

INTRODUCTION TO MARINE SECOND EDITION BIOGEOCHEMISTRY

SUSAN M. LIBES



Introduction to Marine Biogeochemistry

Second Edition

Susan Libes

College of Natural and Applied Sciences
Coastal Carolina University
Conway, South Carolina



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Preface

Seawater covers nearly 71% of Earth's surface making the oceans, at least to us humans, the dominant feature of Planet Earth. International interest in utilizing and conserving this vast resource has given rise to undergraduate and graduate degree programs in oceanography. Most rely on curricula built upon a set of core courses that individually provide surveys of marine biology, geology, physics and chemistry. This text is designed for a one-semester survey in marine chemistry at the advanced undergraduate or introductory graduate level. Students are expected to have completed foundational course work in basic chemistry, biology, physics, and calculus along with an introductory course in marine science.

Segregating oceanographic disciplines for educational purposes has grown increasingly confining as research continues to confirm the importance of a multidisciplinary understanding of ocean processes. This has led to an appreciation of the critical role that the oceans play in regulating atmospheric and thereby, terrestrial processes. Of all the subdisciplines of oceanography, marine chemistry relies most heavily on a multidisciplinary approach, now referred to as marine biogeochemistry. This makes formulation of a suitable introductory textbook challenging given the enormous diversity of important topics and complexity of approaches now in use.

To capture the multidisciplinary nature of marine chemistry, this text highlights the ocean's role in the global biogeochemical cycling of elements that are key to regulation of climate and marine biology. The impact of humans on the oceans and climate is given special emphasis, as are some of the practical triumphs of applied marine biogeochemistry, namely petroleum prospecting and the development of marine natural products, such as drugs and food additives. Part I covers the hydrological cycle and basic physico-chemical processes including chemical speciation. Part II provides an introduction to redox chemistry in the context of microbial ecology. Part III considers how marine processes result in the formation of sediments and the role of the sediments in regulating the chemistry of seawater. Part IV constitutes a survey of the field of marine organic chemistry including coverage of the molecular composition, sources and sinks of organic compounds along with a discussion of the elemental cycling of carbon, nitrogen, oxygen, sulphur, and phosphorus. A comprehensive discussion of marine pollution is the subject of Part V. Special features of the text include: (1) a thematic emphasis on the marine cycling of iron to exemplify marine biogeochemical processes that provide feedbacks regulating global climate and that are thereby linked to terrestrial processes, (2) basic details on introductory chemical principles including equilibria, rate laws, redox energetics, and organic chemistry on an as needed basis, (3) advances in paleoceanographic reconstructions of past ocean chemistry, biology, sedimentology and climate, and (4) human impacts on the ocean including climate change and marine pollution.

By focusing on the "hot" areas of research in marine chemistry, I have attempted to communicate the sense of excitement and discovery that is an essential characteristic of

this relatively young and growing science. The nature of the “hot” topics has changed a bit since my writing of the first edition. Namely, the singular impacts of marine microbes on elemental cycling have come to be recognized as so powerful as to play a critical role in regulating climate and hence, indirectly, ocean circulation and terrestrial erosion rates. Conversely, physical processes, including oceanic circulation, hydrothermal activity, the production of flood basalts, and mountain building, have come to be recognized as having key impacts on ocean chemistry. These phenomena are now thought to have triggered important evolutionary shifts amongst the marine biota, including the Precambrian explosion of metazoans.

This book also includes a few aspects of marine analytical chemistry to address the operational nature of much of our data collection. This includes the use of remote sensing, such as satellite imagery, and in-situ sensing. Exciting advances in the latter include the use of submerged chemical detectors, such as mass spectrometers, and devices powered by natural redox processes, such as those occurring in marine sediments. Examples are provided of a particularly powerful and widespread approach—the use of naturally occurring stable and radioactive isotopes as tracers of biogeochemical processes. Artificial radionuclides, such as those introduced by bomb testing, have also proven to be excellent tracers of ocean circulation. This text seeks to give the reader enough of a background to pursue a more detailed study of this complicated topic.

Research efforts are now being urgently directed at understanding and mitigating the impacts of humans on the oceans as we have come to appreciate the truly global scope and scale of marine pollution and anthropogenically-driven climate change. The field of marine biogeochemistry is uniquely suited to help in this respect and hence represents a critical frontier of knowledge that can help us sustain ourselves and other life forms on planet Earth.

