



The fate of organic carbon in marine sediments - New insights from recent data and analysis



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ABSTRACT

Organic carbon in marine sediments is a critical component of the global carbon cycle, and its degradation influences a wide range of phenomena, including the magnitude of carbon sequestration over geologic time-scales, the recycling of inorganic carbon and nutrients, the dissolution and precipitation of carbonates, the production of methane and the nature of the seafloor biosphere. Although much has been learned about the factors that promote and hinder rates of organic carbon degradation in natural systems, the controls on the distribution of organic carbon in modern and ancient sediments are still not fully understood. In this review, we summarize how recent findings are changing entrenched perspectives on organic matter degradation in marine sediments: a shift from a structurally-based chemical reactivity viewpoint towards an emerging acceptance of the role of the ecosystem in organic matter degradation rates. That is, organic carbon has a range of reactivities determined by not only the nature of the organic compounds, but by the biological, geochemical, and physical attributes of its environment. This shift in mindset has gradually come about due to a greater diversity of sample sites, the molecular revolution in biology, discoveries concerning the extent and limits of life, advances in quantitative modeling, investigations of ocean carbon cycling under a variety of extreme paleo-conditions (e.g. greenhouse environments, euxinic/anoxic oceans), the application of novel analytical techniques and interdisciplinary efforts. Adopting this view across scientific disciplines will enable additional progress in understanding how marine sediments influence the global carbon cycle.

1. Introduction

To contextualize the recent biogeochemical breakthroughs that have been made regarding the fate of organic carbon in marine

sediments, the first section of this review consists of a summary of its role in the global carbon cycle and how this has varied over space and time. Secondly, we describe the sources of new data that are shaping the transformation in how we think about organic carbon in the marine

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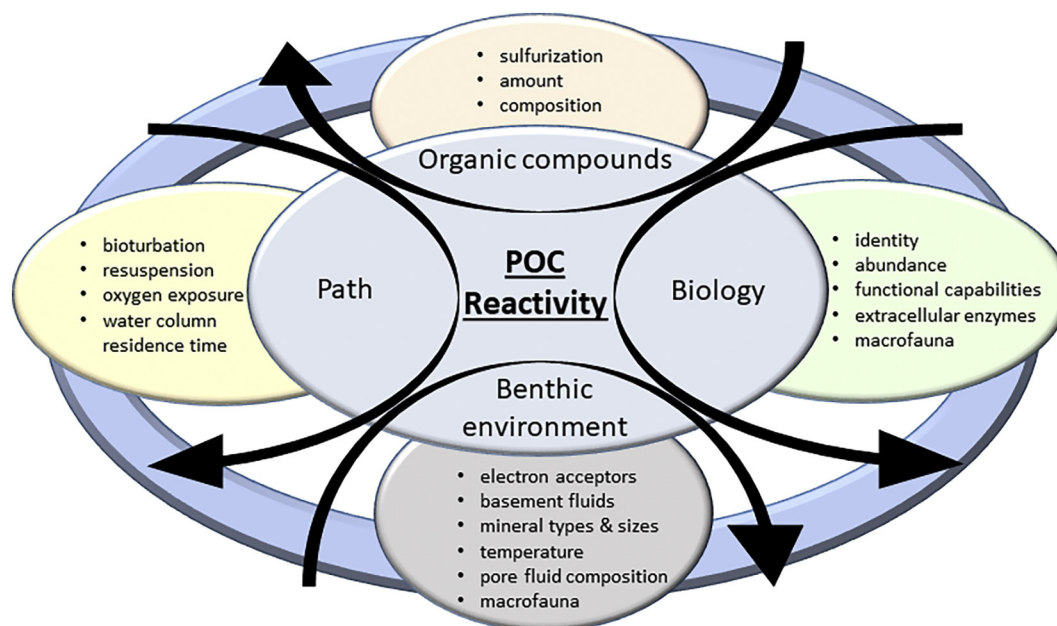


Fig. 1. Schematic of topics discussed in this review: ecosystem factors that influence the reactivity of particulate organic carbon, POC, in marine sediments. The bulleted processes/variables and four categories are not necessarily independent of one another.

system. This is followed by a section on organic carbon in adjacent environments such as hydrothermal systems and the ocean basement, and then a brief overview of modeling advances. The topics covered in this communication are summarized in the schematic shown in Fig. 1.

1.1. Sedimentary organics and the global carbon cycle

Organic carbon (OC) degradation in marine sediments is a critical component of the global carbon cycle and is intricately linked to Earth's climate (Bernier and Canfield, 1989; Bernier, 1990; Siegenthaler and Sarmiento, 1993; Archer and Maier-Reimer, 1994; Mackenzie et al., 2004; Ridgwell and Zeebe, 2005; Ridgwell and Hargreaves, 2007; Hülse et al., 2017). The specific consequences of this process on biogeochemical cycles vary considerably depending on location as well as the temporal and spatial scales of concern. In the upper few meters of relatively recently deposited sediment, the oxidation of organic carbon controls the fluxes of oxygen and nutrients across the sediment-water interface (SWI), ultimately impacting primary productivity in the water column (Van Cappellen and Ingall, 1994; Lenton and Watson, 2000). As organic carbon is aerobically oxidized, pore water pH is decreased, potentially leading to dissolution of calcium carbonate and amplifying the direct effect of OC oxidation on the carbon cycle (Emerson and Bender, 1981; Hales and Emerson, 1996). Deeper in sediments, organic carbon that escapes oxidation can still be microbially reduced to CH_4 , and under some conditions, fuel the slow build-up of methane hydrates (e.g. Wallmann et al., 2012). Although hydrates represent a relatively small carbon reservoir, perturbations in temperature and/or pressure can render hydrates unstable, potentially leading to sudden transfers of carbon back into the ocean-atmosphere system that would have important consequences for global carbon cycling and climate (Ruppel and Kessler, 2017). The small fraction of photosynthetically produced organic carbon that entirely escapes degradation and thus is buried over longer timescales in sediments helps to modulate the long-term evolution of atmospheric CO_2 , has enabled oxygen to accumulate in the atmosphere (e.g. Bernier, 2003) and has led to the formation of large reservoirs of hydrocarbons that provide most of the energy that humans use. Whether marine sediment organic carbon contributes to water column anoxia, becomes trapped in a clathrate, is transformed into petroleum or ends up as atmospheric CO_2 is ultimately based on the flux

of particulate organic carbon (POC) to sediments and the many factors that dictate its rate of degradation.

1.2. POC fluxes and degradation rates

The concentrations of POC shown in Fig. 2 illustrate that the flux of organic carbon to and through sediments vary tremendously (Seiter et al., 2004; Wallmann et al., 2012; LaRowe et al., 2020). In this figure, it can be seen that POC concentrations are highest in recently deposited sediment underlying northern high-latitude and south-east Asian coastal regions and the Humboldt and South Equatorial currents to the west of Peru. They are generally lowest in abyssal regions far from land, and in older and deeper sediments. This span of concentrations is due to variable depositional fluxes and degradation rates.

Field observations have revealed that rates of POC degradation are not constant (e.g. Canfield et al., 2005), leading to burial rates that vary significantly in space (e.g. Canfield, 1994; Blair and Aller, 2012) and time (e.g. Arthur et al., 1985). In fact, first-order rate constants for POC degradation rates derived from field and laboratory data span over eight orders of magnitude, with older sediments having the smallest values (Middelburg, 1989). Many different factors have been invoked to explain this variability. They include, but are not limited to, organic matter composition (e.g. Westrich and Bernier, 1984; Hedges et al., 1988; Tegelaar et al., 1989; Cowie et al., 1992; Canfield, 1994; Hedges and Keil, 1995), electron acceptor (EA) availability (e.g. Demaison and Moore, 1980; Emerson, 1985; Canfield, 1994; Hedges and Keil, 1995; Dauwe et al., 2001), benthic microbial community composition and functional capacities (e.g. Canfield, 1994; Arnosti, 2011; Steen et al., 2019), microbial inhibition by specific metabolites (e.g. Aller and Aller, 1998), priming (e.g. Stevenson, 1986; Graf, 1992; Aller et al., 1996; Sun et al., 2002a; van Nugteren et al., 2009), physical and physicochemical protection (e.g. Keil and Kirchman, 1994; Mayer, 1994; Kennedy et al., 2002; Estes et al., 2019; Hemingway et al., 2019), sediment deposition rate (e.g. Müller and Suess, 1979; Calvert and Pedersen, 1992; Tromp et al., 1995) and macrobenthic activity (e.g. Aller, 1982; Aller and Cochran, 2019; Middelburg, 2019).

The rates of POC degradation in marine sediments are first and foremost controlled by the source and transport of organic carbon. A higher lateral and/or vertical (i.e. sedimentation) transport rate not

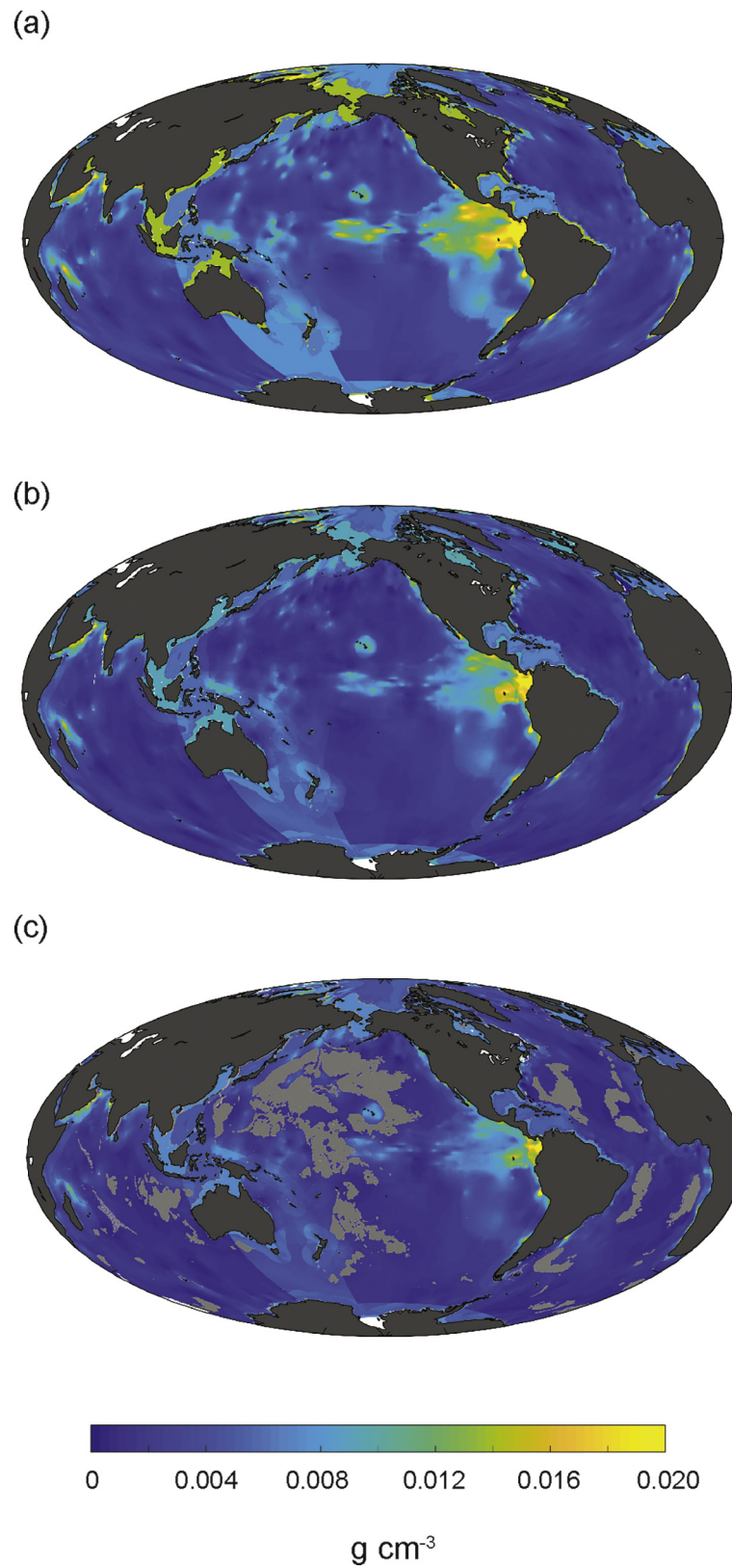


Fig. 2. Concentration of particulate organic carbon (POC) at a) the sea floor, b) 1 m below the sea floor and c) 10 m below the seafloor, based on calculations by LaRowe et al. (2020) and data summarized in Wallmann et al. (2012), which, for Holocene sediments, is taken from a compilation by (Seiter et al., 2004). Grey areas in c) indicate regions where Quaternary sediments (i.e. sediments deposited throughout the last 2.59 million years) are less than 10 m thick. The Quaternary cutoff is the temporal limit for the model used by LaRowe et al. (2020).

