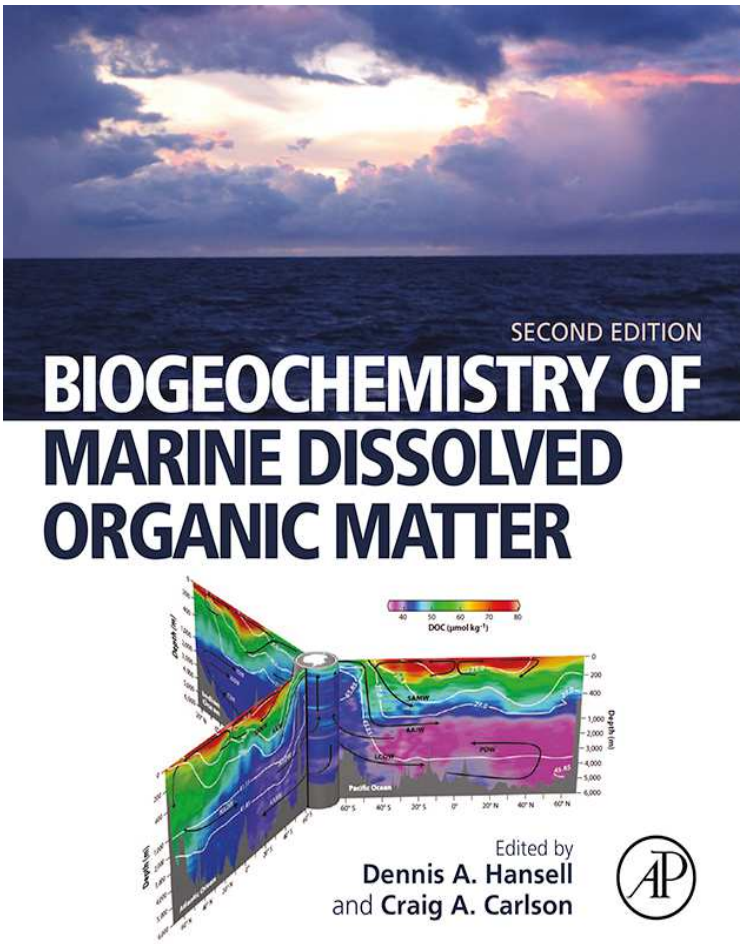

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CHAPTER

12

Sediment Pore Waters

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I PREFACE

Dissolved organic matter (DOM) in marine sediment pore waters plays an important role in sediment carbon and nitrogen remineralization and may also be involved in sediment carbon preservation. It also plays a role in pore water metal complexation, affecting dissolved metal and metal-complexing ligand fluxes from sediments (e.g., Shank et al., 2004).

Since the publication of this chapter in the first edition of this book (Burdige, 2002), a number of key advances have been made in this field. Despite these advances, the following introductory questions from the original chapter still represent an appropriate basis for starting the discussion here:

1. What do we know about the composition and reactivity of pore water DOM, with particular reference to its role in sediment organic matter remineralization?
2. What do we know about the controls on pore water DOM concentrations?
3. What is the role of benthic DOM fluxes in the global ocean cycles of carbon and nitrogen?
4. What is the role of pore water DOM in sediment carbon preservation?

In an effort to be comprehensive, key information from the earlier version of this chapter is presented here along with newer results. However, in a number of places, reference is simply made to this earlier chapter for details that, for brevity and conciseness, we felt could be omitted.

II INTRODUCTION

Dissolved organic matter (DOM) in sediment pore waters is a heterogeneous collection of organic compounds, ranging in size from relatively large macromolecules (e.g., dissolved proteins or humic substances) to smaller molecules such as individual amino acids or short-chain organic acids. As is also the case in the water column (e.g., Benner, 2002; see Chapter 2), much of the pore water DOM remains uncharacterized at the compound-class or molecular-level (see Section IV and Burdige, 2001, 2002 for details).

In many sediments, pore water concentrations of DOM—both dissolved organic carbon (DOC) and dissolved organic nitrogen (DON)—are elevated by up to an order of magnitude over bottom water values (Figure 12.1). This implies that there is net production of DOM in sediments as a result of organic matter degradation processes. Based on diffusive arguments alone, sediments are a potential source of both DOC and DON to the overlying waters (see Section VII). Much of the total pore water DOC and DON is of relatively low-molecular weight (LMW; see Section III.A) and appears to be recalcitrant, at least in a bulk sense. Such observations are consistent with the results of water column studies showing that high-molecular weight (HMW) DOC represents a more reactive and less diagenetically altered fraction of the total DOC than the more abundant, and presumably more recalcitrant, LMW-DOC (e.g., Amon and Benner, 1994; Benner, 2002; Santschi et al., 1995).

Several lines of evidence suggest that the DOM accumulating in sediments is indeed recalcitrant. The first is simply that relatively high

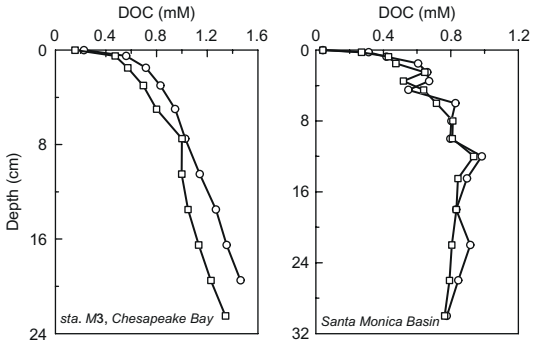

FIGURE 12.1 Pore water DOC concentration profiles in anoxic marine sediments. Symbols on the upper *x*-axes represent concentrations in bottom water samples obtained by hydrocasts. (Left) Cores collected at site M3 in the mesohaline Chesapeake Bay (July 1995, open square; October 1995, open circle); data from Burdige and Zheng (1998). (Right) Replicate cores collected in Santa Monica Basin in March 1994 (Burdige, 2002). Also see Jahnke (1990) and Komada et al. (2013) for general information on the geochemistry of these sediments. See Figure 12.9 for additional DOC profiles in anoxic sediments.

concentrations of this material can be found in sediments and that DOM accumulates with depth in most sediments as rates of particulate organic matter (POM) remineralization and the reactivity of sediment POM both decrease (e.g., Burdige, 1991a; Middelburg, 1989; Westrich and Berner, 1984). Such trends are seen across a wide range of time and space (sediment depth) scales, ranging from ~1 m or less in coastal and nearshore sediments to 100 s of meters or more in deeply buried marine sediments (see Burdige, 2002, and discussions in Section VI for details). If the majority of pore water DOM had a high degree of reactivity, then one might expect its concentration to eventually decrease with depth due to microbial remineralization of the material. Second, in many coastal marine sediments, humic-like fluorescence of pore water DOM is strongly correlated with total DOC concentrations, suggesting that much of the pore water DOM may be considered dissolved humic substances (see Section III.B). Third, a number of incubation experiments support the suggestion that what appears to be recalcitrant DOC can be produced on time scales comparable to those over which POC remineralization and inorganic nutrient regeneration occur (Brüchert and Arnosti, 2003; Chipman et al., 2010; Hee et al., 2001; Komada et al., 2012; Robador et al., 2010; Weston and Joye, 2005).

As a starting point for our discussions, Figure 12.2 shows a conceptual model of DOM cycling in sediments based on the classic anaerobic food chain model (e.g., Fenchel et al., 1998; Megonigal et al., 2003) and the pore water size/reactivity (PWSR) model of Burdige and Gardner (1998). The model in this figure also incorporates DOM production pathway(s) inferred from more recent work (Komada et al., 2012; Robador et al., 2010; Weston and Joye, 2005). In anaerobic settings, the majority of these processes are mediated by bacteria or archaea, with many catalyzed by microbial exoenzymes that must break down organic molecules to sufficiently small sizes to pass into microbial cells for further degradation (e.g., Arnosti, 2004).

In the model in Figure 12.2, we think of the degradation of sediment POM to inorganic end products as occurring by a series of hydrolytic (or oxidative), fermentative, and eventually respiratory processes that produce and consume pore water DOM intermediates with increasingly smaller molecular weights. Although this process leads to a continuum of DOM compounds (in terms of molecular weights and reactivities), the model assumes that there is an initial class of HMW-DOM (box "A" in Figure 12.2) containing biological polymers such as dissolved proteins and polysaccharides resulting from the initial hydrolysis or oxidative cleavage (depolymerization) of sediment POM. Most HMW-DOM is further hydrolyzed and fermented, producing and consuming labile DOM compounds of decreasingly smaller molecular weights (box "B" in Figure 12.2). Eventually, this results in the production of monomeric LMW-DOM compounds

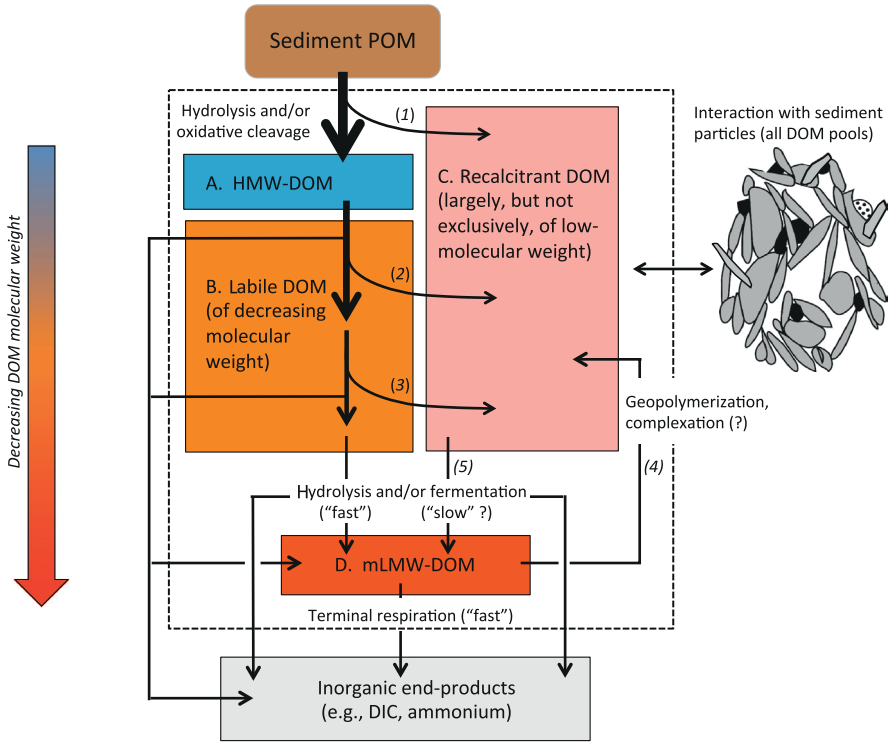

FIGURE 12.2 A conceptual model for DOM cycling in sediments. The processes illustrated here (including pathways (1)-(4)) are discussed in more detail in Section II. The terms "fast" and "slow" are used in a relative sense to imply that the turnover of either labile DOM (box "B") or mLMW-DOM (box "D") occurs much more rapidly than that of recalcitrant DOM (box "C"). This figure is based on information from several sources (e.g., Burdige and Gardner, 1998; Fenchel et al., 1998; Megonigal et al., 2003).

such as acetate, other small organic acids, and individual amino acids (mLMW-DOM; box "D" in Figure 12.2), which are then utilized in terminal respiratory processes such as iron reduction, sulfate reduction, or methanogenesis. A recent food web model for aerobic deep-sea sediments (Rowe and Deming, 2011) also supports the basic aspects of the model in Figure 12.2, although this study notes that the initial breakdown of POM in these sediments occurs by microbial exoenzymes as well as by metazoan feeding (which may in part be mediated by microbes living in the digestive tracts of these higher organisms). In addition, viral lysis of living bacterial cells may be important in adding DOM compounds to these sediment pore waters (Rowe and Deming, 2011).

While boxes "A" and "B" in Figure 12.2 represent labile compounds that generally turn over rapidly, not all carbon flow follows the vertical path along the left side of this figure. Some of the carbon end products of reactions along this pathway may actually be DOM compounds of lower reactivity that appear recalcitrant on the overall time scales of remineralization or the production of inorganic end products (i.e., this DOM falls into box "C" and following pathways (1), (2), or (3) in Figure 12.2; also see discussion in Section V.A). More recent sediment incubation studies point to the importance of direct production of inherently recalcitrant DOM through processes that may be similar to those discussed here (Komada et al., 2012, 2013; Robador et al., 2010; Weston and Joye, 2005).

For example, consider the following hypothetical fermentation reaction (modified after Yao and Conrad, 2000),

$$DOM_1 + aH_2O \rightarrow DOM_2 + DOM_3 + bCH_3COOH + cH_2 + dCO_2, \quad (12.1)$$

where a, b, c, and d are arbitrary coefficients that determine the relative production of acetic acid, H_2, and CO_2 in this process based on the chemical formulae of the three DOM molecules. Here both DOM_2 and DOM_3 have lower molecular weights than DOM_1. If DOM_2 is a labile molecule then this part of the carbon flow in this reaction will follow the vertical path along the left side of Figure 12.2 while if DOM_3 is recalcitrant, then this part of the carbon flow will go into box "C."

In the original PWSR model (Burdige, 2002; Burdige and Gardner, 1998), this recalcitrant DOM was referred to as polymeric LMW-DOM (pLMW-DOM), and in addition to production as discussed above, it was suggested that it might be produced through internal transformations of more reactive precursors (pathway (4) in Figure 12.2). Such processes include the possibility of forming recalcitrant DOM from mLMW-DOM compounds through geopolymerization processes such as the melanoidin or "browning" reaction (an abiotic sugar amino acid condensation reaction; Hedges, 1988) and complexation reactions (Christensen and Blackburn, 1982; Finke et al., 2007; Michelson et al., 1989).

Other recently proposed humification models suggest a slightly different pathway by which recalcitrant or reactive LMW-DOM compounds may serve as precursors for the formation of recalcitrant humic substances (Piccolo, 2001; Sutton and Sposito, 2005). Here, it is suggested that humic substances consist of a supramolecular cluster of relatively LMW-DOM compounds linked together by hydrogen bonds and hydrophobic interactions, as opposed to macromolecules in which covalent bonds formed by geopolymerization-type reactions link LMW-DOM reactants. In the context of the model in Figure 12.2, pathways (1)-(3) could contribute to the formation of recalcitrant dissolved humic substances. However, if such processes do occur on early diagenetic time scales in sediment pore waters, their products apparently still have relatively low molecular weights (Burdige and Gardner, 1998).

In the first edition of this chapter (Burdige, 2002), a reactive-transport (advection-diffusion-reaction) model based on the original PWSR model was presented for both strictly anoxic sediments (the ANS model) and mixed redox (bioturbated and/or bioirrigated) sediments (the BBS model). Carbon flow in the model equations is illustrated in Figure 12.3A while one set of model results, using the ANS model, is shown in Figure 12.3b. A key finding of this modeling effort was that pore water gradients of HMW-DOC and pLMW-DOC near the sediment surface were similar in magnitude, despite the fact that model-derived HMW-DOC concentrations were significantly lower than those of pLMW-DOC throughout most of the sediment column. As a result, in model calculations for both anoxic and mixed redox sediments, benthic fluxes of HMW-DOM were ~50-80% of the total benthic DOC flux (see Burdige, 2002 for details). Thus, in both types of sediments, model results suggest that benthic fluxes of both recalcitrant and reactive DOM can be similar in magnitude. The significance of this result will be discussed in later sections of this chapter.

