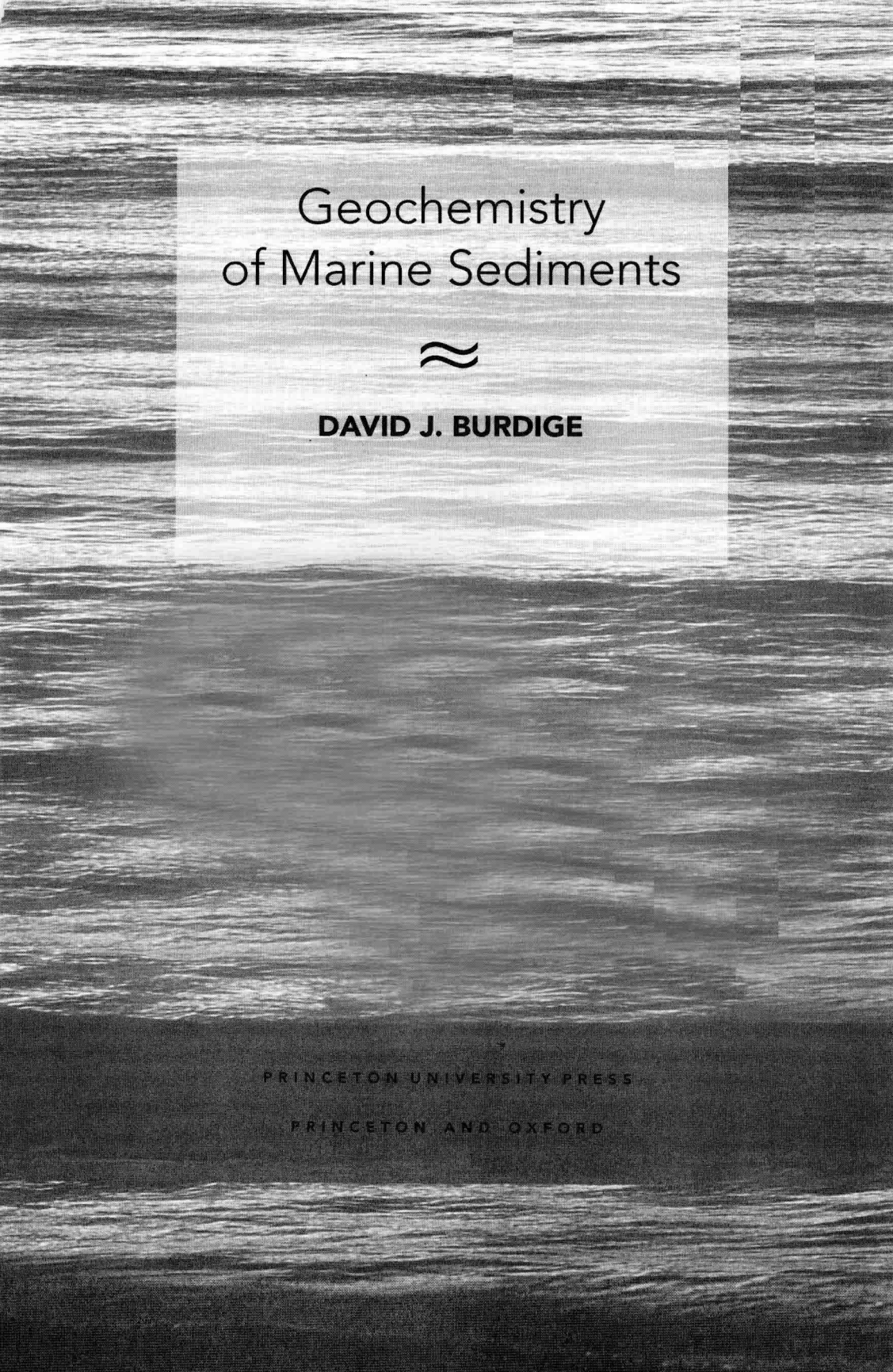


DAVID J. BURDIGE

Geochemistry of Marine Sediments



The background of the book cover is a black and white photograph of ocean waves. The waves are breaking, creating white foam and spray, and the water has a textured, rippled appearance. The lighting suggests a bright day, with the sun reflecting off the water's surface.

