



Systems Biogeochemistry of Major Marine Biomes

EDITED BY
ANINDA MAZUMDAR
WRIDDHIMAN GHOSH

WILEY

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PREFACE

Biological processes have profound roles in the chemical transformations of the marine realm. The nature and extent of biological activities, in turn, are controlled by a number of physical and chemical phenomena such as interaction of the ocean with the atmosphere and earth's crust, oceanic upwelling, oxygenation, sediment accumulation, and inorganic and organic matter fluxes in dissolved and particulate forms from the land and the deep earth. The overall biogeochemical dynamics of the water column and sediment fluid also exert feedback influences on the structure and function of the biota, and, in the entire process, the system evolves holistically in time and space. In this context, a marine biogeochemical system can be thought of as a geographically and geologically defined physiography that transcends latitudes, longitudes and water-depths of the global ocean, and has its characteristic geobiological framework, overarching all the spatiotemporal dynamics of its structural (e.g. chemical and biological species) and functional (e.g. reactions and transformation) components.

Comprehensive understanding of marine biogeochemical regimes entails systemic knowledge of the biomes. Historically, studies of inorganic and organic geochemistry for water-columns and sediments (including both past and present records) contributed the most in deciphering biogeochemical processes within the marine realm. In recent times, remarkable advances in high-throughput meta-omics-based microbiological research, and molecular-taxonomy-based understanding of benthic ecology, have afforded increasing knowledge interfaces between preserved geochemical records and ecosystem structure/function. Such cross-talks of disciplines have led to the discovery of a number of novel (and often cryptic) biogeochemical processes within the global ocean that were impossible to have been revealed previously from preserved chemical records alone. At the same time, increasing cross-disciplinary interfaces have also given rise to biogeochemical enigmas, of which some may well be the potential seeds of future paradigm

changes in marine biogeochemistry. In this intellectual landscape, where our understanding of *in situ* biological processes, their geological manifestations, and cybernetic controls, are evolving faster than ever, this book adopts a systems-based approach to integrate and update the information available on the geochemistry, geophysics, biology and ecology of four major categories of marine physiography: continental margins, ocean depths, polar oceans, and biophysically extreme environments. The idea, at large, is to envision holistic pictures of all biogeochemical happenings within distinct systems of these oceanic provinces.

While some of the biogeochemical regimes mulled over hold crucial implications for planetary health and biosphere sustainability (by virtue of being the bellwethers of perturbations brought about by anthropogenic interference, pollution, global warming and/or climate change), others are central to the understanding of the Earth's early biosphere, so their geobiologies hold critical implications for life-detection during space-exploration missions and potential habitability of differently constituted oceanic systems in extraterrestrial locations.

We expect the biome-based systemic perspective to complement the traditional way of looking at marine biogeochemistry from the standpoint of individual elemental cycles. Systemic consideration of biogeochemical provinces of the global ocean would not only provide an intellectual baseline for integrating chemical records with biome structures/functions but also lay the foundation of holistic policy frameworks for sustainable utilization of marine resources, risk avoidance, and disaster management.

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Biome I

Continental Margins

1

Biogeochemistry of Marine Oxygen Minimum Zones with Special Emphasis on the Northern Indian Ocean

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ABSTRACT

Oxygen minimum zones (OMZs) enclose O₂ depleted subsurface water masses in the global ocean extending approximately 150 to 1200 m below sea level. The most pronounced OMZs occur in Eastern Tropical North Pacific off Mexico and California (ETNP), Eastern Tropical South Pacific off Peru and Chile (ETSP), and the Arabian Sea (AS) defined by secondary nitrite maxima attributed to intense denitrification in the water column. These OMZs sites are critical for biogeochemical processes that control the biodiversity and primary productivity of the ocean. The preservation of organic carbon is efficient within the sediments underlying oxygen-depleted waters as a result of incomplete decomposition as it sinks through the water column and diminished bioturbation activity. The partially degraded (reactive) organic matter fuels microbe-mediated biogeochemical processes in the anoxic marine sediments where sulfate reduction is a significant remineralization pathway. The OMZs exert a strong influence on the abundance, diversity, and composition of microbial communities. Recent geochemical and environmental genomic studies identified the prevalence of C, N, and S cycles in the OMZs. Here, we review the progress and current understanding of the C–S–N cycle in the OMZ sediments with regard to its biogeochemistry and microbial ecology, and present a brief account of the mechanism of the formation of OMZs in the northern Indian Ocean.