A DOC and DON in Sediment Pore Waters: General Observations

Pore water DOC and DON profiles have been published from a wide range of surficial marine sediments, in environments ranging from the deep-sea to shallow water estuaries, salt marshes, and seagrass environments (for reviews of the earlier literature, see Burdige, 2002; Krom and Westrich, 1981; more recent results include Alkhatib et al., 2013; Chipman et al., 2012;

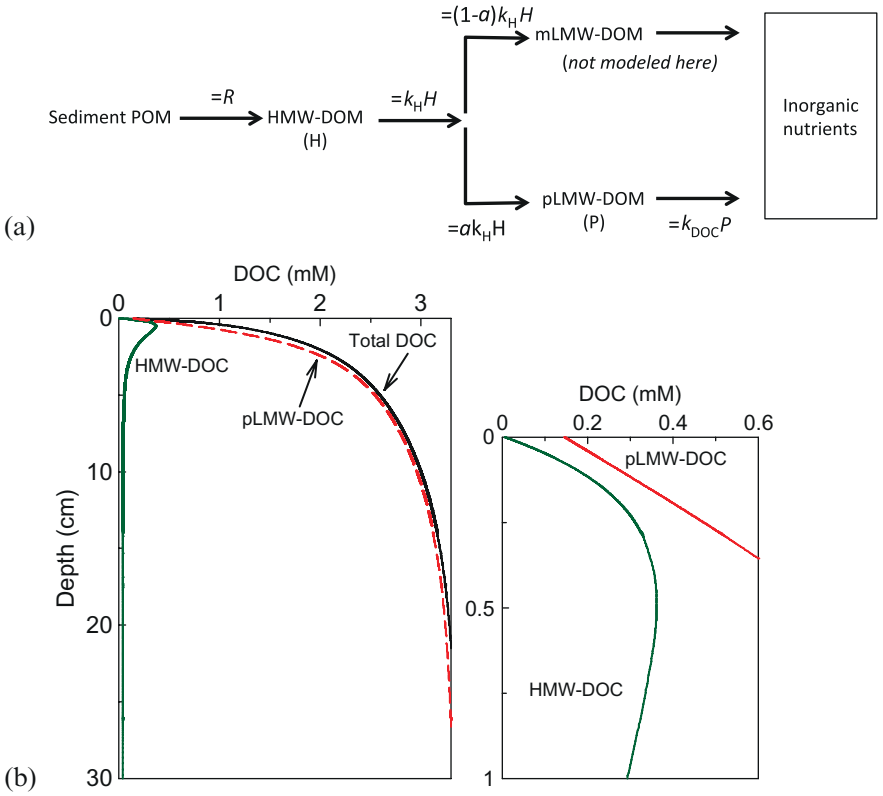

FIGURE 12.3 (a) A schematic representation of DOM remineralization based on the original PWSR model. In this model, production of HMW-DOM from sediment POM is given by Equation (12.2) in the text (see Section VI.A), while the remineralization of either HMW-DOM or pLMW-DOM is assumed to be a first-order process. The parameter *a* represents the fraction of HMW-DOM remineralization that occurs through the lower pathway; in the context of the model illustrated in Figure 12.2, this represents material that is remineralized through the recalcitrant DOM pool on the right side of the figure. The remaining HMW-DOM is then remineralized along the far left side of the figure. Since mLMW-DOM compounds are assumed to be a small fraction of the total DOM pool that are remineralized rapidly to inorganic end products (see Section IV), they are not explicitly modeled here (see Burdige, 2002, for details). This model also does not directly examine production of inorganic end products (i.e., DIC). (b) Model results for strictly anoxic sediments obtained using a reactive-transport model based on the carbon flow illustrated in part A. This model (the ANS model) is described in detail in Burdige (2002), where the specific parameters are also listed. Note that in spite of the fact that throughout most of the sediment column model-derived concentrations of more reactive HMW-DOC are significantly lower than those of more recalcitrant pLMW-DOC (which also makes up the bulk of the pore water DOC pool), the pore water gradients near the sediment surface of these two types of DOC are quite similar in magnitude.

Hall et al., 2007; Heuer et al., 2009; Komada et al., 2004; Lahajnar et al., 2005; Papadimitriou et al., 2002; Pohlman et al., 2010; Ståhl et al., 2004). Profile depths range from 10s of centimeters to several hundred meters.

In early attempts to describe some of the general controls on pore water DOC depth profiles (Krom and Sholkovitz, 1977; Starikova, 1970), it was suggested that these profiles fall into two general categories. In anoxic sediments where benthic macrofaunal processes (bioturbation and/or bioirrigation) are insignificant, pore water DOC (and DON) concentrations generally increase with depth, often approaching "asymptotic"

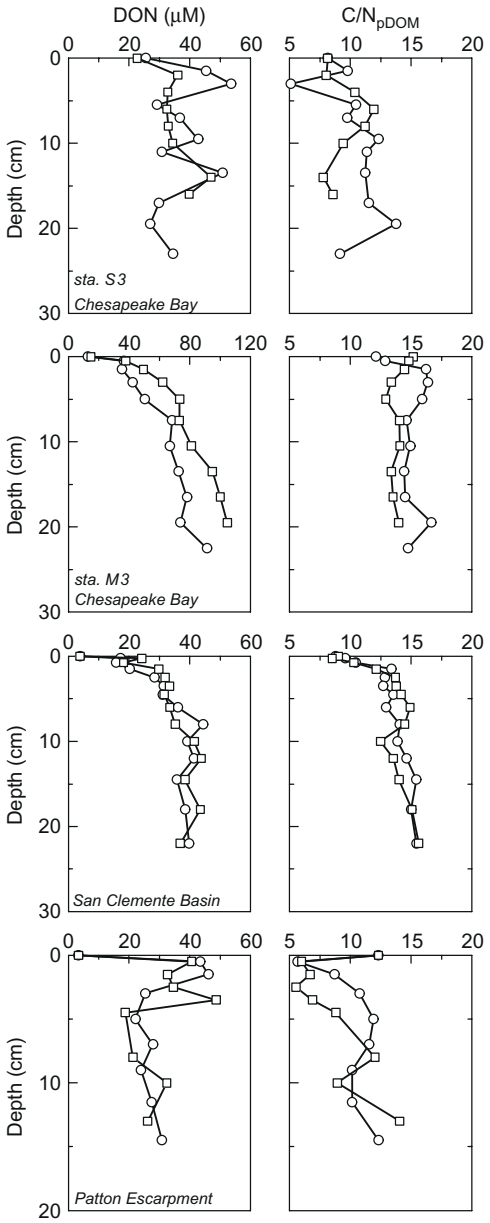

FIGURE 12.4 Pore water DON concentrations (left) and the C/N ratios of pore water DOM (=[DOC]/[DON] and defined here as C/N_{pDOM}) (right) versus depth in contrasting marine sediments. Symbols on the upper x-axes represent values in bottom water samples obtained by hydrocasts. (First row) Cores collected at site S3 in the southern Chesapeake Bay (October 1996, open circle; August 1997, open square); data

concentrations (Figures 12.1 and 12.4). In contrast, in what were then termed "oxic" or "oxidizing" sediments, DOC and DON concentrations are elevated above bottom water values, but are also much more constant with depth in the upper portions of the sediments (Figures 12.4 and 12.5). While some of these sediments may indeed be oxic, it may be more appropriate to recognize that such sediments are often bioturbated and/or bioirrigated and have mixed (or oscillating) redox conditions (sensu Aller, 1994). The three-dimensional, heterogeneous geometry of such sediments leads to a situation in which organic matter remineralization can be thought of as oscillating between oxic and sub-oxic/anoxic processes (also see discussions in Burdige, 2006b).

We also note that among the published DOC and DON depth profiles, one will find some profiles that do not appear to be consistent with the discussions presented here. Our incomplete understanding of DOM cycling in sediments is likely a part of the reason for these differences. At the same time though, several studies have discussed potential sampling artifacts that can affect pore water DOM depth profiles, suggesting another possible explanation for these differences. In particular, in sediments containing abundant benthic macrofaunal populations, pore water collection via sediment centrifugation can lead to elevated DOC concentrations (and potentially elevated

FIGURE 12.4, CONT'D from Burdige and Zheng (1998) and Burdige (2001). (Second row) Cores collected at site M3 in the mesohaline Chesapeake Bay (July 1995, open circle; October 1995, open square); data from Burdige and Zheng (1998). (Third row) Replicate cores collected in San Clemente Basin (March 1994) (Burdige, 2002). (Fourth row) Replicate cores collected at the Patton Escarpment (March 1994) (Burdige, 2002). See Burdige et al. (1999) and McManus et al. (1997) for details on the geochemistry of the San Clemente Basin and Patton Escarpment sediments (also see Table 12.1). Note that DOC data from these Chesapeake Bay site M3 cores are shown in Figure 12.1, and those from the site S3 cores are shown in Figure 12.5.

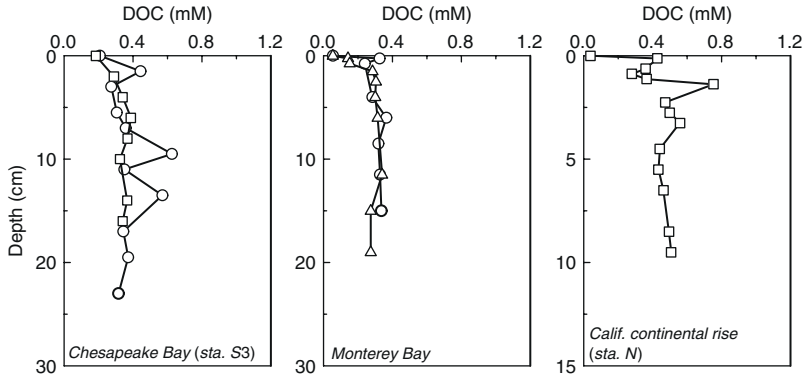

FIGURE 12.5 Pore water DOC profiles in bioturbated and/or bioirrigated (i.e., mixed redox) marine sediments. Symbols on the upper *x*-axes represent concentrations in bottom water samples obtained by hydrocasts. (Left) Cores collected at site S3 in the southern Chespapeake Bay (October 1996, open circle; August 1997, open square); data from Burdige and Zheng (1998) and Burdige (2001). (Center) Replicate cores collected at a site (95-m water depth) in Monterey Bay (Burdige, 2002). See Berelson et al. (2003) for details on the geochemistry of these sediments. (Right) A core collected at station N on the California continental rise (4100-m water depth) at the base of the Monterey deep sea fan (DOC data from Bauer et al., 1995). Also see Cai et al. (1995) for details on the geochemistry of the sediments at this site.

concentrations of individual components of the total DOC pool) as compared to concentrations in pore waters collected by more "gentle" techniques such as with sediment sippers (Alperin et al., 1999; Burdige and Gardner, 1998; Burdige and Martens, 1990; Holcombe et al., 2001; Jørgensen et al., 1981; Martin and McCorkle, 1994). These differences may be due to animal rupture or simple DOM release by benthic organisms during core processing. In deep-sea sediments, distinct maxima in DOC, DON, and dissolved carbohydrates just below the sediment-water interface also appear to be artifacts related to lysis of sediment bacteria due to decompression and/or warming during sediment core collection and recovery (Brunnegård et al., 2004; Hall et al., 2007).

One set of environments where DOM profiles may not follow many of the depth trends and general behaviors discussed here are highly permeable sandy coastal and shelf sediments (e.g., Boudreau et al., 2001; Chipman et al., 2012). These sediments, often described as behaving like a sand filter in a sewage treatment or water purification plant, may act as a DOC sink because of the complex interplay between microbial activity and advective flow through the sediments (see Chipman et al., 2010, and references therein). However, results from Avery et al. (2012) showed that sands from a high-energy beach act as a DOC source, which is more typical of most marine sediments. While the overall significance of net DOC remineralization by permeable sediments is currently unclear (e.g., source vs. sink to the water column), the process could be of large-scale importance because such highly permeable sands represent a major fraction of the continental shelf (Emery, 1968) and because continental shelf sediments are, in general, important sites of organic carbon preservation and remineralization (Burdige, 2007; Hedges and Keil, 1995).

III COMPOSITION AND DYNAMICS OF BULK PORE WATER DOM

A Molecular Weight Distribution

Using ultrafiltration techniques, Burdige and Gardner (1998) and Burdige and Zheng (1998)

showed that the vast majority of the DOC and DON in Chesapeake Bay (estuarine) and Mid-Atlantic Bight (continental margin) sediment pore waters has molecular weights less than ~3 kDa (~80-90% of total DOM in estuarine sediments and ~60-70% of total DOM in continental margin sediments). Studies of DOM from other nearshore marine and freshwater sediments using ultrafiltration and size exclusion chromatography also generally support these conclusions (Chin and Gschwend, 1991; Chin et al., 1994, 1998; Nissenbaum et al., 1972; Ziegelgruber et al., 2013).

In contrast, earlier studies suggested that HMW-DOM (rather than LMW-DOM) accumulates with depth in sediment pore waters (Krom and Sholkovitz, 1977; Orem et al., 1986). However, these studies used filters with smaller nominal molecular weight cut-offs (0.5 and 1 kDa respectively) than those used in the ultrafiltration studies cited above, making a direct comparison of the results difficult. Marine water column studies generally show that the majority of oceanic DOC passes through a membrane with a nominal 1-kDa molecular weight cut-off (Benner, 2002), with LMW-DOC representing 60-75% of the DOC in the surface ocean and 75-80% of the DOC in the deep ocean. Given the bulk radiocarbon age and other chemical characteristics of marine DOM (e.g., Hansell et al., 2009), this provides additional evidence for the recalcitrant nature of LMW marine DOM in general.

B Fluorescence Spectroscopy

Fluorescence spectroscopy has been applied to pore water DOM in a variety of environments including estuarine and marine sediments (Benamou et al., 1994; Burdige et al., 2004; Chen and Bada, 1989; Chen and Bada, 1994; Chen et al., 1993; Coble, 1996; Komada et al., 2004; Komada et al., 2002; Seretti et al., 1997; Sierra et al., 2001; Skoog et al., 1996), intertidal sand flats and subterranean estuaries (Kim et al., 2012; Lübben et al., 2009), mangrove and salt marsh sediments (Marchand et al., 2006; Otero et al., 2007), and deep-sea coral mounds (Larmagnat and Neuweiler, 2011). These studies examined properties of fluorescent DOM (FDOM) through the determination of fluorescence intensity at fixed excitation and emission wavelengths, emission spectra at a limited number of excitation wavelengths, synchronous scan spectra, or full three-dimensional excitation-emission matrix (EEM) spectra.

Regardless of the technique used, pore water FDOM invariably shows broad fluorescence in the spectral region thought to represent fluorescence of humic-like substances. Individual humic-like peaks have also been observed in EEM spectra of pore waters, and possible relationships between these specific humic-like peaks are discussed in Boehme and Coble (2000) and Burdige et al. (2004). Strong fluorescence consistent with emission bands of the aromatic proteins tyrosine and tryptophan is also evident in EEM and synchronous scan spectra of sediment pore waters (see references at the end of this section). The specific nomenclature and characteristic excitation and emission wavelengths of humic-like and protein-like fluorescence peaks seen in EEM spectra are discussed in Coble (1996, 2007), Burdige et al. (2004), and Chapter 10.