How to Use this Book

The study of marine chemistry is challenging but highly satisfying as you will use many of the skills and concepts learned in your basic science and math courses. Please be patient – true mastery takes time. Consider this text as a future reference book that you can return to long after graduation.

Useful features in the text include: (1) a glossary that defines technical terms, abbreviations, and acronyms, whose first appearance in the text is shown in *italic font*, (2) appendices containing various constants, equations, and conversion factors, and (3) a thorough index. Because we learn best from doing, this text has a companion website with resources to support a variety of active learning strategies (<http://elsevierdirect.com/companions/9780120885305>). Online features include: (1) a study guide, (2) homework problems, (3) supplemental content material, (4) a set of lengthy appendices containing geochemical and physical constants and other computational details, (5) color versions of figures as noted in the text's captions, and (6) a list of the full citations for works referenced in the text.

The supplemental content material available at the companion website is briefly described in the text at the relevant locations. For example, information on the evolution of the global carbon cycle over geologic time is briefly presented in Section 25.4 of the text as part of Chapter 25. A lengthier version of Section 25.4 is available online, and is so noted in the text. Text references to figures and tables that are available only online are labeled with a “W”. For example, Figure W25.14 is available only in the online supplemental material for Section 25.4.

Acknowledgements

Many others, besides me, spent long hours working on this textbook. My heartfelt thanks go to them and to my students who provided me with the necessary teaching experience as well as to my fellow faculty members who have been enthusiastic supporters and best friends. Coastal Carolina University has provided a stable and supportive environment since my arrival in 1983. Many administrators and staff have been instrumental in providing essential resources, particularly Paul Gayes, Rob Young, Pete and Betsy Barr, and CCU's librarians. My thanks also go to the editors and publisher of the first edition, John Wiley & Sons. The editors of the second edition, Frank Cynar, Philip Bugeau, Laura Kelleher, and Linda Versteeg of Elsevier Press, provided critical support including an unlimited online subscription to Science Direct! The following colleagues served as reviewers: Tom Tisue, Ron Kiene, Erin Burge, Kevin Xu, Brent Lewis, Paul Haberstroh, Margareta Wedborg, and Courtney Burge.

Important motivation for undertaking this second edition came from numerous highly vocal users of the first edition who have variously threatened and cajoled me since 2003. This effort turned out to be far more of an undertaking than anticipated and required drafting various family members into service, namely Lennie, who proof-read what she could understand and even stuff she couldn't, Sol, who kept me in functioning computers, Don, who served as my book agent, Prashant, who checked all the math and left me alone for very long periods of time, and last but not least, the three best kitties in the world, Prem, Kali and Moti.

My personal interest in marine biogeochemistry stems from my experiences in the early 1980s as a graduate student in the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography and Ocean Engineering where I had first-hand contact with many of the most active researchers in the field. My thanks and admiration goes to them all, as well as to all the researchers and publishers who generously granted permission to use their copyrighted figures and tables herein. It has truly been an honor and a pleasure to summarize and present to the next generation of biogeochemists, the depth and breadth of research now being conducted around the world by an increasingly numerous, diverse, sophisticated and highly dedicated group of marine biogeochemists.

Susan Libes
6/17/08

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PART

The Physical Chemistry of
Seawater

1

CHAPTER The Crustal-Ocean-Atmosphere Factory

1

All figures are available on the companion website in color (if applicable).

1.1 INTRODUCTION

The study of marine chemistry encompasses all chemical changes that occur in seawater and the sediments. The ocean is a place where biological, physical, geological, and chemical processes interact, making the study of marine chemistry very interdisciplinary and more appropriately termed *marine biogeochemistry*. Chemical approaches are now commonly used by marine biologists, marine geologists, and physical oceanographers in support of their research efforts. Likewise, oceanographers recognize the interconnectedness of Earth's hydrosphere with its atmosphere and crust, requiring that a true understanding of the ocean include consideration of its interactions with the rest of the planet. Also important are extraterrestrial forces, such as changes in solar energy and meteorites. For these reasons, this textbook covers topics that range far beyond the margins of the seashore and seafloor, as well as the boundaries of a classical study of chemistry.

