

Chapter 2.7

Biogeochemical Consequences of the Sedimentary Subseafloor Biosphere

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2.7.1 INTRODUCTION

The subseafloor sedimentary ocean comprises a substantial fraction of the Earth's aqueous marine environment. When considering the total volume of sediments (Kennett, 1982, p. 321) and an average porosity of 0.5, the subsurface ocean contains $0.53 \times 10^{18} \text{ m}^3$ of interstitial water (Figure 2.7.1), or 28% of the total water volume in the combined sedimentary and pelagic ($1.37 \times 10^{18} \text{ m}^3$) ocean. Based on sheer volume alone, chemical and biological processes occurring in the deep subsurface ocean will expectedly have consequences for the evolution of the Earth's ocean and chemistry. Much effort in the past decade of deep biosphere research and scientific drilling within the framework of Ocean Drilling Program (ODP) and Integrated Ocean Drilling Program (IODP) has been placed on understanding this habitat, particularly in exploring the abundance, diversity, and physiology of the microbial biocenosis. A stated goal of recent scientific drilling and deep subseafloor biosphere research has been to evaluate the biogeochemical impacts of subseafloor biota. This deep subseafloor biosphere exhibits a strong geological time component that is tightly coupled to variations in climate and ocean circulation. In response, microbial processes leave their imprint on the overall geochemistry of deeply buried sediments and eventually on the global redox cycle. Here, we specifically ask what we have learned about the biogeochemical consequences of microbial activity in deeply buried sediments, on the geochemistry of those sediments, and the overall biogeochemistry of the ocean.

Although the subseafloor sedimentary ocean forms an integral part of the Earth's ocean, important characteristics distinguish it from the overlying pelagic ocean. The pelagic ocean comprises one connected system that mixes on the order of 1000 years (e.g., Libes, 2009), whereas sedimentary systems

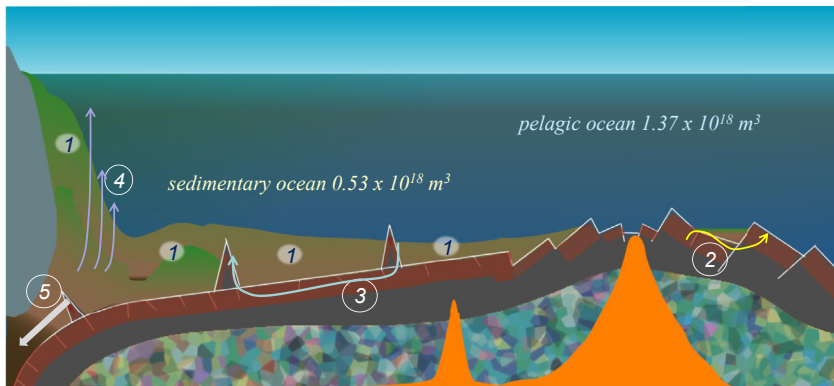


FIGURE 2.7.1 Important environments of the sedimentary subseafloor ocean under consideration in this chapter: (1) diffusive environments, (2) sediment ponds on mid-ocean ridge flanks, (3) sub-sediment flow through crustal aquifers as per [Bekins, Spivack, Davis, and Mayer \(2007\)](#), (4) fluid flow driven by tectonics and sediment accretion at continental margins, and (5) subduction of ocean sediment and removal of oxidants and reductants from the Earth's ocean-atmosphere system.

comprise water constrained in a dense particle matrix, whose varying chemistries depend greatly on the depositional histories of the often isolated basins. With the exception of fluid flow along constrained flow paths in some defined environments, molecular diffusion dominates physical transport in the sedimentary subseafloor ocean ([Figure 2.7.1](#)). The average time required for a dissolved compound to diffuse through to any given depth scales with the square of the diffusion path length (for an excellent discussion of this theme see [Jørgensen, 2006](#)). This has serious consequences for the location and rates of reactions. A medium diffusion time for a dissolved ion, e.g., Cl^- , through the middle of the thinly blanketed South Pacific Gyre sediments (about 20 m thick) is around 4000 years. Thicker sediment packages of 100 m and more, which are typical for the continental margins and high-productivity regions, yield diffusion times of ~400,000 years. Glacial–interglacial changes in ocean chlorinity and $\delta^{18}\text{O}\text{-H}_2\text{O}$ composition can be observed as the diffusion front propagates through sediments (e.g., [Adkins & Schrag, 2001](#); [Adkins, McIntyre, & Schrag, 2002](#); [Insua, Spivack, Graham, D'hondt, & Moran, 2014](#); [Mcduff, 1984](#); [Schrag, Hampt, & Murray, 1996](#); [Schrag et al., 2002](#)). Likewise, at depth scales of 1–50 m the microbial communities can react to changing ocean chemistry and fluxes to the surface on glacial–interglacial timescales, as demonstrated by [Contreras et al. \(2013\)](#) for changes in the sulfate–methane transition (SMT) zone in sediments of ODP Leg 201 Site 1229 on the Peru Margin. At the other extreme, deeply buried layers in the absence of tectonically induced flow through permeable layers are essentially cut off from communication with the overlying pelagic ocean by long diffusion path lengths and extremely low porosities. An example is the Shimokita Oligocene-age coal-bearing sediments (IODP Expedition 337; [Inagaki, Hinrichs, Kubo, & the Expedition 337 Scientists, 2013](#)), which contain an active

biosphere at depths of 2046–2466 mbsf. The consequences of biogeochemical processes within these sediments will be more likely expressed over geological time as the sediments eventually enter the rock record and are weathered.

2.7.2 BIOGEOCHEMICAL ZONATION IN SUBSEAFLOOR SEDIMENTS

The remineralization of deposited organic matter, predominately originating from photosynthetic activity in ocean surface waters and on land, is the main driver for biogeochemical processes in subseafloor sediments (D'Hondt, Rutherford, & Spivack, 2002; D'Hondt et al., 2004). Organic matter oxidation proceeds via a sequence of terminal electron accepting processes (TEAPs), encompassing O_2 , NO_3^- , Mn(IV) and Fe(III) oxides, and SO_4^{2-} , followed by methanogenesis as a function of free energy gain (Froelich et al., 1979; Stumm & Morgan, 1996; Table 2.7.1(a)). In the subseafloor sediment, this progression typically leads to the installation of distinct, yet overlapping biogeochemical zones where the respective oxidation–reduction processes occur. The thicknesses of the different zones are, among other things, controlled by the rate of organic carbon oxidation, electron acceptor availability, and sediment accumulation rates (see Arndt et al., 2013, for review). Consequently, regional and global trends in the distribution of diagenetic processes are identified and continuously updated as studies of previously little-explored ocean regions are being published, integrated into diagenetic models and turned into regional and global estimates of deep sediment respiratory activity (Bowles, Mogollón, Kastner, Zabel, & Hinrichs, 2014; D'Hondt et al., 2004, 2002). For example, the upwelling areas of eastern boundary systems are delineated as high-productivity regions characterized by elevated organic carbon turnover rates. Here, oxygen, nitrate, and reactive metal oxides are consumed during TEAPs or related diagenetic reactions in the upper few centimeters of the sediment, and organic carbon mineralization in the remainder of the sediment column is proceeding via sulfate reduction and methanogenesis (Figure 2.7.2(a)). Sediments underlying the Benguela Upwelling System along the Southwest African margin and the Peru Margin Upwelling System, two of the world's most productive ocean areas, were drilled during ODP Legs 175 and Leg 112 (revisited during Leg 201), respectively. Alkalinity values exceeding 170 mM (Leg 175, Site 1085; Murray, Wigley, & Shipboard Scientific Party, 1998) and 260 mM (Leg 112, Site 688; Kastner et al., 1990), and ammonium concentrations greater than 50 mM, are a direct consequence of the elevated rates of primary productivity in the surface waters reflected in the very high supply and mineralization of organic carbon matter in the underlying sediments. In contrast, central gyres, such as the South Pacific Gyre, drilled during IODP Exp. 329, are extremely oligotrophic regions, and oxygen and nitrate penetrate tens of meters into the sediment (Figure 2.7.2(b); D'Hondt, Inagaki, Alvarez Zarikian, & the IODP Expedition 329 Science Party, 2013; Fischer, Ferdelman, D'Hondt, Røy, & Wenzhöfer, 2009; Røy et al., 2012).