Geochemistry of Marine Sediments



DAVID J. BURDIGE

PRINCETON UNIVERSITY PRESS

PRINCETON AND OXFORD

Copyright © 2006 by Princeton University Press

Published by Princeton University Press, 41 William Street, Princeton,
New Jersey 08540

In the United Kingdom: Princeton University Press, 3 Market Place, Woodstock,
Oxfordshire OX20 1SY

All Rights Reserved

ISBN-13: 978-0-691-09506-X

ISBN-10: 0-691-09506-X

Library of Congress Control Number: 2006925778

British Library Cataloging-in-Publication Data is available

This book has been composed in Utopia

Printed on acid-free paper, ∞

pup.princeton.edu

Printed in the United States of America

1 3 5 7 9 10 8 6 4 2

≈ Preface ≈

FOR MORE THAN A DECADE I have taught a graduate-level course in marine sediment geochemistry that covers many of the topics discussed in this book. The goal now is to present this material to a broader group of students and other interested individuals. In this book I present the fundamentals of marine sediment geochemistry and discuss the ways we can quantify geochemical processes occurring in recent marine sediments.

In my mind, Bob Berner's (1980) *Early Diagenesis, A Theoretical Approach* was the first book to present a clear and concise discussion of how geochemical processes in recent marine sediments can be quantitatively studied. However, tremendous advances have been made in this field since this book was published in 1980. Thus I feel there is the need for a book like this one that picks up (in some senses) where *Early Diagenesis* left off. Other books published since 1980 examine a number of the topics presented here, and do so in an excellent manner (Boudreau, 1997; Boudreau and Jørgensen, 2001; Schulz and Zabel, 2000). However, overall, they do not provide the reader with as broad a view of marine sediment geochemistry as I hope I have presented here.

There are many people I need to thank for their direct and indirect assistance in writing this book. First and foremost, I would like to thank Joris Gieskes, Ken Nealson, Paul Kepkay, and Chris Martens for their advice and guidance over the years. I would never have gotten to the point of writing this book if I hadn't been fortunate to have worked with these fine scientists during the early stages of my scientific career. Over the years many other colleagues and friends provided me with stimulating conversations, good (and some bad) ideas, and a good laugh or two when needed. At the risk of leaving anyone out I won't list these individuals here, but you all know who you are. Thanks for everything.

A part of this book was written while on sabbatical from Old Dominion University, and I would like to thank Larry Atkinson and the Center for Coastal Physical Oceanography at ODU for providing me with an office in which to hide and write. Much of the book was also written while trying to juggle the standard teaching, research, and service activities that come with my faculty position. Thanks go to the three people who served as my department chair during this period (Jim Sanders, Tom Royer, and Dick Zimmerman) for their patience

and understanding. I would also like to thank Princeton University Press for their patience during the entire process of writing this book.

In the course of this project, many people graciously provided me with unpublished manuscripts, answered my email questions, and hunted through old computers and data notebooks to uncover previously published data that is replotted in the book. With the rapid advances in computer technology and software over the past few years, I quickly discovered that data “archaeology” is often not a trivial task! In any event, thanks here go to Bob Aller, Marc Alperin, Dave Archer, Will Berelson, Neal Blair, Bernie Boudreau, Liz Canuel, Jeff Cornwell, Steve Emerson, Yves Gélinas, Marty Goldhaber, Mark Green, Per Hall, Markus Huettel, Christelle Hyacinthe, Rick Jahnke, Karen Johansson, Bo Barker Jørgensen, Mandy Joye, Pete Jumars, Val Klump, Carla Koretsky, Joel Kostka, Karima Khalil, George Luther, Bill Martin, Carrie Masiello, Larry Mayer, Jim McManus, Jack Middelburg, John Morse, Filip Meysman, Christophe Rabouille, Kathleen Ruttenberg, Dan Schrag, Howie Spero, Bjorn Sundby, Brad Tebo, Phillipe Van Cappellen, and Claar van der Zee.

Kim Krecek assisted me with the preparation of some of the figures in the book, and entered a large number of references into EndNote. Debbie Miller of Academic Technology Services at ODU also did a superb job of drafting many of the figures in this book, and put up with my many requests for “just one more change.” Don Emminger (also of Academic Technology Services) was a real life-saver in helping me get the figures into their final format.