1.1. INTRODUCTION

Oxygen minimum zones (OMZs) are oxygen-depleted intermediate-depth water masses in the global ocean, usually between 150 and 1200 m below sea level (mbsl). The upper threshold of dissolved oxygen (DO) concentrations defining the OMZs is ~20 μM (Figure 1.1; Paulmier and Ruiz-Pino, 2009; Ruvalcaba Baroni et al., 2020), while the

lower concentration of DO detected in an OMZ may be <2 nM O₂ (Revsbech et al., 2009), amounting to functionally anoxic conditions. Oceanic regions generally classified as OMZs include (1) the Eastern Tropical North Pacific off Mexico and California (ETNP), (2) the Eastern Tropical South Pacific off Peru and Chile (ETSP), (3) the Bay of Bengal (BoB), and (4) the Arabian Sea (AS). Of these OMZs, the ETNP, ETSP, and the AS have also been classified as anoxic marine zones (Ulloa et al., 2012), owing to the buildup of secondary nitrite maxima (SNM) within the water column. The SNM forms because of denitrification in the water column, which occurs when DO concentrations drop to <5 nM (Anderson et al., 2007; Banse et al., 2017). The functionally anoxic parts of these OMZs occupy only ~0.8% of the world ocean but are responsible for ~35% of the production of N₂ through denitrification (Ward et al., 2009).

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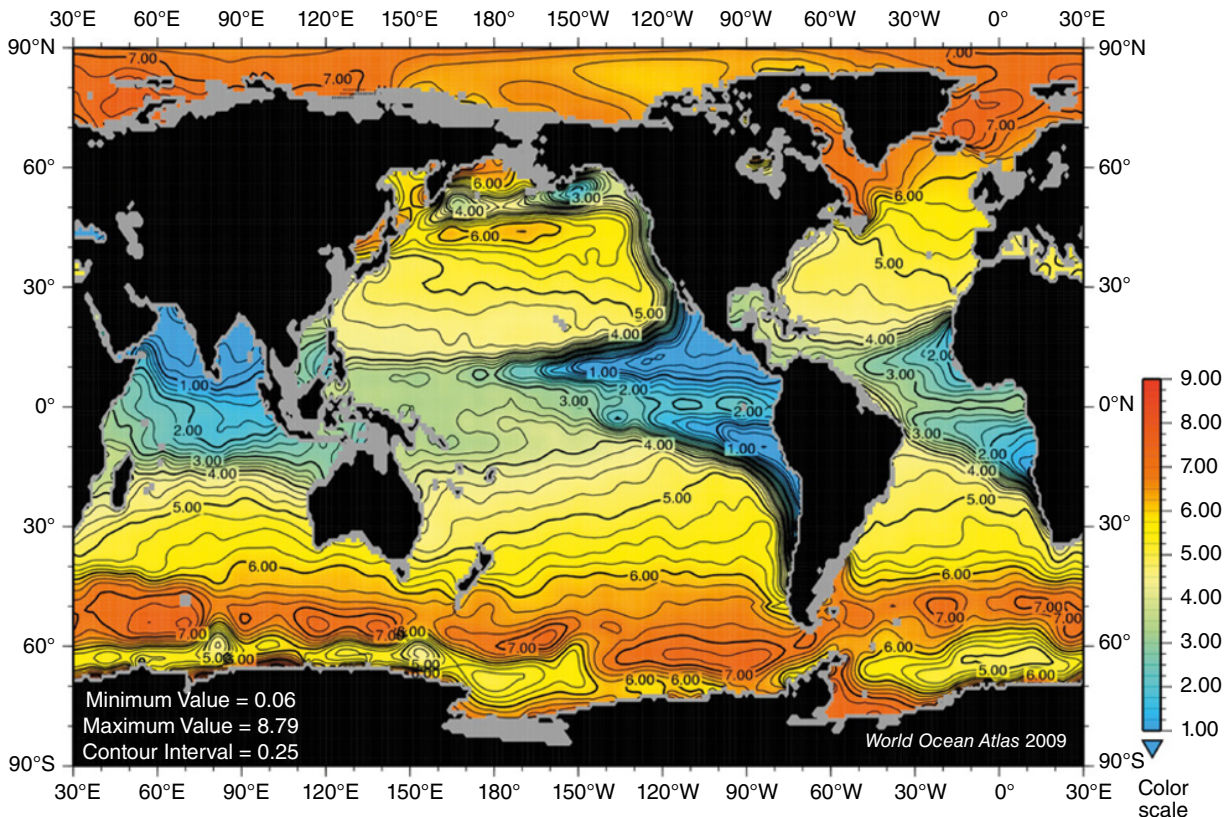


Figure 1.1 Global annual oxygen concentration (ml l^{-1}) at 150 mbsl. *Source:* World Ocean Atlas 2009.

The buildup of OMZs is controlled by the interplay of physical and biological processes coupled with regional geography. Inadequate ventilation of the oxygenated water masses (e.g. the northern Indian Ocean), upwelling of nutrient-rich deep waters (leading to high productivity in the euphotic zone), and subsequent microbial respiration of organic particulates (phytodetritus, fecal pellets, dead organisms, etc.) lead to a depletion of DO in the water column, resulting in the formation of OMZs (Behrenfeld et al., 2006; Regaudie-de-Gioux and Duarte, 2012). OMZs are high in nutrient concentrations and support highly productive fishing regions (Garçon et al., 2019).