only increases the deposition flux but also influences the quality of the organic carbon deposited, since the degree of pelagic degradation during transport through the water column - and thus the nutritive value of POC - is reduced with extended sinking times. A compilation of deep sediment trap data reveals large regional variations in vertical export efficiency (Lutz et al., 2002; Henson et al., 2012; Wilson et al., 2012). For instance, the fraction of the organic carbon export flux that reaches water depths greater than 1.5 km varies between 0.28 and 30% (5.7% average) of the POC that escapes the photic zone (Lutz et al., 2002). Although differences in export efficiencies are most likely not attributable to a single process, factors invoked to explain variations in export efficiency include sinking rates and ballast (e.g. Armstrong et al., 2002; Francois et al., 2002; Klaas and Archer, 2002; Lutz et al., 2002), the seasonality of export production (Antia et al., 2001) and ecosystem structure (Buesseler et al., 2008; Lam et al., 2011; Henson et al., 2012; Mayor et al., 2012). And while export of large particles from surface waters has been extensively investigated, it has also been shown that very small particles ($< 1 \mu\text{m}$) contribute to the chemical composition of exported POC (Close et al., 2013). In addition to the vertical transport of POC from the euphotic zone, the efficient lateral transport of POC in nepheloid layers, benthic storms, mud waves, strong (bottom) water currents or mass wasting events can support an important fraction of the POC deposition flux to continental slope and abyssal sediments in the vicinity of dynamic continental margins (e.g. Ohkouchi et al., 2002; Levin and Gooday, 2003; Mollenhauer et al., 2003; Inthorn et al., 2006b; Mollenhauer et al., 2007; Kusch et al., 2010; Henson et al., 2012; Bao et al., 2019). The efficiency of terrestrial organic matter export from land is even more difficult to predict, given variable controls on residence times in soils, followed by widely varying degrees of alteration during transport through the riverine/estuarine/deltaic system and across the continental shelf (Hedges et al., 1997; Schlünz and Schneider, 2000; Bianchi, 2011; Blair and Aller, 2011; Bauer et al., 2013; Regnier et al., 2013; Canuel and Hardison, 2016; Kandasamy and Nagender Nath, 2016). Organic carbon is also produced in sediments, by phototrophs in shallow waters (Middelburg, 2018, 2019) and chemolithotrophically (Veuger et al., 2012; Sweetman et al., 2017). Although the exact mechanisms controlling the high variability in POC degradation are not well understood, the variety of environments that have been sampled and examined in recent years has provided new insights to constrain which variables are most important in particular settings.

1.3. Observations: increased diversity of sample sites and data types

Over the last several decades, scientific drilling of the seafloor by the International Ocean Discovery Program (IODP) and its precursors, the Integrated Ocean Drilling Program (IODP), the Ocean Drilling Program (ODP) and the Deep Sea Drilling Program (DSDP), have enabled critical expansion of sampled environments and new data that have dramatically increased our knowledge of the distribution of organic carbon in marine sediments. The sample sites targeted by most of these expeditions were motivated by scientific questions about the structure of ocean crust, past climate, and tectonics, leading to drilling locations and sampling methods that were optimized for study of these topics. Although total organic carbon was regularly measured on these samples, tools to study the agents of their transformation, i.e. microorganisms, were relatively rudimentary until culture-independent methods (e.g. DNA and RNA sequencing) became widely available in the early 2000's. Much of the new understanding of controls on organic carbon degradation in marine sediments has to do with recent insight into the role of microorganisms. As pointed out in the ODP Leg 201 summary (D'Hondt et al., 2003), this is despite the fact that deep-sea drilling had revealed indirect evidence of microbial activity as early as the 1980s (Oremland et al., 1982; Whelan et al., 1986; Tarafa et al., 1987) and, by the 1990s, microbial abundances (see Parkes et al., 2014) for a review). Remarkably, ODP Leg 201, the first ODP cruise

dedicated to studying microorganisms, did not sail until 2002. Since this time, a number of IODP expeditions have been focused on studying the limits to life: Expeditions 329 (South Pacific Gyre Subseafloor Life), 331 (Deep Hot Biosphere), 336 (Mid-Atlantic Ridge Microbiology), 337 (Deep Coalbed Biosphere off Shimokita), 357 (Atlantis Massif Seafloor Processes: Serpentinization and Life), 370 (Temperature Limit of the Deep Biosphere off Muroto), and 385 (Guaymas Basin Tectonics and Biosphere). This explicit exploration of microbial communities further informs the perspective that the reactivity of organic carbon in marine sediments is an ecosystem property (Middelburg, 2018).

2. Ecosystem nature of the problem

Organic carbon in natural systems is often referred to as being either labile or recalcitrant (e.g. Hedges et al., 2000). Some have expended considerable effort expanding this classification to intermediate states such as semi-labile and semi-recalcitrant (Hansell, 2013). This reductionist classification system implies that the degradation rate of organic compounds is determined from specific attributes of the chemical compounds themselves. While the reactivity of organic compounds is certainly related to their chemical composition and structure, numerous factors have been invoked to explain the reactivity of organic carbon that are not intrinsic to the compounds, but rather the properties of the surrounding environment (e.g. see Hedges et al., 2000; Burdige, 2007b; Arndt et al., 2013; Middelburg, 2018, 2019 and references therein). Examples include temperature, microbial community structure and benthic ecosystem, mineral types and surface area, redox state, light, nutrient availability, pH, salinity, porosity, permeability, water content and oxygen exposure time. Because these variables are biophysiochemical properties of the environment, the reactivity of organic matter is determined by the interaction between the compound and its ecosystem, not just the chemical nature of the organic compounds. Indeed, a particular organic compound can be extremely resistant to degradation under certain conditions, and be rapidly degraded in a different physiochemical context. For example, aerobic heterotrophic bacteria in incubation experiments have been shown to oxidize and incorporate ^{14}C -free organic carbon preserved in marine black shales for millions of years (Petsch et al., 2001). This idea of ecosystem properties governing organic compound reactivity is not a new one (Middelburg et al., 1993; Canfield, 1994; Harvey et al., 1995; Mayer, 1995), but it is only recently becoming the new paradigm in the soil science community (Marschner et al., 2008; Kleber and Johnson, 2010; Schmidt et al., 2011; Lehmann and Kleber, 2015), and there are indication that it should prevail among sediment scientists as well (Eglington and Repeta, 2014; Middelburg, 2018, 2019). In fact, we suggest that the terms *labile* and *recalcitrant* be retired and replaced with the single term *reactivity*. Similarly, since the fate of organic carbon in natural systems can include oxidation to CO_2 , hydrolysis and fermentation into smaller organics, reduction to methane, adsorption to surfaces, incorporation into biomass and conversion to petroleum products and complex organic compounds, we recommend that the more inclusive term *transformation* be used to refer to the fate of organic carbon rather than the relatively restrictive term *mineralization*. In the following sections, we highlight some of the recent research that seeks to determine how a variety of ecosystem properties influence the rates of organic carbon degradation.

2.1. Source and transit path

A large fraction of the organic carbon that is buried in marine sediments originates from photosynthetic activity in the terrestrial (net primary productivity (NPP) = 56 Pg C yr^{-1}) or marine biosphere (NPP = 49 Pg C yr^{-1}) (Field et al., 1998). In addition, organic carbon can be transported to sediments by other means including the weathering of ancient organic carbon in rocks (Blair et al., 2003), the remobilization of organic matter from thawing permafrost (Mann et al., 2015) and resuspension of already-deposited carbon (see below).

Autotrophic and Chemoautotrophic production as well as secondary production by microorganisms and animals can also contribute to the organic carbon deposition flux (Eglinton and Repeta, 2010; Middelburg, 2011; Lengger et al., 2019). Approximately two-thirds of terrestrially produced OC is rapidly degraded within soils or glacial environments. The remainder that escapes immediate degradation is either partially degraded or temporarily stored before being transported downstream with old, weathered OC within lakes, streams, rivers, estuaries, deltas, fjords, and ultimately, the oceans (Regnier et al., 2013). An estimated $1.9 \text{ Pg C yr}^{-1} \pm 1.0 \text{ Pg C yr}^{-1}$ of total soil carbon (mostly POC and dissolved organic carbon, DOC, but also dissolved inorganic carbon, DIC) is exported to inland waters. Only $0.45 \text{ Pg C yr}^{-1}$ of the terrestrial-derived OC reaches the coastal ocean and $0.1\text{--}0.35 \text{ Pg C yr}^{-1}$ makes it to the open ocean (Bauer et al., 2013; Regnier et al., 2013). Thus, the land-ocean transition zone acts as an important modulator of OC fluxes that not only further degrades and transforms terrestrial OC inputs, but also stores OC on short and long timescales (Canuel and Hardison, 2016). However, the exact amounts of OC that are degraded and temporarily or permanently preserved during transit from land to ocean remain unknown (Regnier et al., 2013).

Similar to terrestrially-derived organic carbon, a large fraction (80–90%) of the OC produced in the surface ocean is rapidly oxidized (Dunne et al., 2007; Hansell and Carlson, 2015). Just over one-quarter (27%) of OC produced in the marine photic zone is DOC that can be transported to the deep ocean by convection and mixing. While most of the exported DOC is degraded at mid-depths, an estimated 0.1 Pg C yr^{-1} is contributed to the large, apparently unreactive, deep ocean DOC reservoir ($\sim 680 \text{ Pg}$) that persists through multiple ocean mixing cycles (Hansell and Carlson, 2015). As POC sinks to the ocean floor, it can be laterally transported by ocean currents (Eglinton and Repeta, 2004) as it is further degraded. Degradation during burial further reduces this flux such that $< 0.3\%$ of the original exported flux is ultimately sequestered in deep marine sediments (Hedges and Keil, 1995; Eglinton and Repeta, 2004; Burdige, 2007b; Dunne et al., 2007; Middelburg and Meysman, 2007; Honjo et al., 2008).