Several people read either all or parts of the first draft of the book and I would like to thank them for their useful comments: Xiping Hu, Scott Kline, Will Berelson, Anitra Ingalls, Rick Murray, Mike Krom, Clare Reimers, and the students in OCEN 613 *Geochemistry of Marine Sediments* (spring 2005): Joy Davis, Hussain Abdulla, Krista Stevens, and Pete Morton. A very special thanks also goes to Bernie Boudreau for his extremely thorough review of the first draft of the book. This is a much better book because of his time and effort, although in the end all of the mistakes, errors, and omissions are still my responsibility.

Finally, a special thanks goes to my parents and sisters for their support over the years. And last but not least, my wife, Juli, and my children, Ben and Emily, showed extraordinary patience and understanding during the entire project. I can't express my appreciation enough.

≈ Commonly Used Abbreviations ≈ and Symbols

Throughout the text (and the literature in general) these symbols are generally used to define the following parameters/quantities.

BE	Burial efficiency (eqn. 8.19)
BFE	Benthic flux enrichment factor (eqns. 12.27 and 12.32)
D	Diffusion coefficient
D_b	Bioturbation (or biodiffusion) coefficient
D_s	Bulk sediment diffusion coefficient (D values corrected for sediment tortuosity)
DBL	Diffusive boundary layer
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DOP	Degree of pyritization
F	Formation factor (used in the determination of sediment tortuosity; see eqn. 6.11)
\mathcal{F}	A factor used to convert solid phase sediment concentration units to pore water concentration units (see eqn. 6.41)
gdw (or g_{dw})	Grams sediment dry weight
HMW	High molecular weight
J	Flux across the sediment-water interface
\mathcal{H}	Hydraulic conductivity (eqn. 4.7)
L	Sediment mixed layer depth
\mathcal{L}	The stoichiometric ratio of the moles of sulfate reduced : carbon oxidized during bacterial sulfate reduction
LMW	Low molecular weight
MU-OM	Molecularly uncharacterized organic matter
ox	The average carbon oxidation state in particulate organic matter (eqns. 11.6 and 11.12)
OET	Oxygen exposure time
POC	Particulate organic carbon
POM	Particulate organic matter
R_{cox}	The depth-integrated rate of sediment organic carbon oxidation. Note that in some sediments this is the

COMMONLY USED ABBREVIATIONS AND SYMBOLS

	portion of the benthic ΣCO_2 flux due to respiration (also see eqn. 11.13). In some works, this term is referred to as C_{ox} .
r_n	The C/N ratio of organic matter undergoing remineralization
TCO_2 (also DIC or ΣCO_2)	Total dissolved inorganic carbon (= $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$)
TOC	Total organic carbon (note that the letter G is often used as a symbol for TOC in diagenetic equations)
TN	Total nitrogen
TOM	Terrestrial organic matter
α or $\alpha(z)$	The depth-dependent non-local bioirrigation coefficient
ϕ	Sediment porosity ($\text{cm}^3_{pw}/\text{cm}^3_{ts}$). Note that in many texts \emptyset is often used as the symbol for sediment porosity. However, here and in other recent works this other form of phi (ϕ) is used for porosity, to unambiguously define these different parameters.
ϕ_s	Sediment solid fraction ($\text{cm}^3_{ds}/\text{cm}^3_{ts}; = 1-\phi$)
\emptyset	Sediment grain size
θ^2	Sediment tortuosity factor (see eqn. 6.12)
ω	Sedimentation rate
Ψ	A geometric parameter that incorporates reaction geometry considerations into α (i.e., solute transport by bioirrigation; see eqn. 12.31)
subscript p or pw	Pore water
subscript ds or s	Sediment (solid phase)
subscript dw	Sediment dry weight
subscript ts	Total sediment (pore water plus solid phase)