TABLE 2.7.1 (a) Metabolic Reactions, Including Reactions of Organic Matter Oxidation in Typical Redfield Stoichiometry (C/N/P) Where x, y, and z are Taken as 106, 16, and 1 (Modified From [Tromp, Van Cappellen, & Key, 1995](#); [Aller, 2014](#)) and (b) Important Secondary Reactions Occurring in Subseafloor Sediments

(a) Metabolic Reactions	
<i>Organic Matter Oxidation Reactions</i>	
Aerobic respiration	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + (x+2y)\text{O}_2 \rightarrow x\text{CO}_2 + (x+y)\text{H}_2\text{O} + y\text{HNO}_3 + z\text{H}_3\text{PO}_4$
Nitrate reduction	$5(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 4x\text{NO}_3^- \rightarrow x\text{CO}_2 + 3x\text{H}_2\text{O} + 4x\text{HCO}_3^- + 2x\text{N}_2 + 5y\text{NH}_3 + 5z\text{H}_3\text{PO}_4$
Dissimilatory manganese oxide reduction	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 2x\text{MnO}_2 + 3x\text{CO}_2 + x\text{H}_2\text{O} \rightarrow 2x\text{Mn}^{2+} + 4x\text{HCO}_3^- + y\text{NH}_3 + z\text{H}_3\text{PO}_4$
Dissimilatory iron oxide reduction	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 4x\text{Fe}(\text{OH})_3 + 7x\text{CO}_2 \rightarrow 4x\text{Fe}^{2+} + 8x\text{HCO}_3^- + 3x\text{H}_2\text{O} + y\text{NH}_3 + z\text{H}_3\text{PO}_4$
Organoclastic sulfate reduction	$2(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + x\text{SO}_4^{2-} \rightarrow x\text{H}_2\text{S} + 2x\text{HCO}_3^- + 2y\text{NH}_3 + 2z\text{H}_3\text{PO}_4$
Hydrogenotrophic methanogenesis	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
Acetoclastic methanogenesis	$\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$
Anaerobic oxidation of methane coupled to sulfate reduction	$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O}$
Anaerobic oxidation of methane coupled to iron reduction	$\text{CH}_4 + 8\text{Fe}(\text{OH})_3 + 15\text{H}^+ \rightarrow \text{HCO}_3^- + 8\text{Fe}^{2+} + 21\text{H}_2\text{O}$
Anammox	$\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ $\text{NH}_4^+ + 3/2\text{MnO}_2 + 2\text{H}^+ \rightarrow 3/2\text{Mn}^{2+} + 1/2\text{N}_2 + 3\text{H}_2\text{O}$

(b) Secondary Reactions	
Oxidation of aqueous metal species	$\mathbf{Mn^{2+}} + \frac{1}{4}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{MnOOH} + 2\text{H}^+$ $\mathbf{Mn^{2+}} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+$ $\mathbf{Fe^{2+}} + \frac{1}{4}\text{O}_2 + \frac{5}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{H}^+$ $\text{MnO}_2 + 2\mathbf{Fe^{2+}} + 4\text{H}_2\text{O} \rightarrow \text{Mn}^{2+} + 2\text{Fe(OH)}_3 + 2\text{H}^+$ $5\mathbf{Fe^{2+}} + \mathbf{NO_3^-} + 12\text{H}_2\text{O} \rightarrow 5\text{Fe(OH)}_3 + \frac{1}{2}\text{N}_2 + 4\text{H}^+$ $\frac{5}{2}\mathbf{Mn^{2+}} + \mathbf{NO_3^-} + 2\text{H}_2\text{O} \rightarrow \frac{5}{2}\text{MnO}_2 + \frac{1}{2}\text{N}_2 + 4\text{H}^+$
Iron monosulfide and pyrite formation	$\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \mathbf{\text{FeS}} + 2\text{H}^+$ $\text{FeS} + \text{S}_x^{2-} \rightarrow \mathbf{\text{FeS}_2} + (x-1)\text{S}_x^{2-}$ $\text{FeS} + \text{H}_2\text{S} \rightarrow \mathbf{\text{FeS}_2} + \text{H}_2$
Manganese oxide reduction	$4\text{H}_2\text{S} + 4\mathbf{\text{MnO}_2} \rightarrow 4\text{S}^0 + 4\text{Mn}^{2+} + 8\text{OH}^-$ $\text{NH}_4^+ + 4\mathbf{\text{MnO}_2} + 6\text{H}^+ \rightarrow 4\text{Mn}^{2+} + \mathbf{\text{NO}_3^-} + 5\text{H}_2\text{O}$
Sulfur oxidation and disproportionation	$2\text{FeOOH} + 3\text{H}_2\text{S} \rightarrow 2\mathbf{\text{FeS}} + \text{S}^0 + 4\text{H}_2\text{O}$ $2\mathbf{\text{H}_2\text{S}} + 8\text{FeOOH} + 14\text{H}^+ \rightarrow \text{S}_2\text{O}_3^{2-} + 8\text{Fe}^{2+} + 13\text{H}_2\text{O}$ $4\text{S}^0 + 4\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{S} + \text{SO}_4^{2-} + 2\text{H}^+$ $8\mathbf{\text{HS}_2^-} + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 7\text{HS}^- + 7\text{H}^+$ $\mathbf{\text{S}_2\text{O}_3^{2-}} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{SO}_4^{2-}$
Alkalinity generation via sulfate reduction	$3\text{SO}_4^{2-} + 6\text{CH}_2\text{O} + 2\text{FeOOH} \rightarrow 6\mathbf{\text{HCO}_3^-} + \text{FeS}_2 + \text{FeS} + 4\text{H}_2\text{O}$ $3\text{SO}_4^{2-} + 3\text{CH}_4 + 2\text{FeOOH} \rightarrow 3\mathbf{\text{CO}_3^{2-}} + \text{FeS}_2 + \text{FeS} + 4\text{H}_2\text{O}$
Bold indicates eponymous reactant.	

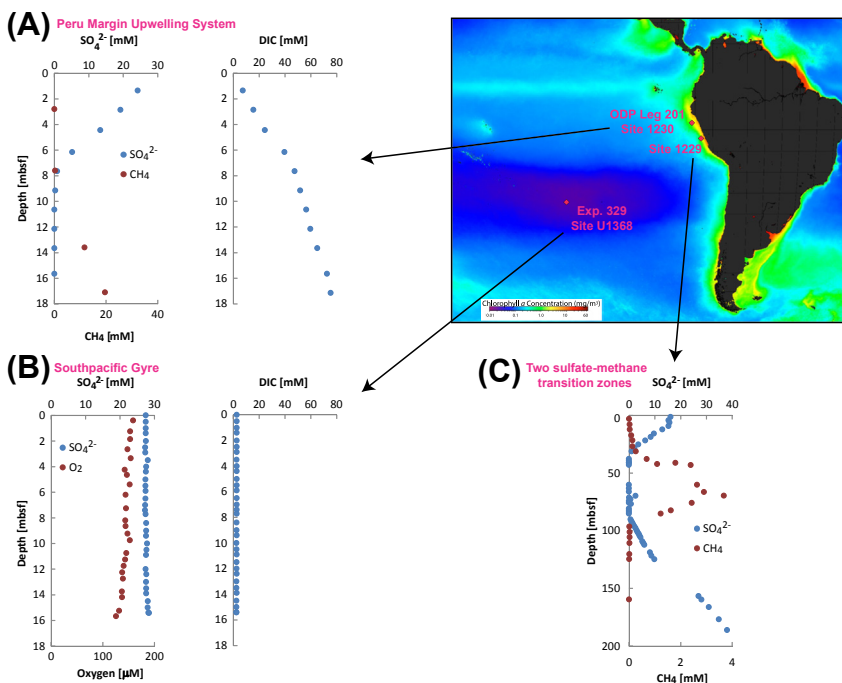


FIGURE 2.7.2 (A) Interstitial water concentration profiles of sulfate (SO_4^{2-}) and dissolved inorganic carbon (DIC), and methane (CH_4) concentration profiles from sediments of the Peru Margin Upwelling System (ODP Leg 201 Site 1230; D'Hondt, Jørgensen, Miller et al., 2003); (B) SO_4^{2-} , oxygen, and DIC concentrations in South Pacific Gyre sediments (IODP Exp. 329 Site U1368; D'Hondt, Inagaki, Alvarez Zarikian et al., 2011), and (C) SO_4^{2-} and CH_4 concentration profiles from ODP Leg 201 Site 1229 sediment, which features two sulfate–methane transition zones. Also shown is the average ocean chlorophyll concentration measured by SeaWiFS (SeaWiFS Project, NASA Goddard Space Flight Center).

A curious biogeochemical feature discovered at many sites drilled during the legacy of Deep Sea Drilling Project (DSDP), ODP, and IODP is the inversion of the sequence of electron acceptor activities near the basement, sometimes even expressed in the occurrence of two SMT zones, e.g., at Site 1229 drilled during ODP Leg 201 (Figure 2.7.2(c); D'Hondt et al., 2004).

2.7.3 SECONDARY BIOGEOCHEMICAL REACTIONS

Microbially mediated diagenetic processes driven by carbon mineralization leave a fundamental imprint on the pore water composition and lithogenic and biogenic solid-phase components of marine sediments (Table 2.7.1; Figure 2.7.3). For instance, the metabolic by-products of the subseafloor microbial carbon cycle, such as hydrogen sulfide and dissolved inorganic carbon (DIC), react with pore water and/or solid-phase components of the sediments. An additional, vast

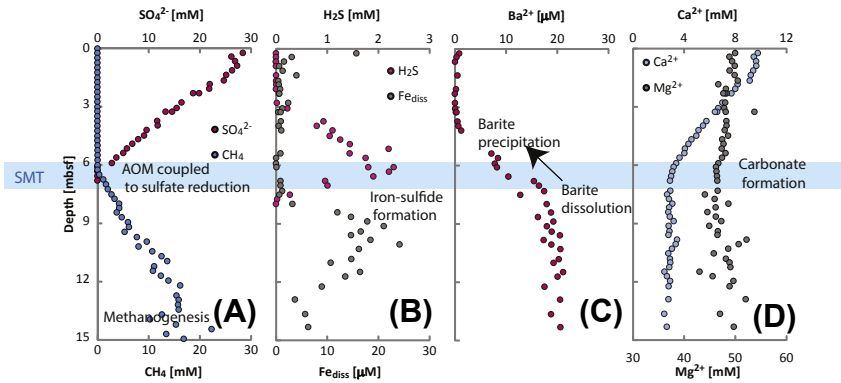


FIGURE 2.7.3 Interstitial water concentration profiles of (A) sulfate SO_4^{2-} and methane (CH_4), (B) hydrogen sulfide (H_2S) and dissolved iron (Fe_{diss}), (C) barium (Ba^{2+}), and (D) calcium (Ca^{2+}) and magnesium (Mg^{2+}) from IODP Expedition 323 Site U1345. *Expedition 323 Scientists, 2011.*

array of diagenetic processes, both inorganic and microbially mediated, occur as a consequence of the initial microbial reactions (Table 2.7.1(b)). These reactions often create a range of short-lived, intermediate compounds that react further via a network of oxidation–reduction reactions. These diagenetic reactions represent important recycling mechanisms that link the carbon, sulfur, phosphorus, silica, and metal cycles.

