY-SA 4.0*

7: Nutrient and Energy Resources - *CC BY-SA 4.0*
- 7.1: Nutrients - *CC BY-SA 4.0*
- 7.2: Extracellular enzymes - *CC BY-SA 4.0*
- 7.3: Nutrient stoichiometry - *CC BY-SA 4.0*
- 7.4: Energy sources for phototrophs - *CC BY-SA 4.0*
- 7.5: Energy sources for chemotrophs - *CC BY-SA 4.0*
  - 7.5.1: Organic matter - *CC BY-SA 4.0*
  - 7.5.2: Reduced inorganic components of minerals - *CC BY-SA 4.0*
  - 7.5.3: Mantle degassing - *CC BY-SA 4.0*
  - 7.5.4: Serpentinization - *CC BY-SA 4.0*
  - 7.5.5: Radiolysis of water - *CC BY-SA 4.0*
  - 7.5.6: Silica radical-based reactions - *CC BY-SA 4.0*
  - 7.5.7: Trace atmospheric gases - *CC BY-SA 4.0*
- 7.6: Electroactive organisms - *CC BY-SA 4.0*
- 7.7: Concept Check Questions - *CC BY-SA 4.0*
- 7.8: References - *CC BY-SA 4.0*

8: Thermodynamic Controls - *CC BY-SA 4.0*
- 8.1: Mass action - *CC BY-SA 4.0*
- 8.2: Gibbs free energy - *CC BY-SA 4.0*
- 8.3: Impacts of changes in product and reactant activities - *CC BY-SA 4.0*
- 8.4: Available, captured, and usable energy - *CC BY-SA 4.0*
- 8.5: Redox zonation - *CC BY-SA 4.0*
- 8.6: Characterizing redox processes in aqueous systems - *CC BY-SA 4.0*
- 8.7: Answers to practice problems - *CC BY-SA 4.0*
- 8.8: Concept Check Questions - *CC BY-SA 4.0*
- 8.9: References - *CC BY-SA 4.0*

9: Kinetic Controls - *CC BY-SA 4.0*
- 9.1: Role of enzymes - *CC BY-SA 4.0*
- 9.2: Influence of pH and temperature on enzyme activity - *CC BY-SA 4.0*
- 9.3: Influence of substrate concentrations - *CC BY-SA 4.0*
- 9.4: Kinetic rate laws - *CC BY-SA 4.0*
- 9.5: Thermodynamic constraints on rates - *CC BY-SA 4.0*
- 9.6: Kinetic constraints on competition between sulfate reducers and methanogens - *CC BY-SA 4.0*
- 9.7: External controls on microbial reaction rates - *CC BY-SA 4.0*
- 9.8: Answers to practice problems - *CC BY-SA 4.0*
- 9.9: Concept Check Questions - *CC BY-SA 4.0*
- 9.10: References - *CC BY-SA 4.0*

10: Biological Environment - *CC BY-SA 4.0*
- 10.1: Microbial interactions - *CC BY-SA 4.0*
- 10.2: Example interactions - *CC BY-SA 4.0*
  - 10.2.1: Viral predation/parasitism of bacteria - *CC BY-SA 4.0*
  - 10.2.2: Mutualisms between plants and soil microorganisms - *CC BY-SA 4.0*
  - 10.2.3: Interactions of anammox microorganisms with other nitrogen cycles - *CC BY-SA 4.0*
  - 10.2.4: Interactions among iron and sulfur cycling microorganisms - *CC BY-SA 4.0*
  - 10.2.5: Interactions among iron reducers, methanogens, and methanotrophs - *CC BY-SA 4.0*
- 10.3: Spatial scales of interactions - *CC BY-SA 4.0*
- 10.4: Concept Check Questions - *CC BY-SA 4.0*
- 10.5: References - *CC BY-SA 4.0*