In addition to the vertical transport from the photic zone to sediments, POC can also be transported after deposition on the seafloor via bioturbation and lateral motion following the resuspension of sediments into the water column. Bioturbation, the biological reworking of sediments near the SWI by macrofauna such as polychaetes and bivalves (Rhoads, 1974; Aller, 1982), can exert an important influence of organic carbon transformation (Meysman et al., 2006; Middelburg, 2018) in the upper 20 cm of sediments (Boudreau, 1994, 1998). These animals can have a complex impact on sediment POC – in some cases accelerating POC degradation through grazing, the redistribution of particles and reintroduction of electron acceptors and DOC, (Kristensen, 1985; Rice, 1986; Kemp, 1988; Aller, 1994; Aller and Aller, 1998; Kristensen and Holmer, 2001; Kristensen et al., 2011) and, in other cases, depositing organics in the form of tube casings that can inhibit organic transformation (Kristensen et al., 1992; Kristensen, 2001). Generally, it seems that bioturbation accelerates POC degradation (Rhoads, 1974; Findlay and Tenore, 1982; Aller and Aller, 1986; Herman et al., 1999; Aller et al., 2001; Kristensen and Holmer, 2001; Kristensen and Kostka, 2005; Aller and Cochran, 2019). Furthermore, benthic macrofauna, in addition to being a source of OC, can affect sediment resuspension (Aller and Cochran, 2019) by altering the bulk properties of sediments (Eckman et al., 1981; Rhoads et al., 1984), which in turn influences their lateral transport.

Sediments, and the POC within, on continental shelves and slopes can also be mobilized after initial deposition and redeposited under open-ocean waters. Not only does this process move organic carbon laterally to parts of the seafloor that typically have low POC deposition rates (Jahnke et al., 1990; Walsh, 1991; Bauer and Druffel, 1998; Ransom et al., 1998a; Thomsen and van Weering, 1998; Jahnke and Jahnke, 2000; Romankevich et al., 2009; Hwang et al., 2010), but it has

the effect of accelerating the oxidation of POC that was buried in margin sediments (see Section 2.5 for a discussion) (de Lange et al., 1987; Prahl et al., 1989; Cowie et al., 1995; Prahl et al., 1997; Cowie et al., 1998; Hoefs et al., 1998; Prahl et al., 2003). However, the scale of this phenomenon, as well as its impact on the global distribution of organic matter reactivity, remains unclear (Eglinton and Repeta, 2014) due to large uncertainties in lateral particle fluxes (Jahnke et al., 1990; Reimers et al., 1992; Inthorn et al., 2006a; Thullner et al., 2009).

2.2. Organic carbon structure and composition

Although the majority of organic carbon inputs to marine sediments originate as POC, these sources can be transformed and contribute to the DOC pool through microbial activities as well as sorption/desorption from mineral surfaces. Chemically, both POC and DOC range in size and complexity from simple monomers to mixtures of large, complex polymers as well as humic substances (de Leeuw and Largeau, 1993; Hedges et al., 2000), the last of which is an ill-defined molecular group of varying sizes that are solely defined by the extraction procedure used to isolate them. Most POC and DOC in marine sediments cannot be chemically identified at the structural level, leading to terms such as “molecularly uncharacterizable carbon, MUC” (Cowie et al., 1995; Prahl et al., 1997; Wakeham et al., 1997; Burdige and Gardner, 1998; Hedges et al., 2000; Burdige, 2007b; Burdige and Komada, 2015). Depending on the sample, anywhere from 50 to 90 wt% of OC in marine sediments is referred to as MUC. Approximately 60–90% of pore water DOC has a molecular weight of less than 3 kDa, and the compounds that can be identified tend to be short-chain organic acids such as acetate, amino acids, and carbohydrates (Burdige and Komada, 2015). High-resolution techniques have shown that thousands of organic compounds are found in pore water (e.g. Repeta et al., 2002; Koch et al., 2005; Schmidt et al., 2009; Fox et al., 2018), but many fall into a rather unsatisfactory category known as CRAM, carboxyl-rich alicyclic molecules – a poorly defined pool of organics thought to be less reactive than other DOC compounds (Hertkorn et al., 2006).

As with DOC, the bulk of organic compounds in the particulate fraction of marine sediments (i.e. POC) is rarely identified and often said to be ‘uncharacterizable’, at least with respect to partitioning it into compound classes such as amino acids, carbohydrates, lignin or lipids (Cowie et al., 1995; Prahl et al., 1997; Wakeham et al., 1997; Hedges et al., 2000; Benner, 2002; Koch et al., 2005; Burdige, 2007a; Mao et al., 2011; Ball and Aluwihare, 2014; Estes et al., 2019). Although it is not clear why this is the case, one of the explanatory hypotheses, that organics attach to mineral surfaces and condense into large macromolecules that are less accessible by exoenzymes, e.g. (Hedges et al., 1988; Keil and Kirchman, 1994; Hedges et al., 2000), no longer holds in the soil science community. Briefly, it was long thought that complex macromolecular carbon compounds form in soils through abiotic processes and that these large compounds were especially resistant to biological degradation. More recently, however, there is a growing consensus that these larger compounds are an artifact of extraction procedures and there is no evidence for their presence *in situ* (Kelleher and Simpson, 2006; Lehmann and Kleber, 2015).

The structure and composition of organic matter serves as the first guidepost to determining its reactivity. For instance, relatively weak bonds between monomers render a biopolymer more reactive over a wide range of environmental conditions, than aliphatic moieties cross-linked by ether bonds (Tegelaar et al., 1989; de Leeuw and Largeau, 1993). At the most fundamental level, this structural heterogeneity is responsible for the higher reactivities of most algal organic carbon over most terrestrial organic matter (Canuel and Martens, 1996; Hedges and Oades, 1997; Dauwe and Middelburg, 1998; Camacho-Ibar et al., 2003; Burdige, 2005; Dai and Sun, 2007), the selective preservation of certain compounds in the geological record and the widely observed decrease of organic carbon with depth and or transport/burial time (Goth et al., 1988; Tegelaar et al., 1989). However, the relative importance of

organic structure and composition in controlling overall preservation/degradation remains unclear (see de Leeuw et al., 2006; Gupta et al., 2007; Gupta, 2015). In addition, because of the extremely limited availability of compound-specific kinetic data (e.g. Ming-Yi et al., 1993; Harvey and Macko, 1997; Sun et al., 2002b), a comprehensive knowledge of organic structure and composition does not help in quantifying organic matter reactivity. Ultimately, linking the identity of individual organic compounds to their reactivity would require knowledge of how many other biophysiochemical variables impact it as well.

2.3. Sediment matrix

Mineral surfaces are thought to slow or prevent the degradation of organic carbon, largely based on observations that there is a positive correlation between mineral surface area and the amount of organic matter in sediments (e.g. Mayer et al., 1985; Keil et al., 1994; Mayer, 1994). Most hypotheses explaining this phenomenon rest upon the notion that extracellular enzymes cannot access mineral-associated organic compounds. Compounds can associate with minerals via a number of mechanisms, both physical and chemical, including 1) physisorption (physical adsorption) in surface irregularities, 2) strong mineral surface bonding, 3) insertion into clay interlayers, 4) formation of mineral-OC aggregates, 5) co-precipitation with Fe-oxides and other authigenic minerals, 6) seclusion by exopolymeric substances (EPS) and 7) protection within biogenic minerals such as diatom frustules (Keil and Hedges, 1993; Keil et al., 1994; Mayer, 1994; Hedges and Keil, 1995; Ransom et al., 1997; Ransom et al., 1998b; Mayer, 1999; Arnarson and Keil, 2001; Mayer and Xing, 2001; Kennedy et al., 2002; Ingalls et al., 2003; Paction et al., 2007a; Paction et al., 2007b; Kennedy and Wagner, 2011; Lalonde et al., 2012; Hemingway et al., 2019). Chemical preservation mechanisms, in particular, are likely important, since OC concentration often correlates more strongly with the abundance of specific mineral classes such as smectite clays (Ransom et al., 1998a), metal oxides (Lalonde et al., 2012; Roy et al., 2013; Barber et al., 2017) or tephra (Longman et al., 2019) rather than total mineral surface area, suggesting that the specific chemical bonds formed by these minerals with organic compounds are essential to decreased reactivity.

Given the large variety of organic compounds and minerals found in marine sediments, it is probable that all of the mechanistic hypotheses noted above contribute to the long-term preservation of OC. The array of explanations is likely due to the fact that the samples used to generate them have come from different places and therefore are characterized by a variety of different biogeochemical conditions and timescales of preservation. Although there is a growing appreciation of the complexity of mineral-organic reactions, disentangling which mechanism operates under what set of environmental conditions is complicated by a lack of data that more fully contextualizes mineralogical observations such as oxygen exposure times (OETs). For example a study examining how OETs affect mineral-organic associations in northeast Pacific sediments (Arnarson and Keil, 2007) found that for OETs shorter than a year, OC was mostly in a mineral-free state. For sediments with OETs ranging from years to decades, OC was largely in mineral-organic aggregates. For longer OETs (centuries to millennia), the aggregates broke down and most OC was found sorbed to mineral surfaces or protected inside biogenic diatom frustules (see Section 2.5 for a discussion on electron acceptor availability).

The exposure to a variety of geochemical conditions over varying timescales also impacts how solid phases can control organic carbon reactivity. For instance, microorganisms use Fe- and Mn-oxide minerals to oxidize organic carbon in marine sediments (Ehrlich, 1971; Aller, 1980; Berner, 1981; Jones, 1983; Burdige and Nealson, 1986; Lovley, 1991; Thamdrup, 2000; Hyun et al., 2017), especially where manganese- and iron-oxides are abundant or rapidly recycled due to fluctuating redox conditions (Sørensen and Jeørgensen, 1987; Aller et al., 1990; Canfield et al., 1993). In fact, it has been estimated that 3% of the

POC degraded in the top 50 cm of global marine sediments is coupled to Fe-oxide reduction (Thullner et al., 2009), though this is spatially quite variable (Burdige, 2012; Dale et al., 2015). Yet, these same mineral phases provide protection and stabilization of organic matter (Lalonde et al., 2012; Johnson et al., 2015; Barber et al., 2017). Substantially more OC is associated with Fe oxides via inner-sphere complexation in coastal environments with short OETs than in low OC, deep-sea sediment (Barber et al., 2017). Experimental evidence additionally demonstrates that the composition of OC matters in determining the balance between degradation and preservation by minerals: the presence of disaccharides inhibits the abiotic degradation of protein by the manganese oxide mineral birnessite (Reardon et al., 2018). Furthermore, carbon compounds can serve as templates for mineral nucleation, and co-precipitate with minerals during mineral growth and aggregation (Mann et al., 1993; Moreau et al., 2007; Kleber et al., 2015 and references therein). Beyond redox chemistry, (Taylor, 1995) showed that under some conditions sorbed proteins are hydrolyzed much faster than dissolved proteins, indicating that surface sorption can in fact enhance organic carbon degradation.