In the upper sediment column and in sediments above the ocean crust, reactions involving oxygen, nitrogen compounds, and dissolved and particulate metal species often play a prevalent role (Table 2.7.1(b)), for example, the oxidation of (up- or downward diffusing) aqueous iron and manganese to new metal oxide phases, and the oxidation of aqueous iron via manganese oxides phases. At depths where sulfate reduction is occurring, processes involving intermediate sulfur species and hydrogen sulfide are important, such as the reaction of these sulfur compounds with dissolved iron and solid-phase iron (oxyhydr)oxides to form elemental sulfur, iron monosulfide, and pyrite (Figure 2.7.3(b); Berner, 1970, 1984). Throughout the sediment column, the production of DIC during organic carbon mineralization and increasing alkalinity affects the saturation of carbonate mineral phases as outlined below.

2.7.4 INTERACTION OF BIOGEOCHEMICAL PROCESSES AND THE SEDIMENT

The diagenetic processes in subseafloor sediments lead to the dissolution, oxidation, reduction, and/or recrystallization of sedimentary deposits, and the formation of new authigenic precipitates. The genesis of authigenic mineral phases, such as carbonates (Figure 2.7.3(d)), can change sediment properties, e.g., by facilitating lithification and thus reducing sediment permeability. The occurrence and elemental and isotopic composition of these mineral phases often

allow reconstruction of the microbially mediated processes and associated early diagenetic reactions in the past and present, and can reveal changes of the environmental conditions in the overlying water column over time, including oxygenation conditions (Figure 2.7.4; e.g., Goldhaber, 2003; Lyons & Severmann, 2006; Raiswell, Buckley, Berner, & Anderson, 1988; Raiswell & Canfield, 1998;). The alteration of primary sediment components by diagenetic processes, however, can also affect paleoproxies commonly used in paleoceanographic studies, e.g., by dissolution of skeletal fossils and alteration of initial biogenic constituents such as barite (Brumsack & Gieskes, 1983; McManus et al., 1998; Von Breymann, Brumsack, & Emeis, 1992; see Figure 2.7.3(c)). Biogeochemical reactions in subseafloor sediments play an important role in the global carbon, sulfur, phosphorus, silica, and metal cycles, by regulating their oceanic reservoirs through transformation, deposition, and burial of aqueous species (e.g., sulfate), and particulate lithogenic and biogenic components in the form of more stable diagenetic products (e.g., authigenic pyrite, carbonate, and apatite phases). Aside from dissolution–precipitation reactions, cation exchange on mineral surfaces is central for the distribution of pore water ions, and thus the availability of reactants for further authigenic mineral formation in the sediment. For instance, the adsorption of ammonium, produced during organic carbon oxidation, onto clay minerals can play an important role for the concentrations and isotopic composition of calcium and magnesium in marine pore waters (Figure 2.7.4; Mavromatis, Meister, & Oelkers, 2014; Ockert, Gussone, Kaufhold, & Teichert, 2013; Teichert, Gussone, & Torres, 2009; Von Breymann, Collier, & Suess, 1990; Von Breymann, Ungerer, & Suess, 1988).

One of the most fundamental reactions of the subseafloor microbial carbon cycle is the formation of diagenetic carbonate phases, such as magnesian calcite and dolomite (Baker & Kastner, 1981; Kelts & McKenzie, 1982; Pisciotto & Mahoney, 1981). This process ultimately controls the amount of DIC that is released back into the ocean and the fraction of carbon that is buried in the sedimentary record over longer timescales (Falkowski et al., 2000; Higgins, Fischer, & Schrag, 2009; Milliman, 1993; Schrag, Higgins, Macdonald, & Johnston, 2013). It is estimated that diagenetic carbonates may account for at least 10% of global carbonate accumulation at present and may thus play an important role in the removal of carbon from the Earth's surface (Sun & Turchyn, 2014). Additionally, changes in the volume of the global authigenic carbon reservoir over time may have significantly affected the global carbon cycle in the past. This carbon sink should therefore be included in global carbon mass balance estimates throughout Earth's history (Canfield & Kump, 2013; Higgins et al., 2009; Schrag et al., 2013).

Organoclastic sulfate reduction has been proposed as a driver for diagenetic carbonate formation in marine subseafloor sediments (e.g., Burns, Baker, & Showers, 1988; Mazzullo, 2000). This process is dependent on the availability of reactive iron (oxyhydr)oxide phases to form iron sulfides and the concomitant build-up of hydrogen sulfide in the pore water (Morse & McKenzie, 1990;

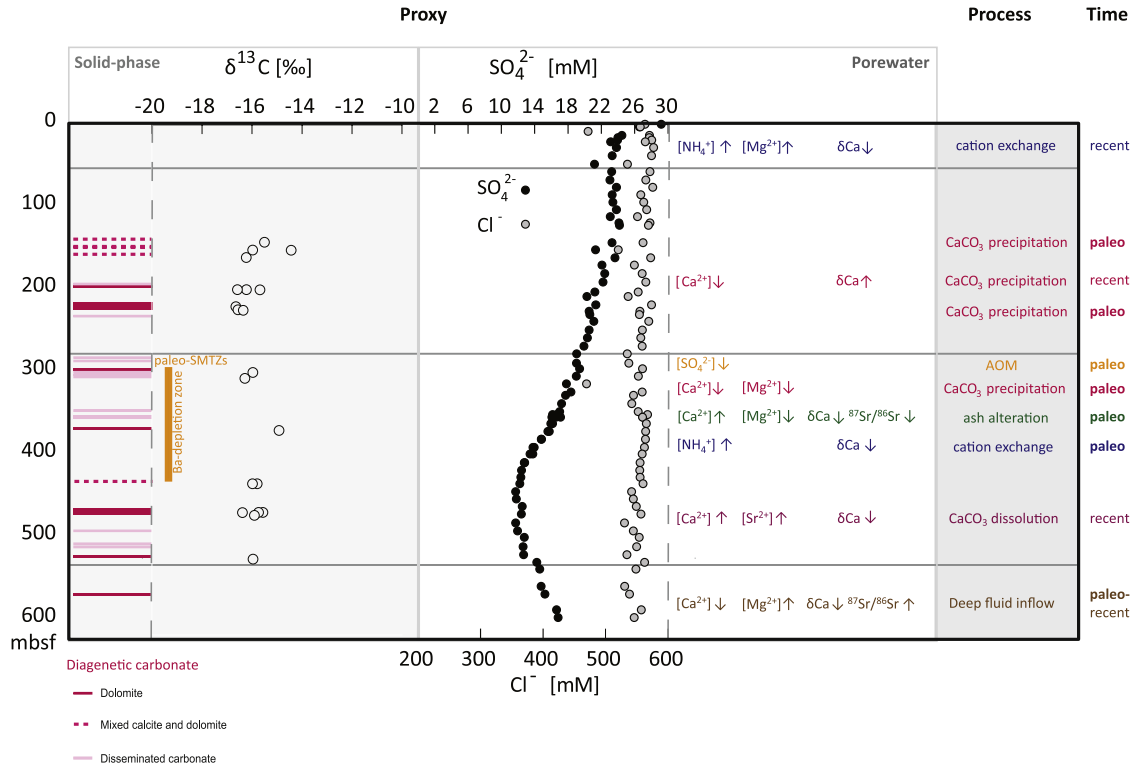


FIGURE 2.7.4 Example of linking biogeochemical processes to solid phase carbonate chemistry (distribution of diagenetic carbonate phases and carbon isotopic composition ($\delta^{13}\text{C}$) of carbonates) and interstitial water profiles (sulfate (SO_4^{2-}) and chloride (Cl^-)) at IODP Expedition 323 Site U1341 (Bowers Ridge, Bering Sea; after Wehrmann et al., in press). The present (recent) and past (paleo) biogeochemical processes and their effects on pore water concentrations and isotope values with depth are summarized. Brackets denote concentration, a delta sign the isotopic ratio. Up- and downward arrows indicate that the concentration or isotope ratio is increasing or decreasing at this depth.

Walter & Burton, 1990). In both advective fluid flow systems and diffusive systems, sulfate reduction coupled with reductive iron oxide dissolution and precipitation of pyrite represents an important source of carbonate alkalinity for the marine environment.

As written in Table 2.7.1(b), both organoclastic and methanotrophic sulfate reduction yield equivalent amounts of alkalinity per sulfate reduced. Significant net alkalinity production may result from deep subseafloor sulfate reduction activity (D'Hondt et al., 2002) even given the various wide range of estimates of organic carbon burial within ocean sediments and various estimates of net sulfate reduction (Bowles et al., 2014; D'Hondt et al., 2002). In the absence of reactive iron, a shift in the carbonate equilibrium during the initial stages of sulfate consumption leads to carbonate undersaturation and can facilitate carbonate dissolution until elevated DIC concentrations are high enough to reach carbonate saturation (Meister, 2013; Morse & McKenzie, 1990). Excursions in pore water calcium and magnesium concentrations in the sulfate zone of ocean drilling sites, for example, ODP Leg 201 Site 1226 (D'Hondt et al., 2004), indicate ongoing carbonate formation, which typically encompasses the disseminated precipitation of a variety of authigenic carbonates (Aller, 2014), while distinct diagenetic carbonate nodules at these sites are typically absent.