11: Mechanisms of Microbial Impacts - *CC BY-SA 4.0*
- 11.1: Catalyzing reactions - *CC BY-SA 4.0*
  - 11.1.1: Direct impacts - *CC BY-SA 4.0*
  - 11.1.2: Indirect impacts - *CC BY-SA 4.0*
  - 11.1.3: Practice - *CC BY-SA 4.0*
- 11.2: Generating biomass - *CC BY-SA 4.0*
- 11.3: Forming minerals - *CC BY-SA 4.0*
- 11.4: Dissolving minerals - *CC BY-SA 4.0*
  - 11.4.1: Redox mechanism - *CC BY-SA 4.0*
  - 11.4.2: Acid mechanism - *CC BY-SA 4.0*

- 11.4.3: Chelation mechanism - *CC BY-SA 4.0*
- 11.5: Answers to practice problems - *CC BY-SA 4.0*
- 11.6: Concept Check Questions - *CC BY-SA 4.0*
- 11.7: References - *CC BY-SA 4.0*

12: Impacts to the Lithosphere - *CC BY-SA 4.0*

- 12.1: Examples of biomineralization - *CC BY-SA 4.0*
  - 12.1.1: Carbonates - *CC BY-SA 4.0*
  - 12.1.2: Amorphous silica - *CC BY-SA 4.0*
  - 12.1.3: Iron (oxyhydr)oxides - *CC BY-SA 4.0*
  - 12.1.4: Sulfides - *CC BY-SA 4.0*
  - 12.1.5: Clay minerals - *CC BY-SA 4.0*
- 12.2: Microbial influence on marine sediments - *CC BY-SA 4.0*
- 12.3: Microbial influences on tectonic activity - *CC BY-SA 4.0*
- 12.4: Mineral evolution - *CC BY-SA 4.0*
- 12.5: Concept Check Questions - *CC BY-SA 4.0*
- 12.6: 12.6 References - *CC BY-SA 4.0*

13: Impacts to the Atmosphere - *CC BY-SA 4.0*

- 13.1: Oxygen - *CC BY-SA 4.0*
- 13.2: Trends in greenhouse gases - *CC BY-SA 4.0*
- 13.3: Carbon dioxide - *CC BY-SA 4.0*
- 13.4: Methane - *CC BY-SA 4.0*
- 13.5: Nitrous oxide - *CC BY-SA 4.0*
- 13.6: Responses of microorganisms to climate change - *CC BY-SA 4.0*
- 13.7: Managing greenhouse gas emissions - *CC BY-SA 4.0*
- 13.8: Answers to practice problems - *CC BY-SA 4.0*
- 13.9: Concept Check Questions - *CC BY-SA 4.0*
- 13.10: References - *CC BY-SA 4.0*

14: Impacts to the Hydrosphere - *CC BY-SA 4.0*

- 14.1: Pathogens - *CC BY-SA 4.0*
- 14.2: Groundwater quality - *CC BY-SA 4.0*
  - 14.2.1: Chemical evolution of groundwater - *CC BY-SA 4.0*
  - 14.2.2: Middendorf aquifer - *CC BY-SA 4.0*
- 14.3: Surface water quality - *CC BY-SA 4.0*
  - 14.3.1: Connections to groundwater - *CC BY-SA 4.0*
  - 14.3.2: Algal blooms - *CC BY-SA 4.0*
- 14.4: Examples of microbial impacts to chemical contaminants - *CC BY-SA 4.0*
  - 14.4.1: Nitrate - *CC BY-SA 4.0*
  - 14.4.2: Arsenic - *CC BY-SA 4.0*
  - 14.4.3: Acid mine drainage - *CC BY-SA 4.0*
  - 14.4.4: Chlorinated solvents - *CC BY-SA 4.0*
  - 14.4.5: Petroleum hydrocarbons - *CC BY-SA 4.0*
- 14.5: Applying microbiology to remediate contaminated water - *CC BY-SA 4.0*
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15: Appendix A- Thermodynamic Data for Select Reactions - *Undeclared*

- 15.1: Redox Reactions - *Undeclared*
- 15.2: Gas Solubility Reactions - *Undeclared*
- 15.3: Mineral Reactions - *Undeclared*

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