Fluorescence intensity of sediment pore waters is in many cases markedly higher than that of the overlying water column and typically increases with sediment depth (Chen and Bada, 1994; Chen et al., 1993; Komada et al., 2004; Lübben et al., 2009; Marchand et al., 2006; Sierra et al., 2001). This increase is due in part to the higher concentration of DOC (and hence FDOM) in sediments relative to bottom water. However, results from organic-rich, anoxic sediments also show considerably higher DOC-normalized fluorescence intensities in pore waters relative to the overlying bottom water (Burdige et al., 2004; Chen et al., 1993), indicating that pore water FDOM fluoresces more intensely than its water column counterpart, at least for these types of sediments. Combined with the fact that

marine sediments are net sources of DOC to the water column (Section VII), sediments are also net sources of FDOM to the water column (Boss et al., 2001; Burdige et al., 2004; Chen et al., 1993; Lübben et al., 2009; Skoog et al., 1996).

A positive correlation between humic-like fluorescence intensity and DOC appears to be the norm in pore waters (e.g., Chen et al., 1993; Seretti et al., 1997; Sierra et al., 2001; Skoog et al., 1996). This is in contrast to water column FDOM, where this relationship can be of an inverse nature depending on the area of study (Coble, 2007). The intercept of the FDOM-DOC regression line further suggests that the overwhelming majority of pore water DOC is fluorescent (Burdige et al., 2004; Chen et al., 1993; Komada et al., 2004). These observations again support the hypothesis that humic-like fluorescence arises from molecularly complex (uncharacterized), poorly reactive DOC that comprises the bulk of the pore water DOC pool (Section II).

There are several lines of evidence supporting a direct link between FDOM and the molecularly uncharacterized, poorly reactive component of bulk DOC. First, slopes of humic-like fluorescence versus DOC concentration have been found to vary with redox potential, with lower slopes observed under more oxidizing (or mixed redox) conditions, both across a redox gradient within a given core (Komada et al., 2004) and across different sedimentary settings (Burdige et al., 2004). In a laboratory incubation experiment using coastal sediments, Skoog et al. (1996) also observed higher benthic FDOM fluxes under anoxic versus oxic conditions. As is discussed in Section VI.C, greater exposure to stronger oxidants such as O_2 appears to result in greater loss of more recalcitrant organic matter (e.g., Blair and Aller, 2012; Burdige, 2007; Zonneveld et al., 2010).

At present, it is not possible to link humic-like fluorescence to specific compounds or fluorophores because the molecular basis for natural DOM fluorescence is unclear (Boehme and Coble, 2000; Del Vecchio and Blough, 2004). Nonetheless, the presence of specific peaks in EEM spectra should hold important clues regarding the composition of FDOM (e.g., Burdige et al., 2004; Coble, 2007; Komada et al., 2002; also see Chapter 10).

Pore water EEM spectra also contain peaks that coincide with those observed in spectra of the aromatic amino acids tryptophan and tyrosine (Burdige et al., 2004; Coble, 1996; Kim et al., 2012; Komada et al., 2002). These protein-like peaks have been associated with high biological activity in the water column (Coble, 2007) and with degradation of fresh biomass (Parlanti et al., 2000). Some studies have observed these peaks to be most pronounced near the sediment-water interface (e.g., Coble, 1996; Seretti et al., 1997), although Burdige et al. (2004) observed protein-like fluorescence to co-vary with bulk DOC, and proposed that protein-like fluorescence is associated with both labile DON that escapes the sediments as a benthic flux and DON that is part of the recalcitrant bulk DOM that accumulates in the pore waters (see Section III.F).

C Carbon Isotope Ratios

Abundances of natural ^{13}C and ^{14}C provide insight into the composition and dynamics of pore water DOC cycling that complement molecular and other compositional studies (e.g., McNichol and Aluwihare, 2007; Raymond and Bauer, 2001b). To the best of the authors' knowledge, only a handful of $\Delta^{14}C$ and $\delta^{13}C$ values for marine pore water DOC ($\Delta^{14}C_{DOC}$ and $\delta^{13}C_{DOC}$, respectively) have been published (Bauer et al., 1995; Heuer et al., 2009; Ijiri et al., 2012; Komada et al., 2013; Valentine et al., 2005). The scarcity of data may be due, in part, to the analytical challenges associated with determining natural C isotope ratios in marine DOC, especially $\Delta^{14}C$ (Bauer, 2002; Johnson and Komada, 2011; also see Chapter 6).

Pore water $\Delta^{14}C_{DOC}$ profiles have been reported for two sites in the northeastern Pacific

Ocean: station N on the continental rise at the base of the Monterey deep-sea fan (Bauer et al., 1995) and Santa Monica Basin (SMB) in the California Borderland (Bauer et al., 1995; Komada et al., 2013). At both sites, $\Delta^{14}C_{DOC}$ values are invariably higher than the $\Delta^{14}C$ value of the overlying bottom water DOC by >100‰ (e.g., see Section V.B), and pore water $\delta^{13}C_{DOC}$ values generally fall between −24‰ and −20‰. These results clearly indicate that DOC flux out of these sediments is dominated by material that is much younger than the DOC found in the deep ocean and that this material appears to be of marine origin. However, as discussed in Section VII.C, these observations belie the more complex role of sediments as a possible source of ^{14}C-depleted (and recalcitrant) DOC to the oceans.

Strongly ^{14}C-depleted DOC has been reported for waters associated with hydrothermal systems and methane seeps. McCarthy et al. (2011) determined $\Delta^{14}C$ and $\delta^{13}C$ signatures of DOC and DIC in ridge-flank and on-axis hydrothermal fluids from the Juan de Fuca Ridge, concluding that DOC in these fluids is synthesized from ^{14}C-depleted DIC by chemosynthetic bacteria. They further suggested that ridge-flank systems might be sources of new, yet ^{14}C-depleted, DOC to the deep ocean. Pohlman et al. (2010) observed that pore water DOC in northern Cascadia margin seep sediments was strongly depleted in both ^{14}C and ^{13}C, concluding that a significant amount of this DOC is derived from fossil methane.

$\delta^{13}C$ values of pore water DOC have been used to gain insight into carbon cycling and metabolic pathways in methane-bearing environments. Heuer et al. (2009) reported $\delta^{13}C$ values of acetate, lactate, and bulk DOC in the upper 190 m of sediments in the northern Cascadia Margin. $\delta^{13}C$ signatures of DOC and lactate ranged from ~−20‰ to −24‰ and were similar to, or slightly higher than, the $\delta^{13}C$ value of bulk sedimentary POC, suggesting little to no ^{13}C-fractionation during fermentation. In contrast, $\delta^{13}C$ signatures of acetate varied widely with depth, which was attributed to the interplay among pathways, and the associated isotope fractionation, of acetate production (fermentation, acetogenesis) and consumption (sulfate reduction, acetoclastic methanogenesis). Ijiri et al. (2012) drew similar conclusions for the uppermost 14 m of sediments of the Bering Sea shelf break.

Valentine et al. (2005) reported $\delta^{13}C$ values for pore water DOC in the uppermost 25 cm of sediments of Hydrate Ridge, a site of intense methane seepage off the coast of Oregon (USA). In contrast to the findings of Heuer et al. (2009) and Ijiri et al. (2012), pore water DOC at this site had $\delta^{13}C$ signatures that deviated from those of bulk sedimentary POC by as much as ±10‰. Also, $\delta^{13}C$ signatures of DOC were as low as −38.3‰. Through mass balance calculations, these authors concluded that pore water DOC was an important carbon source for both heterotrophy and organic carbon accumulation at this site.

D Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS)

Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) is a relatively new analytical technique with very high mass resolution and accuracy, capable of providing exact chemical formulas of LMW (<~1 kDa) DOM compounds (Sleighter and Hatcher, 2007). With this technique, many thousands of DOM compounds can be identified in a single sample, although quantification of the concentrations of these individual compounds is currently not possible (e.g., Kujawinski et al., 2004). Nevertheless, results to date provide important insights into the nature of recalcitrant LMW-DOM in natural systems.

Only a relatively small number of pore water samples have been analyzed by FTICR-MS (Koch et al., 2005; McKee, 2011; Schmidt et al., 2009, 2011; Tremblay et al., 2007), and so few conclusions can be drawn. A wide range of aliphatic

and aromatic compounds have been observed in these studies, with suggested marine and terrestrial sources. Based on elemental ratios and inferred reaction pathways determined using a van Krevelen diagram (e.g., Sleighter and Hatcher, 2007) many of the compounds detected by FTICR-MS appear to represent recalcitrant compounds produced by microbial and/or photochemical degradation processes (also see related discussions in Chipman et al., 2010).

More specifically, weighted average H/C (~1.2-1.3) and O/C (~0.4-0.5) values for these pore water samples (Koch et al., 2005; Schmidt et al., 2009) plot within the region on a van Krevelen diagram that Hertkorn et al. (2006) identify as representing carboxyl-rich alicyclic molecules (CRAM). CRAM is thought to represent a major component of recalcitrant DOM in the oceans. When these results are examined in the context of Figure 12.2, we see that they support the notion of relatively LMW recalcitrant DOM being produced during the course of organic matter remineralization in sediments. FTICR-MS studies focusing on N-containing compounds in Black Sea sediment pore waters (Schmidt et al., 2011) similarly suggest that when these DON compounds are plotted on a van Krevelen diagram they too fall within the region discussed above for recalcitrant DOM.

In two contrasting organic-rich sediments (Mangrove Lake sediments and sediments on the northwest Iberian continental margin off Spain), a relatively large number of sulfur-containing DOM compounds were observed in pore waters by FTICR-MS (McKee, 2011; Schmidt et al., 2011). In both studies, it was suggested that organic matter sulfurization is responsible for these compounds. However, it is not clear whether this sulfur addition occurs to DOM precursors or whether sulfur addition to POM itself is the precursor to S-containing DOM compounds. Regardless of their mode of formation, S-containing DOM molecules are likely to be fairly recalcitrant (e.g., see related discussions in Kohnen et al., 1992; Tegelaar et al., 1989).

E Nuclear Magnetic Resonance (NMR)

Only a small number of pore water samples have been analyzed by nuclear magnetic resonance (NMR), and in all cases only HMW extracts (>0.5 or 1 kDa, depending on the study) were examined (Orem and Hatcher, 1987; Orem et al., 1986; Repeta et al., 2002). In the suite of samples studied by Orem and Hatcher (1987), they observed that samples from predominantly anoxic settings were dominated by carbohydrate resonances, while DOM from more aerobic settings had NMR spectra with diminished carbohydrate character and greater aromatic character. They suggested that these differences might be the result of more effective decomposition of carbohydrates under oxidizing conditions plus significantly lower rates of lignin degradation (as the source of the observed aromatic resonances) under anoxic conditions.

The HMW pore water DOM extracts analyzed by Repeta et al. (2002), all from settings that could be considered anoxic in the context of the definitions from the Orem and Hatcher (1987) study, also had major contributions to their NMR spectra from carbohydrates, as well as bound acetate, and lipids. Acetate and carbohydrate resonances, when coupled with monosaccharide analyses of acid-hydrolyzed extracts, were interpreted as being indicative of relatively high concentrations of acylated polysaccharides in these pore waters (see Section V.B for details).

F DON and the C/N Ratio of Pore Water DOM

Much of what has been said about DOC in sediment pore waters applies equally well to pore water DON, in that nitrogen-containing DOM is also a heterogeneous class of organic compounds that range from well-defined biochemicals such as urea or amino acids, to larger dissolved proteins and peptides, to more complex (and poorly characterized) N-containing humic and fulvic acids (see recent reviews in Aluwihare and

Meador, 2008; Worsfold et al., 2008). Similarly, much of the DON in pore waters is uncharacterized at the compound level. Lomstein et al. (1998) were able to quantify ~40% of the DON in Danish coastal sediment pore waters as dissolved free and combined amino acids, although as discussed in Section IV.C the details about what these combined amino acids actually represent is uncertain.

Nitrogen found in marine DOM can have several types of functionality, although in HMW-DOM in the water column much of this functionality appears to be in the amide ($-CONH_2$) form (e.g., Aluwihare and Meador, 2008). This issue has not yet been examined in sediment pore waters, although given the important role of proteins (in general) and amino acids (in particular) in sedimentary carbon and nitrogen remineralization (Burdige and Martens, 1988; Cowie et al., 1992; Henrichs and Farrington, 1987) and preservation (e.g., Moore et al., 2012), amide or amine ($-NH_2$) functionality for much of the pore water DON seems likely. The factors controlling the preservation of nitrogen in marine sediments is an important topic of research (Derenne et al., 1998; McKee and Hatcher, 2010) and reactions involving DON intermediates might be expected to play some role in the preservation process (see discussions in Burdige, 2001; Schmidt et al., 2011).

Despite the lack of detailed information regarding the specific components that make up DOM in pore waters, the simultaneous determination of pore water DOC and DON does allow for the examination of the C/N ratio of pore water DOM ($=C/N_{pDOM}$), which can yield insights into the composition, reactivity, and cycling of pore water DOM. Pore water profiles of DON and C/N_{pDOM} from selected marine sediments are shown in Figure 12.4 and Table 12.1 contains a more detailed summary of C/N_{pDOM} values and depth trends from a wide range of marine sediments.

At least four general conclusions can be made from these observations. The first is that when C/N_{pDOM} values in estuarine Chesapeake Bay sediments are compared with the C/N ratio of DOM benthic fluxes, we see that DOM accumulating in sediment pore waters is depleted in nitrogen as compared to that which escapes the sediments as a benthic flux (Figure 12.6). This uncoupling is consistent with other field observations (Blackburn et al., 1996; Landén-Hillmeyr, 1998) and model results (Burdige, 2002; and Figure 12.3) and will be discussed in further detail in Section VII.C.

A second observation is that in sediments where there is a significant input of terrestrial organic matter (e.g., site N3 in the Chesapeake Bay and ODP core 1075 from the Southwest African Margin), C/N_{pDOM} values tend to be higher. This is consistent with the fact that terrestrially derived organic matter is generally depleted in nitrogen as compared to marine organic matter (C/N values of ~20-80 vs. ~6-8; e.g., Burdige, 2006b).

