

≈ CHAPTER ONE ≈

Introduction

**T**HE PROCESSES OCCURRING in the upper several meters of marine sediments<sup>1</sup> 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<sub>2</sub>, 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

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

## INTRODUCTION

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,<sup>2</sup> 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

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

## INTRODUCTION

roughly equivalent to a decrease of only 0.02%  $\text{CaCO}_3$  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-

## INTRODUCTION

gests that the opposite is the case, and that true steady-state conditions may be far less common in marine sediments than has been previously assumed.

Chapter 15 builds on much of what has been discussed in earlier chapters by examining the controls on organic carbon preservation in marine sediments, a process that occurs largely in continental margin sediments. Chapters 16 and 17 further examine processes occurring in continental margin, coastal, and estuarine sediments from the standpoint of the sediment cycling of trace metals and nutrients. The book concludes by examining sediment biogeochemical processes in the context of the global cycles of the major elements.

An appendix at the end of the book briefly describes many of the field sites discussed in the text.

In writing this book I have assumed that the reader has some basic knowledge of geology, chemistry, and biology. Readers who come across unfamiliar terms or concepts may want to consult introductory texts in these fields. In contrast, many readers may not be as familiar with some of the concepts of chemical oceanography that are brought into the discussions here. Several good texts have been published in this area that readers may find useful (Broecker and Peng, 1982; Libes, 1992; Millero, 1996; Pilson, 1998; Chester, 2000; Gianguzza et al., 2002). Where appropriate I cite these works in the text.