Generalizations about organic-mineral interactions are further complicated by the fact that sediment types may vary on the centimeter scale and might be dominated by an array of mineral types that have distinct physiochemical properties. Common sediment lithologies include chert, siliceous ooze, carbonate, clay, silt and sand in the form of turbidites, volcanoclastics and limestone (Plank and Langmuir, 1998). Sediments made of these various constituents respond differently to increasing pressures and temperatures during diagenesis, leading to dissolution, precipitation, and solid-phase reordering reactions (Prothero and Schwab, 2004) that will certainly impact organic-mineral associations. How specific mineral-organic associations change across environmental gradients is not well known, but potentially crucial to understanding the fate of OC in marine sediments. The common clay mineral smectite provides an illustrative example since it has been shown to preferentially sequester organics, relative to chlorite-rich clays (Ransom et al., 1998a). With as little as 1.3 MPa pressure (Hüpers and Kopf, 2012), the interlayer in smectite begins to dewater and collapse, a process that also depends on temperature, the identities of interlayer cations and the concentrations of cations present in solution (Ransom and Helgeson, 1995). If organics are sequestered in this interlayer, they could be expelled during this transition and transported into other parts of the sediment. Likewise, the reductive dissolution of metal oxides may liberate chemically or physically adsorbed organics (Coppola et al., 2007). Other recent work suggests that the salinity gradient experienced by smectite during transport from the terrestrial to marine environments induces cation exchange reactions and the removal of associated pedogenic organic carbon, followed by repopulation of the mineral surface with marine OC (Blattmann et al., 2019). On the other end of the size spectrum, sandy sediments - half of continental shelf seafloor - allow for water column POC to be pumped biologically or tidally into the subsurface. This reactive DOC stimulates organisms (Huettel et al., 2014) to consume it and more of the particulate organic fraction, contributing to low POC in sandy sediments (Boudreau et al., 2001).

2.4. Hydrolysis and Fermentation

When free oxygen has been exhausted in sediments, OC is thought to be transformed through a series of steps that include the extracellular enzymatic hydrolysis of large, complex organic compounds into smaller ones that are then fermented into volatile fatty acids, H₂ and other simple chemical species, some of which are then oxidized by microorganisms using electron acceptors such as nitrate, metal-oxides and sulfate, or reduced to methane (Schulz, 2006). Thought to be the rate limiting step in organic matter degradation, extracellular enzymes produced by microorganisms are known to break large and/or complex organic compounds to supply microorganisms with energy and

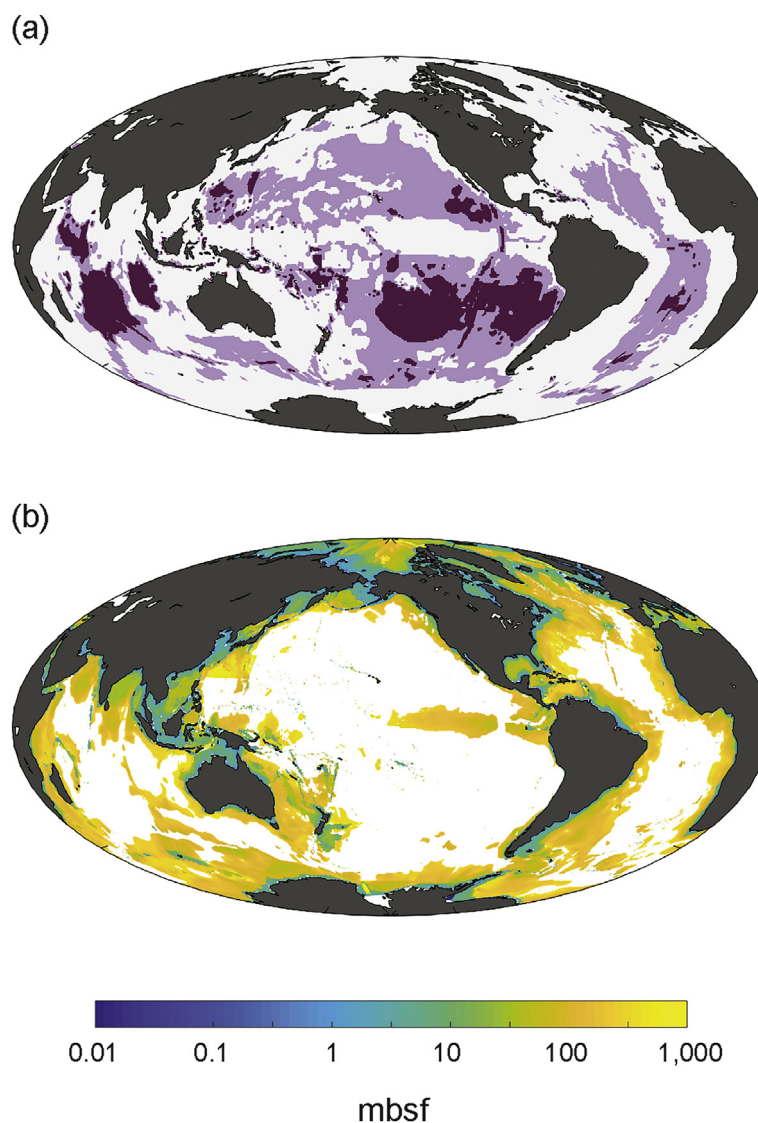


Fig. 3. Estimated a) regions of the seafloor where dissolved O_2 is modeled to be present throughout the sediment to the underlying oceanic basement and b) depth of the sulfate-methane transition (SMT) zone. The dark shading in a) refers to the minimum extent of modeled O_2 -penetrating regions while the light shading, together with the dark shading, indicate the maximum extent, based on [D'Hondt et al. \(2015\)](#). The white regions in b) denote regions where there is no SMT. All data for b) from [Egger et al. \(2018\)](#).

nutrients such as nitrogen and phosphorous ([Arnosti, 2011](#)). Extracellular enzymes are diverse and present in low concentrations in marine sediments ([Steen et al., 2019](#)). Although temperature and pH are dominant controls on rates of enzyme-catalyzed reactions, patterns of activity across ecosystem types do not necessarily correlate with such physio-chemical variables ([Mahmoudi et al., 2020](#)). It seems that the functional diversity of microbial communities, nutrient availability and organic matter reactivity are likely to better explain patterns of extracellular enzyme activities, with a notably strong correlation with particle composition, size and abundance ([Arnosti et al., 2014](#)).

It is difficult to locate fermenting microorganisms in sediment columns since they do not leave a distinct chemical trace of their activity ([Nealson, 1997](#)). A near-limitless number of organic compounds can serve as reactants and products, and a considerable number of inorganic species can be produced and consumed by both fermentative and non-fermentative processes ([LaRowe and Amend, 2019](#)). In addition, many organisms can switch between fermentation and other catabolic strategies, and macrofauna can also leave signatures reminiscent of fermentative pathways as they partially digest organic matter during gut passage ([McInerney et al., 2008](#); [Jochum et al., 2017](#)). Consequently,

the specific forms of fermentation and diversity of fermentative mechanisms in marine sediments remain largely unknown.

Recent analyses of biomolecular data (see Section 2.6) from sediments confirm that fermentation generally appears to be a widespread survival strategy for many cosmopolitan groups of microorganisms in anoxic sediments. For example, Bathyarchaeota, Hadesarchaea, and the Atribacteria that are common in marine sediments all utilize fermentative strategies – using peptides, aldehydes, sugars and lignin as substrates ([Lloyd et al., 2013](#); [Baker et al., 2016](#); [Nobu et al., 2016](#); [Orsi, 2018](#); [Yu et al., 2018a](#)). As has been often presumed, fermenting bacteria have now been found throughout the anoxic sediment column across multiple geochemical zones ([Orsi et al., 2017](#); [Beulig et al., 2018](#)). Many bacteria with the capability to ferment (in particular alpha- and gamma-proteobacteria) have also been found in oxic marine sediment such as deep-sea red clay, though they respire oxygen in these settings ([Vuillemin et al., 2019](#)). Eukaryotic microorganisms are also involved in fermentation processes in sediments. For example, the majority of H_2 produced in anoxic permeable sediments results from fermentation by eukaryotic algae ([Bourke et al., 2016](#)). In deeper sediments down to at least 2000 m below the seafloor (mbsf), fermenting

fungal cells can still persist (Ciobanu et al., 2014), suggesting that they have the ability to contribute to H_2 production since this can be a product of their fermentative pathway (Orsi, 2018). Finally, metagenomic and proteomic data taken from terrestrial settings suggest that fermenting organisms constitute a large fraction of the Candidate Phyla Radiation, an uncultured but geographically widespread and genetically diverse group of bacteria (Wrighton et al., 2012; Wrighton et al., 2014; Anantharaman et al., 2016; Danczak et al., 2017).

2.5. Electron acceptors

Most sedimentary POC – and its hydrolysis and fermentation products – are consumed by microorganisms using an array of electron acceptors. The identities and concentrations of EAs are in turn determined by the composition of the overlying seawater and the types of mineral phases that are deposited along with organic compounds. The principal EAs encountered in marine sediments, O_2 , NO_3^- , Mn(IV), Fe(III), SO_4^{2-} and CO_2 , are traditionally thought to be consumed in the order listed based on the idea that this sequence follows the order of decreasing Gibbs energy yield of the corresponding organic matter oxidation reactions (Claypool and Kaplan, 1974; Froelich et al., 1979; Stumm and Morgan, 1996), though it should be noted that the range of Gibbs energies for reactions involving these EAs can overlap depending on the environmental conditions (LaRowe and Van Cappellen, 2011; LaRowe and Amend, 2014, 2015a). This hierarchy leads to redox zonation in marine sediments – oxic sediments nearest the SWI, followed by so-called sub-oxic zones where NO_3^- and Mn(IV) reduction occurs, a ferruginous layer if Fe(III)-bearing minerals are present, then a sulfidic layer where the bulk of SO_4^{2-} reduction takes place and finally a methanogenic zone at the bottom of the sediment column. Not all of these redox zones will necessarily be present in any given sediment column. The thickness of the zones can vary dramatically (Glud, 2008; D'Hondt et al., 2015; Egger et al., 2018) and the order of them can exhibit complex patterns (see Jørgensen et al., 2019). For instance, in many coastal sediments where POC fluxes are high, the oxic zone might be vanishingly thin (Glud, 2008), while the oxic layer in sediments underlying ocean gyres can penetrate tens of meters to the basement since POC fluxes are so low (Røy et al., 2012; D'Hondt et al., 2015). In fact, D'Hondt et al. (2015) estimate that 9–37% of the global sediment-basement interface is oxic (Fig. 3a).

In an undetermined volume of the ocean crust, deep sediment layers can exhibit higher concentrations of dissolved oxygen than in upper or middle layers due to the penetration and circulation of deep, oxygenated seawater into unsedimented adjacent basaltic outcrops (Orcutt et al., 2013b; Mewes et al., 2016; Kuhn et al., 2017). This subsediment, rapid movement of low-temperature seawater allows oxygen to diffuse upward from basement basalt into sediments, thus creating a C-shaped O_2 curve in these sediments. An example of this is shown in Fig. 4 for a sediment pond near the mid-Atlantic Ridge, though it should be noted that these kinds of oxygen profiles have also been observed in the North Pacific near a fracture zone (Mewes et al., 2016; Kuhn et al., 2017). The upward transport of such microbial energy sources could be common globally due to the vast number of seamounts that jut above the sediment-water interface (Wheat et al., 2019 and references therein).