1.2 WHY THE STUDY OF MARINE BIOGEOCHEMISTRY IS IMPORTANT

Most of the water on Earth's surface is in the ocean; relatively little is present in the atmosphere or on land. Because of its chemical and physical properties, this water has had a great influence on the continuing biogeochemical evolution of our planet. Most notably, water is an excellent solvent. As such, the oceans contain at least a little bit of almost every substance present on this planet. Reaction probability is enhanced if the reactants are in dissolved form as compared with their gaseous or solid phases. Many of the chemical changes that occur in seawater and the sediments are mediated by marine organisms. In some cases, marine organisms have developed unique biosynthetic pathways to help them survive the environmental conditions found only in the oceans. Some of their metabolic products have proven useful to humans as pharmaceuticals, nutraceuticals, food additives, and cosmeceuticals.

Another important characteristic of water is its ability to absorb a great deal of heat without undergoing much of an increase in temperature. This enables the ocean to act as a huge heat absorber, thereby influencing weather and climate.

Thus through many means, water sustains life, both marine and terrestrial. Scientific evidence supports the hypothesis that on Earth, life first evolved in a wet environment, such as an early ocean or submarine hydrothermal system. In turn, biological activity has had important effects on the chemical evolution of the planet. For example, the photosynthetic metabolism of plants is responsible for the relatively high concentration of oxygen gas (O_2) in our present-day atmosphere. Most of this oxygen was originally present as CO_2 emitted onto Earth's surface as part of volcanic gases. Over the millennia, photosynthesizers, such as marine phytoplankton, have converted this CO_2 into O_2 and organic matter (their biomass). Burial of their dead biomass (organic matter) in marine sediments has enabled O_2 to accumulate in the atmosphere. In this way, microscopic organisms have effected a global-scale transformation and transport of chemicals. This is only one example of many in which microscopic organisms serve as global bioengineers.

In studying the ocean, marine biogeochemists focus on exchanges of energy and material between the crust, atmosphere, and ocean. These exchanges exert a central influence on the continuing biogeochemical evolution of Earth. Particular concern is currently focused on the role of the ocean in the uptake and release of greenhouse gases, such as CO_2 . As part of the atmosphere, these gases influence solar heat retention and, hence, influence important aspects of climate, such as global temperatures, the hydrological cycle, and weather, including tropical storms. Exchanges of material between the land and sea control the distribution of marine life. For example, transport of nutrients from the nearby continents causes marine organisms to grow in greater abundance in coastal waters than in the open ocean. The exchange rates of many substances have been or are being altered by human activities. Thus, the study of marine chemistry has great practical significance in helping us learn how to use the ocean's vast mineral and biological resources in a sustainable fashion to ensure its health for future generations of humans and other organisms.

1.3 THE CRUSTAL-OCEAN-ATMOSPHERE FACTORY AND GLOBAL BIOGEOCHEMICAL CYCLES

As illustrated in Figure 1.1, the planet can be viewed as a giant chemical factory in which elements are transported from one location to another. Along the way, some undergo chemical transformations. These changes are promoted by the ubiquitous presence of liquid water, which is also the most important transporting agent on Earth's surface. It carries dissolved and particulate chemicals from the land and the inner earth into the ocean via rivers and hydrothermal vents. Chemical changes that occur in the ocean cause most of these materials to eventually become buried as sediments or diffuse across the sea surface to accumulate in the atmosphere. Geological processes uplift marine sediments to locations where terrestrial weathering followed by river transport