In the northern Indian Ocean, OMZs occur in both the AS and the BoB (Figure 1.2) because of their closed northern geographical boundaries and monsoon-driven seasonal upwelling (Naqvi, 1991; Stramma et al., 2008). The DO concentration within the Arabian Sea (ASOMZ) reflects a balance between biological O_2 consumption and O_2 replenishment. The primary source of intermediate water (Indian Ocean Central Water: ICW) (Stramma et al., 1996; Schott and McCreary, 2001; Rixen et al., 2020) in the northern Indian Ocean include contributions from the Antarctic Intermediate Water (AAIW), Subantarctic Mode Water (SAMW) and the Indonesian intermediate waters (Lachkar et al., 2019). The dense and

highly saline Persian Gulf water (PGW) and relatively less saline but denser Red Sea water (RSW) are the lateral sources of intermediate water in the AS (Bower et al., 2005).

1.1.1. The Arabian Sea Oxygen Minimum Zone

The AS is believed to contain the thickest and most intense of the OMZs (Agnihotri et al., 2003; Naqvi et al., 2010a; Prakash et al., 2012; Banse et al., 2014; Acharya and Panigrahi, 2016), extending over the entire sea, with its upper boundary occurring at 100–150 m, and its lower boundary at 1000–1200 m (Wyrтки, 1971; Banse et al., 2005; Banse et al., 2014), impinging upon a large area of the continental slope (Naqvi et al., 2006). The benthic area of the upper slope underlying hypoxic water in the AS is computed to be 230 440 km^2 , making it responsible for over one-quarter of the world's naturally hypoxic seafloor (Global estimate = 764 000 km^2 ; Helly and Levin, 2004). The ASOMZ arises from its landlocked geography, mainly owing to the presence of the Asian landmass that restricts the flow of oxygenated water from the north. Monsoonal upwelling, wind-driven mixing, Ekman pumping during summer (Kumar et al., 2009), convective mixing during winter (Madhupratap et al., 1996;

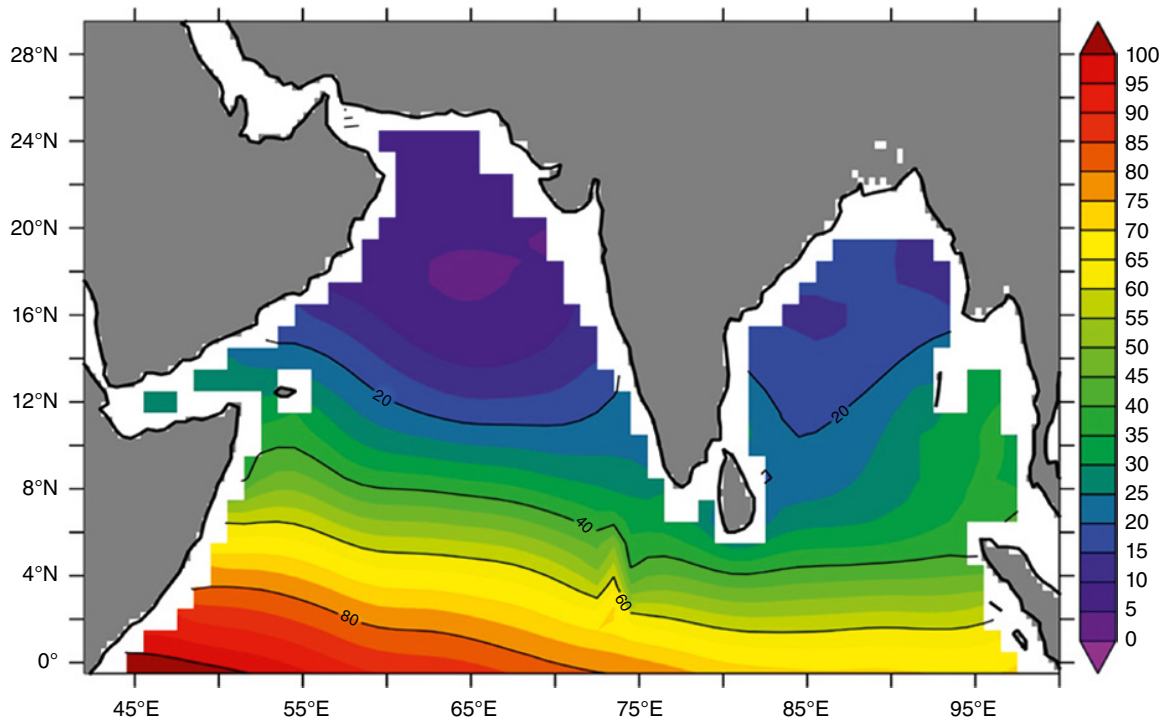


Figure 1.2 Annual oxygen concentration ($\mu\text{mol l}^{-1}$) in the water column of the Indian Ocean. The data is obtained from the World Ocean Atlas 2013 (Boyer et al., 2013). The map was produced using generic mapping tool software.