A third observation is that in oxic or mixed redox sediments, C/N_{pDOM} values tend to be relatively low as compared to more strict anoxic sediments. This result can be seen in Chesapeake Bay site S3 sediments, in Patton Escarpment sediments, and in oxic, pelagic sediments in the southwest Pacific. One possible explanation for these observations involves benthic macrofaunal processes that may produce low C/N ratio organic compounds, such as urea ($C/N = 0.5$) (Burdige and Zheng, 1998; Lomstein et al., 1989). However, in the bioturbated sediments at site S3 in Chesapeake Bay, urea is not a significant component of the pore water DOM pool (Burdige, 2001). Another possible source of low C/N ratio pore water DOM compounds in mixed redox sediments are bacteria. Bacteria have C/N ratios that range from ~3 to 5 (Fenchel et al., 1998), so grazing of bacteria by higher organisms in oxic or mixed redox sediments (Kemp, 1990; Lee, 1992) could lead to the production of DOM with a low C/N ratio (e.g., certain amino acids; see Section IV.C for further details). The absence of bacterial grazing in anoxic sediments would

TABLE 12.1 C/N Ratios of Pore Water DOM (C/N_{pDOM}) in Marine Sediments

Site	Sediment Depth (max.)	C/N_{pDOM} (range)	C/N_{pDOM} (Depth Variations)	Sediment Characteristics
Coastal, estuarine sediments				
Chesapeake Bay site M3[a]	30 cm	~12-18	No coherent trend with depth, but depth-weighted averages show seasonal variations and are highest when remineralization rates are lowest	Anoxic, non-bioturbated; sulfate reduction and methanogenesis dominate organic matter remineralization
Chesapeake Bay site S3[a]	30 cm	~8-14	No coherent depth trends	Mixed redox conditions; sediments are bioturbated and bioirrigated
Chesapeake Bay site N3[a]	30 cm	~10-30	Increase with depth	Sediment organic matter is largely terrestrially derived; some bioturbation in the upper ~5 cm of sediment
Danish coastal sediments[b]	5 cm	~10-20	~20 (upper 1 cm), constant below this depth (=~10-11)	Shallow water depth (4 m); upper ~10 cm of sediment is bioturbated
Lower St. Lawrence estuary (CA)/Gulf of St. Lawrence[c]	~2-3 cm	~5-14	Sediment depth variations not reported, although average C/N_{pDOM} values increase as one moves from the lower estuary into the Gulf	As one moves from the lower estuary into the Gulf sediment organic matter reactivity decreases, sediment oxygen exposure increases, and the relative importance of terrestrial organic matter in the sediments decreases; salinity is high (>30) in the bottom waters, with little variation along this transect
Continental margin and deep sea sediments				
Mid-Atlantic shelf/slope break (400-750 m water depths) [d]	30 cm	~7-17	Increase with depth in most cores	Sub-oxic sediments with minimal bioturbation in the upper 20-30 cm of sediments; nitrate becomes undetectable in the upper 1-4 cm of sediment; linear sulfate gradients in the upper 25 cm of sediment
Santa Monica Basin (California Borderlands; 900 m water depth)[e]	30 cm	~7-18	Increase with depth (7-12 near sediment surface, 7-18 at depth)	Anoxic, sulfidic sediments with no bioturbation or bioirrigation
San Clemente Basin (California Borderlands; ~2000 m water depth)[e]	30 cm	~7-17	Increase with depth (7-10 near sediment surface, ~17 at depth)	Sub-oxic sediments; pore water O_2 depleted in the upper 1 cm of sediment, nitrate depleted by ~2-5 cm sediment depth

TABLE 12.1 C/N Ratios of Pore Water DOM (C/NpDOM) in Marine Sediments—cont'd

Site	Sediment Depth (max.)	C/N_{pDOM} (range)	C/N_{pDOM} (Depth Variations)	Sediment Characteristics
Patton Escarpment (eastern North Pacific; ~3700 m water depth)[e]	30 cm	~5-15	Minimum value observed ~1-2 cm below the sediment surface; increase with depth below	Pore water O_2 depleted at a sediment depth of ~2.5 cm, nitrate depleted by ~4-10 cm sediment depth; some sediment bioturbation and bioirrigation
Hatteras continental rise (northwest Atlantic; ~4200 m)[f]	30 cm	~6-11	No obvious depth trends	Sub-oxic sediments; nitrate depleted by ~8 cm sediment depth after an initial increase in the upper 1-2 cm of sediment
Southwest Pacific pelagic sediments (~2800-5400 m water depths)[g]	30-50 cm	~2-7	No obvious depth trends	Oxic sediments; nitrate increases with depth in an exponential-like fashion
"Deep" sediment cores (Southwest African Margin)[h]				
Lower Congo Basin (ODP Leg 175, core 1075; ~3000 m water depth)	60 m	20 (±7)	No obvious depth trends	Anoxic sediments; sulfate is depleted by ~30 m sediment depth; marine and terrestrial organic matter sources
Walvis Basin (ODP Leg 175, core 1082; ~1300 m water depth)	360 m	11.3 (±3.2)	No obvious depth trends	Anoxic sediments; sulfate is depleted by ~20 m sediment depth; predominant marine organic matter sources

[a]*Data from Burdige and Zheng (1998) and Burdige (2001).*

[b]*Data from Lomstein et al. (1998).*

[c]*Data from Alkhatib et al. (2012, 2013).*

[d]*Data from Burdige and Gardner (1998) and Burdige et al. (2000, unpub. data).*

[e]*DOC and DON data from Burdige et al. (1999, unpub. data). Other data from Shaw et al. (1990), Berelson et al. (1996), and W. Berelson (pers. comm.).*

[f]*Data from Heggie et al. (1987).*

[g]*Data from Suess et al. (1980).*

[h]*DOC and DON data from Burdige et al. (unpub. data); other data from Wefer et al. (1998).*

then minimize the production of low C/N ratio and bacterially derived DOM (also see discussions in Burdige, 2001).

However, studies conducted in the lower St. Lawrence estuary, Canada contrast with the second and third general observations discussed above. As one moves down this estuary into the Gulf of St. Lawrence, there is an increase in C/N_{pDOM} from ~5 to ~14 in surface (upper ~2-3 cm) sediment pore waters as the relative input of terrestrial organic matter to the sediments decreases and sediment oxygen exposure time increases (Alkhatib et al., 2013). These authors attribute these trends in C/N_{pDOM} to a decrease in sediment organic matter reactivity along with the increase in sediment oxygen exposure time (also see Alkhatib et al., 2012). Additional work is needed to examine the reasons for contrasting trends among these environments.

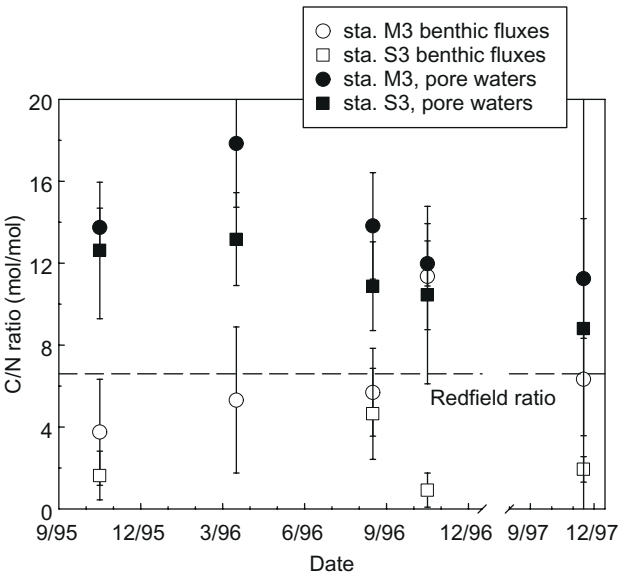

FIGURE 12.6 Temporal changes in the depth-weighted average value of C/N_{pDOM} (e.g., see Figure 12.4) in the pore waters (closed symbols) and the C/N ratio of the DOM escaping the sediments (i.e., the ratio of the DOC benthic flux to the DON benthic flux, open symbols) at stations S3 and M3 in the Chesapeake Bay. *Data from Burdige and Zheng (1998) and Burdige et al. (2004).*

The final observation based on the results in Table 12.1 is that in most of the continental margin sediments examined to date, C/N_{pDOM} values increase with sediment depth (also see the San Clemente Basin profiles in Figure 12.4). Since there is evidence for the occurrence of terrestrially derived organic matter in such continental margin sediments (see reviews in Blair and Aller, 2012; Burdige, 2006b), one explanation of these C/N_{pDOM} values is that the increased remineralization of terrestrially derived organic matter becomes increasingly important with depth, leading to the production of DOM with higher C/N ratios. Implicit in this assumption is that N-depleted, terrestrially derived organic matter deposited in these sediments is less reactive than marine-derived POM (e.g., see Burdige, 1991a).

In contrast, C/N_{pDOM} values in Chesapeake Bay estuarine sediments do not increase with sediment depth (Burdige and Zheng, 1998), despite decomposition studies suggesting that terrestrially derived POM undergoes remineralization with depth in these sediments (Burdige, 1991a). The reasons for these differences are not understood, although the results suggest that there may not be a tight coupling between the C/N ratio of sediment POM undergoing remineralization and that of its DOM intermediates (or its recalcitrant "end products," e.g., DOM in box "C" in Figure 12.2; also see discussions in Alkhatib et al., 2013). Schmidt et al. (2011) similarly suggested that FTICR-MS analyses of N-containing DOM compounds in sediment pore waters can be explained by proteins and peptides undergoing reactions that reduce the molecular size, nitrogen content, and potentially the reactivity of the products.

IV COMPOSITION AND DYNAMICS OF DOM AT THE COMPOUND AND COMPOUND-CLASS LEVELS

When looking at studies that have characterized pore water DOM at the compound or compound-class level, we note that most efforts have focused on examining concentrations and cycling of compounds that fall into the mLMW-DOM category (box "D" in Figure 12.2; also see Henrichs, 1993 for an earlier summary). While some work has been carried out

examining the dynamics of the HMW-DOM pool (Arnosti, 2000; Boschker et al., 1995; Mayer and Rice, 1992; Pantoja and Lee, 1999; Robador et al., 2010), few studies have examined its chemical composition.

A Short Chain Organic Acids (SCOAs)

Interest in the study of short-chain organic acids (SCOAs) such acetate, lactate, formate, propionate, and butyrate in marine sediments stems from the observation that these compounds are important in situ substrates/electron donors (along with H_2) for terminal anaerobic remineralization processes such as iron reduction, sulfate reduction, and methanogenesis (e.g., Finke et al., 2007; Lovley and Phillips, 1987; Parkes et al., 1989; Sansone and Martens, 1982; Sørensen et al., 1981; Thamdrup, 2000; Valdemarsen and Kristensen, 2010). These organic acids are largely produced by fermentation reactions that fall along the left side of Figure 12.2 (e.g., Thauer et al., 1977). However, acetate can also be produced by CO_2 reduction using H_2 in a microbial process referred to as acetogenesis (Ragsdale and Pierce, 2008).

In the uppermost ~30 cm of most anoxic sediments, acetate concentrations range from <1 to up to ~100 μM, generally increasing with sediment depth (Albert and Martens, 1997; Barcelona, 1980; Christensen and Blackburn, 1982; Heuer et al., 2009; Hines et al., 1994; Knab et al., 2008; Novelli et al., 1988; also see Burdige, 2002 for a more detailed list of earlier publications). In many of these studies, total DOC concentrations were generally not determined along with acetate, although where both measurements were made (or where DOC concentrations can be obtained from other published studies), acetate usually accounts for at most ~5%, and often times <1%, of the total pore water DOC.

Concentrations of other SCOAs such as formate or propionate have not been determined as frequently as acetate although when determined, their concentrations can be comparable to those of acetate (Albert and Martens, 1997; Barcelona, 1980). Previous studies (summarized in Henrichs, 1993) have also concluded that much of the acetate and other SCOAs that can be chemically measured may not be biologically available, possibly due to complexation in the pore waters; Finke et al. (2007) support these earlier suggestions. Given the importance of SCOAs as substrates for terminal anaerobic remineralization processes, all of these observations reinforce the notion that material in the mLMW-DOM pool (Figure 12.2) represents a small fraction of the total sediment pore water DOM pool whose concentration is held at relatively low levels due to rapid microbial utilization.

It is generally thought that competition for key substrates (electron donors) such as acetate or H_2 plays a major role in regulating the biogeochemical zonation of different anaerobic terminal remineralization processes (Canfield et al., 2005; Hoehler et al., 1998; Lovley and Goodwin, 1988; Lovley and Phillips, 1987). Furthermore, concentrations of these key substrates increase with decreasing energy yield of the remineralization process. For example, iron reducers appear able to maintain H_2 concentrations at levels that are too low for sulfate reducers to utilize H_2, as sulfate reducers similarly do to out-compete methanogens for this substrate (Hoehler et al., 1998; Lovley and Goodwin, 1988).

Incubations of freshwater sediments by Lovley and Phillips (1987) show an overall order of magnitude increase in the acetate concentration when the dominant terminal remineralization process changes from iron reduction to sulfate reduction to methanogenesis. In contrast, similar competitive inhibition of acetate uptake did not affect sulfate reduction and iron reduction in surface (0-2 cm) Arctic marine sediments (Finke et al., 2007). However, field data, as well as other sediment incubation studies and bioenergetics model calculations, generally do show that the transition in marine sediments (either spatially or temporally) from sulfate reduction to methanogenesis results in an increase in acetate concentrations (Alperin

et al., 1994; Dale et al., 2006; Heuer et al., 2009; Hoehler et al., 1998; Knab et al., 2008).

Slightly different trends have been observed in deeply buried sediments (the so-called deep marine biosphere; i.e., depths beginning at 10s to 100s of meters below the seafloor, mbsf). For example, in gas hydrate-containing sediments on the Blake Ridge on the southeast US continental margin, acetate increases to a maximum concentration of ~15 mM (~15% of the total DOC) in methanogenic sediments at depths of ~750 mbsf (Egeberg and Dickens, 1999) while complete sulfate depletion in the pore waters occurs at a significantly shallower sediment depth, that is, ~20 mbsf. This acetate buildup is attributed to a temperature increase with depth (due to the natural geothermal gradient) that stimulates acetate production over acetate consumption by methanogens (Wellsbury et al., 1997). Of equal importance is the fact that acetate consumption appears to occur several hundred meters shallower in the sediment column relative to its depth of production (Egeberg and Dickens, 1999). Similar depth trends were also observed in hydrate-containing sediments on the Peru margin (site 1230, Leg 201; D'Hondt et al., 2003). Here acetate concentrations increase from <20 μM to ~60 μM at ~10 mbsf, where sulfate concentrations go to zero, and then increase again dramatically to ~200 μM (~2% of total DOC) at ~140 mbsf. This spatial separation between acetate production and consumption in the deep marine biosphere is very different than that seen in anoxic surficial sediments (see references above) where acetate production and consumption do not show such dramatic spatial uncoupling. Further study is required to assess the significance of these observations in terms of general biogeochemical dynamics of the deep marine biosphere.

B Carbohydrates

Total dissolved carbohydrates (TDCHOs) have been determined in a limited number of coastal and continental margin sediments, with concentrations that generally range from ~10 to 400 μM C (Arnosti and Holmer, 1999; Burdige et al., 2000; Jensen et al., 2005; Lyons et al., 1979; Robador et al., 2010). In most cases TDCHO concentrations increase with depth in the upper ~20-30 cm of sediment and represent ~10-40% of the total DOC. Such relative TDCHO concentrations generally decrease in this sediment depth range although the magnitude of these changes vary among the few sites that have been examined (see Burdige et al., 2000, for details).

There have been few studies of individual aldoses (monomeric neutral sugars) in sediment pore waters. In selected pore water samples from Chesapeake Bay and mid-Atlantic shelf/slope break sediments, after acid hydrolysis ~30-50% of the TDCHOs could be identified as individual aldoses (Burdige et al., 2000), although lower percentages were observed in Danish continental margin sediments of the Skagerrak, Kattegat, and Belt Seas (Jensen et al., 2005). In the Burdige et al. (2000) study, total aldose yields (total individual aldose concentrations as a percentage of DOC) are higher in continental margin sediment pore waters (~9%) than they are in the estuarine sediment pore waters (<5%), while values in the Danish continental margin sediments range from 0.05% to 4% (Jensen et al., 2005). In both studies, dissolved glucose is the predominant aldose.

These results suggest that dissolved carbohydrate concentrations in sediment pore waters are not strongly tied to particulate (sediment) carbohydrate concentrations, and TDCHO concentrations may be more strongly controlled by sediment remineralization processes (Burdige et al., 2000). Early studies also suggested that these TDCHOs likely represent some of the initial HMW intermediates produced and consumed during sediment POC remineralization (Arnosti and Holmer, 1999; Burdige et al., 2000). However, several recent studies indicate that this may not necessarily be the case.