Other chemical compounds that can provide energy for microorganisms have been found to be transported upward in sediments. In one such case near the Peru Margin, sulfate diffused upward from a brine in the oceanic basement (D'Hondt et al., 2004; Parkes et al., 2005; Engelen et al., 2008). In another, Cretaceous-aged organic-rich horizons support methane production that seem to, in turn, provide energy for microbial communities in and above it, driving unexpected distributions of EAs that differ from classical expectations (Arndt et al., 2006). In many anoxic sedimentary settings, the reduced products of POC oxidation, compounds such as Fe^{2+} , H_2S and NH_4^+ , diffuse upwards to be oxidized by chemolithotrophic microorganisms for energy. If redox conditions oscillate, this process can cycle, creating the impression that

POC is being transformed more rapidly than it is (Thullner et al., 2009), though OC oxidation rates can be accelerated due to these oscillations (Sun et al., 1993; Aller, 1994; Sun et al., 2002a; Caradec et al., 2004).

The deepest extent of the sulfate-reducing zone and thus the beginning of the methanogenic zone (sulfate-methane transition, SMT) varies widely on a global scale, and has been shown to strongly depend on sedimentation rates and associated organic matter burial fluxes (Berner, 1978; Borowski et al., 1999; Egger et al., 2018). In fact, Egger et al. (2018) recently used a compilation of 1704 observations to correlate sedimentation rates with SMT depth to map the extent of the SMT globally (Fig. 3b). It can be seen in this figure that SMT depth is spatially highly variable: in many shallow continental shelf and slope settings, SMT depth is < 1 mbsf, and up to 10 mbsf. In deeper sediments, particularly water depths > 2000 m, SMT depth is at least 10 mbsf and in many instances, hundreds of meters deep. The majority of sediments in the abyssal plain ($> 66\%$) exhibit no SMT.

The preservation of POC in sediments is sometimes attributed to anoxia, and therefore ascribed to the identities of the electron acceptors present (e.g. Demaison and Moore, 1980; Emerson, 1985; Calvert and Pedersen, 1992; Lee, 1992; Aller, 1994; Canfield, 1994; Wignall, 1994), and to some extent the types of organic compounds deposited (Harvey et al., 1995; Harvey and Macko, 1997; Sun et al., 1997; Bianchi et al., 2000; Grossi et al., 2001; Sun et al., 2002a). Though there are many datasets and reports arguing for and against the idea that the presence of free oxygen plays a decisive role in POC reactivity (see Hulthe et al., 1998), there seems to be a growing consensus that the presence O_2 typically enhances organic carbon reactivity in many marine sediments (Hartnett et al., 1998; Hedges et al., 1999; Keil and Cowie, 1999; Keil et al., 2004; Moodley et al., 2005; Cowie et al., 2009; Middelburg and Levin, 2009; Aller, 2014; Eglinton and Repeta, 2014; Keil et al., 2016). Notable exceptions to these observations include studies that show that rates of POC degradation in anoxic sediments have been observed to be nearly equal to (e.g. Henrichs and Reeburgh, 1987; Lee, 1992; Kristensen and Holmer, 2001) or far exceeding those in oxic settings (Røy et al., 2012; D'Hondt et al., 2015). On a molecular level, fatty acids can be degraded at similar rates independently of their degree of saturation in the presence of oxygen, whereas unsaturated acids are preferentially degraded under anoxic conditions (Harvey and Macko, 1997; Sun et al., 1997; Grossi et al., 2001). In sediments dominated by sulfate reduction, measured cell specific sulfate-reduction rates vary by 10 orders of magnitude (Jørgensen et al., 2019). Furthermore, recent incubation experiments have built on other studies (e.g. Lee, 1992, b) showing that the identity of the electron acceptors used during POC transformation processes has little to no influence on the overall rate of organic carbon degradation (Beulig et al., 2018). Taken together, these studies suggest that the identity of the oxidant/reductant does not necessarily determine the reactivity of organic carbon, but that O_2 has a special role among EAs in evaluating the reactivity of POC.

2.6. Microorganisms

Although many factors influence the reactivity of organic carbon in sediments, one of the most unifying is microorganisms. The extent to which organic carbon reactivity is influenced by the taxonomic and functional distribution of microorganisms is only beginning to be explored, after an era in which little attention was paid to microbial life in sediments (see Section 1.3). In the last decade or so, there has been a revolution in understanding the number, identity, functional capabilities and extent of life in marine sediments, and their role in OC degradation.

2.6.1. Abundance

Microbial cell numbers correlate with mean sedimentation rate and distance from continental landmasses (Kallmeyer et al., 2012), as well as with the amount of organic matter in sediments (Jørgensen and Marshall, 2016). For surface sediments, those on continental margins

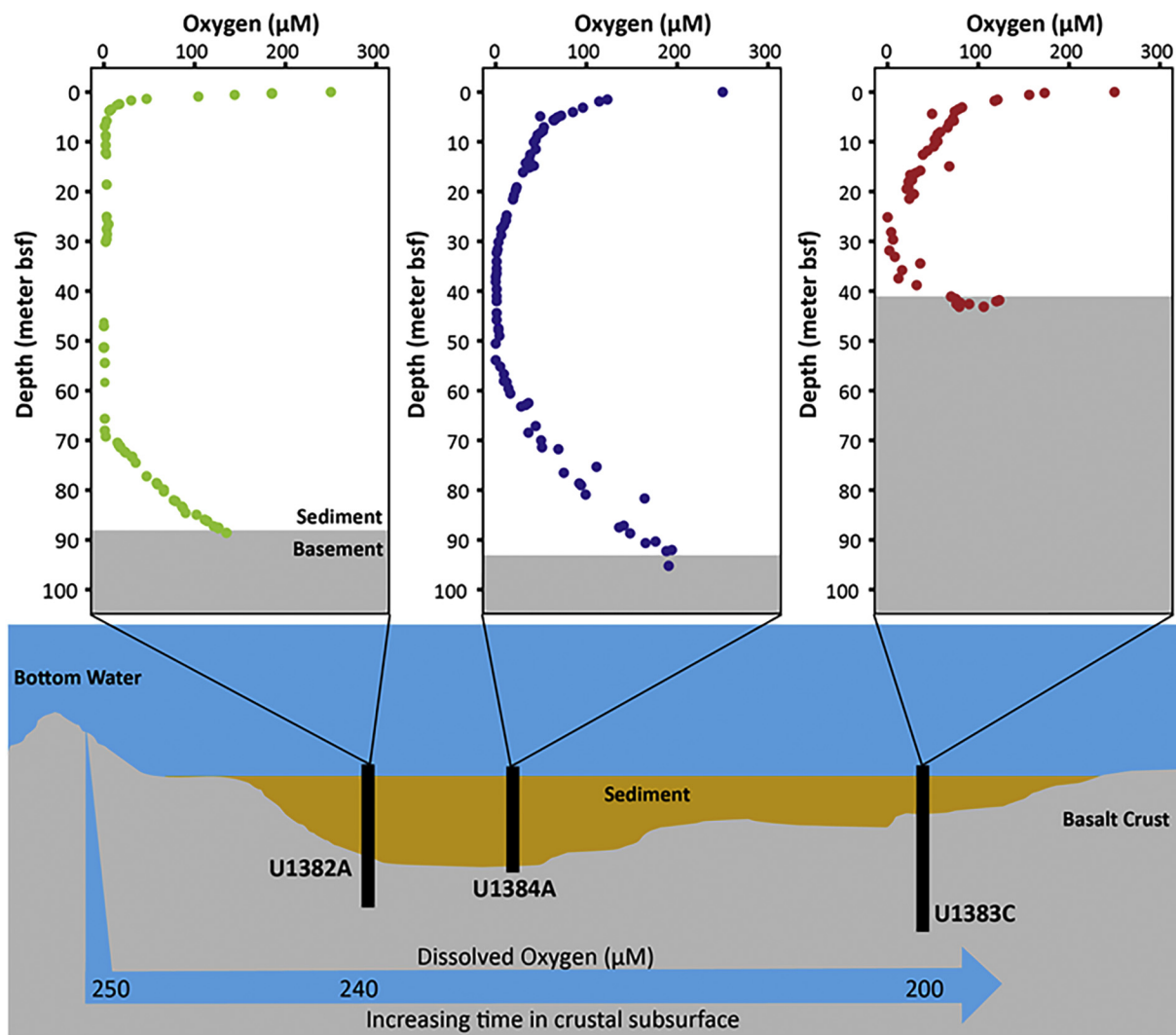


Fig. 4. Oxygen concentration profiles as a function of depth in marine sediments and ocean basement crust from three IODP drill cores located on ~ 8 Ma flank of the mid-Atlantic Ridge (also known as North Pond – see [Orcutt et al., 2013b](#)). The bottom panel contains a cross section schematic of what is thought to be the mechanism of O_2 delivery to basal sediments – upward diffusion from oxygenated fluid flowing rapidly in the basement. This fluid is chemically very similar to local bottom seawater and is likely introduced to the subsurface from locally outcropping basalt (see [Meyer et al., 2016](#)). Oxygen loss in flowing fluids is thought to result from both diffusion into sediments and consumption during microbial oxidation of DOC.

contain 10^8 – 10^{10} cells cm^{-3} , whereas those underlying oligotrophic gyres contain 10^5 – 10^7 cells cm^{-3} ([Kallmeyer et al., 2012](#)) (Fig. 5). In most sediments, cell concentrations decrease with increasing depth below the seafloor, according to a power law. In OC-poor, oxic sediments, cell concentrations drop below $\sim 10^2$ cells cm^{-3} between 10 and 15 mbsf ([Kallmeyer et al., 2012](#); [Vuillemin et al., 2019](#)). Cell abundance in OC-rich, anoxic sediments on continental shelves remain relatively high at great depths in the sediment, and only fall to $\sim 10^2$ cells cm^{-3} between 1000 and 2500 mbsf ([Kallmeyer et al., 2012](#)).

2.6.2. Identity

Rapid progress in high-throughput DNA sequencing and analytical tools over the last decade has completely revised our understanding of the tree of life ([Hug et al., 2016](#)). Many of the phylogenetic groups found in sediments are candidate phyla that are not yet cultivated, so their role in organic matter transformation is not entirely clear ([Lloyd et al., 2018](#)). Though common types of fungi, bacteria, and archaea have been found in sediments ([Richards et al., 2012](#); [Orsi et al., 2013](#)), many new groups of microorganisms reside in the subsurface that appear to be endemic to this environment. These endemic groups are repeatedly found to be relatively abundant in subsurface settings

([Anantharaman et al., 2016](#); [Orsi, 2018](#)), with widely differing diversity in oxic and anoxic sediments ([Orsi, 2018](#)). In addition, sediments of varying redox state reveal evidence of viruses ([Engelhardt et al., 2015](#); [Tully and Heidelberg, 2016](#); [Bäckström et al., 2019](#); [Cai et al., 2019](#)), which may contribute to organic processing via lysis of microbial biomass ([Danovaro et al., 2008](#); [Orsi, 2018](#)), with archaea potentially being disproportionately lysed in surface sediments under deep waters ([Danovaro et al., 2016](#)).