Methanotrophic sulfate reduction is a major contributor to diagenetic carbonate formation in subseafloor sediments (Meister et al., 2007; Raiswell, 1988; Ussler & Paull, 2008). During the anaerobic oxidation of methane coupled to sulfate reduction, DIC is produced while at the same time the pore water pH converges to 7.9, resulting in carbonate oversaturation and the formation of carbonate phases (Soetaert, Hofmann, Middelburg, Meysman, & Greenwood, 2007). The SMT zone has thus been identified as an important zone of carbonate formation, including the precipitation of dolomite (Figure 2.7.3(d); Malone, Claypool, Martin, & Dickens, 2002; Meister et al., 2007; Meister, Bernasconi, Vasconcelos & Mckenzie, 2008; Moore, Murray, Kurtz, & Schrag, 2004; Rodriguez, Paull, & Borowski, 2000). Here, the anaerobic oxidation of ^{13}C -depleted methane (Alperin, Reeburgh, & Whiticar, 1988; Martens, Albert, & Alperin, 1999; Mccorkle, Emerson, & Quay, 1985) leads to the production of strongly ^{13}C -depleted DIC, which is subsequently recorded in the carbon isotopic composition of the precipitating carbonate phases (Meister et al. 2007; Ritger, Carson, & Suess, 1987; Ussler & Paull, 2008; Wehrmann et al., 2011, Wehrmann et al., 2014). Diagenetic carbonates formed in the SMT zone are often observed as distinct light colored, semilithified bands in unconsolidated, siliciclastic sediments and hold a characteristic light carbon isotope composition (e.g., Meister, Mckenzie, Warthmann, & Vasconcelos, 2006; Meister et al., 2007; Pisciotto & Mahoney, 1981).

Several lines of evidence indicate that diagenetic carbonate phases may also form in and below the active methanogenic zone. At several DSDP, ODP, and IODP sites, diagenetic carbonate phases with a ^{13}C -enriched carbon isotopic signal were found, e.g., at DSDP Leg 64 Hole 479 (maximum $\delta^{13}\text{C}$ -values $> 11\text{‰}$;

Kelts & McKenzie, 1982), at ODP Leg 175 Site 1081 (+7.7‰; Pufahl & Wefer, 2001), at ODP Leg 201 Site 1227 (+11.5‰; Meister et al., 2007), and at IODP Exp. 323 Site U1343 (+11.37‰; Pierre et al., 2014). The strong ^{13}C -enrichment of the diagenetic carbonate phases is explained by carbonate formation in the methanogenic zone and/or the mixing of ^{13}C -depleted DIC formed during organoclastic and methanogenic sulfate reduction and ^{13}C -enriched DIC produced during methanogenesis, during the downward movement of the SMT zone in the sediment (Meister et al., 2008; Wehrmann et al., 2014; see Figure 2.7.4). Wehrmann et al. (2011) and Pierre et al., 2014 furthermore provided geochemical and mineralogical evidence for the existence of a deep carbonate formation zone, where dolomite is precipitating at low rates, below the depth of the methanogenic zone at several high-productivity sites drilled during IODP Exp. 323.

An important precondition to the formation of diagenetic carbonate in the methanogenic zone may be the contemporaneous transformation of CO_2 , produced during methanogenesis, to bicarbonate (HCO_3^-) via marine silicate weathering (Scholz, Hensen, Schmidt, & Geersen, 2013; Wallmann et al., 2008, 2006). During both acetoclastic and hydrogenotrophic methanogenesis CO_2 is produced whose subsequent (partial) dissociation produces protons and lowers the pH (Soaetert et al., 2007) to conditions unfavorable for carbonate formation. During silicate weathering, however, reactive silicates (e.g., plagioclase feldspars, olivine, and pyroxene) react with CO_2 to form clay minerals and bicarbonate (Wallmann et al., 2008). These reactions can be summarized as follows:

Reactive silicates + $\text{CO}_2 \rightarrow$ clay minerals + dissolved cations + dissolved silica + HCO_3^-

This process also releases cations such as magnesium, calcium, and iron, previously bound in the silicate matrix, into the pore water, which can subsequently take part in the precipitation of carbonate. Accordingly, Pierre et al., 2014 describe the occurrence of iron-rich carbonates in Expedition 323 sediments below 130–260 mbsf, which presumably formed as a result of methanogenesis coupled to the microbially assisted low-temperature transformation of Fe-rich clay minerals (smectite and chlorite) to illite.

The diagenesis of biogenic silica in subseafloor sediments, potential linkages to microbially mediated processes, and, more directly, microbe–mineral interactions with silicates and clays in the sedimentary subseafloor biosphere remain poorly investigated. Silicate diagenesis is important in the control of alkalinity and pH in the deep sediments, and may play an important role in the subseafloor phosphorus cycle. The alteration of biogenic silica proceeds via a range of reactions (see Aller, 2014; Loucaides, Van Cappellen, Roubex, Moriceau, & Ragueneau, 2012; for review) that depend on the availability and interaction of different aqueous and particulate sediment components, for example Al^{3+} and Fe^{3+} (Aplin, 1993; Dixit & Van Cappellen, 2002; Dixit, Van Cappellen, & Van Bennekom, 2001; Mackin & Aller, 1989; Michalopoulos & Aller, 2004; Van Bennekom, Fred Jansen, Van Der Gaast, Van Iperen, & Pieters, 1989). An important process in biogenic opal-rich sediments is the conversion of biogenic silica to aluminosilicates via reverse

weathering (Mackenzie & Garrels, 1966; Mackin & Aller, 1984, 1989), which occurs at very early stages of silica diagenesis, i.e., shallow sediment depths (Loucaides et al., 2010; Michalopoulos & Aller, 1995; Michalopoulos, Aller, & Reeder, 2000; Wallmann et al., 2008). Meister et al. (2014) directly link the early diagenetic formation of chert at ODP Site 1226 to the formation of authigenic, poorly crystallized iron oxides and illite. The authors propose that these authigenic iron oxide and iron-bearing silicate phases precipitate at a deep, inverted redox front (400 mbsf) where microbes utilize upward diffusing nitrate to oxidize downward diffusing ferrous iron. The availability of lithogenic Al- and Fe-rich components is also likely a main controlling factor for reverse weathering in open-ocean areas such as the Southern Ocean (Van Cappellen & Qiu, 1997), while Scholz et al. (2013) suggested that the availability of CO₂ deriving from methanogenesis regulates the rate of silicate weathering in underlying methanogenic sediments. Overall, both processes strongly alter the primary biogenic silica component of marine sediments, affect the subseafloor carbonate system through CO₂ production and consumption, respectively, and lead to the uptake or release of specific cations and anions (e.g., K, Mg, and Li).

The reaction of hydrogen sulfide, produced during both organoclastic and methanogenic sulfate reduction, with dissolved iron and reactive iron(oxyhydr) oxide to form iron monosulfide, elemental sulfur, and pyrite also strongly affects the composition of marine sediments, the latter being most important over the extended diagenetic timescales for subseafloor sediments. Several reaction pathways are proposed for the formation of pyrite and other associated iron sulfide phases, e.g., mackinawite (FeS) and greigite (Fe₃S₄) (Goldhaber, 2003; Rickard & Luther, 2007; Rickard, Schoonen, & Luther, 1995; Schoonen, 2004; Table 2.7.1(b)). Pyritization is of fundamental importance for the global sulfur cycle, as the burial of solid-phase sulfur compounds represents a major sink for seawater sulfate, in addition to the formation and burial of organic sulfur and the precipitation of calcium sulfates in evaporites (Raiswell & Canfield, 2012; Vairavamurthy, Orr, & Manowitz, 1995).

The interactions between the iron and sulfur cycles in subseafloor sediments are observed not only in varying concentrations of diagenetic mineral phases such as pyrite, but also in the alteration of magnetic susceptibility records. These records are commonly used in oceanographic studies as a proxy for stratigraphic changes in sediment composition that may be linked to palaeoclimate-controlled depositional processes. In this case, the magnetic signal is created by primary (detrital) iron phases including magnetite and metastable iron sulfides, e.g., greigite and pyrrhothite. The dissolution of primary iron oxide phases during reaction with sulfide and the formation of metastable iron sulfide phases during diagenesis can thus significantly deteriorate the original magnetic susceptibility signal (Figure 2.7.5; e.g., Abrajevitch & Kodama, 2011; Fu, Von Döbeneck, Franke, Heslop, & Kasten, 2008; Karlin & Levi, 1983; März, Hoffmann, Bleil, De Lange, & Kasten, 2008; Reitz, Hensen, Kasten, Funk, & De Lange, 2004; Riedinger et al., 2005).

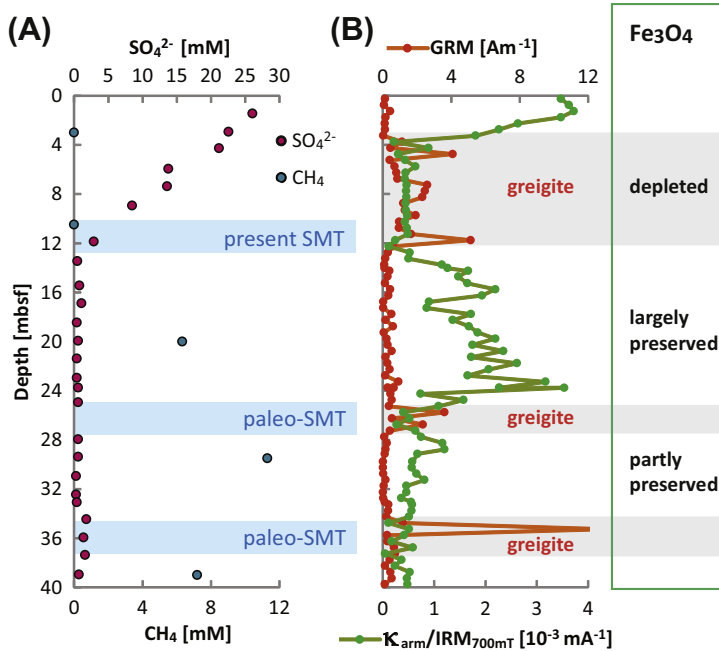


FIGURE 2.7.5 (A) Interstitial water sulfate (SO_4^{2-}) and methane (CH_4) concentrations, (B) distribution of the greigite-sensitive rock magnetic parameter gyromagnetic remanent magnetization (GRM) and the $\text{K}_{\text{arm}}/\text{IRM}_{700\text{mT}}$ parameter, which is sensitive to changes in grain-size variations within magnetite, as well as geochemical interpretation of these records based on Fu et al. (2008).