Prasanna Kumar et al., 2001; Kumar et al., 2009), and advection of NO_3^- rich upwelled water mass off the Oman, Yemen, and Somalia margins leads to large-scale fertilization of the euphotic zone (Naqvi et al., 2006; 2010b). The productivity in this region is controlled by the NO_3^- and Fe (aeolian) limitations which also show seasonal variation (Naqvi et al., 2010b; Banerjee and Kumar, 2014).

The ASOMZ shows an east–west variation in structure, where the upper part (400 m) is located in the central/eastern basin, and the lower part (below 400 m) extends to the Omani coast, indicating a northward intensification of the ASOMZ (McCreary et al., 2013). The PGW water enters the ASOMZ from the northwest at shallow depths of ~ 300 m and spreads around the perimeter of the basin and southward along the Omani coast (Prasad et al., 2001), and the denser RSW encroaches to depths of 600–1000 m and spreads across the basin (Shankar et al., 2005; Shenoi et al., 2005).

A poleward undercurrent (West India Undercurrent, WIUC) carries the ICW northwards into the eastern Arabian Sea (EAS) up to 16°N at a water depth of ~ 500 m (Shenoy et al., 2020; Schmidt et al., 2020a). In the EAS, the OMZ expands southwards during the SW monsoon ($\sim 9^\circ\text{N}$) and retreats northwards during the NE monsoon (11°N) (Shenoy et al., 2020). Although the productivity across the EAS is significantly lower

compared with that of the Western Arabian Sea (WAS), the OMZ is more intense in the central and eastern AS (Naqvi, 1991). This observation may be attributed to one or more hypotheses, including:

- water column O_2 consumption (via respiration of organic matter) during eastward transit of ICW from Somali coast to the west coast of India (McCreary et al., 2013; Acharyya and Panigrahi, 2016; Rixen et al., 2020);

- rapid sinking of the large phytoplankton detritus in the upwelling regions of the WAS (Naqvi et al., 2010b) results in minimum respiration, alternatively, the slow sinking rate of organic matter (Hood et al., 2009) produced in the WAS and subsequent eastwardly advection of the organic particulates leads to DO depletion in central and eastern AS;

- effective renewal of subsurface water along the western boundary of the AS, by advection from the south, from the Red Sea and from the Persian Gulf (Naqvi et al., 2006). The prolonged ventilation times 7–8 years for RSW and (2–3 years) for PGW in the EAS compared with the ventilation time of (3–4 years and 1–2 years, respectively, in WAS lead to more significant DO depletion in the EAS (Schmidt et al., 2020a)

- physical processes such as mesoscale eddies prevailing in the WAS are expected to contribute towards effective oxygen renewal in the water column (McCreary et al., 2013; Schmidt et al., 2020b);

the cross-shelf transport of organic-rich sediments from the western continental shelf of India (Somayajulu et al., 1996; Sarma et al., 2020) and subsequent respiration, causing suboxia in the EAS.

the warming of the PGW. Recent observations have seen warming of the PGW (shallow semi-enclosed sea with an average depth of 35 m) at a rate of two to three times faster than the global average rate, increasing its buoyancy and may lead to poor, intermediate water ventilation (Lachkar et al., 2019).

In addition to the perennial OMZ (pOMZ), the AS experiences seasonal suboxia and denitrification over the inner and mid-shelf off the west coast of India during and shortly after the southwest monsoon (Sharma, 1978; Shetye et al., 1990; Naqvi et al., 2000, 2006). This coastal oxygen-deficient zone is separated from the pOMZ in the central AS by the presence of slightly more oxygenated waters of the WIUC that flow poleward (Naqvi et al., 2006). During the peak of upwelling season (in September), almost the entire Indian shelf (and some of the Pakistan shelf) is severely hypoxic having an O_2 concentration $<0.5 \text{ ml l}^{-1}$ covering an area of about $180\,000 \text{ km}^2$ (Naqvi et al., 2000). The seasonal suboxia (even anoxia) reported in this region occurs because of coastal upwelling occurring along the western Indian shelf during June to November. Upwelling begins in April, along the southwest coast of India (along with Kerala), and gradually moves northward. The intense DO depletion in both the seasonal OMZ (sOMZ) and pOMZ enhances the deposition of organic matter in the underlying sediments as a result of a combination of high (upwelling-driven) primary productivity and inefficient degradation during sinking in the oxygen-depleted water column (Paropkari et al., 1992, 1993; Cowie, 2005). The intense DO depletion has a profound influence on the underlying sediments, with respect to the redox conditions, microbial community, nature and activity of benthic communities, pore water redox processes, and consequently on the diagenetic pathways (e.g. Cowie, 2005).