In long-term (24 months) sediment incubations with Arctic and temperate sediments, Robador et al. (2010) observed an absolute and relative increase with time in TDCHO concen-

trations. They interpret this as being the result of the accumulation of recalcitrant carbohydrates, although the absence of molecular weight data does not allow us to determine whether these are HMW or LMW entities. At the same time, in pore waters collected from sediment depths of ~100-300 mbsf in the equatorial Pacific and Peru margin (ODP Leg 201; Burdige, 2006a), TDCHOs represent up to three quarters of the total DOC (0.76 ± 0.46, at the three open ocean sites; Figure 12.7). Furthermore, in these deeply buried sediments, as is also seen in shallow estuarine and continental margin sediments, there appears to be an inverse relationship between the relative concentrations of pore water TDCHOs and rates of sediment carbon oxidation (Figure 12.7).

One interpretation of these observations is that recalcitrant carbohydrates may be directly produced through the decomposition of more recalcitrant components of the POC pool; this has also been discussed in terms of a "decoupling" of initial hydrolysis of POC and downstream fermentative and/or terminal metabolism (Robador et al., 2010). This observation is discussed in a more general sense in Section V. However, little is known about these recalcitrant carbohydrates. One suggestion regarding their occurrence is that structural changes (e.g., methylation, sulfurization) may render reactive carbohydrates less susceptible to further degradation. Such changes may also make individual aldoses in these carbohydrates difficult to identify after acid hydrolysis, yet may not impact their detection by the colorimetric procedures used in many of these studies to determine total dissolved carbohydrates (Burdige et al., 2000; Robador et al., 2010). Studies of the HMW isolates of three pore water samples from coastal and organic-rich continental margin sediments further indicate relatively high concentrations of acylated polysaccharides (APS) in pore waters (Repeta et al., 2002). APS represents a group of compounds that appear to be produced by marine phytoplankton and are

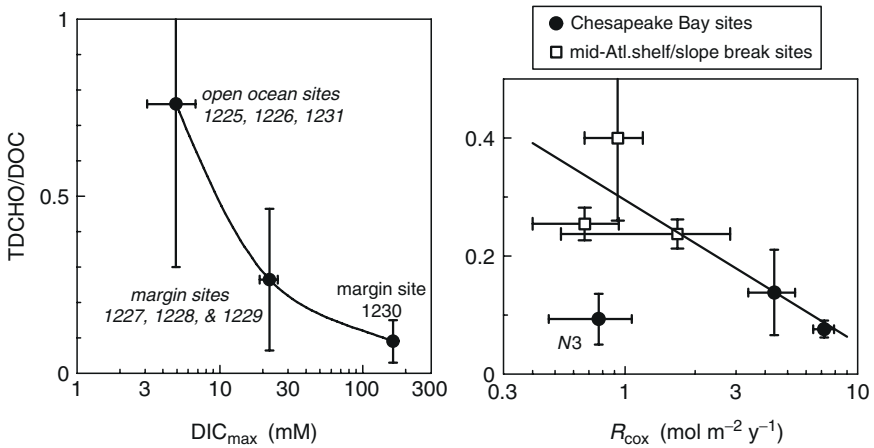

FIGURE 12.7 Apparent inverse relationship between the relative concentration of pore water TDCHOs and the rate of sediment carbon oxidation. (left panel) The relative concentrations of total dissolved carbohydrates (TDCHO/DOC) versus the maximum concentrations of DIC in the pore waters (DIC_{max}) at open-ocean and Peru margin sites from ODP Leg 201; data from Burdige (2006a). Note that here DIC_{max} is used as a proxy for the sediment carbon oxidation rate. (right panel) TDCHO/DOC versus the depth-integrated rate of sediment carbon oxidation at Chesapeake Bay (closed circles) and mid-Atlantic shelf/slope break sites (open squares); data from Burdige et al. (2000). Also shown here is the best fit line through this semi-log plot of the data ($y = -10.54 \ln(x) + 29.48$; $r^2 = 0.73$), excluding the data point from sta. N3. In contrast to the other sites in this panel, terrestrial organic matter predominates over marine organic matter in sta. N3 sediments (Burdige et al., 2000; Marvin-DiPasquale and Capone, 1998), which may explain why its values do not fall on the best fit line shown here.

defined as being "semi-reactive" in the surface ocean, i.e., having turnover times on the order of years to decades (Repeta and Aluwihare, 2006). While APS production might explain the results from the incubation studies of Robador et al. (2010), it is difficult to see how it could explain high relative concentrations of recalcitrant carbohydrates in the pore waters of deeply buried sediments where the time scales of remineralization are clearly significantly longer than decades (Burdige, 2006a).

C Amino Acids

Amino acids comprise significant amounts of the carbon and nitrogen that are remineralized in marine sediments (e.g., Burdige and Martens, 1988; Cowie and Hedges, 1992; Henrichs and Farrington, 1987) and pore water dissolved amino acids are likely important intermediates in this process (also see references cited below in this section). Dissolved amino acids in sediment pore waters may be "free" monomeric amino acids (DFAAs) as well as combined amino acids (DCAAs); the latter generally either represent dissolved peptides (originally produced by the hydrolysis of larger proteins, e.g., Roth and Harvey, 2006) or may be incorporated into humic-like substances. Combined amino acids (at least those found in dissolved peptides) can be further hydrolyzed and deaminated to produce, among other end products, smaller peptides, ammonium, and DFAAs (e.g., Jacobsen et al., 1987; Pantoja and Lee, 1999). DFAAs can be used in a wide range of fermentation reactions, generally producing H_2 and short-chain organic acids such as acetate (Barker, 1981; Thauer et al., 1977). DFAAs can also be used directly by sulfate-reducing bacteria (e.g., Takii et al., 2008).

Studies to date in anoxic sediments suggest that most remineralization of DFAAs occurs by fermentation rather than by sulfate reduction (Burdige, 1991b; Hansen and Blackburn, 1995; Valdemarsen and Kristensen, 2010), although there appear to be exceptions (Hansen et al., 1993; Wang and Lee, 1995). In any event, when compared to H_2 or short-chain organic acids such as acetate, free amino acids are likely minor electron donors, at best, for total sulfate reduction in sediments (Burdige, 1989; Parkes et al., 1989; Valdemarsen and Kristensen, 2010)

DFAAs in pore waters have been examined in a wide range of sediments, including those in salt marsh, estuarine, coastal, continental margin, and deep-sea settings (e.g., Burdige and Martens, 1990; Haberstroh and Karl, 1989; Henrichs et al., 1984; Landén and Hall, 1998, 2000; Lomstein et al., 1998). Several of these studies have examined amino acid adsorption to sediments as well as DFAA turnover rates (also see Christensen and Blackburn, 1980; Ding and Henrichs, 2002; Henrichs and Sugai, 1993; Liu and Lee, 2007; Rosenfeld, 1979; Wang and Lee, 1993). Concentrations of total dissolved free amino acids (TDFAAs) generally decrease with sediment depth, with surface pore water concentrations usually ranging from ~20 to 200 μM and concentrations below 10-20 cm being <5-10 μM. In the few studies where total DOC and DON have been examined along with amino acids, TDFAAs represent 1-13% of the DON and <4% of the DOC (Henrichs and Farrington, 1987; Landén and Hall, 2000; Lomstein et al., 1998).

The predominant amino acids in the DFAA pool include glutamic acid, alanine, glycine, aspartic acid, and, in some sediments, the nonprotein amino acid β-aminoglutaric acid (β-aga), an isomer of glutamic acid. Among the protein amino acids, the DFAA pool is generally enriched in glutamic acid relative to the sediment hydrolyzable amino acid pool. Other nonprotein amino acids in addition to β-aga, such as β-alanine, can also be enriched in pore waters relative to the sediments. These and other compositional differences between pore water and sediment amino acids are likely related to both biological and physical (e.g., adsorption) processes that affect amino acids as they undergo remineralization (Burdige and Martens, 1990; Henrichs and Farrington, 1987).

In anoxic sediments, the mole percentage of β-aga generally increases with depth (upper ~30 cm), with β-aga often becoming the predominant DFAA in pore waters (> ~40 mol%) (Burdige and Martens, 1990; Henrichs and Farrington, 1979; Henrichs et al., 1984). In contrast, β-aga appears to be a much less important component of the pore water DFAA pool in oxic or mixed redox sediments (Caughey, 1982; Henrichs and Farrington, 1980; Landén and Hall, 2000). The source(s) of β-aga in sediment pore waters are not well characterized (Burdige, 1989; Henrichs and Cuhel, 1985) and its relative accumulation with depth in anoxic sediments may occur because it is more recalcitrant than other amino acids (Henrichs and Farrington, 1979). The proposed recalcitrant nature of β-aga may also be a function of sediment redox conditions, similar to that observed for other recalcitrant components of the pore water DOM pool (Burdige, 2001; also see Section VI.C).

Along similar lines, there could be broader compositional differences in the dissolved amino acid pool in anoxic versus oxic/mixed redox sediments that might help explain the low C/N_{pDOM} values in these latter sediments (see Section III.F). Specifically, Burdige (2002) suggested that glycine (C/N = 2) may be preferentially enriched in the pore waters of mixed redox versus strictly anoxic sediments. However, glycine is also an abundant amino acid in many benthic invertebrates (Henrichs and Farrington, 1980), and so elevated glycine levels may simply result from the release of this amino acid by benthic organisms during core collection and/or pore water processing (Burdige and Martens, 1990; Jørgensen et al., 1981). Further studies will be needed to critically examine these observations (also see discussions in Burdige, 2001).

In contrast to studies of DFAAs, there have been far fewer studies of DCAAs in marine sediment pore waters (Caughey, 1982; Kawahata and Ishizuka, 2000; Lomstein et al., 1998; Ogasawara et al., 2001; Pantoja and Lee, 1999). In general, concentrations of total DCAAs are ~1.5-4 times that of total DFAAs. Given the small data set on pore water DCAAs, it is difficult to determine whether the composition of the DCAA pool is more similar to that of DFAAs or hydrolyzable sediment amino acids. Such information could be important in determining the extent to which the DCAA pool represents dissolved peptides or proteins (i.e., "reactive" HMW intermediates of sediment organic matter remineralization) or perhaps abiotic condensation products of, for example, melanoidin-type reactions. In the former case, the DCAA pool might be expected to be more similar to that of sediment (hydrolysable) amino acids, while in the latter case the amino acid distribution in DCAAs might be expected to look more like DFAAs (for further discussions, see Burdige, 2002).

V MODELING DOC CYCLING IN MARINE SEDIMENTS

A Production of Recalcitrant DOC: General Observations

Consistent with Figure 12.2 and discussions in Section II, a number of incubation studies show production of DOC that appears recalcitrant on time scales comparable to those over which organic matter remineralization and inorganic nutrient regeneration occur (Brüchert and Arnosti, 2003; Chipman et al., 2010; Hee et al., 2001; Komada et al., 2012; Robador et al., 2010; Weston and Joye, 2005). Production of recalcitrant DOC was observed in flow through column reactor studies run for only several hours (Chipman et al., 2010) to closed system sediment incubations lasting months (Komada et al., 2012) to years (Robador et al., 2010). In at least one of these studies (Chipman et al., 2010), FTICR-MS analyses of the produced DOM indicated the presence of lignin- and tannin-like compounds. These compounds are presumed to be fairly recalcitrant, in part because of their high degree of aromaticity (e.g., Bianchi and Canuel, 2011).

In cases where such compositional information is not available, accumulation of "recalcitrant" DOC in incubation studies could also be due to a decoupling between DOC production and degradation, as opposed to production of inherently recalcitrant DOC (Robador et al., 2010; Weston and Joye, 2005). Looking at Figure 12.2, a decrease in carbon flow from box "A" to "B" or box "B" to "D" relative to the initial organic matter breakdown (sediment POM to box "A") could, for example, result in the accumulation of DOM in boxes "A" or "B." This suggestion also reinforces the point that describing the DOC accumulating in these experiments as "recalcitrant" is somewhat subjective and in part may be a function of the time scale of the study.

In considering the production of recalcitrant DOC during overall POC remineralization, it may also be difficult to distinguish between "direct" production of recalcitrant DOC from POC or HWM intermediates (i.e., pathways *1-3* in Figure 12.2) versus pathways by which more labile LMW intermediates are transformed into recalcitrant components (i.e., pathway *4* in Figure 12.2). While there is evidence that complexation reactions can decrease the reactivity, or bioavailability, of simple monomers such as acetate (Christensen and Blackburn, 1982; Finke et al., 2007; Michelson et al., 1989), the long-term fate of these complexes is uncertain. At the same time, there is little direct evidence for the occurrence of aqueous phase geopolymerization reactions in nature (Hedges, 1988; Hedges and Oades, 1997; Henrichs, 1992), and abiotic condensation reactions involving LMW monomeric reactants are likely to be quite slow in comparison to their biological uptake or remineralization to inorganic end products (Alperin et al., 1994). If these internal conversion processes are indeed slow, it is unlikely that they would have been detected in incubation experiments such as those discussed here (also see discussions in Section VI.B).

Another important constraint on in situ production of recalcitrant DOC from labile intermediates comes from radiocarbon (^{14}C) analysis of the DOC produced in the incubation study of Komada et al. (2012). They saw net production of DOC depleted in ^{14}C by at least 200‰ relative to the DIC produced by fermentation and/or terminal respiration of POC, itself enriched in ^{14}C and containing at least some bomb-^{14}C. Given the extremely short time period of this incubation study (~4 months) relative to the half-life of ^{14}C (5730 year), in situ production and ageing of recalcitrant DOC is not possible and its production from pre-aged (^{14}C-depleted) POC is therefore a plausible explanation. Related discussions of this point are also presented in the next section.

B The Multi-*G* + DOC Model

In applying the model in Figure 12.2 to the incubation studies discussed above, an important point to recall is that different types of POC undergo remineralization with time, or in the case of sediments in situ, with depth in the sediment column. Remineralization therefore continually fractionates POC by preferentially using the most reactive material available and thus decreases the overall reactivity of that remaining (e.g., Cowie and Hedges, 1994; Middelburg, 1989). One approach to parameterizing these changes assumes that POC can be "quantized" into discrete classes with different reactivities and chemical properties, as in the multi-*G* model (Burdige, 1991a; Westrich and Berner, 1984). Other formulations allow for changes (decreases) in POC reactivity to be viewed as a continuous function of the age of the material, and therefore depth in a sediment column (Boudreau and Ruddick, 1991; Middelburg, 1989). There are some advantages to this latter approach to describe sediment organic matter reactivity. However, in the context of modeling DOC cycling in sediments (or in sediment incubation studies), this approach has distinct disadvantages with regard to parameterizing the changing properties of sediment POC undergoing remineralization beyond its bulk reactivity

and therefore linking POC remineralization to DOC cycling. Thus, in the following discussions, we will use a multi-*G* approach to link DOC cycling to POC remineralization.

Referring to Figure 12.2, the specific DOC transformation pathways, their rates, and the types of recalcitrant DOC that may be produced, could all depend on the source POC. Further complicating this discussion is that there are few field data with which to parameterize the types of DOC cycling illustrated in Figure 12.2 in reactive-transport (early diagenesis) models. The model illustrated in Figure 12.3 (Burdige, 2002) was one such attempt (albeit highly simplified), as was the work of Dale et al. (2008). However, this latter study focused on DOC cycling as it primarily relates to mLMW-DOC compounds (box "D" in Figure 12.2), that is, substrates such as acetate and H_2 that are directly utilized by sulfate-reducing and methanogenic bacteria.