The dissolution of iron (oxyhydr)oxide by dissimilatory iron reducers or during the reaction with hydrogen sulfide and the mineralization of organic matter release phosphorus into the pore water of marine sediments (Anschutz, Zhong, Sundby, Mucci, & Gobeil, 1998; Filippelli & Delaney, 1996). The phosphorus from these “labile phases” is transformed into an amorphous Ca-phosphate precursor (Gunnars, Blomqvist, & Martinsson, 2004; Van Cappellen & Berner, 1988) and further altered to diagenetically more stable authigenic carbonate fluorapatite over time (Filippelli & Delaney, 1996; Rutenberg & Berner, 1993). These biogeochemical transformations of phosphorus increase the burial efficiency of labile phosphorus in marine sediments, and distinguish authigenic phosphorus phases in this environment as an important sink in the global phosphorus cycle (Delaney, 1998; Wallmann, 2010). In biosilica-dominated ocean regions, e.g., the Southern Ocean and the North Pacific, biogenic opal-bound phosphorus represents an additional contributor to the reactive phosphorus pool (Figure 2.7.6; Latimer, Filippelli, Hendy, & Newkirk, 2006; März, Poulton, Wagner, Schnetger, & Brumsack, 2014). However, the impact of microbial activity on the opal-bound phosphorus pool and its linkage to opal diagenesis in marine sediments remains poorly investigated (Figure 2.7.6; Latimer et al., 2006; März et al., 2014).

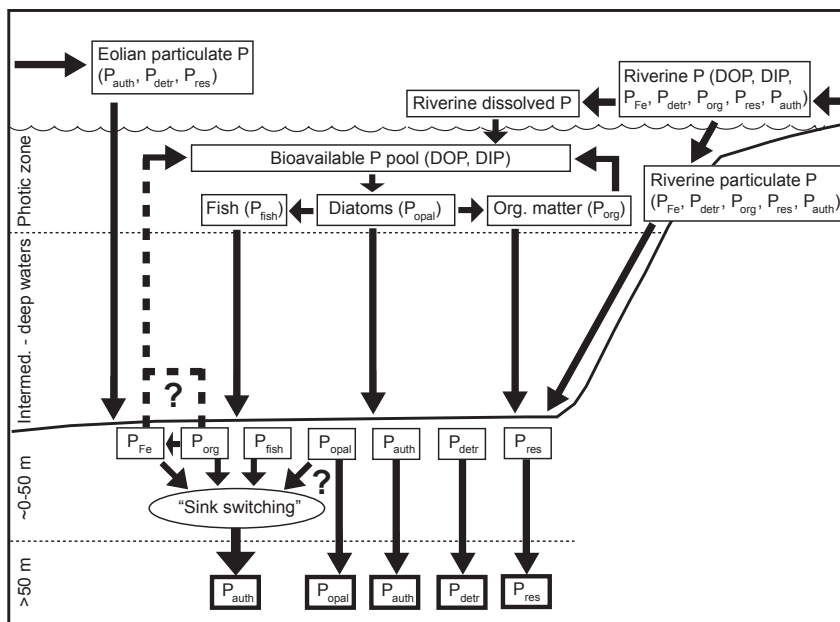


FIGURE 2.7.6 Schematic illustration of the Bering Sea phosphorus cycle including input pathways (eolian, riverine); transformation and recycling processes within surface waters, deep/intermediate waters, surface (<50 m) and deeper (>50 m) marine sediments; and buried phosphorus fractions. *From März et al., 2014.*

At open-ocean sites away from areas of high productivity, the cycling of iron and manganese can play a prevalent role for microbial processes occurring in the subseafloor sediments. Here, extended zones of elevated pore water iron and manganese concentrations have been observed, for example, at ODP Leg 201 Site 1331, and point to the predominance of these TEAPs for carbon mineralization. In particular, if sediments additionally receive increased input of metal oxide phases, such as close to hydrothermal sources in the Eastern Equatorial Pacific (Leg 201 Site 1226; [Meister, Bernasconi, Aiello, Vasconcelos, & Mckenzie, 2009](#)) and in the Arctic Ocean ([Löwemark, Jakobsson, Mörth, & Backman, 2008](#); [März et al., 2011](#)), the diagenetic Mn (and Fe) cycling facilitates the formation of distinct authigenic mineral phases, including Ca-rhodochrosite, and authigenic Mn-rich layers ([Meister et al., 2009](#); [März et al., 2011](#)).

In paleoceanographic studies, sedimentary barite contents, barium to aluminum ratios (Ba/Al), or excess barium concentration over the composition of average crust (Ba_{xs}) are often used as tracers for paleoproductivity, and the strontium isotope composition of deposited barite can give insight into the past seawater strontium composition (e.g., [Gingele & Dahmke, 1994](#); [Gingele, Zabel, Kasten, Bonn, & Nürnberg, 1999](#); [Mearon, Paytan, & Bralower, 2003](#); [Paytan, Kastner, & Chavez, 1996](#); [Paytan, Kastner, Martin, Macdougall, & Herbert,](#)

1993s). Microbially mediated diagenetic processes, however, can strongly alter the primary barite and/or barium signal of subseafloor sediments (Brumsack & Gieskes, 1983; McManus et al., 1998; Von Breymann et al., 1992). Specifically, pore water sulfate depletion results in the dissolution of solid-phase barite and the release of barium into the pore water (Figure 2.7.3(c)). Following the subsequent upward diffusion of the released barium, authigenic barite layers form at the interface with downward diffusing sulfate, i.e., immediately above the SMT zone (Dean & Schreiber, 1978; Riedinger, Kasten, Groger, Franke, & Pfeifer, 2006; Torres, Brumsack, Bohrmann, & Emeis, 1996). These barite fronts can persist in marine subseafloor sediments over timescales of several thousands of years, and thus serve as distinct indicators for the past location and shifts of the depth of the SMT zone over time (Arndt, Hetzel, & Brumsack, 2009; Henkel et al., 2012; Riedinger et al., 2006).

2.7.5 TIME AND THE DEEP SUBSEAFLOOR BIOSPHERE

The extended sediment sequences that are retrieved in the framework of IODP not only offer the unique opportunity to study the paleoceanographic and paleoenvironmental history of ocean regions, but these deep-time records also provide the required data to investigate the evolution of biogeochemical processes in seafloor sediments as a function of depth and time. Much of our understanding of deep subseafloor biogeochemistry derives from modeling of concentration–depth profiles, where conditions of steady state, which eliminates any time-dependent variations in input and composition of the sediment can be reasonably assumed (e.g., Berner, 1980; Bowles, Mogollón, Kasten, Zabel, & Hinrichs, 2014; Wang, Spivack, Rutherford, Manor, & D’Hondt, 2008). Nevertheless, non-steady state conditions must be considered at many ODP and IODP sites.

Variations in the amount of the input and the quality of deposited organic matter driving subseafloor biogeochemical processes result from numerous, often co-occurring, factors, including changes in surface water primary productivity, sea ice coverage, the depositional environment, as well as lateral transport processes. Other factors can also influence the magnitude of the input and the quality of organic matter reaching the seafloor, such as water column oxygen levels, the amount and composition of terrigenous ballast material, the community composition of primary producers, and the fraction and degradability of terrestrial organic matter delivered to the ocean (e.g., Arndt et al., 2013; Hedges & Keil, 1995; Hedges et al., 1994; Henson, Sanders, & Madsen, 2012; Hulthe, Hulth, & Hall, 1998; Mollenhauer et al., 2007; Simon, Poulicek, Velimirov, & Mackenzie, 1994; Wilson, Barker, & Ridgwell, 2012; Zonnefeld et al., 2010). Variations of these features are often the result of large-scale changes of the oceanographic regime, e.g., over glacial–interglacial timescales. Important oceanographic changes are modifications in ocean stratification (Gebhardt et al., 2008; Jaccard et al., 2005; Sigman, Jaccard, & Haug, 2004), the location

and extent of oxygen minimum zones (e.g., [Altabet, Murray, & Prell, 1999](#)), and/or the prevailing current regime ([Berger, 1970](#); [Haug & Tiedemann, 1998](#)).

Non-steady state geochemical regimes can furthermore develop as a result of more extreme changes in organic carbon input. This includes periods following the deposition of organic carbon-rich shales and sapropels during oceanic anoxic events, e.g., in the Cretaceous and Neogene ([Arthur, Brumsack, Jenkyns, & Schlanger, 1990](#); [Jenkyns, 1980](#); [Wilson & Norris, 2001](#)). Cretaceous black shales, drilled during ODP Leg 207 on Demerara Rise, still imprint the biogeochemical signatures in pore water and the sediment at present; i.e., they are still microbially active “bioreactors,” even after almost 100 million years ([Arndt, Brumsack, & Wirtz, 2006](#); [Arndt et al., 2009](#)). Similarly, major changes in the environmental setting, such as repeated transitions from freshwater to saltwater conditions like those described for the Baltic Sea and the Black Sea ([Björck, 1995](#); [Degens & Ross, 1972](#); [Ryan et al., 1997](#); [Voipio, 1981](#), p. 418), can drive non-steady state conditions in associated subseafloor sediments.