≈ Contents ≈

Preface	xv
Common Abbreviations and Symbols	xvii
CHAPTER ONE	
Introduction	1
CHAPTER TWO	
The Components of Marine Sediments	5
2.1 DETRITAL COMPONENTS	5
2.2 BIOGENIC COMPONENTS	8
2.2.1 Biogenic Carbonates	9
2.2.2 Biogenic Silica	10
2.2.3 Distribution of Biogenic Components in Marine Sediments	10
2.3 AUTHIGENIC MINERALS	12
2.3.1 Nonbiogenic Carbonates	13
2.3.2 Mn Crusts, Layers, and Nodules	13
2.3.3 Phosphorites	14
2.3.4 Sulfides	15
2.4 CLAYS AND CLAY MINERALS	15
2.4.1 Distribution of Clay Minerals in Surface Marine Sediments	18
2.4.2 Ion Exchange/Adsorption	20
2.5 THE CLASSIFICATION OF MARINE SEDIMENTS AND SEDIMENTARY REGIMES	24
CHAPTER THREE	
Isotope Geochemistry	27
3.1 INTRODUCTION	27
3.2 PRINCIPLES OF ISOTOPE FRACTIONATION	28
3.2.1 Terminology	30
3.2.2 Equilibrium Isotope Exchange Reactions	31
3.3 ISOTOPE FRACTIONATION IN INORGANIC MATERIALS IN NATURE	32
3.3.1 Isotope Fractionation in the Hydrosphere and in Ice Cores	32

CONTENTS

3.3.2 <i>Isotope Fractionation during Clay Mineral Formation</i>	34
3.3.3 <i>Oxygen and Carbon Isotopes in Calcite</i>	35
3.4 CARBON ISOTOPES IN ORGANIC MATTER	36
3.4.1 <i>Photosynthesis</i>	37
3.4.2 <i>Respiration (Early Diagenesis in Sediments)</i>	38
3.5 OXYGEN AND CARBON ISOTOPES IN SEDIMENT PORE-WATERS	38
3.5.1 <i>Carbon Isotopes</i>	38
3.5.2 <i>Oxygen Isotopes</i>	39
3.6 NITROGEN ISOTOPES	39
3.7 SULFUR ISOTOPES	40
3.8 RADIOACTIVE ISOTOPES	40
3.8.1 <i>Basic Principles</i>	40
3.8.2 <i>Radiocarbon</i>	43
 CHAPTER FOUR	
Physical Properties of Sediments	46
4.1 GRAIN SIZE	46
4.2 POROSITY AND SEDIMENT DENSITY	47
4.3 PERMEABILITY	55
 CHAPTER FIVE	
An Introduction to Transport Processes in Sediments	59
5.1 DIFFUSION	59
5.2 SEDIMENT ACCUMULATION, STEADY STATE, AND THE FRAME OF REFERENCE FOR PROCESSES IN MARINE SEDIMENTS	61
5.3 AN INTRODUCTION TO BIOTURBATION AND BIOIRRIGATION	65
5.4 TIME AND SPACE SCALES OF SEDIMENT PROCESSES	67
5.5 THE CLASSIFICATION OF MARINE SEDIMENTS ON THE BASIS OF THEIR FUNCTIONAL DIAGENETIC CHARACTERISTICS	70
 CHAPTER SIX	
Models of Sediment Diagenesis	72
6.1 THE GENERAL DIAGENETIC EQUATION	72
6.1.1 <i>Diffusion</i>	74
6.1.2 <i>Advection, Sediment Compaction, and Bioturbation</i>	78
6.1.3 <i>Adsorption</i>	83
6.2 SOLUTIONS TO THE DIAGENETIC EQUATION	84
6.2.1 <i>Boundary Conditions</i>	86
6.3 SOLUTIONS TO SPECIFIC DIAGENETIC EQUATIONS	87
6.3.1 <i>Organic Matter Remineralization without Bioturbation</i>	88