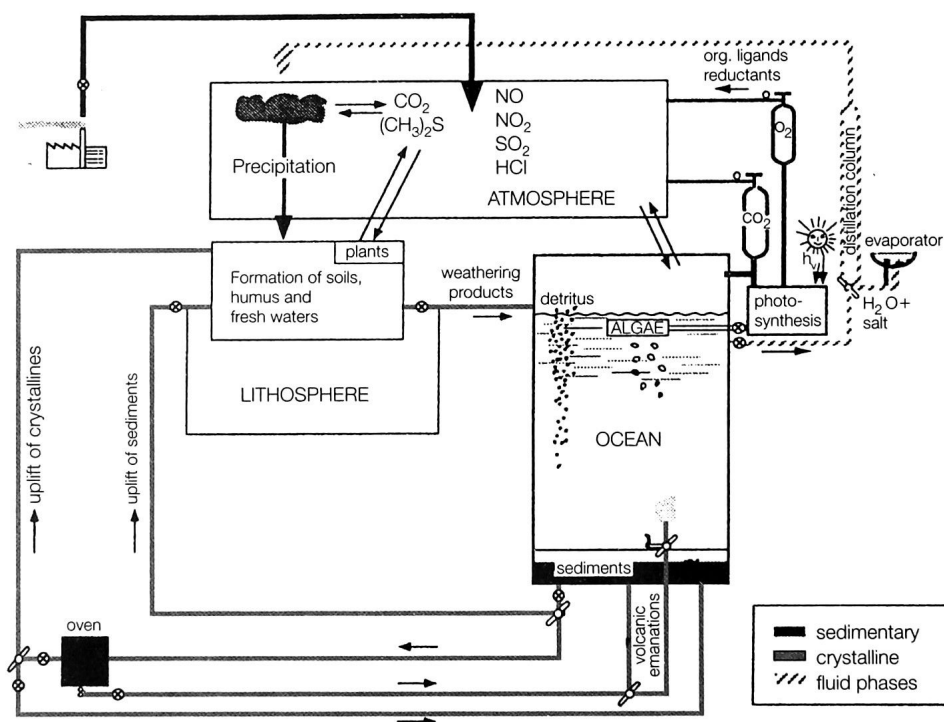


FIGURE 1.1

The crustal-ocean-atmosphere factory. Source: Stumm, W. and J. J. Morgan (1996) *Aquatic Chemistry*, 3rd ed. Wiley-Interscience, p. 874.

returns the chemicals to the ocean. The mobility of chemicals within the crustal-ocean-atmosphere factory is strongly affected by partitioning at interfaces. In the ocean, these include the air-sea and sediment-water interfaces, as well as the contact zone between seawater and suspended or sinking particulate matter. Thus, the ocean acts as a giant stirred flow-through reactor in which solutes and solids are added, transformed, and removed.

The representation of the ocean presented in Figure 1.1 is not a complete description of the ocean but serves to illustrate aspects important to the discussion at hand. Scientists refer to these simplified descriptions as a *model*. Models are useful ways of summarizing knowledge and identifying avenues for further study. Those that include mathematical information can be used to make quantitative predictions. The model illustrated in Figure 1.1 is a mechanistic one that emphasizes the flow of materials between various reservoirs. Because most material flows appear to follow closed circuits (if observed for long enough periods of time), the entire loop is referred to as a *biogeochemical cycle*. Such a cycle can be defined for any particular substance, whether it be an element, molecule, or solid. An example of the latter, the rock cycle, is given in Figure 1.2. This type of depiction is called a *box model* because each reservoir, or form that a substance occurs in, is symbolized by a box (e.g., sedimentary rock). The flow

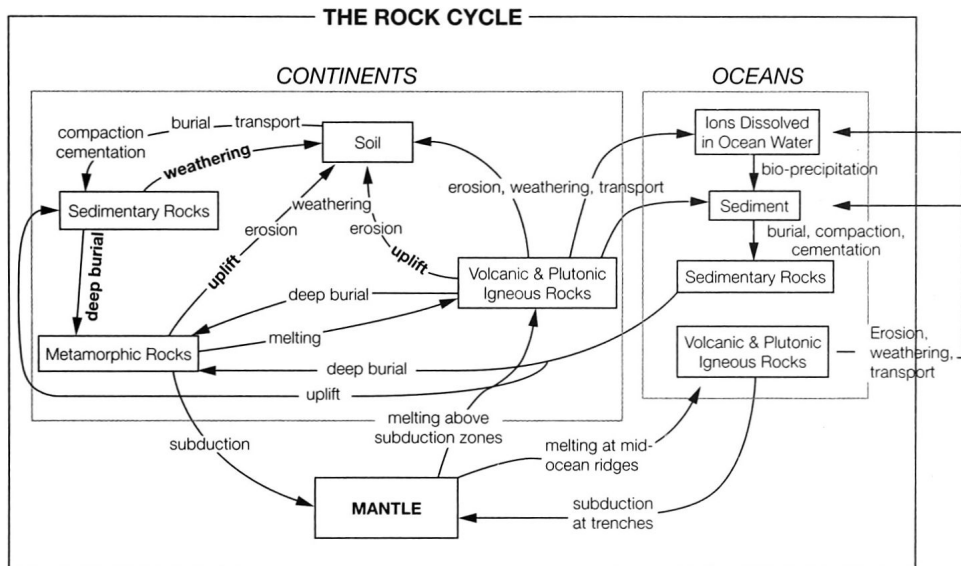


FIGURE 1.2

The global rock cycle. Source: After Bice, D. Exploring the Dynamics of Earth Systems: Modeling Earth's Rock Cycle. http://www.carleton.edu/departments/geol/DaveSTELLA/Rock%20Cycle/rock_cycle.htm.