The occurrence of erosional events is another major cause for non-steady state processes, often linked to changes in the (bottom water) current regime. This process essentially removes the uppermost part of the sediment column, and thus of the pore water profiles. As the geochemical profiles reequilibrate during the downward diffusion of seawater into the sediment column, transient “concave-down” geochemical profiles develop (e.g., [Hensen et al., 2003](#)). Erosional events can also lead to the expression of multiple sequences of TEAP in the metabolite profiles, as, for example, observed at IODP Expedition 307 Site U1318 on the Porcupine Seabight continental margin ([Figure 2.7.7](#); [Ferdelman, Kano, Williams, Henriët, & the Expedition 307 Scientists, 2006](#)). This submarine weathering of the diagenetically altered deep sediment may have implications for the geochemistry of the ocean and seafloor over geological time frames. On the other hand, the subsequent deposition of eroded sediments downslope can result in the rapid burial of reworked organic matter and fresh iron (oxyhydr)oxides, formed during the oxidation of sedimentary iron monosulfide and pyrite in oxic seawater ([Morse, 1991](#)), into deep sediments ([Hensen, Zabel, & Schulz, 2000](#); [Hensen et al., 2003](#); [Riedinger et al., 2005](#); [Riedinger, Formolo, Lyons, Henkel, Beck, & Kasten, 2014](#)). Such a depositional environment is, for example, observed along the Argentine Basin, where it led to the burial reactive iron (oxyhydr)oxides below the SMT zone ([Hensen et al., 2003](#); [Riedinger et al., 2005](#)). Intriguingly, in this setting the anaerobic oxidation of methane coupled to iron reduction ([Beal, House, & Orphan, 2009](#); [Sivan et al., 2011](#)) may play an important role for methane consumption in the deep biosphere ([Riedinger et al., 2014](#)).

The long-term evolution of the biogeochemical setting of subseafloor sites is further controlled by plate tectonic movement from the point of original location across the seafloor, for instance, from ocean spreading centers to the continental margins. As a consequence of this drift, the sites cross ocean regions characterized by different extents of surface water productivity, varying inputs

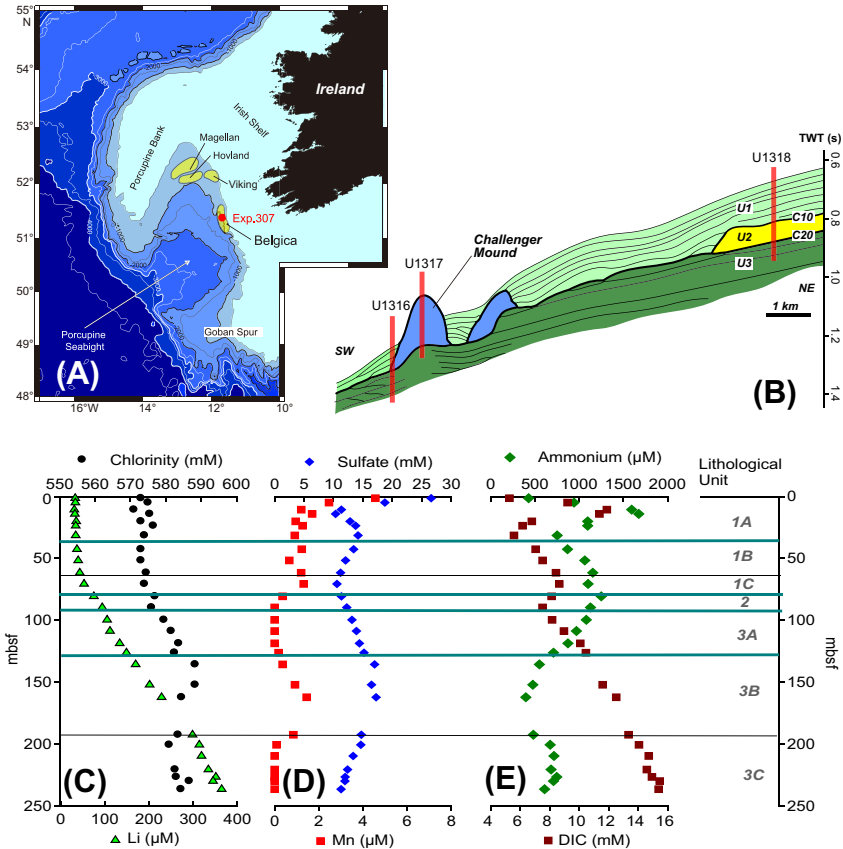


FIGURE 2.7.7 Interstitial water chemistry influenced by periods of rapid sedimentation lying over hiatuses and erosive surfaces at IODP Expedition 307 Site 1318 (Ferdelman et al., 2006). (A) Site 1318 is located upslope from the Porcupine Basin Belgica cold-water coral mound province near SW Ireland. (B) The location and interpreted seismic section of the continental margin sampled during Expedition 307 (after De Mol et al., 2002; Kano, Ferdelman, & Williams, 2010) is shown. The upper seismic unit (U1) corresponds to rapidly buried recent and late Pleistocene sediments from Lithological Unit 1 and Early Pleistocene sediments from Lithological Unit 2. Seismic Units U2 and U3 represent Tertiary (Pliocene and Miocene) deposits ascribed to Lithological Units 3A and 3B & C. The strong seismic reflectors are attributed to erosive unconformities as indicated by the thick blue lines in panels (C)–(E). (C) The distribution of lithium (Li) in the surface 100 m of the sediments indicates rapid burial of seawater Li within the surface sediments that has not come into steady state with respect to a deep source of Li, whereas the chlorinity profile reflects downward propagating changes in ocean salinity. (D, E) Interstitial water profiles of the metabolites sulfate, manganese (Mn), ammonium, and dissolved inorganic carbon (DIC).

of terrigenous and hydrothermal material, and different sedimentation rates. This is often reflected in changes in the amount and quality of deposited organic carbon and in the availability of terminal electron acceptors such as Mn- and Fe-(oxyhydr)oxides. For example, ODP Leg 202 Site 1237 has moved $\sim 3^\circ$ eastward

over the past 6 million years. (Leg 202 Shipboard Scientific Party, 2003a) from a region of higher, to an area of lower temperature, salinity, nutrient concentration, and surface water primary productivity (Wara & Ravelo, 2006). Site 1236, drilled during the same expedition, moved $\sim 20^\circ$ westward into an area with primary productivity that is $\sim 50\%$ higher than it probably was 25 million years ago at its past location (Leg 202 Shipboard Scientific Party, 2003b).

Ultimately, the result of these important non-steady state diagenetic regimes are changes in metabolic rates and concomitant vertical shifts of biogeochemical zones and diagenetic reaction fronts, including the SMT zone (Arndt et al., 2009; Contreras et al., 2013; Holstein & Wirtz, 2010; Meister et al. 2007; Meister, Liu, Ferdelman, Jørgensen, & Khalili, 2013; Riedinger et al., 2006). Resulting transient geochemical signals remain visible in solid-phase and pore water records over long timescales, e.g., as upward-moving sulfurization fronts (e.g., Eckert et al., 2013; Jørgensen, Böttcher, Lüschen, Neretin, & Volkov, 2004; Neretin et al., 2004) and associated nonlinear geochemical pore water gradients (Contreras et al., 2013; Dickens, 2001; Hensen et al., 2003; Wehrmann, Arndt, März, Ferdelman, & Brunner, 2013). In the sediment these fluctuations are recorded in multiple layers of specific diagenetic phases, e.g., authigenic barite (Arndt et al., 2009; Contreras et al., 2013; Riedinger et al., 2006) and dolomite (Meister et al., 2008; Contreras et al., 2013; Wehrmann et al., 2014), pronounced enrichment of authigenic iron sulfides, and distinct sulfur isotopic excursions of pyrites (Holmkvist, Ferdelman, & Jørgensen, 2011; Kasten, Freudenthal, Gingele, & Schulz, 1998). Furthermore, such changes can be reinforced by variations in sea level and sedimentation rates over time (Kasten et al., 1998; Meister et al., 2008; Riedinger et al., 2005).

Reaction-transport modeling represents an important tool for investigating the biogeochemical history of subseafloor sediments, allowing researchers to infer past and present rates of microbial activity, and helps to reconstruct the evolution of diagenetic processes over geological timescales (Arndt et al., 2006, 2009; Dale, Van Cappellen, Aguilera, & Regnier, 2008; Marquart, Hensen, Piñero, Wallmann, & Haeckel, 2010; Reed, Slomp, & De Lange, 2011). These models have been applied to several sites that have undergone major changes in their diagenetic history due to variations in the supply and quality of organic carbon to the sediment, including the Demerara Rise (ODP Leg 207, Site 1258; Arndt et al., 2009), the Peruvian Shelf (ODP Leg 201, Site 1229; Contreras et al., 2013), the Bering Sea (IODP Exp. 323, Site U1341; Wehrmann et al., 2013), and the Black Sea continental margin (Henkel et al., 2012).