2.6.3. Functional capabilities

Before the molecular biology revolution, the functional capabilities of microbial communities in sediments were inferred from pore water profiles, with little to no direct biological information. For example, decreases in sulfate and increases in sulfide suggested microbial sulfate reduction and amendment experiments revealed that the addition of fermentation end products (H_2 , acetate) stimulated rates of sulfate reduction ([Goldhaber et al., 1977](#); [Iverson and Jørgensen, 1985](#)). The ability to sequence and identify genes with known functions, and determine their expression levels, allowed for the discovery of new types of microorganisms as well as new functional capabilities ([Biddle et al., 2006](#); [Biddle et al., 2008](#)), which could then be correlated to

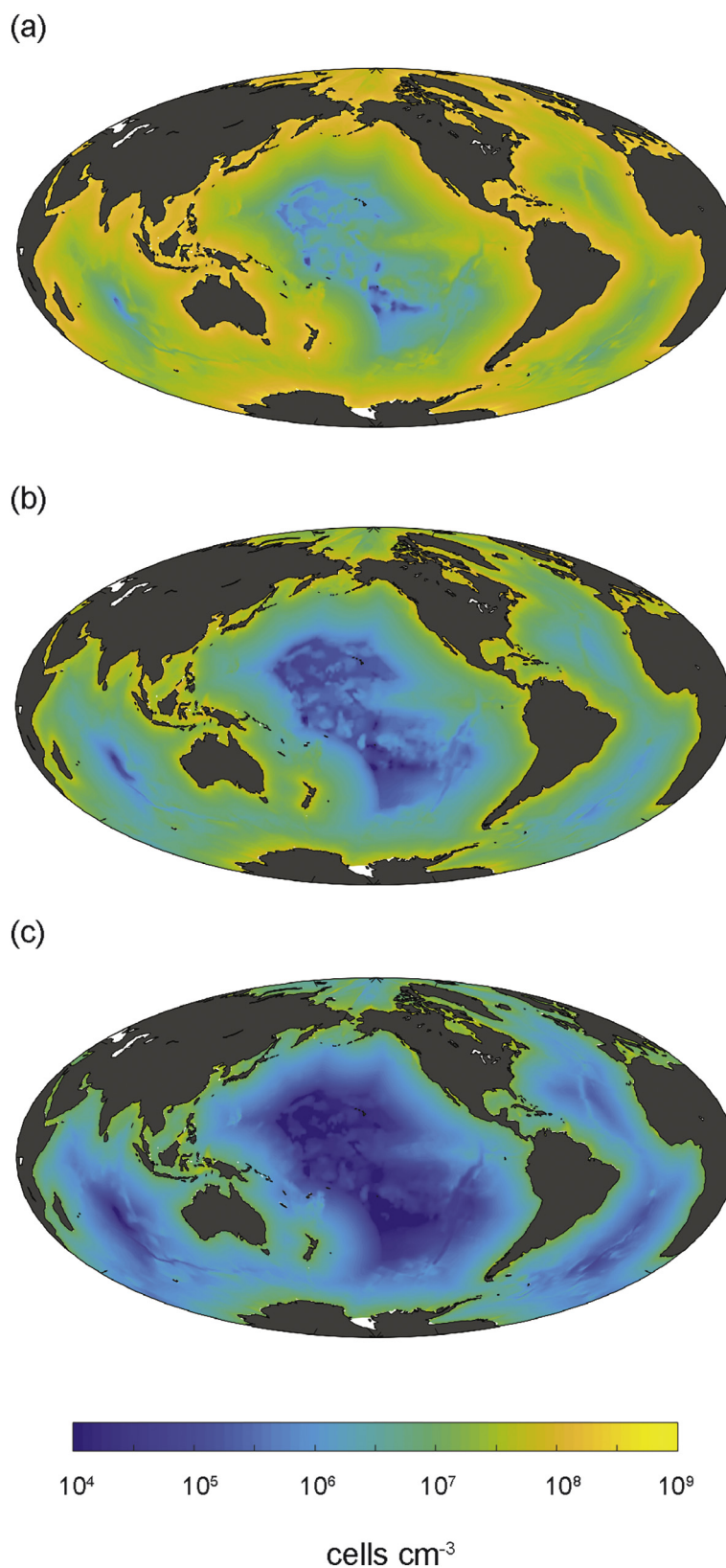


Fig. 5. Calculated cell concentrations in marine sediment at a) the seafloor, b) 1 m below the sea floor and c) 10 m below the seafloor using the data compilation and approach described by [Kallmeyer et al. \(2012\)](#).

geochemical profiles.

Knowledge of microbial functionality from environmental 'omics data (the term 'omics is commonly used to refer to the analysis of DNA, RNA, metabolite and protein sequences extracted from samples) can be

inferred from a close similarity of protein encoding genes from environmental samples to those found in genomes of cultured microbes that have been assigned a function based on biochemical experiments ([de Bruijn, 2010](#)). Marine sediment communities are dominated by

microorganisms that are not closely related to any current pure culture (Parkes et al., 2005; Biddle et al., 2006; Inagaki et al., 2006; Lloyd et al., 2018). Therefore, it is speculative to assume that distant genetic similarities from the in situ microorganisms to cultured strains imply that those genes are enabling microorganisms to perform the same function. A large number of genes encoding hypothetical proteins in marine metagenomes, which are digital libraries of all the DNA present from all the microorganisms in a natural sample, remain difficult to annotate with information about their identities or functions. For instance, in the large TARA Oceans metagenomic data set, only about 16% percent of DNA sequences that encoded a hypothetical protein had a statistically significant similarity to proteins with an experimentally determined function. Furthermore, 44% of the hypothetical proteins had no significant similarity to gene families that share general biochemical functions (Sunagawa et al., 2015). This problem is difficult to solve using traditional bioinformatic approaches, which rely on comparing environmental sequences to genes whose function has been identified.

A further complicating factor is that databases of known genes are dominated by well-characterized microorganisms, particularly from a single phylogenetic group (Proteobacteria), whereas marine environments are dominated by uncultured organisms from diverse lineages (Lloyd et al., 2018). Physiologies from some of these uncultured microbes have been inferred from whole genome reconstructions in marine sediments (Lloyd et al., 2013), metatranscriptomics showing which genes were being transcribed at the time of sampling (Orsi et al., 2013), compositions of natural isotopes of biomass (Biddle et al., 2006; Shah et al., 2008; Meador et al., 2015), stable isotope probing (Morono et al., 2011; Trembath-Reichert et al., 2017), direct measurement of metabolites (Bird et al., 2019) and tracking increases in a microbial group's cell abundance during laboratory enrichment of natural marine sediments (Kevorkian et al., 2018; Yu et al., 2018b). The limitations of these approaches are that DNA and RNA sequences from environmental samples can only be given functional annotations based on their similarity to known cultures. Therefore, truly novel functions cannot be determined from sequencing methods alone. Heterologous expression and characterization can be used to identify novel functions (Cottrell et al., 2005; Michalska et al., 2015; Wrighton et al., 2016), but such methods have only been applied to enzymes with enough homology to a known protein to develop a hypothesis. Determining the functions of genes encoding truly novel "hypothetical" proteins will be very important for inferring functions of uncultured microorganisms in marine sediments.

It should be noted that genome representation in databases represents one of the largest issues for making correct assignments of protein encoding genes in environmental genomics datasets. For example, the number of genomes from archaea in databases that derive from subsurface environments has grown substantially in recent years (Lloyd et al., 2013; Spang et al., 2015; Anantharaman et al., 2016; Baker et al., 2016; Jungbluth et al., 2017; Dombrowski et al., 2018; Tully et al., 2018; Seitz et al., 2019). Before these genomes were available, protein encoding genes expressed by archaea in marine sediments were estimated to be about 1% to 2% of total genes expressed (Orsi et al., 2013). However, a re-analysis of that same data including these new archaeal genomes in the database showed that archaea actually express 25% of the total genes (Orsi, 2018), clearly demonstrating a database bias. Thus, we imagine that as more genomes from archaea are sequenced, their representation in environmental 'omics datasets will continue to increase. The archaea are thus likely to be critically important for subsurface carbon cycling, as predicted by earlier studies from the marine subsurface (Biddle et al., 2006; Lloyd et al., 2013).

2.6.4. OC Degradation potential based on biomolecular data

The advent of inexpensive nucleic acid sequencing technology combined with the availability of user-friendly bioinformatics processing platforms has made it possible for non-specialists in bioinformatics

to substantiate biogeochemical work with 'omics data. 'Omics approaches that have proven valuable in sediment biogeochemistry include single-cell genomics, metagenomics and the related practice of "binning" metagenomic sequences into "metagenome-assembled genomes" (Albertsen et al., 2013), metaproteomics, and metabolomics (for a review see Gutleben et al., 2018). These approaches, especially when used in concert, have enabled insight into the mechanisms of organic matter degradation that would be impossible from purely geochemical techniques. For instance, in deep sediments of the Baltic Sea, it appears that Atribacteria have the potential to act as a keystone species, accessing a wide range of organic carbon using a broad spectrum of extracellular enzymes, and then exporting the resulting free amino acids, possibly supporting the rest of the microbial community (Bird et al., 2019).

Ideally, the integration of multiple molecular approaches will yield information on the rates and potentials of organic matter oxidation by microbial communities. Progress along this path has been made in studies of the nitrogen cycle, for which the genomic pathways of important transformations (N_2 fixation, nitrification, etc.) are well-characterized and the relevant genes are highly conserved (Pachiadaki et al., 2017). This information has been used to construct a "gene-centric" model of the nitrogen cycle in the Arabian Sea oxygen minimum zone, revealing interactions between the cryptic sulfur cycle and the nitrogen cycle which would have been difficult to observe using purely biogeochemical techniques (Reed et al., 2014).

The use of biomolecular data to better understand organic carbon cycling is a nascent area of inquiry that presents researchers with many avenues of research to make sense of the tremendous diversity and complexity of organic structures, and therefore enzymes that catalyze organic matter transformations. One aspect of this complexity is illustrated in Fig. 6, which shows that the phylogenetic diversity of putative secreted organic-degrading enzymes in anoxic marine sediments spans the tree of life (Orsi, 2018). Peptidases provide a more specific example: even though all peptidases catalyze essentially the same reaction, breaking a peptide bond, this can be performed by 268 different structural families of proteins via eight separate catalytic mechanisms (Rawlings et al., 2016). Other categories of enzymes related to organic carbon degradation are similarly diverse, obscuring relationships between enzyme structure and function (Michalska et al., 2015). Because many enzymes relevant to OC degradation can catalyze reactions beyond those including their "preferred" substrates, caution must be used when inferring degradation processes from genomic data or enzyme assays (Steen et al., 2015). It is also possible that novel uncultured clades harbor catalytic enzymes not identifiable by current annotation methods. Therefore, even if particular genes are present in an ecosystem, biomolecular data sets alone might not be sufficient for making specific predictions about the rate, quantity and type of organic carbon reacted in a given system. Lastly, recent experimental work using bioreactor incubations with marine sediments and different marine heterotrophs has directly demonstrated species-to-species differences in the rate, quantity, and type of organic matter oxidized, illustrating that the reactivity of organic carbon is also a function of the microorganisms that are present and active in a given environment (Mahmoudi et al., 2019).