of materials between reservoirs is indicated by arrows that point from the source of a substance to its *sink*. The magnitude of the exchange rates and sizes of the reservoirs are often included in these diagrams. For some substances, such as carbon and nitrogen, humans have significantly altered exchange rates and reservoir sizes. In these cases, the box model approach has proven valuable in assessing current impacts of human activities. These insights are used to predict how the crustal-ocean-atmosphere factory is likely to respond in the future, enabling a cost-benefit analysis of various environmental management strategies.

1.3.1 Steady State, Residence Times, and Turnover Times

If the size of a reservoir remains constant over time, the combined rates of input (J_{in}) to each box must equal the combined rates of output (J_{out}):

$$-\frac{dM_C}{dt} = 0 = J_{\text{in}} - J_{\text{out}} \quad (1.1)$$

where M_C is the amount of material, C , in the reservoir, and J has the units of amount per unit time.¹ This condition is referred to as *steady state*. The average period of time

¹ Typically, M_C has units of mass.

that a specified unit of a substance spends in a particular reservoir is called its *residence time*. This steady-state residence time is given by

$$\text{Residence time} = \frac{\text{Total amount of a substance in a reservoir}}{\text{Total rate of supply to or removal of the substance from the reservoir}} = \frac{M_C}{J_{\text{in}} \text{ or } J_{\text{out}}} \quad (1.2)$$

In the case of water,

$$\text{Residence time} = \frac{\text{Total volume of water in the ocean}}{\text{Annual volumetric rate of water input}} = \frac{V_{\text{SW}}}{Q_{\text{RW}}} \quad (1.3)$$

As shown in the next chapter, the average molecule of water spends 3800 years in the ocean before being removed, mostly via the process of evaporation.

The steady-state concentration of a chemical with an oceanic residence time much longer than that of water can be predicted if it is assumed that its removal rate is directly proportional to its abundance in seawater, i.e.,

$$J_{\text{out}} = kM = kC_{\text{SSW}}V_{\text{SW}} \quad (1.4)$$

where k is a removal rate constant and C_{SSW} is the steady-state concentration of C in seawater. Since river input is the major source of most elements to seawater,

$$J_{\text{in}} = Q_{\text{RW}}C_{\text{RW}} \quad (1.5)$$

where C_{RW} is the concentration of C in riverwater. Substituting Eqs. 1.3 and 1.4 into Eq. 1.1 and solving for C_{SSW} yields

$$[C]_{\text{SSW}} = \frac{[C]_{\text{RW}}}{RT \times k} \quad (1.6)$$

where RT is the residence time of water in the ocean. Equation 1.5 indicates that the steady-state concentration of a given chemical is dependent on the relative magnitudes of its k and $[C]_{\text{RW}}$. Steady-state concentrations can shift given a sustained change in k and/or $[C]_{\text{RW}}$. In many biogeochemical cycles, changes in the steady-state concentration are difficult to achieve because natural systems tend to have feedbacks that act to reduce the effects of rate and/or concentration changes and, hence, stabilize biogeochemical cycles against perturbations.

Equation 1.6 is built upon the assumption that each of the removal processes that C undergoes follows first-order behavior. If these are chemical reactions, a first-order rate law can be written for each (individual) process in which

$$\text{Rate of change of } C \text{ due to reaction } i = - \left(\frac{d[C]_{\text{SW}}}{dt} \right)_i = k_i [C]_{\text{SW}} \quad (1.7)$$

where k_i is the first-order reaction rate constant that has a positive value if C is lost from the ocean through chemical reaction. These rate constants are additive so the k used in Eq. 1.7 can be computed as the sum of the individual reaction rate constants:

$$k = \sum_i^n k_i \quad (1.8)$$

First-order chemical behavior is commonly assumed because reaction rate laws are generally not known. Although this approach is accepted as a reasonable and practical