CONTENTS

6.3.2 <i>Organic Matter Remineralization with Bioturbation</i>	89
6.3.3 <i>Organic Matter Remineralization Coupled to Sulfate Reduction</i>	91
6.3.4 <i>Ammonium Production in Anoxic Sediments</i>	92
6.3.5 <i>Determination of Sediment Accumulation Rates</i>	95
CHAPTER SEVEN	
Biogeochemical Processes in Sediments	97
7.1 BACTERIAL METABOLISM: GENERAL CONSIDERATIONS	98
7.2 BACTERIAL RESPIRATION AND BIOGEOCHEMICAL ZONATION IN SEDIMENTS	99
7.3 BACTERIAL RESPIRATION: SPECIFIC PROCESSES	105
7.3.1 <i>Aerobic Respiration</i>	105
7.3.2 <i>Denitrification</i>	105
7.3.3 <i>Manganese and Iron Reduction</i>	107
7.3.4 <i>Sulfate Reduction</i>	110
7.3.5 <i>Methanogenesis</i>	111
7.4 CHEMOLITHOTROPHIC REACTIONS	114
7.4.1 <i>Aerobic Processes</i>	114
7.4.2 <i>Anaerobic Processes</i>	116
7.4.3 <i>Linkages between Chemolithotrophic and Organic Matter Remineralization Processes</i>	116
7.5 THE DISTRIBUTION OF ORGANIC MATTER REMINERALIZATION PROCESSES IN MARINE SEDIMENTS	120
7.5.1 <i>Depth Scales of Biogeochemical Zonation</i>	120
7.5.2 <i>General Trends with Water Column Depth or Sediment Type</i>	124
7.6 DYNAMICS OF ORGANIC MATTER DECOMPOSITION IN SEDIMENTS	134
7.6.1 <i>General Considerations</i>	134
7.6.2 <i>Anaerobic "Foodchains"</i>	135
7.6.3 <i>Dynamics of Organic Matter Decomposition under Mixed Redox Conditions</i>	139
CHAPTER EIGHT	
Quantifying Carbon and Nutrient Remineralization in Sediments	142
8.1 MODELS OF ORGANIC MATTER DECOMPOSITION IN SEDIMENTS	142
8.2 SEDIMENT BUDGETS FOR REACTIVE COMPONENTS	150
8.2.1 <i>Theoretical Considerations</i>	151

CONTENTS

8.2.2 <i>Sediment Nutrient Budgets Using Cape Lookout Bight as an Example</i>	153
8.3 CARBON BURIAL IN SEDIMENTS	161
8.4 LAYERED AND COUPLED MODELS OF SEDIMENT DIAGENESIS	162
CHAPTER NINE	
An Introduction to the Organic Geochemistry of Marine Sediments	171
9.1 GENERAL CONSIDERATIONS	172
9.2 CONCENTRATIONS AND SOURCES OF ORGANIC MATTER IN MARINE SEDIMENTS	174
9.3 THE BULK CHEMICAL COMPOSITION OF MARINE SEDIMENT ORGANIC MATTER	175
9.4 AMINO ACIDS	179
9.5 CARBOHYDRATES	189
9.6 LIGNINS	193
9.7 LIPIDS	194
9.8 HUMIC SUBSTANCES AND MOLECULARLY UNCHARACTERIZED ORGANIC MATTER	204
9.8.1 <i>Black Carbon</i>	206
9.8.2 <i>Molecularly Uncharacterized Organic Matter (MU-OM): General Considerations</i>	207
9.8.3 <i>Geopolymerization: The Formation of Humic Substances</i>	209
9.8.4 <i>Selective Preservation of Refractory Biomacromolecules</i>	212
9.8.5 <i>Physical Protection</i>	213
9.9 ORGANIC NITROGEN DIAGENESIS IN SEDIMENTS	215
CHAPTER TEN	
Dissolved Organic Matter in Marine Sediments	218
10.1 GENERAL OBSERVATIONS	218
10.2 DIAGENETIC MODELS OF PORE-WATER DOM CYCLING IN SEDIMENTS	227
10.3 PORE-WATER DOM COMPOSITIONAL DATA	228
10.3.1 <i>Short-Chain Organic Acids</i>	230
10.3.2 <i>Carbohydrates</i>	231
10.3.3 <i>Amino Acids</i>	231
10.4 FLUXES OF DOM FROM MARINE SEDIMENTS	232
10.5 DOM ADSORPTION AND SEDIMENT-ORGANIC MATTER INTERACTIONS	234