2.6.5. Energetic and power constraints

Absent photosynthesis, all microbial energy is derived from catalyzing redox reactions, nearly all of which are ultimately driven by the degradation of organic carbon. The amount of Gibbs energy available in a number of sedimentary settings has been determined (e.g. Schrum et al., 2009; Wang et al., 2010; LaRowe and Amend, 2014; Teske et al., 2014), as have the metabolic rates in a number of subsurface habitats (Orcutt et al., 2013a). However, the rate at which this energy is used, microbial power utilization, is less well constrained, despite being critical for understanding activity levels and growth state (Hoehler and Jørgensen, 2013; LaRowe and Amend, 2015a). In situ measurements of

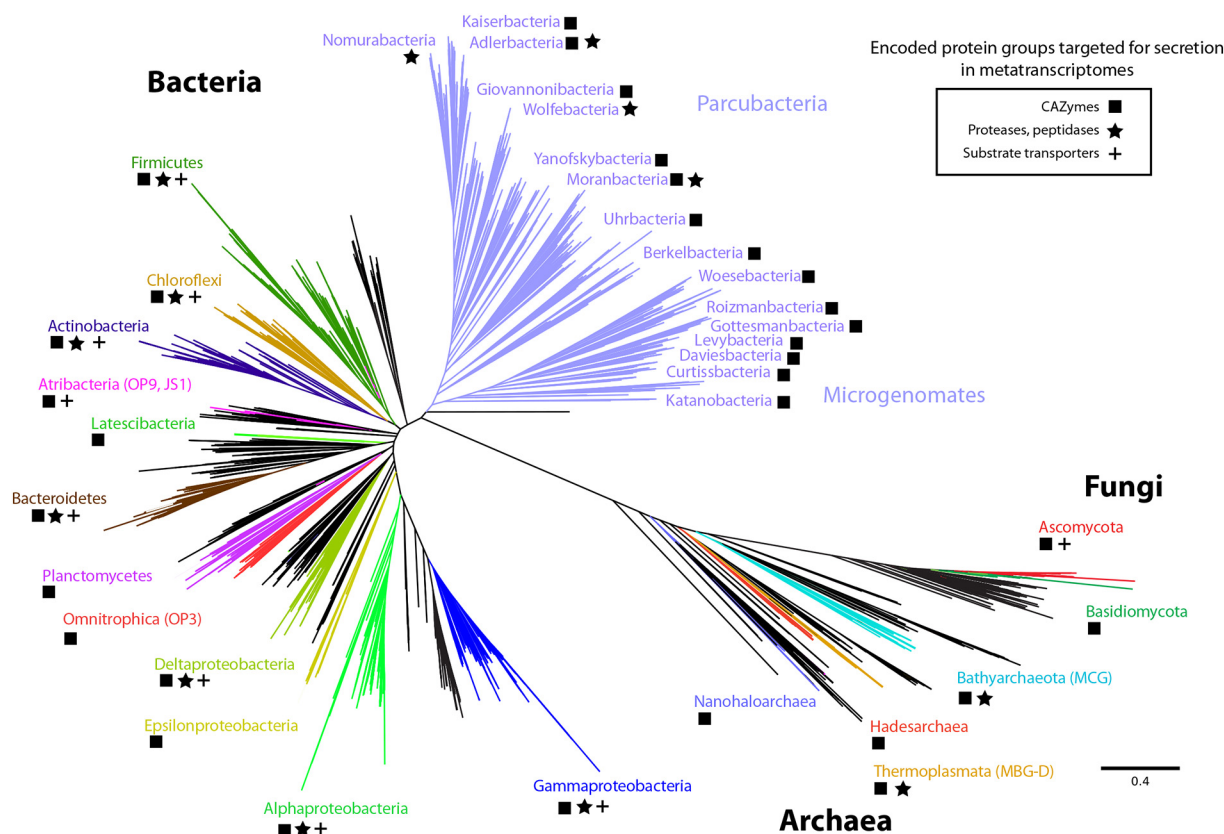


Fig. 6. Phylogenetic tree showing microbial groups containing genes encoding putatively secreted enzymes capable of degrading proteins and carbohydrates in anoxic marine sediments (modified from Orsi et al., 2018). The term CAZymes refers to carbohydrate-active enzymes (Lombard et al., 2013).

microbial power utilization are not yet feasible, but calorimetric measurements carried out in the laboratory have begun to assess low rates of heat production from small numbers of cells taken from the subsurface (Robador et al., 2016). However, a growing number of studies have computed power usage by combining geochemical data with modeling tools (e.g. LaRowe and Amend, 2015a, b; Bradley et al., 2018b). In these studies, data gathered by scientific drilling is used to inform POC degradation models (see Section 4) while the energetics of organic carbon degradation can be constrained by either using the total molecular composition of dead microbial cells (Bradley et al., 2018b) or by relating the nominal oxidation state of organic carbon to its energy content (LaRowe and Van Cappellen, 2011).

The results of these power studies have shown that in low-energy sediments, such as those underlying the South Pacific Gyre (SPG), microbial activity is limited, more or less, to maintaining cellular integrity through biomolecular repair and replacement (Bradley et al., 2018a), a state akin to dormancy (see Section 4.3). Thus, maintenance activities (the sum of activities that do not produce growth) constitute a much greater fraction of total power utilization by microbial communities in habitats where growth is minimal. Indeed, bioenergetic modeling of the SPG sediments suggested that < 0.1% of the power from organic carbon oxidation can be attributed to growth, with maintenance accounting for the rest (Bradley et al., 2019).

Power calculations have also been used to constrain the cell-specific power requirement of microorganisms in sediments. Assuming that all counted cells are involved in organic matter degradation, minimal cell-specific power requirement of microbial cells in SPG sediments have been estimated to be around 1.9×10^{-19} W cell⁻¹ (LaRowe and Amend, 2015b). Assuming this value for the non-growing cells in SPG sediments, the degradation of cells that died in the sediments, necromass, was estimated to provide 2 to 13% of the power used by microbial communities in shallow and relatively young sediments

(< 10,000 years) from SPG (Bradley et al., 2018b). In a similar study, mean cell-specific metabolic rates of functional groups involved in nitrogen cycling in oligotrophic North Pond sediments (on the western flank of the Mid-Atlantic Ridge) showed that an increased power supply in transition zones between oxic and anoxic regimes may be responsible for the revival of organisms from a maintenance state, and even for growth (Zhao et al., 2019).

The lack of quantitative data accurately describing the distribution of various functional groups of microorganisms in marine sediments has impeded the calculation of cell-specific power requirements for particular catabolic groups. This has led to sometimes-untested assumptions about the fraction of a community catalyzing a particular reaction (e.g. that ~10% of the total cells in organic-rich sediments are sulfate reducers (Hoehler and Jørgensen, 2013)). Quantification methods like marker-gene-based qPCR and FISH are useful means to measure the abundances of various functional groups in marine sediments (Schippers and Neretin, 2006; Lever, 2013; Buongiorno et al., 2017), though their application is limited by primer and probe biases.

One of the goals motivating calculation of cell-specific power requirements for different types of functional groups (e.g. Zhao et al., 2019) under a wide range of natural conditions is to determine the limits that the environment imposes on basal power requirements (Hoehler and Jørgensen, 2013). Knowing what the ultimate limits are would greatly facilitate the prediction of the standing stock of biomass of different functional groups in marine sediments on a global scale using geochemical and physical data (e.g. Bowles et al., 2014; Egger et al., 2018) and without the requirement for the collection, analysis and assembly of biological samples on such a vast scale.

2.6.6. Microbial turnover rates

Most early studies focusing on microorganisms in marine sediments were largely conducted in the upper tens of centimeters of sediment,

which are both younger and often more carbon-rich than deeper sediments (see Fig. 2). While some studies measured microbial activities in subsurface sediments as deep as 1.5 mbsf at the Peru Margin (Parkes et al., 1990), these studies generally depended on laboratory incubations to measure metabolic rates, which tend to overestimate the in situ rate.

In recent years, new approaches that are incubation-independent and sensitive to low activities have revealed that a large, active, yet slow-growing microbial community inhabits the deep subsurface. These microbes subsist on low power levels and have been ascribed some of the slowest turnover times ever documented. Amino acid racemization modeling has been used to estimate that some marine sediment microorganisms require hundreds to thousands of years to grow or replace all of their biomass (Lomstein et al., 2012), though these estimates have been adjusted to span years to hundreds of years (Braun et al., 2017). It should be noted that this work was carried out in relatively young, organic-rich sediments, (especially when compared to ancient sediments, e.g. from SPG). A different and perhaps more sensitive method, deuterium incorporation into lipids, has been used to estimate microbial community turnover times from tens to hundreds of years in relatively shallow (< 1 mbsf) subsurface sediments from the Baltic Sea (Wegener et al., 2012), as well as in very deep (up to 2000 mbsf) sediments from offshore Japan (Trembath-Reichert et al., 2017). In all cases, these turnover times are several orders of magnitude slower than the doubling times of laboratory cultures, which are typically on the order of hours to days.

With such slow replication rates, it is unlikely that subsurface sedimentary microorganisms have experienced a sufficient number of generations for specific adaptations to have evolved and spread through the community (Starnawski et al., 2017), calling into question whether these organisms can be considered endemic (see Section 2.6.2). Under this scenario, it is more likely that a community that is able to tolerate this increasing energy limitation is selected for as it is buried deeper in the sediment column (Marshall et al., 2019). This idea is substantiated by evidence that the microbial taxa that dominate deep subsurface sediments are common across a wide range of locations (Petro et al., 2017) and are often found in surficial sediments (Walsh et al., 2015; Starnawski et al., 2017), while the converse is not the case – surficial sediments contain microbial taxa that are not found deeper in the sediment column. In fact, it has recently been shown that at sites as diverse as the Indian Ocean and the Bering Sea, the operational taxonomic units that are most abundant at depth are a subset of the local seafloor community (Kirkpatrick et al., 2019). That is, net replication was not required to produce the microbial population observed in deep sediment, which could instead have been produced by differential mortality rates. These lines of evidence suggest that microbial community members with a slow-metabolizing survival strategy are selected for in the energy-limited deep subsurface environment, though it is unclear that these traits are passed on as in Darwinian selection. As noted above, the importance of energetic efficiency as a selective advantage for long-term microbial survival has been supported by modeling (Bradley et al., 2019) and experimental (Vuillemin et al., 2019) work. Metabolomic and transcriptional evidence has identified some specific mechanisms that likely underlie the slow-metabolizing survival strategy – for example, the use of chemical protectants to stabilize nucleic acids and proteins, and metabolic interdependencies among members of the microbial community (Bird et al., 2019). However, many of these mechanisms – and the impact of these slow metabolizers on the long-term carbon cycle – remain underexplored.