In our most recent work (Komada et al., 2013), we approached this problem using what we refer to as the multi-*G*+DOC model (Figure 12.8). In this model, it is assumed that isotopically and kinetically heterogeneous DOC is produced and consumed during remineralization of multiple pools of metabolizable organic matter (G_i), each of which is characterized by distinct $\Delta^{14}C$ and $\delta^{13}C$ signatures (Δ_i and δ_i in Figure 12.8). Different DOC fractions (DOC_i) are produced by first-order degradation of G_i with degradation rate constant k_i, and it is assumed that DOC_i has the same isotopic values as its parent. This DOC_i is then oxidized to DIC without isotopic fractionation (Boehme et al., 1996; Heuer et al., 2009; Penning and Conrad, 2006) with rate constant k_{DOCi}. In the context of the conceptual model in Figure 12.2, the multi-*G*+DOC model takes the complexity of DOC cycling in this figure and simplifies it such that the k_{DOCi} value for each DOC_i pool effectively integrates (or averages) over the reactivity of all DOC intermediates produced and consumed downstream of the parent, particulate G_i material.

The multi-*G*+DOC model was used in the interpretation of pore water $\Delta^{14}C_{DOC}$ and $\delta^{13}C_{DOC}$ profiles obtained from the Santa Monica Basin (Komada et al., 2013; Figure 12.9). These kinetics were implemented in a steady-state, variable-porosity, reactive-transport model for carbon species in the uppermost 45 cm of the sediment column. The values of $\Delta^{14}C_{DOC}$ are about the same as, or slightly higher than, $\Delta^{14}C$ values of bulk POC, while $\Delta^{14}C_{DIC}$ is higher than $\Delta^{14}C$ values of bulk POC and DOC, indicating that POC remineralization is a selective process in which net oxidation of younger components of the POC pool to DIC occurs at a faster rate than older counterparts. Furthermore, the $\Delta^{14}C_{DOC}$ profile shows a large drop (~200‰) from the maximum value observed in the uppermost 2 cm to that observed at 30-cm sediment depth (Figure 12.9); this drop is too large

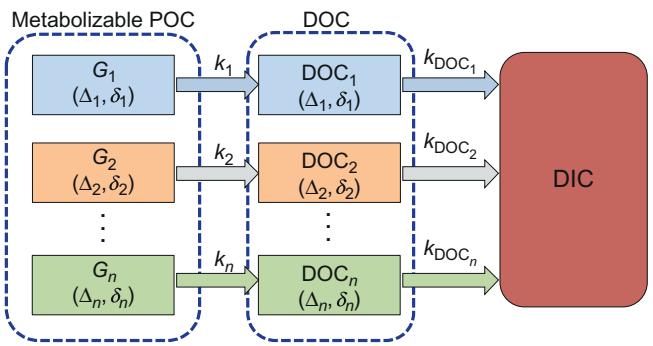

FIGURE 12.8 The multi-*G*+DOC model. Metabolizable POC is divided into *n* components, each with its own unique first-order degradation rate constant (k_i) and $\delta^{13}C$ and $\Delta^{14}C$ signatures (δ_i and Δ_i respectively). Each POC fraction (G_i) is metabolized to DOC_i without isotopic fractionation and each DOC_i fraction is oxidized to DIC (again without isotopic fractionation) with first-order rate constant k_{DOCi}. *Figure modified after Komada et al. (2013).*

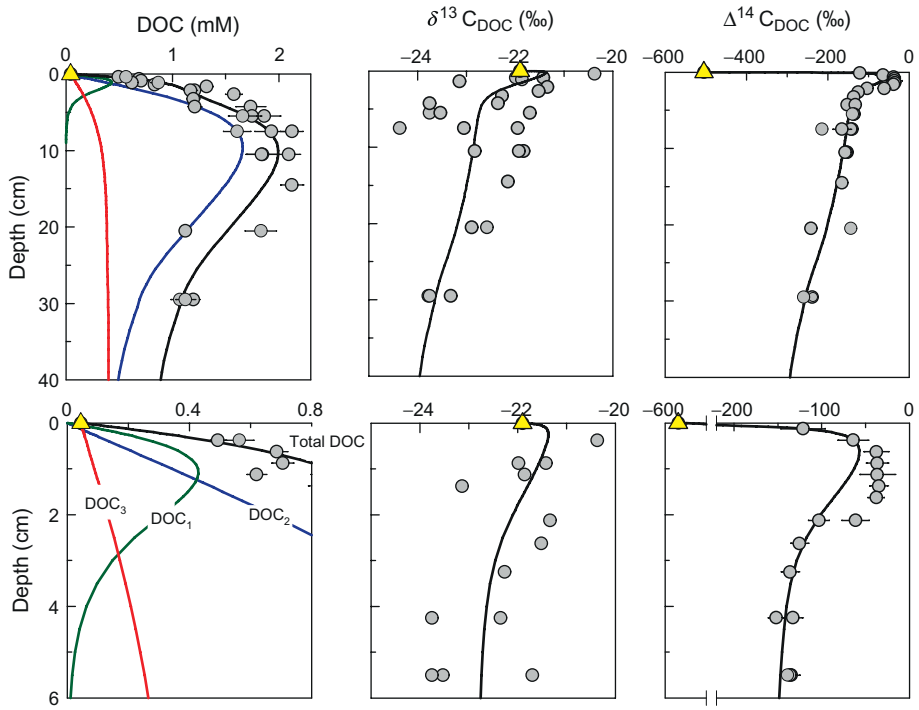

FIGURE 12.9 Pore water DOC concentration and isotopic signature profiles from Santa Monica Basin sediments (symbols) and best fit model results (lines) using the multi-*G* + DOC model (Figure 12.8) in a steady-state reactive-transport model (for details see Komada et al., 2013). Upper panels show the complete profiles over 40 cm, while the lower panels highlight the upper 6 cm of sediment. Shown in the concentration plots (far left) are the model results for the three DOC sub-fractions along with modeled bulk DOC (i.e., the sum of the three fractions). Yellow filled triangles are bottom water values. Where error bars are not visible, they are smaller than the symbols. *Figure modified after Komada et al. (2013).*

to be attributed to radioactive decay during diffusive transport over this distance. While it is possible that this gradient is caused by upward diffusion of ^{14}C-depleted DOC produced in deeper sediments, the relatively small DOC concentration gradient with depth (Figure 12.9) suggests this to be of minor importance. A more plausible explanation is that the isotopic composition of DIC and bulk DOC in the pore waters changes with depth as a result of the differential reactivities of the different G_i and DOC_i pools, and their associated $\Delta^{14}C$ and $\delta^{13}C$ signatures.

The isotopic composition and k_{DOCi} values for the three DOC fractions obtained by the model are presented in Table 12.2 and a subset of the model curves are shown in Figure 12.9. DOC_1 dominates the bulk DOC pool in the uppermost ~1 cm of the sediments, is highly reactive, and contains bomb-^{14}C. DOC_2 dominates the bulk DOC pool throughout much of the sediment column, exhibits intermediate reactivity, and has a modern (but pre-bomb) $\Delta^{14}C$ signature. DOC_3, which steadily increases with depth, is virtually nonreactive and has a $\Delta^{14}C$ signature of ~−500‰. DOC_1 and DOC_2 appear to be of marine origin, while DOC_3 appears slightly depleted in ^{13}C. These model results are discussed below in more detail in Sections VI.A and VII.C.

TABLE 12.2 Model-derived Rate Constants (k_{DOC}) and Turnover Times ($\tau_{DOC} = 1/k_{DOC}$) for Sediment DOC Consumption and Estimated Isotopic Values for Different Pore Water DOC Pools

Site	Depth Interval of Fit	k_{DOC} (year^{-1})	τ_{DOC} (year)	$\delta^{13}C$ (‰) [a]	$\Delta^{14}C$ (‰)[a]
Chesapeake Bay (site M3)[b]	0-25 cm	6.4 ± 2.1	~0.1-0.3		
North Carolina continental slope[c]	25-225 cm	$1.7 \pm 0.7 \times 10^{-3}$	~300-800		
Southwest African Margin (Walvis Bay, site 1082)[d]	1.5-115 m 1.5-370 m	$4.6 \pm 1.2 \times 10^{-5}$ $9.3 \pm 2.9 \times 10^{-5}$	~16,000-30,000 ~7000-14,000		
Santa Monica Basin (SMB)[e]	0-45 cm				
DOC_1		33-80	~0.01-0.03	−17 to -20.6	−58 to +68
DOC_2		0.16-0.23	~4-6	−22 to −23	−45 to −66
DOC_3		$\sim 1 \times 10^{-4}$	$\sim 10^4$	−26 to −27	−480 to −520

[a]*These isotopic values are derived from fitting the depth profiles of pore water DOC and DIC concentration and isotopic signatures to the multi-G + DOC model discussed in Section V.B and illustrated in Figures 12.8 and 12.9 (see Komada et al., 2013, for details). The values listed here are the δ_i and Δ_i values shown in Figure 12.8. Similar isotopic values are not available for pore water DOC at the three other sites discussed in this table.*

[b]*Data from Burdige and Zheng (1998). Model results from Burdige (2002). See Figure 12.11 for best fit profiles.*

[c]*Data from Alperin et al. (1999), model results from Burdige (2002). See Figure 12.11 for best fit profiles.*

[d]*Data and model results from Burdige (2002). See Figure 12.11 for best fit profiles.*

[e]*Data and model results from Komada et al. (2013). The ranges reported here for k_{DOC}, $\delta^{13}C$ and $\Delta^{14}C$ are based on different assumptions made in the model fits to the data.*

VI CONTROLS ON DOC CONCENTRATIONS IN SEDIMENTS

A Controls on DOC Concentrations in Surficial Sediments

DOC (and DON) accumulate with depth in sediment pore waters due to a slight imbalance between production and consumption (e.g., Alperin et al., 1999; Burdige and Gardner, 1998). Because this accumulation occurs predominantly in the form of recalcitrant DOM, understanding the controls on DOC concentration at depth (or the asymptotic concentration, in cases where the DOC concentration gradient diminishes to zero) may provide useful information about the origin and dynamics of recalcitrant DOC. We start this discussion by noting that in Figure 12.10 there is a positive relationship between maximum pore water DOC concentrations in anoxic surficial sediments ($[DOC]_\infty$) and depth-integrated rates of sediment carbon oxidation (R_{Cox}). Bioturbated/bioirrigated sediments do not appear to fall on the trend line for anoxic sediments, for reasons discussed below in Section VI.C.

Two possibilities may explain the observations in Figure 12.10 for anoxic sediments. The first is that a balance occurs at depth between DOC production and DOC consumption (Alperin et al., 1994; Burdige and Gardner, 1998). This explanation was implicitly incorporated into the DOC reactive-transport model presented in Burdige (2002) and illustrated in Figure 12.3, in which it was assumed that the rate of DOC production from POC (R_{DOC}) could be expressed by an equation of the form,

$$R_{DOC} = (R_o - R_\infty)e^{-\alpha z} + R_\infty, \qquad (12.2)$$

where R_i is the rate of DOC production at the sediment surface ($i=0$) or at depth ($i=\infty$) and α is the attenuation constant for this rate expression. It was also shown in Burdige (2002) that model equations containing Equation (12.2) are consistent with the observations in Figure 12.10. Interestingly, Alperin et al. (1999) used a very different modeling approach to examine sediment DOC cycling and obtained the following relationship,

$$[DOC]_\infty \propto R_{cox} z^*, \qquad (12.3)$$

where z^* is the e-folding depth for remineralization. Assuming that z^* is roughly constant in all of the anoxic sediments shown in Figure 12.10, this equation is similarly consistent with the observations in this figure.

The second explanation for asymptotic DOC concentrations with depth is that DOC production rates go to zero and biotic or abiotic changes in the composition of the pore water DOC pool continually decreases its bulk reactivity. This scenario would eventually lead to a situation in which pore water DOC found at depth is effectively nonreactive on early diagenetic time scales and is therefore selectively preserved (see Burdige, 2006b). In this case, one might think of this DOC at depth much like one thinks of "inert" inorganic remineralization end products such as phosphate, ammonium, or DIC, which also show similar exponential-like profiles in anoxic sediments (e.g., Berner, 1980). This analogy would then predict that greater amounts of DOC would accumulate with depth in sediment pore waters as rates of sediment carbon oxidation increase (e.g., Krom and Westrich, 1981), as is seen in Figure 12.10. However, several lines of evidence (see Section V.A and references cited therein) argue against some aspects of this second suggestion, at least over the time and depth scales of surficial sediments.

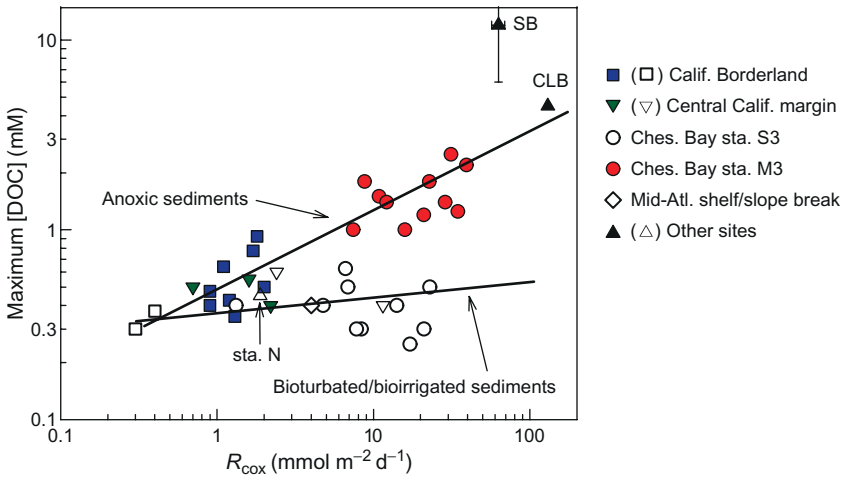

FIGURE 12.10 The maximum DOC concentration in the upper ~20-30 cm of sediment versus the depth-integrated sediment carbon oxidation rate. Open symbols represent bioturbated/bioirrigated sediments while closed symbols represent strictly anoxic sediments. The two lines highlight the general trends in the data sets but do not imply any functional relationships. Data sources: Chesapeake Bay sites M3 and S3—Burdige and Homstead (1994), Burdige and Zheng (1998), and Burdige (2001); California Borderlands and central California margin sites—Berelson et al. (1996) and Burdige et al. (1999, unpub. data); mid-Atlantic-shelf/slope break (site WC4)—Burdige et al. (2000, unpub. data); Cape Lookout Bight, NC (CLB)—Martens et al. (1992) and Alperin et al. (1994); Skan Bay (SB), Alaska—Alperin et al. (1992); station N (see Figure 12.2)—Bauer et al. (1995).

The multi-G+DOC model provides some insight into reconciling the two suggestions discussed above for explaining the accumulation of recalcitrant DOC with depth in anoxic sediments. Regarding the second suggestion, this model provides an explanation for how DOC reactivity decreases with depth in the absence of in situ processes that specifically produce recalcitrant material from more reactive constituents. Here, less reactive DOC is produced from less reactive POC, versus it being rendered less reactive as a result of in situ ageing or chemical transformation. This DOC also inherits it radiocarbon signature directly from its parent POC, again as opposed to acquiring it via in situ ageing.