CONTENTS

CHAPTER ELEVEN

Linking Sediment Organic Geochemistry and Sediment Diagenesis	237
11.1 THE SOURCES OF ORGANIC MATTER TO MARINE SEDIMENTS	237
11.1.1 <i>Carbon and Nitrogen Isotopic Tracers of Organic Matter Sources</i>	238
11.1.2 <i>Elemental Ratios as Tracers of Organic Matter Sources</i>	241
11.1.3 <i>Spatial Trends in the Sources of Organic Matter to Marine Sediments: Marine versus Terrestrial</i>	244
11.1.4 <i>Other Sources of Organic Matter to Marine Sediments: Black Carbon and Recycled Kerogen</i>	249
11.1.5 <i>Production of Bacterial Biomass in Sediments</i>	250
11.2 THE COMPOSITION OF ORGANIC MATTER UNDERGOING REMINERALIZATION IN MARINE SEDIMENTS	253
11.2.1 <i>Pore-Water Stoichiometric Models for Nutrient Regeneration/Organic Matter Remineralization</i>	254
11.2.2 <i>Benthic Flux and Sediment POM Stoichiometric Models for Nutrient Regeneration</i>	260
11.2.3 <i>The Composition of Organic Matter Undergoing Remineralization: Elemental Ratios and Stable Isotopic Composition</i>	261
11.2.4 <i>The Composition of Organic Matter Undergoing Remineralization: Organic Geochemical Composition</i>	265

CHAPTER TWELVE

Processes at the Sediment-Water Interface	271
12.1 THE DETERMINATION OF BENTHIC FLUXES	272
12.2 DIFFUSIVE TRANSPORT AND THE BENTHIC BOUNDARY LAYER	274
12.3 SEDIMENT-WATER EXCHANGE PROCESSES IN PERMEABLE SEDIMENTS	283
12.4 BIOTURBATION	286
12.4.1 <i>General Considerations</i>	286
12.4.2 <i>Models of Bioturbation</i>	289
12.4.3 <i>Nonlocal Sediment Mixing</i>	299
12.5 BIOIRRIGATION	302
12.5.1 <i>The Diffusive Openness of Bioirrigated Sediments</i>	313
12.5.2 <i>Methods for Quantifying Bioirrigation in Sediments</i>	316
12.5.3 <i>Rates of Bioirrigation in Marine Sediments</i>	319
12.6 OTHER SEDIMENT-WATER INTERFACE PROCESSES: METHANE GAS EBULLITION	326

CONTENTS

CHAPTER THIRTEEN

Biogeochemical Processes in Pelagic (Deep-Sea) Sediments	328
13.1 ORGANIC MATTER REMINERALIZATION	328
13.2 TRACE METAL DIAGENESIS	332
13.3 MANGANESE NODULES AND CRUSTS	344
13.4 DIAGENESIS OF OPALINE SILICA	352
13.5 DIAGENESIS OF CALCIUM CARBONATE	359

CHAPTER FOURTEEN

Nonsteady-State Processes in Marine Sediments	373
14.1 GENERAL CONSIDERATIONS	373
14.2 PERIODIC INPUT PROCESSES	374
14.3 SEASONALITY IN SEDIMENT PROCESSES	378
14.4 DIAGENETIC PROCESSES IN DEEP-SEA TURBIDITES	382
14.4.1 <i>Organic Geochemical Studies of Turbidite Diagenesis</i>	391
14.5 MULTIPLE MN PEAKS IN SEDIMENTS: NONSTEADY-STATE DIAGENETIC PROCESSES ASSOCIATED WITH PALEOCEANOGRAPHIC CHANGES	395
14.5.1 <i>Multiple Mn Peaks and the Glacial-Holocene Transition</i>	400
14.5.2 <i>Multiple Mn Peaks and Pleistocene Climate Cycles</i>	402
14.5.3 <i>Multiple Mn Peaks in Holocene Sediments</i>	404

CHAPTER FIFTEEN

The Controls on Organic Carbon Preservation in Marine Sediments	408
15.1 ORGANIC MATTER-MINERAL INTERACTIONS	412
15.2 THE ROLE OF OXYGEN IN SEDIMENT CARBON REMINERALIZATION AND PRESERVATION	417
15.3 THE ROLE OF BENTHIC MACROFAUNAL PROCESSES IN SEDIMENT CARBON REMINERALIZATION AND PRESERVATION	419
15.4 OXYGEN EXPOSURE TIME AS A DETERMINANT OF ORGANIC CARBON PRESERVATION IN SEDIMENTS	421
15.4.1 <i>What Exactly Does Sediment Oxygen Exposure "Mean"?</i>	425
15.4.2 <i>Organic Carbon Burial and Controls on Atmospheric O₂</i>	428
15.5 THE COMPOSITION OF ORGANIC MATTER PRESERVED IN MARINE SEDIMENTS AND THE FATE OF TERRESTRIAL ORGANIC MATTER IN MARINE SEDIMENTS	432

