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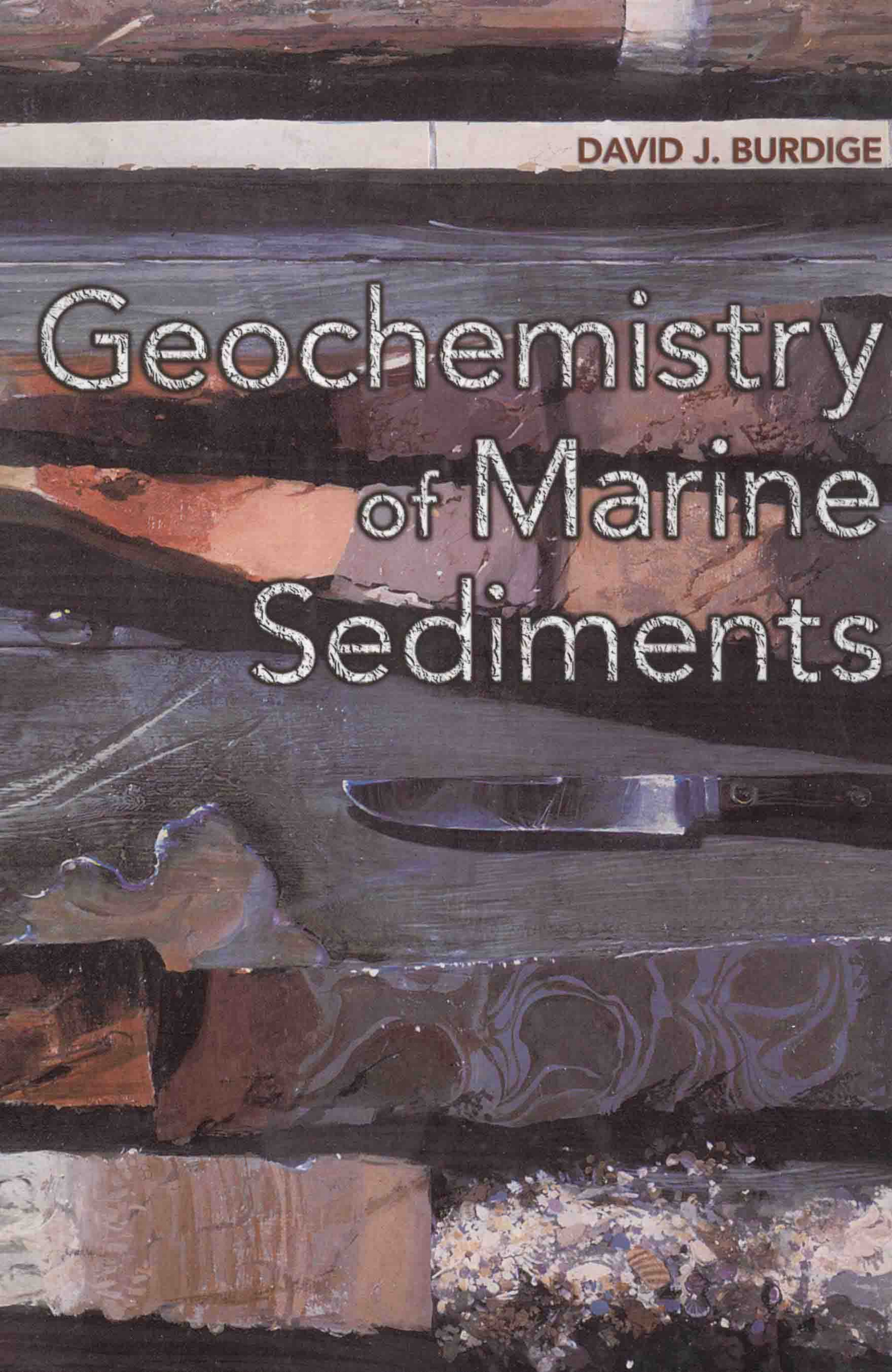

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≈ *Preface* ≈

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 Johannesson, 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: Xinping 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
$\mathcal{K}$	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

	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 (= $[CO_2] + [HCO_3^-] + [CO_3^{-2}]$)
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 (cm^3_{pw}/cm^3_{ts}). Note that in many texts ø 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 (cm^3_{ds}/cm^3_{ts}; = 1-φ)
ø	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* ≈

≈ CHAPTER ONE ≈

Introduction

THE PROCESSES OCCURRING in the upper several meters of marine sediments[1] 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 discus 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-