1.1.2. The Bay of Bengal Oxygen Minimum Zone

The BoB, in the northern Indian Ocean, is the largest bay in the world, bordered by India, Bangladesh, Sri Lanka, and Myanmar. The BoB receives a large amount of freshwater from several river systems, which drain into it. The rivers Ganga-Brahmaputra (G-B), Irrawaddy, Godavari, Mahanadi, Krishna, and Kaveri contribute 60% of the total freshwater received by the BoB. Riverine water flux of $2.95 \times 10^{12} \text{ m}^3 \text{ year}^{-1}$ (Sengupta et al., 2006) combined with an excess of precipitation over evaporation results in a salinity stratified water column (Prasanna Kumar et al., 2007). The BoB is one of the major global OMZs. Although the conditions appear to be conducive

for denitrification/anammox to occur, there has been no indication of nitrogen loss via denitrification in the BoB. Anammox reaction involves oxidation of NH_4^+ to N_2 gas using NO_2^- as the electron acceptor under anoxic conditions. The relatively less intense OMZ in the BoB may be attributed to weaker upwelling along the east coast of India than in Oman and Somalia. McCreary et al. (2013) attributed lower respiration in the BoB to the absence of an advective flux of additional organic matter, as observed in the EAS. The aggregation of organic matter with mineral particles supplied by high river discharge in the BoB increases the sinking speed of the organic detritus, thereby decreasing its remineralization rate and impacting on the OMZ structure and intensity (Al Azhar et al., 2017). In contrast, Sarma et al. (2018) suggested the activities of cyclonic and anticyclonic eddies to be one of the possible reasons for excess DO in the BoB reported by Bristow et al. (2017). The cyclonic eddies bring up nutrient-rich water, causing enhanced productivity and subsequent DO drawdown as a result of respiration. In contrast, the anticyclonic eddies cause the downwelling of DO-rich surface water to deeper layers causing the weakening of the OMZ. In addition, Sarma and Bhaskar (2018) suggested westward advection of oxygenated waters within the 150–300 mbsl depth zone driven by anticyclonic eddies originating in the Andaman waters. Recently, however, Bristow et al. (2017) observed extremely low levels of DO in the BoB and hypothesized that future increases in the deposition of nutrients from atmospheric sources combined with the varying intensity of the summer monsoon could enhance organic matter decomposition and O_2 consumption leading to anammox and nitrogen loss. The vertical distribution of O_2 and NO_2^- in the AS (Lam et al., 2011) and BoB (Bristow et al., 2017) is plotted in Figure 1.3.

1.2. PRESERVATION OF ORGANIC MATTER AND SEDIMENT BIOGEOCHEMISTRY

The preservation of organic carbon (OC) is efficient within the sediments underlying oxygen-depleted waters (Paropkari et al., 1993; Eglinton et al., 1994; Van der Weijden et al., 1999; Hartnett et al., 1998; Hartnett and Devol, 2003; Böning et al., 2004; Jessen et al., 2017; More et al., 2018) because of incomplete breakdown while sinking through the water column as well as diminished bioturbation activity. A more significant proportion of labile organic matter escapes degradation while sinking through hypoxic or oxygen minimum regions of the modern ocean than oxic zones (Van Mooy et al., 2002). The partly degraded (reactive) organic matter fuels microbe-mediated sediment biogeochemical processes during burial, which results in modification of the pore fluid composition and precipitation/dissolution

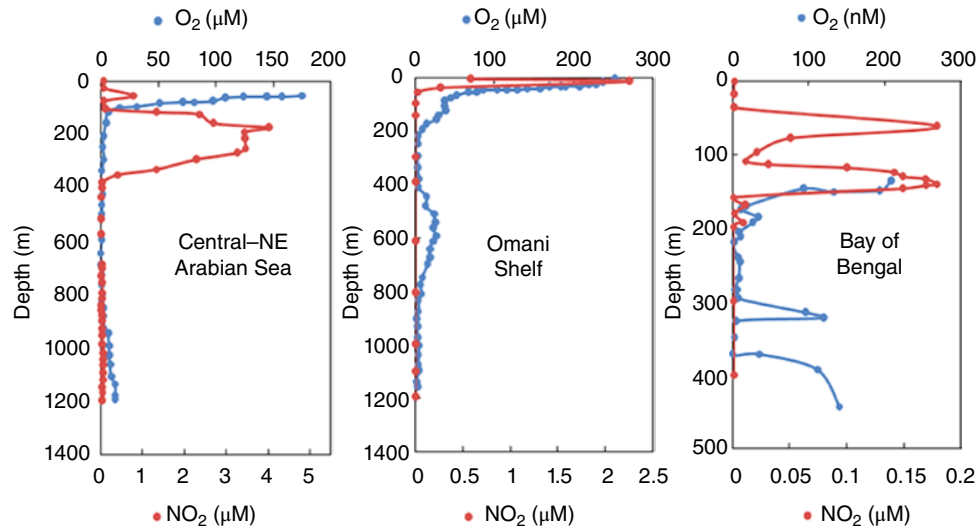


Figure 1.3 Vertical distribution of oxygen (solid blue circle) and nitrite concentrations (solid red circle) over the Central–northeast Arabian Sea, Omani Shelf and the Bay of Bengal. Redrawn from Lam et al. (2011) and Bristow et al. (2017).