CONTENTS

15.6 THE RELATIONSHIP BETWEEN PHYSICAL PROTECTION, OXYGEN EXPOSURE, AND POSSIBLE ABIOTIC CONDENSATION REACTIONS IN SEDIMENT CARBON PRESERVATION	439
CHAPTER SIXTEEN	
Biogeochemical Processes in Continental Margin Sediments.	
I. The CO ₂ System and Nitrogen and Phosphorus Cycling	442
16.1 PORE-WATER pH AND CARBONATE CHEMISTRY UNDER SUBOXIC AND ANOXIC CONDITIONS	442
16.2 SEDIMENT NITROGEN CYCLING	452
16.2.1 <i>Benthic DON Fluxes</i>	463
16.3 SEDIMENT PHOSPHORUS CYCLING	464
16.3.1 <i>Formation of Authigenic CFA and Phosphorus Burial in Sediments</i>	474
CHAPTER SEVENTEEN	
Biogeochemical Processes in Continental Margin Sediments.	
II. Sulfur, Methane, and Trace Metal Cycling	478
17.1 SEDIMENT SULFUR CYCLING	478
17.1.1 <i>Sulfur Burial Efficiency</i>	486
17.1.2 <i>Long-Term Changes in the Sedimentary Sulfur Cycle</i>	489
17.2 METHANOGENESIS AND ANAEROBIC METHANE OXIDATION	490
17.2.1 <i>Shallow (Coastal) Sediments</i>	490
17.2.2 <i>Continental Margin Sediments</i>	493
17.3 TRACE METAL CYCLING	500
CHAPTER EIGHTEEN	
Linking Sediment Processes to Global Elemental Cycles:	
Authigenic Clay Mineral Formation and Reverse Weathering	509
18.1 SEDIMENT SILICA BUDGETS	514
18.2 FINAL THOUGHTS	515
<i>Appendix</i>	
Some of the Field Sites Discussed in the Text	517
<i>References</i>	521
<i>Index</i>	593

≈ CHAPTER ONE ≈

Introduction

THE PROCESSES OCCURRING in the upper several meters of marine sediments¹ have a profound effect on the local and global cycling of many elements. For example, the balance between carbon preservation and remineralization represents the key link between carbon cycling in active surface reservoirs in the oceans, in the atmosphere, and on land, and carbon that cycles on much longer, geological time scales—in sedimentary rock, and in coal and petroleum deposits (Berner, 1989; Hedges, 1992). Denitrification in marine sediments, i.e., the reduction of nitrate to gaseous N_2 , is an important component of the global nitrogen cycle, and on glacial-interglacial time scales may play a role in regulating the oceanic inventory of reactive nitrogen (Ganeshram et al., 1995; Codispoti et al., 2001). On more local scales, nitrogen and phosphorus remineralization in coastal and estuarine sediments can provide a significant fraction of the nutrients required by primary producers in the water column (Klump and Martens, 1983; Kemp and Boynton, 1984). In deep-sea sediments, trace metal remineralization may play a role in the growth and genesis of manganese nodules (Glasby, 2000). Similarly, in coastal and estuarine sediments subjected to elevated anthropogenic inputs of certain toxic metals, sediment processes affect the extent to which these sediments represent “permanent” versus “temporary” sinks for these metals (e.g., Huerta-Diaz and Morse, 1992; Riedel et al., 1997).

Understanding processes occurring in surficial marine sediment is also important in the accurate interpretation of paleoceanographic sediment records, since sediment processes can sometimes significantly alter the primary “depositional” signal recorded in the sediments (e.g., Martin and Sayles, 2003). At the same time, temporal changes in ocean conditions can lead to the occurrence of nonsteady-state conditions in sediments (Wilson et al., 1985; Finney et al., 1988). The ability to recognize and accurately quantify nonsteady-state processes in sediments may therefore provide important paleoceanographic

¹ Throughout the book, this portion of the sediments is referred to as surface or surficial marine sediments.

information that is complementary to that obtained using more traditional tracer approaches such as carbon or oxygen isotopes.