Regarding the first suggestion that asymptotic DOC concentrations at depth represent a balance between production and consumption, we start by recognizing that in the multi-G+DOC model we express total DOC production as $\sum k_i G_i$ (Komada et al., 2013). We also assume here, for the sake of this argument, that the concentration of reactive POC in each fraction decreases exponentially with depth (e.g., Berner, 1980; Burdige, 2006b). In this case, the total rate of DOC production can be expressed as:

$$\sum k_i G_i \approx k_1 G^o,\ e^{-\alpha_1 z} + k_2 G_2^o e^{-\alpha_2 z} + k_3 G_3^o e^{-\alpha_3 z} + \ldots \quad (12.4)$$

where $\alpha_i = k_i/\omega$, ω is the sediment accumulation rate, and G_i^o is the initial concentration of organic matter in the ith fraction. However, in a given sedimentary setting (i.e., over specific time and depth scales), data analysis methods generally used to extract information about sediment organic matter reactivity can only determine, at most, two or three fractions of material, regardless of the number of fractions that may actually exist (e.g., Middelburg, 1989). Furthermore, since the various k_i values decrease for higher-order organic matter fractions, this implies that the e-folding depth for the remineralization of higher-order G_i fractions ($=1/\alpha_i = \omega/k_i$) will increase and eventually become large relative to the depth scale of the sediment system. Higher-order exponential terms in Equation (12.4) will therefore be roughly constant with depth in this sediment (or roughly equal to zero as k_i values continually decrease) and as a result, this equation will simplify to either a single or double exponential function of depth plus a constant term, as in Equation. (12.2).

B Controls on DOC Concentrations in Deeply Buried Sediments

In contrast to the numerous DOC profiles that have been collected in surficial sediments (see Section II and earlier reviews in Burdige, 2002 and Krom and Westrich, 1981), far fewer studies have examined pore water DOC concentrations over larger depth and time scales (Burdige, 2002; Egeberg and Barth, 1998; Heuer et al., 2009; Smith et al., 2005). Additional DOC pore water data from deeply buried sediments are available in the scientific reports of selected ODP (Ocean Drilling Program) and IODP (International Ocean Drilling Program) cruises (see, most recently, Fisher et al., 2005; Tréhu et al., 2003; Wilson et al., 2003). Interestingly, when such DOC profiles are compared with results from surficial sediments (Figure 12.11) one often observes a general similarity in the exponential-like shape of the profiles, in spite of significant differences in both the depth and concentration scales for the profiles. Examining these observations in the context of Equation (12.3) leads to the conclusion that z^* (i.e., the increasing depth scale over which organic matter remineralization and its associated DOC production and consumption occurs) rather than R_{cox} plays a major role in explaining the shapes of these DOC profiles. Specifically, between site M3 in Chesapeake Bay and site C on the North Carolina (NC) continental slope, R_{cox} values actually decrease from ~20 to ~5 mmol m^{-2} d^{-1} while $[DOC]_\infty$ increases (Alperin et al., 1999; Burdige and Zheng, 1998). In addition, as one moves to deeply buried sediments (such as the Walvis Bay sediments), values of R_{cox} also presumably continue to decrease as $[DOC]_\infty$ increases.

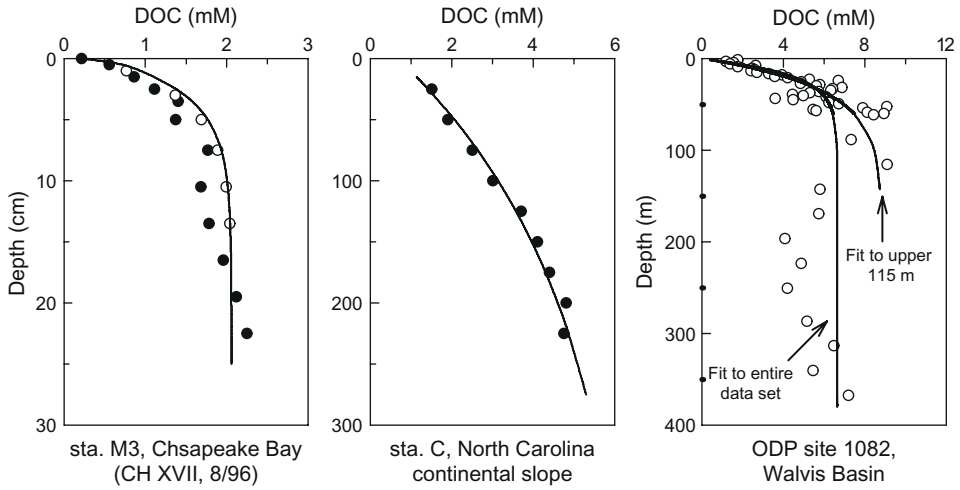

FIGURE 12.11 Pore water DOC concentration profiles from three contrasting anoxic marine sediments fit to the ANS model in Burdige (2002). The best fit rate constants for DOC consumption (k_{DOC}) are listed in Table 12.2, while the remaining fitting parameters are listed in the original reference. Note the factor of 4 difference in concentration scales and factor of >1000 difference in depth scales as one moves from the estuarine Chesapeake Bay sediments to the deep sediment (ODP) cores collected in Walvis Basin (also note that the depth scale for the Walvis Basin core is in units of meters while the depth scales for the other two sites are in units of centimeters). The different symbols for the Chesapeake Bay plot (left) represent replicate cores collected on this date at this site. At site C on the North Carolina continental slope (center) the data were fit starting at a sediment depth of 25 cm based on the observation that the upper portion of these sediments are extensively bioturbated (Alperin et al., 1999). Finally, for the Walvis Basin sediments (right) the entire data set and the upper 115 m of sediment were fit separately to the model. Although there are factor of ~2 differences in the resulting fitting parameters of each fit (see Table 12.2), both sets of results are consistent with the general trends discussed in the text regarding the comparison of the fitting parameters from all three sediments. Data sources: Chesapeake Bay—Burdige and Zheng (1998); North Carolina continental slope—Alperin et al. (1999); Walvis Bay—DOC data from Burdige et al. (unpubl. data), other model input parameters from Wefer et al. (1998).

The significance of z^* in describing the shape of DOC profiles in deeply buried sediments also has implications for POC remineralization over these longer depth and time scales as expressed, for example, in Equation (12.4). Here, we see that lower-order organic matter fractions are "rapidly" remineralized near the sediment surface (i.e., on early diagenetic time scales) while higher-order, less reactive fractions that appear recalcitrant (or even inert) on these short time scales become increasingly more important for fueling remineralization in much deeper sediments (see, e.g., recent discussions in Hoehler and Jørgensen, 2013 and Lomstein et al., 2012).

The results in Figure 12.11 along with those in Figure 12.9 from SMB sediments can be used to further examine the questions posed in the previous section regarding the controls on pore water DOC concentrations in sediments. We begin by comparing in Table 12.2 model-derived DOC remineralization rate constants (k_{DOC}) and the DOC turnover times ($\tau_{DOC}=1/k_{DOC}$) for the four sites. For the three sites shown in Figure 12.11, these rate constants were determined using the steady-state reactive-transport model described in Burdige (2002), assuming that only one type of DOC is produced from POC according to Equation (12.2). In contrast, DOC consumption in SMB sediment pore waters was modeled using the multi-G+DOC model illustrated in Figure 12.10 with three reactive fractions of organic matter and therefore three DOC pools undergoing decomposition.

As a first observation, we note that even the largest k_{DOC} values listed here are, for the most part, much smaller (by up to two orders of magnitude) than analogous first-order rate constants for the decomposition of monomeric DOM such as acetate or amino acids (see summaries in Finke et al., 2007 and Henrichs, 1993). This observation is consistent with previous discussions that the bulk of the pore water DOC pool represents relatively recalcitrant material that turns over much more slowly than components of the mLMW-DOC pool. At the same time, rate constants for the degradation of synthetic melanoidins determined in studies with Alaska coastal sediments (Henrichs and Doyle, 1986) ranged from 0.7 to <0.09 year^{-1} (τ_{DOC} from ~1 to >10 year) and are more comparable to some of the k_{DOC} and τ_{DOC} values in Table 12.2. Since melanoidins have been proposed as models for recalcitrant marine humic materials (Hedges, 1988; Krom and Sholkovitz, 1977; Nissenbaum et al., 1972), this observation is perhaps not surprising.

A comparison of the SMB results with those from the other three sites indicates that the Chesapeake Bay rate constant is intermediate between the SMB k_{DOC1} and k_{DOC2} values while the NC continental slope value is intermediate between k_{DOC2} and $k_{DOC3.}$ Given the broad types of POC deposited in these sediments, and their assumed reactivity, these observations suggest that rate constants derived from models assuming only one type of pore water DOC undergoing remineralization likely "average" over the rate constants one obtains by assuming the existence of multiple DOC pools with differing reactivities (see similar discussions in Arndt et al., 2013, regarding 1−G vs. multi-G POC-only degradation models).

Overall, these observations suggest that POC degradation through DOC intermediates can be minimally described as a two-step process as defined by the multi-G+DOC model in Figure 12.9. However, as noted above, this approach is clearly an oversimplification of the dynamics of DOC production and consumption illustrated in Figure 12.2, despite the success of the multi-G+DOC model in linking bulk POC reactivity to its isotopic signatures (δ^{13}C and Δ^{14}C) and those of its downstream DOC intermediates and remineralization end products (i.e., DIC). Future work should therefore be aimed at better incorporating aspects of the conceptual model in Figure 12.2 into kinetic models like the multi-G+DOC model, and eventually into DOC reactive-transport models.

Also of equal interest here is the almost seven orders-of-magnitude decrease in k_{DOC} values (or increase in τ_{DOC} values) as one moves from the most reactive DOC fraction in surficial SMB sediments to deep Walvis Basin sediments. When looked at in the context of the discussion above, these trends are most easily explained by the remineralization of increasingly recalcitrant sediment POC leading to the net production of increasingly recalcitrant pore water DOC.

Within SMB sediments (Komada et al., 2013), the depth distribution of $\Delta^{14}C_{DOC}$ (Figure 12.9) places important constraints on possible sources of recalcitrant DOC in these sediments and suggests that it is highly unlikely that this material forms within the pore waters from labile moieties (see Section V.B for details). However, when this problem is examined over the much longer time and depth scales of deeply buried sediments, the possibility exists that some amount of the pore water DOC also undergoes internal transformations (by any number of possible mechanisms discussed in Section II) that lead to a decrease in its reactivity (also see discussions in Section V.A and in Burdige, 2002). With time, such processes could play a role in the accumulation of higher concentrations of more recalcitrant DOC and ultimately be involved in overall sediment carbon preservation (see Section VI.D for further discussions). More detailed compositional and/or structural studies of pore water DOC from a wide range of sedimentary settings may be able to provide additional insights into this problem.

C Possible Redox Controls on Pore Water DOC Concentrations

Results in Figure 12.10 illustrate that asymptotic DOC concentrations in mixed redox sediments are in general lower than those in strictly anoxic sediments. As noted in Section II, similar observations date back to studies of DOC cycling as early as the 1970s. Model calculations presented in Burdige (2002) illustrate that changes in sediment redox conditions alter carbon flow through DOM intermediates and lead to the buildup of recalcitrant DOM under anoxic conditions (also see discussions in Burdige, 2001). This accumulation appears to occur as a result of some combination, under mixed redox conditions, of either enhanced consumption of recalcitrant DOM (pathway 5 in Figure 12.2 or the lower pathway in Figure 12.3) or preferential carbon flow through mLMW-DOM intermediates (i.e., carbon flow via the vertical arrows on the left side of Figure 12.2 or the upper pathway in Figure 12.3 (a)).

Evidence in support of the former suggestion comes from observations that the ratio of humic-like fluorescence to total DOC concentration is higher in pore waters of strictly anoxic versus mixed redox sediments (Burdige et al., 2004; Komada et al., 2004; also see Section III.B). One possible explanation for this is that by analogy with discussions of the factors controlling the preservations of POM in sediments (see reviews in Blair and Aller, 2012; Burdige, 2007; Hedges and Keil, 1995; Zonneveld et al., 2010), the presence of O_2 and/or the occurrence of mixed redox conditions may similarly enhance the remineralization of certain types of recalcitrant DOM in sediment pore waters. Such "oxygen" effects may express themselves in a number of different direct and indirect ways that are described in greater detail in the reviews cited above.

The cycling of DOC in sediment pore waters may also be impacted by iron redox cycling, given the strong affinity of DOC compounds to adsorb to iron oxide surfaces (see discussions in Chin et al., 1998; Lalonde et al., 2012; Skoog and Arias-Esquivel, 2009). However, the broader-scale significance that this may have on redox controls of pore water DOC concentrations requires further study.

D Interactions Between DOM and Sediment Particles and the Possible Role of DOM in Sediment Carbon Preservation

In addition to biological processes that affect DOM, physical interactions with sediment particles, for example, adsorption, are also of some importance (Figure 12.2). If we assume adsorption is a reversible, equilibrium process, then a simple linear adsorption isotherm can be used to describe the process (Stumm and Morgan, 1996),

$$\overline{C} = K^{*}C, \tag{12.5}$$

where $\overline{C}$ is the concentration of the adsorbed compound (in units of, e.g., $\mathrm{mmol\,kg^{-1}}$, where kg is kilograms of dry sediment), C is the concentration of the compound in solution (in units of, e.g., mM), and K^* is the adsorption coefficient with units of $\mathrm{L\,kg^{-1}}$.

Adsorption can decrease the availability of DOM to microbial degradation (e.g., Sugai and Henrichs, 1992) and may play a role in sediment carbon preservation (see the discussion at the end of this section). Ionic interactions or weaker Van der Waals interactions appear to be the predominant mechanisms by which reversible adsorption occurs (Arnarson and Keil, 2001; Henrichs and Sugai, 1993; Liu and Lee, 2007; Wang and Lee, 1993). For simple LMW-DOM such as glucose, amino acids, and short-chain organic acids, adsorption coefficients range from ~0.1 to ~300 $\mathrm{L\,kg^{-1}}$ (e.g., Henrichs, 1992, 1995; Liu and Lee, 2007; Sansone et al., 1987), while larger molecules such as proteins or synthetic melanoidins have K^* values that range from 50 to 600 $\mathrm{L\,kg^{-1}}$ (Ding and Henrichs, 2002; Henrichs, 1995; Henrichs and Doyle, 1986). Adsorption studies using natural assemblages of pore water DOM yield K^* values that range from 1 to 3200 $\mathrm{L\,kg^{-1}}$ (Arnarson and Keil, 2001; Thimsen and Keil, 1998).

Positively charged organic molecules, for example, basic amino acids such as lysine, are more strongly adsorbed than neutral or negatively charged organic molecules; this has historically been attributed to the fact that most natural sediments have a negative surface charge (see Henrichs, 1992 for a summary). However, recent studies also suggest that in some marine sediments adsorption of LMW-DOM to sediment organic matter itself may be more important than adsorption to mineral surfaces (Liu and Lee, 2007). Furthermore, organic matter architecture as well as diagenetic history (also sometimes referred to as diagenetic maturity; e.g., Cowie and Hedges, 1994) appears to influence not only the overall extent of adsorption but also changes in the extent of adsorption as a function of DOM characteristics such as hydrophobicity (Liu and Lee, 2006, 2007; Wang and Lee, 1993). Increasing molecular weight and increasing hydrophobicity may enhance adsorption (Henrichs, 1992, 1995), although in the context of the recent studies discussed above, this generalization may require reexamination.

Several studies have also shown that much of this DOM adsorption is only partially reversible and in some cases is effectively irreversible (Ding and Henrichs, 2002; Henrichs and Sugai, 1993; Liu and Lee, 2007; Wang and Lee, 1993). The causes of this behavior may include: attachment of molecules to multiple binding sites that slow down desorption (Collins et al., 1995; Henrichs and Sugai, 1993), chemical reactions between adsorbed molecules and sedimentary organic matter (Henrichs and Sugai, 1993), and enzyme-type adsorption sites with high desorption activation energies (Liu and Lee, 2007).