2.7.6 BEYOND INTERSTITIAL WATER AND SOLID PHASE CHEMISTRY?

Our understanding of the biogeochemistry of deeply buried sediments derives primarily from the fitting of reaction-transport models to high-resolution depth distributions of dissolved metabolic reactants and products. Diagenetic modeling

provides robust estimates of net reaction rates and fluxes, but may miss processes of biogeochemical importance. For instance, rapid production and consumption of a compound may go unnoticed as the compound's concentration falls below detection limits, or similar rates of consumption and production leave no measurable change in concentration with depth (Fossing, Ferdelman, & Berg, 2000). Experimental rate measurements can lead to additional insight on selected samples and at specific depths. Isotope tracer methods, in particular radiotracer methods, allow the experimental detection of vanishingly small changes in concentration over time. The 10,000-fold increase in the detection limit of sulfate reduction using radiotracers is elaborated upon in the Explanatory Methods of ODP Expedition 201 (D'Hondt, Jørgensen, Miller et al., 2003).

Direct measurement of sulfate turnover using the highly sensitive radiolabel technique affords further insight into sulfur cycling within deep subseafloor sediments. ODP Leg 201 sites along the Peru Continental Margin and Equatorial Pacific have been sampled at high depth resolution from the sediment–water interface down to depths of 300 mbsf for the determination of microbiological sulfate reduction rates (Parkes et al., 2005; see Figure 2.7.8). Based on these studies as well as investigations of other ocean margin sites (Fossing et al., 2000; Holmkvist et al., 2011), direct experimental measurements of sulfate reduction suggest that methane-dependent sulfate reduction appears to consume only a fraction of the total integrated sulfate reduction, and more than 90% of the sulfate turnover (not to be confused with net flux) can be attributed to oxidation of compounds other than methane. Furthermore, sulfate reduction may continue

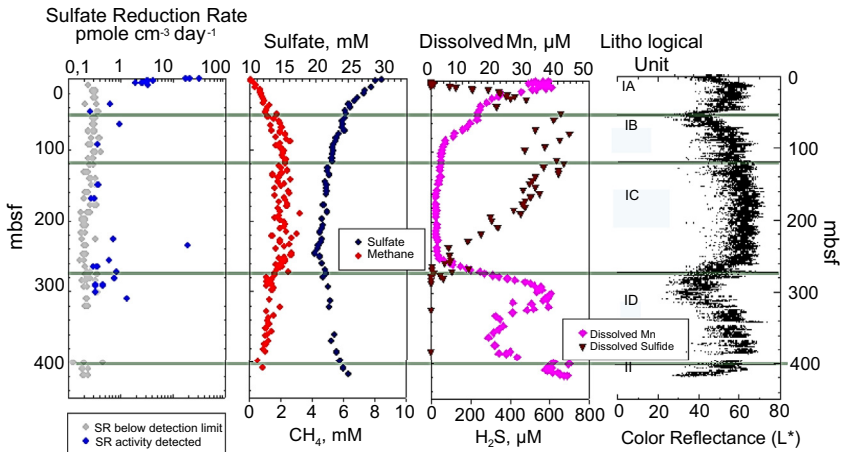


FIGURE 2.7.8 Experimentally determined sulfate reduction rates, interstitial water chemistry, and sediment color reflectance from ODP Leg 201 Site 1226 in the Equatorial Pacific (after Parkes et al., 2005). Sulfate reduction activity was detected using the highly sensitive ^{35}S radiotracer method in a small fraction of the sediments tested, including the darker intervals at depths of 290–320 mbsf that contain Miocene-age diatom and organic-rich sediment. Note the influence of basement seawater flow on the profiles of dissolved sulfate and manganese at depths >380 mbsf. D'Hondt et al., 2004.

as an important process even below the sulfate–methane zone (Holmkvist et al., 2011). Alternative sources of sulfate include oxidative or mineral dissolution processes, e.g., dissolution of barite- and gypsum-bearing facies. Other tracer methods used to elucidate key biogeochemical processes include the determination of (radiolabeled) methane, bicarbonate, and acetate turnover (e.g., Parkes et al., 2011; Webster et al., 2009) or hydrogen turnover using tritiated H₂ (Soffientino, Spivack, Smith, Roggenstein, & D'hondt, 2006; Soffientino, Spivack, Smith, & D'hondt, 2009).

Shortcomings of any isotope-experimental approach (radioisotope or stable-isotope probing) are that isotope tracers are limited to a few elements, and that the time and costs of processing such experiments are extensive. It is also important to state that all such isotope rate measurements are experiments whose underlying assumptions and variables must be understood and constrained. An intriguing example is the back flux of tracer from a labeled product pool into the substrate pool under conditions where extreme energy limitation conditions prevail, i.e., conditions typical of the deep subsurface ocean. During the sulfate-dependent oxidation of methane, one of the most endergonic microbial processes known, experimental data show that a transfer of the radiolabeled ¹⁴C from ¹⁴CO₂ to methane during the net oxidation of methane to CO₂ occurs (Holler et al., 2011). The total transfer of ¹⁴C (or ¹³C for that matter) becomes decoupled from a straightforward stoichiometric relationship to C reduction or oxidation. Such catabolic back fluxes may occur in the sulfate-reducing system under low-energy conditions as well, with striking consequences for stable sulfur isotope distributions in deeply buried sediments (Sim, Bosak, & Ono, 2011). Tracer experiments nevertheless provide invaluable insight. Such biologically induced back flux or tracer exchange clearly indicates the presence of active, functional enzyme systems, for example, sulfate reduction detected at a depth of approximately 300 mbsf at ODP Site 1226 (Figure 2.7.8). Thus, an important microbial process may be localized that would otherwise remain undiscovered when only evaluating interstitial water chemistry.

These microbial-mediated processes can strongly alter the initial sediment composition of marine sediments during diagenesis within distinct and narrow horizons (as described previously); in turn, sediment lithology influences the composition, population size, and metabolic activity of the local microbial community. For example, Aiello and Bekins (2010) demonstrate that microbial cell counts vary an order of magnitude between organic-rich diatom and nannofossil oozes of a drill site in the eastern equatorial Pacific (ODP Leg 201, Site 1226). The authors suggest that these small-scale variations are ultimately controlled by Milankovitch frequency variations in past oceanographic conditions. Similarly, Picard and Ferdelman (2011) describe changes in microbial heterotrophic activity linked to specific lithologies such as dark clay-rich layers and sandy intervals in oligotrophic sediments of the North Atlantic Gyre. Microbial activity measured with the radiotracer method reveals a tight coupling between sediment lithology and microbial activity in the Equatorial Pacific, along the Peru

Margin (Figure 2.7.8; Parkes et al., 2005), and in the cold-water coral-bearing sediments drilled during IODP Expedition 307 (Webster et al., 2009).

2.7.7 CONNECTING THE PELAGIC OCEAN AND SUBSEAFLOOR SEDIMENTARY OCEAN

Hydrothermal circulation at mid-ocean ridges influences ocean water chemistry through seawater–basement rock chemical reactions. Further off-axis, outcropping of permeable basement rock and seamounts allows conductive flow beneath layers of impermeable sediment accumulating on young ridge flanks (Figure 2.7.1; Fisher et al., 2003; Sclater, 2003). If we consider the sediments as boundaries overlying the hydrologically active crustal environment, then using profiles of bioactive compounds measured within/through the sediment layer is an obvious approach to understanding the role of subseafloor microbial life in the chemistry of the water flowing below the sediment cover. Diagenetic modeling of the overlying sediment has been successfully used to estimate water and heat flow within off-axis, sediment-covered systems such as at the Juan de Fuca Ridge (Elderfield, Wheat, Mottl, Monnin, & Spiro, 1999; Giambalvo, Steefel, Fisher, Rosenberg, & Wheat, 2002; Rudnicki, Elderfield, & Mottl, 2001). Seawater altered by water–rock interactions diffuses into and reacts with the overlying organic-rich sediment. Subsequently, microbial terminal electron acceptor processes such as organoclastic sulfate reduction and metal oxide dissolution; precipitation reactions of carbonates, iron sulfides, and apatite; and silica dissolution alter the chemical composition of the water seeping out at discharge sites. Model estimates and extrapolation to the global scale suggest that these sediment–hydrothermal reactions enhance fluxes of sulfate, ammonium, phosphate, and silica (Giambalvo et al., 2002). When compared to basement hydrothermal and riverine fluxes, these sediment–hydrothermal fluxes, with perhaps the exception of dissolved Si, appear to be insignificant (Giambalvo et al., 2002). However, with the advent of new borehole sampling technologies, and the growing realization that the inflow and outflow paths around basement outcrops are extremely complex (Wheat, Hulme, Fisher, Orcutt, & Becker, 2013), estimates of overall fluxes are under continual revision. Fluxes of trace elements (Wheat, Jannasch, Kastner, Plant, & Decarlo, 2003) and nitrogen (Bouronnais et al., 2012) in and out of hydrothermally influenced off-axis sediments are low, but significant. Wankel et al. (2011) have suggested that subsurface microbial processes may remove more than 50% of the expected flux of H₂ from diffuse venting at the Endeavour hydrothermal field on Juan de Fuca Ridge.