The geochemistry of marine sediments is controlled by both the composition of the material initially deposited in the sediments and the chemical, biological, or physical processes that affect this material after its deposition. These processes fall within the general category of what is commonly referred to as early diagenesis (*sensu* Berner, 1980). Since these processes occur in the upper portions of the sediments, temperatures are generally not elevated above bottom water values. Sediment pore spaces are also still water saturated,² although in some sediments gas bubbles may also occur (e.g., see section 12.6).

More importantly, though, a key fact that has emerged in the past 20–30 years of research in marine sediment geochemistry is that the oxidation, or remineralization, of organic matter deposited in sediments is either the direct or the indirect causative agent for many early diagenetic changes. Thus in many ways, we are actually examining the biogeochemistry of these sediments. Much of this organic matter remineralization is mediated by bacteria, since marine sediments often become anoxic (i.e., devoid of oxygen) close to the sediment-water interface (generally <1 cm in coastal sediments to several centimeters or more in some deep-sea sediments). At the same time, surficial marine sediments are often colonized by benthic macrofauna such as burrowing clams and shrimp and tube-dwelling polychaetes. The presence of these benthic macrofauna and their resulting activities can also have a profound effect on sediment geochemistry (e.g., Aller, 1982b).

Given the key role that organic matter remineralization plays in many early diagenetic processes, significant efforts have gone into understanding and quantifying these processes. Such studies have taken both organic and inorganic approaches, with the latter often carried out through studies of the pore-water chemistry of remineralization products or reactants. Studies of pore-water geochemistry are particularly useful in this effort because they are very sensitive indicators of diagenetic changes occurring in the sediments. As an example of this, Berner (1980) notes that a 20% increase of dissolved calcium in the pore waters from the dissolution of calcium carbonate is

² As will be discussed in chapter 3, the water found in these pore spaces is referred to as *pore waters* or *interstitial waters*.

roughly equivalent to a decrease of only 0.02% CaCO_3 by weight. While the former is easily measurable, the latter is not. Thus, a great deal of effort has gone into the study of pore-water geochemistry and the development of diagenetic models of the processes affecting pore water solutes.

Historically, there has been more of a tendency to use inorganic geochemical studies to quantify rates of sediment carbon remineralization processes. However, an increasing number of workers have also begun to use organic geochemical measurements to examine the rates of these processes. Such efforts have built important links between inorganic and organic geochemical approaches to the study of sediment biogeochemistry. They have also played a major role in advancing not only what we know about sediment geochemical processes, but also how we approach their study.

The remainder of this book is divided up as follows. Chapters 2–6 contain a basic introduction to the study of marine sediment geochemistry. These chapters also begin to discuss the ways we can quantify processes occurring in sediments using mathematical models of early diagenesis. Chapters 7–12 further examine sediment organic matter remineralization and early diagenetic processes from the standpoint of: the potential reactions that may occur; the relationships between these reactions, e.g., thermodynamic vs. kinetic controls; the composition and reactivity of sediment organic matter; and the role that external factors play in controlling these reactions, e.g., carbon rain rate to the sediments or bioturbation.

Chapters 13–17 build on these previous chapters in more specific discussions examining processes occurring in pelagic and continental margin sediments. The division of the material presented here is perhaps somewhat arbitrary since changes in sediment geochemical processes are clearly a continuum as one moves from deep-sea to nearshore settings (e.g., see discussions in section 7.5.2). Nevertheless, I believe that this approach is as good as any other to present this material.

Chapter 13 describes processes occurring in pelagic sediments; this discussion then leads to a discussion in chapter 14 of nonsteady-state, or time-dependent, diagenetic processes occurring in sediments. By presenting a discussion of nonsteady-state processes in a separate chapter the intent is not to suggest that the occurrence of nonsteady-state conditions is “unusual,” or the exception, as compared to steady-state conditions. In fact, evidence increasingly sug-