Sorption of DOC to sediment particles can affect pore water DOC concentrations (Hedges and Keil, 1995; Henrichs, 1995; Papadimitriou et al., 2002), and it has been suggested that pore water DOC concentrations may be "buffered" by reversibly sorbed DOC in equilibrium with the pore waters (Thimsen and Keil, 1998). However, Alperin et al. (1999) concluded that buffering of pore water DOC concentrations by reversible sorption is not an important controlling factor in explaining pore water DOC concentrations in NC continental slope sediments. Furthermore, in situations where rates of sediment accumulation and bioturbation are sufficiently low, reversible adsorption can be neglected in reactive-transport models (Berner, 1980; Komada et al., 2004), further minimizing the importance of reversible adsorption in impacting pore water DOC concentrations.

DOM-particle interactions such as those discussed above have also been examined in terms of broader, and more general, questions of how these interactions may impact sediment carbon preservation. Many aspects of this have been discussed previously (Burdige, 2007; Hedges and Keil, 1995; Henrichs, 1995) and for details the interested reader is urged to consult these publications. A more recent study examining the role of reactive iron in promoting organic carbon preservation in marine sediments also discusses the role pore water DOC may play in this type of sediment carbon preservation (Lalonde et al., 2012).

Similarly, given other recent studies examining the ways in which humic substances may form (Piccolo, 2001; Sutton and Sposito, 2005), many properties of pore water DOM (LMW, low degree of "bulk" reactivity) also argue for pore water DOM playing a potentially important role in the formation of presumably recalcitrant humic materials (see Section II for details). However, more work is needed to examine the role this may ultimately play in sediment carbon preservation.

VII THE ROLE OF BENTHIC DOM FLUXES IN THE OCEAN CARBON AND NITROGEN CYCLES

A Benthic DOC Fluxes

The fact that concentrations of both DOC and DON in sediment pore waters are often elevated over bottom water concentrations implies that sediments can be a potential source of DOM to

overlying waters. The occurrence of these benthic fluxes was discussed in the literature beginning in the 1980s (e.g., Hedges, 1992; Heggie et al., 1987; Williams and Druffel, 1987) where it was suggested that sediments might represent a significant source of DOC to the deep ocean and that benthic DOC fluxes might provide an explanation for the apparent discrepancy between the "old" (~6000 ybp) ^{14}C age of deep water DOC and the average oceanic mixing time of ~1000 year (for details also see Burdige, 2002). The direct measurement of these fluxes was undertaken in studies beginning in the 1990s using either core incubation techniques or in situ benthic landers or chambers (see Burdige et al., 1999, for a summary). Benthic DOC fluxes determined in this manner in a number of estuarine, coastal, and continental margin sediments range from ~0.1 to 3 mmol m^{-2} d^{-1}.

In a compilation and synthesis of these results, Burdige et al. (1999) observed the following positive, but nonlinear, relationship between benthic DOC fluxes (BDF) and depth-integrated sediment carbon oxidation rates (R_{cox}):

$$BDF = 0.36 R_{cox}^{0.29} \qquad (12.6)$$

(BDF and R_{cox} both expressed here in units of mmol m^{-2} d^{-1}). The relationship implies that the ratio of BDF to R_{cox} increases with decreasing R_{cox}. Using Equation (12.6) Burdige et al. (1999) estimated that the integrated DOC flux from coastal and continental margin sediments (0-2000 m water depth) was ~180 Tg C $year^{-1}$. Three other estimates of this quantity for this sedimentary region, determined using different approaches, have also been presented; in one case, a near-identical value was obtained (Dunne et al., 2007), while in the other two cases, smaller values of 40 Tg C $year^{-1}$ (Alperin et al., 1999) and 90 Tg C $year^{-1}$ were obtained (Maher and Eyre, 2010). However, the Maher and Eyre (2010) value is based on a definition of the continental shelf that is significantly smaller in surface area (factor of ~10) than that used in the other studies.

In addition to coastal and continental margin sediments, Maher and Eyre (2010) estimated the integrated benthic DOC flux from intertidal and vegetated (seagrass, macroalgae, salt marsh, and mangrove) sediments not explicitly considered in the other estimates discussed above. For these sediments they obtained a value of ~170 Tg C $year^{-1}$, with vegetated sediments accounting for >90% of this flux. Their work (also see Maher and Eyre, 2011) further shows while these sites are net sources of DOC over diel cycles, this is often a balance between DOC uptake in the dark and release during daylight. These observations further highlight the role that higher plants may play in such environments in mediating DOC fluxes to the water column (also see discussions in Section VII.B).

Dunne et al. (2007) also estimated an integrated DOC flux of ~100 Tg C $year^{-1}$ from sediments in water depths >2000 m. This estimate is extrapolated from calculated fluxes determined with DOC pore water profiles from cores collected at a single site at a water depth of 3500 m (Papadimitriou et al., 2002). Based on a comparison of these pore water profiles with those presented by Hall et al. (2007), and the discussion in Section II.A of possible artifacts associated with deep-sea pore water DOC determinations, it seems possible that this estimate of the integrated benthic DOC flux from deep-sea sediments may be an overestimate (also see discussions in Brunnegård et al., 2004). More work will be needed to evaluate deep-sea benthic DOC fluxes and noninvasive in situ techniques for measuring benthic fluxes may hold promise here (e.g., Swett, 2010).

Returning to the examination of benthic DOC fluxes from non-vegetated coastal and continental margin sediments, we note that these fluxes are generally less than ~10% of sediment carbon oxidation rates (for details see Burdige et al., 1999). Thus, these sediments are quite efficient in oxidizing DOM produced during remineralization processes, consistent with past discussions in this chapter. Similar trends also appear to be

the case for sediment DON cycling (see next section) and both observations imply that net sediment DOM production is small in comparison to gross sediment DOM production. These trends are consistent with prior discussions regarding carbon and nitrogen flow through DOM intermediates during sediment POM remineralization and the role of DOM as an intermediate in the overall remineralization process.

A second implication of these results is that the integrated benthic DOC flux from coastal and continental margin sediments including vegetated sediments (~350 Tg C $year^{-1}$) is comparable to (or even larger than) estimates of the riverine DOC input of ~210 Tg C $year^{-1}$ (Ludwig and Probst, 1996). Thus, marine sediments may be an important net source of DOC to the oceans (Burdige et al., 1999). However, the actual impact these fluxes have on the oceanic carbon cycle ultimately depends on the extent to which sediment-derived DOM is reactive in the water column. This point will be discussed in greater detail in Section VII.C (also see discussions in Alperin et al., 1999 and Maher and Eyre, 2010).

B Benthic DON Fluxes

Interest in benthic DON fluxes and their role in the marine nitrogen cycle is similar to that discussed above for benthic DOC fluxes and the marine carbon cycle. However, because nitrogen is a limiting nutrient in marine ecosystems (Gruber, 2008) and because marine phytoplankton can use DON as their nitrogen source (Mulholland and Lomas, 2008), there is additional interest in understanding the role of sediments as a source of DON to the water column.

A number of studies have examined benthic DON fluxes from coastal, estuarine, and continental margin sediments (see reviews in Bronk and Steinberg, 2008 and Burdige, 2002). Benthic DON fluxes show a tremendous range in both absolute magnitude and direction (into and out of the sediments). However, at estuarine or coastal sites where repeated (or seasonal) studies have been carried out, mean or annual averages generally suggest that benthic DON fluxes are small, usually out of the sediments, and are only a small percentage of the benthic dissolved inorganic nitrogen (DIN) flux (e.g., see Burdige and Zheng, 1998 for more details; DIN = the sum of ammonium, nitrate, and nitrite). For example, in Chesapeake Bay sediments, benthic DON fluxes range from ~0.08 to 0.2 mmol m^{-2} d^{-1} in the anoxic sediments at site M3 and 0-0.4 mmol m^{-2} d^{-1} in the bioturbated and bioirrigated sediments at site S3 (Burdige, 2001; Burdige and Zheng, 1998). At both sites, benthic DON fluxes were only ~3-4% of benthic DIN fluxes.

In contrast, at some sites, benthic DON fluxes are comparable to, or even exceed, benthic DIN fluxes or integrated rates of sediment denitrification. These include high latitude (Arctic) sediments (Blackburn et al., 1996), North Sea continental margin sediments (Landén-Hillmeyr, 1998), estuarine mudflat sediments (Cook et al., 2004), microtidal fjord sediments (Sundbäck et al., 2004), and subtropical estuarine euphotic sediments (Ferguson et al., 2004).

The reasons for widely varying differences in the relative magnitude as well as the direction of benthic DON fluxes are not well understood. In some cases, they may be the result of transient (non-steady-state) events; for example, Blackburn et al. (1996) suggested that the large DON fluxes observed may have been a temporary phenomena associated with the recent sedimentation of fresh detrital material. Similarly, as is the case for benthic DOC fluxes (see the previous section), the presence of macroalgae, microphytobenthos, and benthic macrofauna can impact the magnitude and direction of benthic DON fluxes over a range of time scales (see discussions in Bronk and Steinberg, 2008; Ferguson et al., 2004; Maher and Eyre, 2011; Sundbäck et al., 2004; Tyler et al., 2003). Additional discussions on the controls of benthic DON fluxes can be found in Burdige and Zheng (1998) and Alkhatib et al. (2013).

C The Impact of Benthic DOM Fluxes on the Composition and Reactivity of Oceanic DOM

Interest in DOM fluxes from marine sediments stems in part from a recognition of the need to better understand the sources and sinks of DOM in the oceans (Hansell et al., 2009, 2012). Although benthic fluxes of DOC (Burdige et al., 1999; Dunne et al., 2007; Maher and Eyre, 2010) and DON (Alkhatib et al., 2013; Brunnegård et al., 2004; Burdige and Zheng, 1998) appear to be of similar magnitude to their riverine inputs, the impact of these fluxes on water column DOM concentrations and properties depends on the reactivity of sediment-derived DOM in the water column. If sediment-derived DOC (or DON) is reactive in the water column and undergoes remineralization on time scales shorter than that required for transport out of the benthic boundary region, or deep water residence times, then these fluxes will have a minimal impact on deep water DOM properties. Conversely, if this material is sufficiently recalcitrant, then these fluxes could represent an important source of DOM to the deep ocean and might also help explain, for example, the ^{14}C content of deep water DOC.

Several lines of evidence from contrasting marine sediments suggest that not all of the DOM escaping from sediments as a benthic flux is recalcitrant, and that it has the potential to be reactive in the water column. In estuarine Chesapeake Bay sediments, a comparison of measured benthic DOM fluxes versus calculated, diffusive DOM fluxes suggests that there is enhanced production of N-rich DOM at or near the sediment-water interface relative to the DOM accumulating in these sediment pore waters (Figure 12.6). Similar trends in DOM elemental ratios have been observed in other sediments (Blackburn et al., 1996; Landén-Hillmeyr, 1998) and were explained as being due to the diffusional loss of low C/N ratio DOM produced during the initial hydrolysis of fresh detrital organic matter near the sediment surface. This explanation is consistent with discussions in Burdige and Gardner (1998) regarding the spatial separation between sediment processes that produce the initial HMW intermediates of sediment POM remineralization and those responsible for the production of bulk recalcitrant pore water DOM. Such spatial separation of these processes can also be inferred from model results illustrated here in Figure 12.3 (Burdige, 2002).

Isotope studies of pore water DOC provide another approach to examining this problem. At two sites in the eastern North Pacific examined by Bauer et al. (1995), pore water DOC near the sediment surface was greatly enriched in ^{14}C as compared to bottom water DOC (also see Figure 12.9 and Section III.C), and based on these observations these authors concluded that sediments are not a major source of pre-aged (^{14}C-depleted) DOC to the oceans. However, it is important to remember that the ^{14}C signature of bulk DOC is actually a weighted average value based on the distribution of ^{14}C signatures of all of the molecules present in the sample (e.g., Loh et al., 2004). Recent work by Komada et al. (2013) supports this observation for sediment pore waters (Table 12.2 and Figure 12.9), suggesting that pore water DOC at any given depth is a mixture of components of varying reactivities and isotopic signatures. Pore water DOC near the surface of SMB sediments appears ^{14}C-young and labile (as was also noted by Bauer et al., 1995), and upon escaping the sediments as a benthic flux, the majority of this material is indeed likely oxidized in the bottom waters. However, modeling these pore water data also indicates the presence of an aged, recalcitrant DOC component. This recalcitrant (i.e., DOC_3) material represents ~3-8% of the total benthic DOC flux from these sediments (Komada et al., 2013), and as is shown in Table 12.2, is also depleted in ^{14}C. The significance of this is that the input of ^{14}C-depleted DOC to the ocean complicates the linkage between the apparent radiocarbon "age" of DOC in the deep ocean and its true deep ocean turnover time (Bauer and Druffel, 1998; Guo and

Santschi, 2000; McCarthy et al., 2011; Raymond and Bauer, 2001a)

On a global scale, the benthic DOC flux from non-vegetated coastal and continental margin sediments has been estimated at ~180 Tg C year^{-1} (see Burdige et al., 1999, and Section VII.A). If, based on the discussion above, we now assume that 3-8% of this material survives remineralization in the near-bottom waters, then 5-14 Tg C year^{-1} of recalcitrant DOC from coastal and continental margin sediments is added to the oceans (Komada et al., 2013). This flux represents 12-33% of the turnover rate of recalcitrant DOC in the deep ocean (=43 Tg C year^{-1}), the latter determined by modeling DOC distributions in the global oceans (Hansell et al., 2012). These results argue strongly for the important role of sediment processes and benthic DOC fluxes in adding recalcitrant and ^{14}C-depleted DOC to the deep oceans, although further work is needed to better constrain the production rate of recalcitrant pore water DOC in sediments and the role it plays in determining the Δ^{14}C value (and turnover time) of deep ocean DOC.

Finally, sediment pore water DOC interactions (Section VI.D) could play a role in a slightly different fashion in adding ^{14}C-depleted DOC to the deep ocean. This possibility is based on results from Guo and Santschi (2000), who observed that simple desorption of colloidal (>1 kDa) organic matter from continental margin sediments yields DOC that has a substantially greater ^{14}C-age than the bulk sediment organic matter (~3000 vs. 700 year, respectively). While the details of how this material ages in the sediments is somewhat uncertain, desorption of this material from sediments in the benthic nepheloid layer, coupled with its off-shore transport (e.g., Bauer and Druffel, 1998), could add pre-aged DOC to the deep ocean DOC.

VIII CONCLUDING THOUGHTS

Throughout this chapter, we have attempted to summarize and synthesize the existing data on DOM in marine sediment pore waters and present explanations that (at least to us) appear to best explain the observations. Addressing many of the important problems and questions that still remain will involve studies linking DOM composition, structure, and reactivity with a better understanding of the pathways and processes that are illustrated in Figure 12.2. Studies of the chemical composition and structure of the parent POM should also be useful here in understanding DOM cycling. As was noted in the first edition of this chapter (Burdige, 2002), many of these questions can be (and will continue to be) addressed in carefully conducted sediment incubation experiments, such as those discussed in Section V.A.

The general role of sediment redox conditions in DOM cycling, and the ways it may link DOM cycling and overall sediment carbon preservation, remain a continuing area of interest and inquiry. Finally, in terms of DOM cycling in specific sedimentary environments, a number of important and interesting questions remain about these processes in the very different realms of shallow, permeable sediments and deeply buried sediments (deep marine biosphere).

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