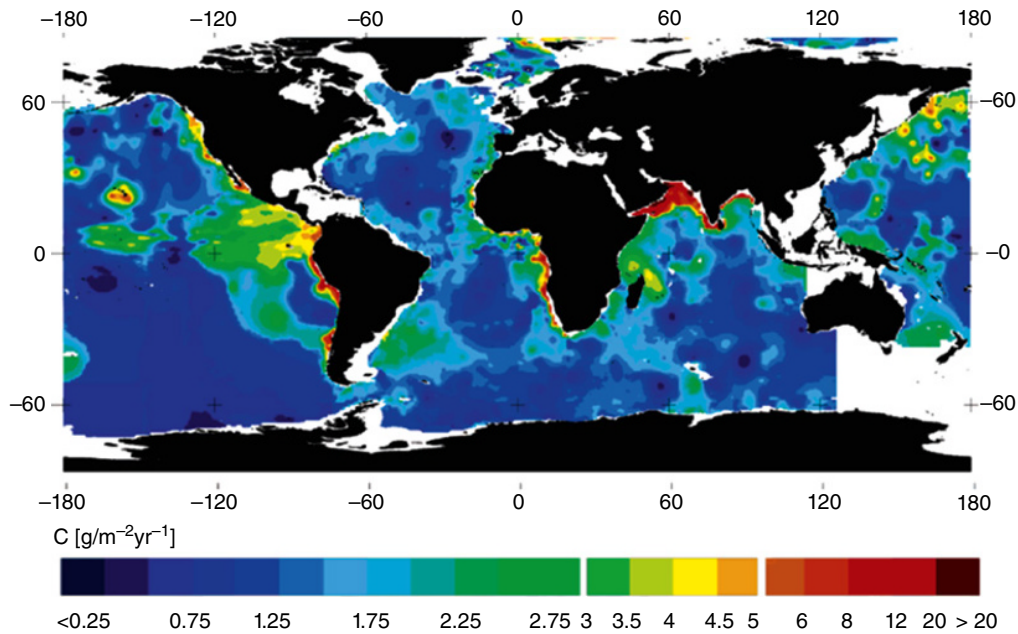


Figure 1.4 Global distribution pattern of particulate carbon flux to the seafloor. *Source:* Reimers (2007) with permission from American Chemical Society.

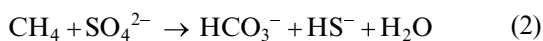
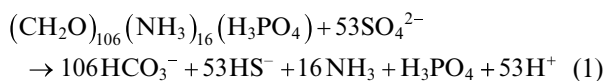
of inorganic mineral species (Madigan et al., 2000; Middelburg and Levin, 2009) Fernandes et al., 2018). The global distribution pattern of particulate organic carbon flux (Reimers, 2007) is depicted in Figure 1.4.

Remineralization of the partly degraded organic matter is strongly influenced by benthic biotic activity controlled by sediment–water interface conditions such as DO concentration, diffusion of $\text{CH}_4/\text{H}_2\text{S}$, sedimentation rate,

organic matter content, and sediment grain size. The upper and lower boundaries of the ASOMZ have a lower TOC content than the OMZ core, which is attributed to lack of bioturbation and high organic matter flux from the DO-depleted water column in the latter (Fernandes et al., 2018). In contrast, the upper and lower edges of the OMZ are associated with a relatively high remineralization rate due to higher DO availability.