Away from the focused hydrothermal flow fields, subsurface sediment habitats grow and evolve as ocean basins are formed. Off-axis hills and valleys are filled and eventually covered as abyssal deposits accumulate over millions of years of seafloor spreading and subsidence (Figure 2.7.9; Ewing & Ewing, 1967; Tominaga, Lyle, & Mitchell, 2011; Webb & Jordan, 1993). The biogeochemical story of how these sediment basins form and evolve is

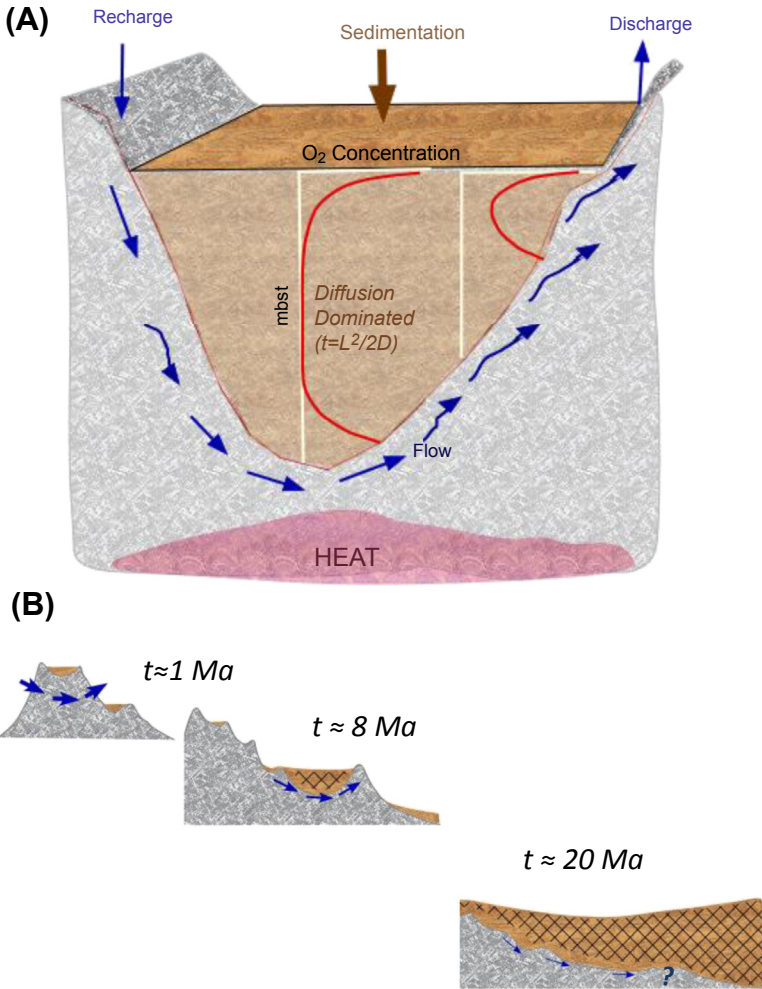


FIGURE 2.7.9 (A) Conceptual model of sediment accumulation, fluid flow, and dissolved oxygen distributions in the middle and nearer to the edges of North Pond, a ponded sediment basin on the flank of the Mid-Atlantic Ridge (figure modified after Ziebis et al., 2012; Sclater, 2003). (B) Conceptual model of the development of an anoxic subsurface biosphere in the open ocean basins, moving from young, about 8Ma crustal age (e.g., North Pond) to older crust overlain with thick sediment deposits. Arrows indicate decreasing subsediment flow with increasing age, and the hatched area denotes where anaerobic electron acceptor processes dominate (e.g., metal oxide reduction, sulfate reduction, methanogenesis). Note that dissolved oxygen typically penetrates less than a meter below surface in sediments outside of extremely oligotrophic regions.

crucial to understanding the development of a deep sedimentary biosphere. A typical example of younger sediment basin development is the vast area of seafloor on the western flank of the Mid-Atlantic Ridge, which is characterized by depressions filled with sediment and surrounded by high-relief topography.

The largest depressions are 5–20 km wide and sediment thickness varies but can reach 400 m (Langseth, Becker, Von Herzen, & Schultheiss, 1992). They are believed to overly recharge zones for the venting of fluids that takes place locally through unsedimented young ocean crust.

Deep oxygen profiles obtained from an IODP site survey expedition onboard RV *Maria S. Merian* to North Pond (Figure 2.7.9(a); Ziebis et al., 2012) and the subsequent IODP Expedition 336 provided the first proof of this principal (Orcutt et al., 2013). North Pond is one of the larger (70 km²) and best studied sediment ponds. While surface profiles show typical downward decreasing concentration profiles of dissolved oxygen, indicating oxidation of deposited organic carbon, near the basalt–sediment interface dissolved O₂ concentrations increase (Figure 2.7.9(a)). Degradation of organic carbon within the sediment package creates chemical gradients that drive the diffusive transport of oxidants, from both above and below the sediment. Mean diffusion times scale to the square of length; therefore, in the thicker deposits to be found in the center of the basin, any potential diffusive supply of oxygen, either from above or below, cannot keep up with the low but continual organic carbon remineralization. Ziebis et al. (2012) suggested that the sediment would eventually become anoxic at depth, particularly considering that the sediment package is hundreds of meters deep (Figure 2.7.9). With low to no appreciable rates of aerobic respiration within the sediment, the sediment would remain fully oxic, as is seen in sediments underlying the South Pacific Gyre (D’Hondt et al., 2009). Based on further O₂ measurements during IODP Expedition 336, Orcutt et al. (2013) were able to validate this model and further estimate rates of oxygen consumption in the underlying crust, putatively mediated by microorganisms.

Subsediment, basement flow also functions at much larger scales, for instance, in the equatorial Pacific. The distribution of electron acceptor activities near the basement sediment–water interface is inverted (D’Hondt et al., 2004). Nitrate penetrates 20 m upward from the basalt–sediment interface into the sediment. Sulfate also shows a distinct upward diffusion from seawater-like concentrations from within the basaltic aquifer, and indications are that oxygen penetrates upward from the sediment–water interface. Bekins, Spivack, Davis, and Mayer (2007) provide an elegant mechanism for the convective transport of fluids over these huge distances. They suggest that seawater enters off-axis recharge zones, warms, and allows calcium carbonates to precipitate. As this seawater percolates upward through buried seamounts, the cooling, undersaturated seawater dissolves the overlying biogenic carbonates, thus keeping the discharge zones free. Such a deep thermo-chemo-circulation through the crust may influence sedimentary biogeochemistry over extensive regions of the sedimentary subseafloor ocean. The extent of this flow and sediment alteration is not clear. Initial measurements from IODP Expedition 329 suggest that older basalt crust overlain with deep-sea clays does not show any indication of ongoing basement circulation (Expedition 329 Scientists, 2011). Only near the mid-ocean ridge sediments are there indications for diffusive fluxes of oxygen and nitrate into the sediment.

2.7.8 TOWARD A GLOBAL OCEAN VIEW

Mapping the extent of upward oxidation of reduced sediments in the subseafloor sedimentary ocean and the biogeochemical evolution of sediments will continue to be a major research focus for the coming decade.

The overall effect of this diffuse fluid flow and reaction with overlying sediments on ocean chemistry has not been accurately constrained. More progress has been made with estimating fluxes associated with fluid flow that are advected along fault lines and other permeable horizons, for example, from mud volcanoes at the continental margin of Costa Rica (Hensen & Wallmann, 2005). Boetius and Wenzhöfer (2013) estimate that approximately 0.02 Gt a^{-1} of methane may reach the pelagic ocean from cold venting of methane-containing fluids along continental margins.

Marine sediments are the ultimate and largest reservoir of carbon, bound in both organic carbon and carbonates (DeMarais, 1997). Processes occurring within the deeply buried sediments over Earth's history have controlled the redox poise of the Earth's ocean and atmosphere over most of geological time. In a seminal paper, Hayes and Waldbauer (2006) have examined how the carbon cycle regulates the overall redox state of the planet. In essence, CO_2 that is continuously released from the Earth's mantle is reduced principally through photoautotrophy, thus releasing oxidizing power in the forms of O_2 , Fe III (ferric iron), and sulfate. The amount of organic carbon stored in the crust should balance the oxidizing power represented by crustal inventories of Fe^{3+} , SO_4^{2-} , and O_2 . A flux of organic carbon from the crust to the mantle, for instance, through burial and subduction along with H_2 loss from the atmosphere, contributes to the accumulation of oxidizing power.

The efficiency of nutrient retention with organic matter buried in marine sediments regulates the overall effectiveness of photosynthesis in the ocean. Lomstein, Langerhuus, D'Hondt, Jørgensen, and Spivack (2012) have shown that amino acids are recycled and retained in so-called necromass in Peru Margin sediments. In the oxic sediments of the South Pacific Gyre, the dominance of aerobic degradation throughout the sediment leads to the situation where there is a flux of nitrate out of the sediments and into the deep waters (D'Hondt et al., 2009). Ocean phosphorus concentrations are strongly regulated by the burial of phosphorus with organic carbon. The efficiency by which phosphorus is removed and leached from organic carbon deposits and made available for photosynthesis will impact the rate of organic carbon formation and burial. Current ongoing studies of phosphorus distributions in sediments obtained from IODP expeditions, in particular in the Pacific Ocean (IODP Expeditions 320, 321, and 329), will better constrain the global phosphorus budget.

The main oxidants released into today's ocean in order of increasing abundance are oxygen, sulfate, and ferric iron. The fluxes of ferric iron and sulfate within deeply buried sediments are key parameters ultimately affecting the overall degradation of organic carbon even at depths below where sulfate reduction and

iron reduction expectedly cease (Holmkvist et al., 2011; Riedinger et al., 2005, 2014). In vast swaths of the open ocean, the sediments accumulate slowly and are, more importantly, fully oxic. Data from IODP Expedition 329 (Figure 2.7.2(b); D’Hondt, Inagaki, Alvarez Zarikian et al., 2011) suggest that, although rates are slow, organic carbon decomposition continues over long geological periods of time. Furthermore, the sediment that ultimately becomes subducted may represent a significant sink of oxidants from the global ocean, particularly as Fe(III).

Major insights into biogeochemical processes and implications for sediment diagenetic systems have been gained over the last decade of scientific ocean drilling in the subseafloor sedimentary ocean. The outlines of the consequences for the Earth’s climate, ocean chemistry, and biology are broadly apparent. Greater understanding of the subseafloor “plumbing” and transfer of energy and reactants between the deep sediments and the overlying pelagic ocean will certainly progress as data from the most recent scientific drilling investigations of the deep subsurface ocean habitat emerge.

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