1.3. PORE FLUID GEOCHEMISTRY

The chemical compositions of sediment pore-waters are altered from their original seawater-like compositions by various microbially mediated biogeochemical reactions taking place at and below the sediment–water interface. The biogeochemical reactions are associated with the remineralization of organic matter. Thermodynamically, O_2 is the most favorable terminal electron acceptor for the remineralization of organic matter. When the aerobic respiration entirely consumes O_2 , other electron acceptors (in order of decreasing energy gain) such as nitrate (NO_3^-), manganese oxides (Mn (IV)), iron oxides (Fe (III)), and sulfate (SO_4^{2-}) are used, depending on their concentration in solution and their thermodynamic efficiency (Froelich et al., 1979; Pattan et al., 2013; Turchyn and Schrag, 2006; Turchyn et al., 2016; Müller, 2018). Thus, there is a geochemical zonation in the sediments, with redox conditions ranging from oxic to methanic. The sediment layer where NO_3^- , Mn (IV) and Fe (III) reduction controls organic matter remineralization is termed the suboxic zone (Froelich et al., 1979). Although energetically more favorable than SO_4^{2-} , electron acceptors in the suboxic zone are usually limited in supply, which makes them biogeochemically less significant (Aller, 1994; Thamdrup et al., 1994; Jørgensen and Kasten, 2006; Seitaj et al., 2015). Microbial sulfate reduction is the major pathway of organic carbon oxidation in the anoxic zone as the high concentration of SO_4^{2-} in seawater makes it a dominant electron acceptor (Heinrich and Reeburgh, 1987; Widdel et al., 2007). The global estimate of marine sulfate reduction is 11.3 teramoles of sulfate per year, which accounts for the oxidation of 12–29% of organic carbon that reaches the sea floor (Bowles et al., 2014). The organoclastic sulfate reduction (OSR) (Froelich et al., 1979; Treude et al., 2005; Jørgensen and Kasten, 2006; Riedinger et al., 2017) and anaerobic oxidation of methane (AOM) (Froelich et al., 1979; Reeburgh, 1980; Valentine and Reeburgh, 2000; Boetius et al., 2000) are the two pathways of microbial sulfate reduction in marine sediments, represented by equations (1) and (2).



The AOM involves a syntrophic consortium of sulfate-reducing bacteria and methanotrophic archaea (Boetius et al., 2000; Knittel and Boetius, 2009). The AOM process results in the formation of SMTZ, which is a redox interface in the sediment where porewater SO_4^{2-} and CH_4 inter-

sect and are depleted to near-zero levels (Treude et al., 2005; Sultan et al., 2016). The depth of SMTZ depends on the organic matter availability, oxygen exposure time (OET) of organic matter, flux of CH_4 and SO_4^{2-} , and the activity of sulfate-reducing bacteria and methanotrophic archaea and bioturbation (Niewöhner et al., 1998; Hong et al., 2014; Komada et al., 2016; Lin et al., 2016; Hu et al., 2017). The AOM process at the SMTZ leads to high pore water alkalinity owing to bicarbonate (HCO_3^-) and hydrogen sulfide (HS^-) production. The sulfate reduction rates in marine sediment pore waters are controlled by the availability of labile organic matter, SO_4^{2-} concentration, bottom water temperature (OET), bioturbation, bacterial distribution, and abundance (Aller, 1994; Kristensen, 2000; Hedges and Keil, 1995; Nierop et al., 2017; Jessen et al., 2017). Depth integrated sulfate reduction rates have been reported to be maximum around continental margins (Bowles et al., 2014), apparently linked to the higher deposition/preservation of organic carbon in these areas of the global ocean (Dean et al., 1994; Littke et al., 1997; Van der Weijden et al., 1999; Böning et al., 2004; Seiter et al., 2004, 2005; Rasiq et al., 2016; Dale et al., 2015; Fernandes et al., 2018).

Bottom water DO depletion and high preservation of reactive organic matter within the OMZ sediment led to considerably higher sulfate reduction rates. The higher sulfate reduction rate is associated with higher porewater NH_4^+ and dissolved inorganic carbon (DIC) concentrations and shallow SMTZ (Mazumdar et al., 2009, 2012; Fernandes et al., 2018; Fernandes et al., 2020).

Studies from the Oman margin sediments by Pedersen and Shimmiel (1991) show depletion of porewater SO_4^{2-} concentration (<1 mM) within 50 to 100 meters below seafloor (mbsf). Furthermore, Passier et al. (1997) (from Oman margin), Schenau et al. (2002) (from Pakistan and Oman margins), and Van der Weijden et al. (1999) (Oman margin) reported low sulfate reduction in the sediments. Lower sulfate reduction in the Oman margin sediment is also supported by a very low concentration of reduced sulfur compounds (Fe-sulfide) relative to total organic carbon content (Emeis et al., 1991). The low sulfate reduction rate in the ASOMZ sediments may result from the incorporation of sulfur into the organic matter, which renders the organic matter refractory (Passier et al., 1997; Lückge et al., 1999; Schenau et al., 2002; Law et al., 2009). In contrast, Law et al. (2009) attributed low sulfate reduction rates ($0-0.45 \text{ mmol m}^{-2} \text{ d}^{-1}$) from the Pakistan margin sediments to the dominance of other metabolic pathways (Fe cycling) or lack of reactive organic matter. The low sulfate reduction rates in the ASOMZ sediments compared with other upwelling regions (e.g. Namibian and Peruvian margins) is attributed to the low availability of labile organic matter and supply of reactive Fe in the sediments (Lückge et al., 1999; Law et al., 2009; Naik

Table 1.1 Summarizes the calculated depth-integrated sedimentary sulfate reduction rates (SRRs) from different oxygen minimum zones (OMZs) regions of the global ocean.

Area	OMZ water depth (mbsl)	SRR (mmol cm ⁻² yr ⁻¹)	Reference
Eastern Arabian Sea OMZ	200–1200	0.0008–0.0113	Fernandes et al. (2018)
Pakistan margin	200–1200	0.00036–0.01642	Law et al. (2009)
Oman margin	200–1000	0.000035–0.00011	Pedersen and Shimmield (1991)
Off central Chile	70–450	0.3504–1.09135	Ferdelman et al., (1997), Thamdrup and Canfield (1996)
Off central Peru	50–650	0.3212–1.25195	Fossing (1990)
Off NW Mexico	150–800	0.011315–0.06862	Hartnett and Devol (2003)

et al., 2017). See Table 1.1 for depth-integrated sedimentary SRRs from different OMZ regions of the global Ocean.

1.4. SEDIMENTARY SULFIDIZATION AND SULFURIZATION

Hydrogen sulfide produced during sulfate reduction in sediments is diffused from the microbial cell into the surrounding pore water and is trapped in the sediment as Fe sulfide minerals (sulfidization) and organosulfur compounds (sulfurization). A significant fraction of H₂S may diffuse out of the sediment–water interface and be oxidized to SO₄²⁻ or elemental sulfur (S⁰). Porewater H₂S is oxidized to intermediate species such as S⁰, thiosulfate (polysulfides: S_x²⁻, HS_x²⁻) and sulfoxyanoids (sulfite, thio-sulfate, and polythionates) (Chen and Morris, 1972; Berner and Westrich, 1985; Thamdrup et al., 1994; Canfield et al., 2005). Sulfide oxidation can be microbe-mediated (e.g. Nielsen et al., 2010; Eckert et al., 2011; Rao et al., 2016) or abiotic, by reaction with oxides such as MnO₂ or FeO(OH) (Berner and Westrich, 1985; Thamdrup et al., 1993; Yao and Millero, 1993, 1995, 1996; Canfield et al., 2005). The intermediate sulfur species produced from sulfide oxidation can undergo disproportionation reactions where the sulfur intermediates are simultaneously transformed to both H₂S and SO₄²⁻; these reactions are often referred to as inorganic fermentation because they do not involve any other electron donor or acceptor (Bak and Cypionka, 1987, Canfield and

Thamdrup, 1994; Habicht et al., 1998; Böttcher et al., 2001). The burial of Fe sulfide minerals and sulfurized organic matter depends on the availability of reactive Fe (Yucel et al., 2010; Zhu et al., 2016), sedimentation rate, reactive organic matter flux (Berner, 1985; Raiswell and Berner, 1985; Wilkin and Barnes, 1997; Werne et al., 2003; Markovic et al., 2015), and bottom water DO concentration. The degree of pyritization (DOP) values in sediments underlying the oxygenated waters are < 0.45, whereas, under dysoxic and euxinic waters the values range between 0.46 and 0.75 and > 0.75, respectively (Raiswell and Berner, 1985; Raiswell and Canfield, 2012). In the ASOMZ, pyritization is limited by the availability of reactive Fe oxides attributed to the reductive dissolution of Fe in the water column or at the sediment–water interface as a result of low DO concentration (Scheneau et al., 2002). The bottom water DO concentrations and detrital organic matter availability controls the spatial extent and the degree of bioturbation and bioirrigation. The activity of benthic organisms not only modifies the porewater concentration profiles it also plays an important role by oxidizing Fe-sulfide minerals close to the sediment–water interface. The sediments underlying OMZs show the minimum influence of bioturbation (Levin, 2003, Cowie and Levin, 2009). The absence of burrowing/irrigation would minimize the exposure of early diagenetic Fe-sulfides to oxidants such as NO₃⁻/NO₂⁻ thereby enhancing the preservation of early sulfidization. The relative significance of organic matter sulfurization depends on the availability of labile organic molecules and the extent and rate of reactive Fe consumption (Zaback and Pratt, 1992; Passier et al., 1997; Werne et al., 2004). Loss of sedimentary reactive Fe through reductive dissolution and enhanced preservation of highly labile organic matter in the sediments underlying OMZs would promote enhanced organic matter sulfurization (Lückge et al., 2002; Scheneau et al., 2002). The OBS constitutes an estimated 50% of the total sedimentary sulfur in the Peru margin following the polysulfide pathway (Mossman et al., 1991). The incorporation of sulfur in organic molecules (sulfurization) occurs either intramolecularly (as cyclo sulfo groups such as thiolane, thiane, and thiophene) or intermolecularly through S²⁻ or S_x²⁻ bonds between larger molecules (Sinninghe Damsté and de Leeuw, 1990; Abdulla et al., 2020). Lallier-Verges et al. (1993) found pyrite infillings in pore spaces and pyrite framboids in sediment rich in autochthonous organic matter from the Oman margin. Furthermore, they suggested that 50% of organic matter degradation in organic poor sediments is supported by sulfate reduction and attributed it to the deposition of zooplankton debris (in addition to phytoplankton) with mineral skeletons, which increase porosity and enhance sulfate reduction. While in organic-rich sediments, only