2.7. Sulfurization

Sulfurization is one of the mechanisms thought to be responsible for the preservation of organic carbon in marine sediments (for reviews see Sinninghe Damsté and De Leeuw, 1990; Werne et al., 2004; Amrani, 2014). Sulfurization is the process whereby sulfur atoms ultimately

replace carbon atoms in organic compounds, producing organic sulfur compounds (OSC). OSCs are thought to be less accessible to microbial degradation since S replaces reactive functional groups that tend to be the easiest parts for microorganisms and/or their exoenzymes to access (Kohnen and Sinninghe Damsté, 1989). Sulfur has been found in a wide variety of organic compound types in sediments (Werne et al., 2004), occupying the full range of sulfur oxidation states (−2 to +6) (Amrani, 2014). The preservation potential of OSCs is based on a) observations that the S:C in POC increases with depth in sedimentary systems (Francois, 1987; Eglinton et al., 1994; Hetzel et al., 2009; Amrani, 2014), b) the isotopic composition of organically bound S (Francois, 1987; Mossmann et al., 1991), c) intense sulfurization of POC-rich Cretaceous and Jurassic deposits (van Kaam-Peters et al., 1997; Sinninghe Damsté et al., 1998; Van Kaam-Peters et al., 1998; Kolonic et al., 2002; Kolonic et al., 2005; Böttcher et al., 2006; van Dongen et al., 2006; Hetzel et al., 2009; Raven et al., 2018; Raven et al., 2019) d) observations that many fossil fuels and their precursors have high levels of OSCs (Sinninghe Damsté et al., 1989a; Sinninghe Damsté et al., 1989b) and e) laboratory studies (Krein and Aizenshtat, 1994; Schouten et al., 1994).

Sulfurization is thought to proceed in anoxic environments in which sufficiently high concentrations of POC and H₂S coexist in the absence of metals such as reactive Fe (Gransch and Posthuma, 1974; Werne et al., 2004; Amrani, 2014), although there is some evidence that sulfurization can happen in the presence of reactive iron species since it can lead to the formation of polysulfides which in turn seem to enhance the incorporation of S atoms into organic structures (Kohnen and Sinninghe Damsté, 1989; Werne et al., 2004; Heitmann and Blodau, 2006). Somewhat paradoxically, sulfurization is thought to be an abiotic process, yet the requisite sulfide is attributed to microbial sulfate reduction, leading to the observation that high organic content is sometimes required for its preservation (Quijada et al., 2016).

Sulfurization takes place in a variety of environments on a range of timescales. Although it was traditionally thought to be a relatively slow process taking place in sediments and petroleum reservoirs (Sinninghe Damsté and De Leeuw, 1990; Werne et al., 2004), more recent research has shown that it can take place in hydrothermal systems (Gomez-Saez et al., 2016), in sinking marine particles on a timescale of hours (Raven et al., 2016; Raven et al., 2019), and surface sediments subjected to oscillating redox conditions (Jessen et al., 2017). It has been shown that such rapid sulfurization of organic carbon likely exerted an important feedback on ocean redox geochemistry and climate during the end of a major Cretaceous extinction event (OAE2), ultimately terminating the extreme environmental conditions that caused it (Raven et al., 2019; Hülse et al., 2019).

2.8. Terrestrial studies

Investigations on the cycling of organic carbon in terrestrial settings offer valuable insights to analogous processes within the marine subsurface. Moreover, terrestrial settings are easier to access than deep marine environments, and thus they are more amenable to long term observations and manipulation for field and laboratory-based experiments. Through such studies, the stability of organic carbon has been found to be largely dependent on the complex interplay of the physicochemical (e.g. OC-mineral interaction and aggregation, temperature, moisture, salinity, etc.) and biological (e.g. microbial community composition, nutrient availability, extracellular enzyme production, etc.) properties of the environment rather than on the molecular properties of the OC itself (e.g. elemental composition, presence of functional groups, molecular conformation, etc.). Given that a substantial fraction of POC buried in marine sediments is of terrestrial origin (Burdige, 2007a), understanding the factors governing OC stability in terrestrial ecosystems provides valuable insight into the marine carbon cycle.

Within soils, certain organic compounds such as lignin have

classically been viewed as resistant to biodegradation due to their large and complex molecular structures. However, lignin and lignocellulose compounds are no more likely to persist in soils than other organics given the proper conditions (Marschner et al., 2008; Klotzbücher et al., 2011; Schmidt et al., 2011). This is largely due to the activity of fungi, who play a critical role in the degradation of poorly reactive organic substrates on land (Treseder and Lennon, 2015) and thus may also play a similar role in marine sediments containing soil-derived organics. In fact, new experiments show that fungi living in coastal marine sediments play a role in degrading lignocellulose at the land-sea interface (Ortega-Arbulú et al., 2019).

The ability of microorganisms to degrade soil OC may, at times, also be restricted by nutrient or energy limitations. This is especially pronounced in deep soil layers where turnover times are on the order of thousands to tens of thousands of years (Schmidt et al., 2011). Recent studies suggest that this long turnover time cannot be solely attributed to the chemical structure of OC as there is not always a significant change in composition with depth (e.g. Fontaine et al., 2007). However, amendments with fresh OC to subsoil via root exudates or decomposition (often called priming) has been shown to stimulate increased degradation of the old OC, indicating that the fresh OC may provide a needed energy source to promote the activity of existing microbial degraders (Fontaine et al., 2007; Marschner et al., 2008; Kuzyakov, 2010). This mechanism has also been shown to occur to marine OC as well (Steen et al., 2016). The mechanism behind priming effects, however, is unclear. Common root exudates such as oxalic acid may enhance organic carbon degradation by removing organic carbon from mineral surfaces, thereby increasing its reactivity (Keiluweit et al., 2015). In the case of permafrost, which is also primarily composed of old organic carbon, temperature has been found to be a dominant factor governing its degradation. While frozen, decreased water availability and microbial and enzymatic activity lead to an increase in OC stability. With rising temperatures, these limitations are largely erased and OC degradation rates increase (Schuur et al., 2009; Schmidt et al., 2011) and references therein).

Molecular biological tools have revealed that anoxic freshwater sediments contain similar microbial groups that exist in their marine counterparts (Vuillemin et al., 2018). The presence of the common phylum, Bathyarchaeota, in deep terrestrial sediments that contain high amounts of unreactive plant derived organic matter (e.g. lignocellulose) is thought to be due to their ability to use lignin as an energy source (Yu et al., 2018b). Bathyarchaeota might also be involved in the turnover of terrestrially derived organic matter, such as lignin, in marine sediments in coastal settings where land-derived OC is commonly deposited. Other bacterial “dark matter” groups that are present in marine sediments such as the candidatus groups *Latescibacteria*, *Omnitrophica*, and *Parcubacteria* have been shown to have similar rates of organic carbon turnover in freshwater sediments relative to more well-studied groups such as the *Proteobacteria* (Coskun et al., 2018). Given their transcriptional activities in marine sediments (Orsi, 2018), these groups could also be important for benthic carbon cycling in the ocean.

3. Old, hot and deep organic carbon

Most studies concerning the rates of POC degradation in marine sediments focus on the shallowest, most recently deposited material. However, it is becoming clear that deeply-buried organic carbon is actively being consumed and that fluid circulation in the ocean basement can impact OC reactivity through the modification of organic compounds as well as the composition of sediment pore water.

3.1. Ancient sediments

Throughout Earth's history there have been numerous periods of time when the deposition flux of organic carbon into sediments has been much higher than the present day (Pedersen and Calvert, 1990). A

fraction of this ancient OC persists in modern marine sediments within layers of elevated OC concentrations (Condie et al., 2001; Jenkyns, 2010; Ohkouchi et al., 2015). Although the details vary depending on the time period, there is evidence that large-scale tectonic processes and volcanism are ultimately responsible for the relatively high concentrations of OC deposited in the past (Berry and Wilde, 1978; Condie et al., 2001; Jenkyns, 2010; Trabucho-Alexandre et al., 2012; Ohkouchi et al., 2015). One such example is a section of Cretaceous-aged sediments located in an area of the equatorial Atlantic known as the Demerara Rise, where drill cores from ODP Leg 207 have revealed shales that typically contain between 2 and 15 wt% POC in layers ranging from 56 to 94 m thick (ShipboardScientificParty, 2004). Biogeochemical reaction transport modeling has revealed that deep Demerara organic-rich strata likely host organisms that convert the POC in these shales into CH_4 which is subsequently consumed by anaerobic methane oxidizing microbial consortia using SO_4^{2-} as the oxidant (Arndt et al., 2006). Although data on microbial abundance are not available, it is likely that biomass concentration is higher in POC-rich sediment layers as well as the adjacent sulfate-reducing zone than in the hundreds of meters of sediment separating these layers from the SWI, in which the POC content is far lower. Supporting this notion, cell abundances in core sections 1500 to 2500 mbsf near the Shimokita Peninsula, Japan, are orders of magnitude higher in organic-rich lignite layers than surrounding, organic-poor sediments (Inagaki et al., 2015). Although much of this deeply-buried organic matter looks to have escaped microbial degradation, it seems as if it is actually hosting a very slowly metabolizing community. Observations and diagenetic modeling results show that the organic matter in ancient, deeply buried organic carbon-rich strata still provides a suitable substrate for ongoing microbial respiration (Krumholz et al., 1997; Coolen et al., 2002; Krumholz et al., 2002; Moodley et al., 2005; Arndt et al., 2006; Arndt et al., 2009). Microbial biomass and cell activity have also been shown to peak at redox transition zones, including at oxic-anoxic transition zones in North Pond sediments (Zhao et al., 2019), and in deep (~90 m below the SWI) Peru Margin sediments associated with ODP Leg 201 (site 1229) where there is a convergence of methane and sulfate, the latter of which is diffusing upwards from a brine (Jørgensen et al., 2003).

The rate at which old, deeply buried organic carbon is metabolized by microorganisms in marine sediments becomes extremely slow with depth (Middelburg, 1989), but as these organics are exposed to sufficient pressure and temperature, they can be converted abiotically into petroleum through a process known as catagenesis. Although it is thought that the principle zone of oil formation in organic-bearing sediments occurs from ~ 50 - 160 °C, with pressure playing a lesser role, hydrocarbons and methane can be generated abiotically from complex organic matter at lower temperatures (Tissot and Welte, 1984; Hunt, 1996). As noted by LaRowe et al. (2017a), nearly 35% of the volume of marine sediments are above 60 °C, and even if sediments do not contain enough OC to be commercial sources of petroleum (TOC > 0.5% by weight), the remaining organic carbon in them can still be converted to microbially accessible hydrocarbons through abiotic processes. Some fraction of small-molecular weight hydrocarbons and CH_4 produced abiotically in sedimentary basins could be expelled and migrate to regions that are more conducive for life. Both petroleum and natural gas can migrate hundreds of kilometers from source rocks (Selley, 1998), and there are certainly thermophilic anaerobes capable of oxidizing common products of catagenesis such as alkanes and benzyl-compounds (Teske et al., 2014). In addition, water, CO_2 and H_2S can also be produced in large amounts during the catagenesis of Type II kerogens (Tissot and Welte, 1984), fueling microbial activities with carbon and electron acceptors and donors. Furthermore, it has been estimated that more CH_4 has been produced by methanogens degrading petroleum reservoirs than there is primary CH_4 produced from catagenesis (Milkov, 2011). In total, $1.97\text{--}3.94 \times 10^{13}$ kg of free CH_4 generated from the microbial degradation of petroleum is estimated to exist in sedimentary basins (Milkov, 2011). Taken together, catagenesis could

be fueling microbial communities deep in marine sediments of unknown size.

3.2. Hydrothermal sediments

Sediments that are deposited in regions near spreading centers or volcanic hot spots are subjected to advecting hot fluids that transform organic molecules. The effects are particularly pronounced near continental settings, such as the Guaymas Basin in the Gulf of California (Simoneit and Lonsdale, 1982) and at Middle Valley on the Juan de Fuca Ridge, off the coast of Washington State (Cruse and Seewald, 2006). The transformations that occur have been compared to the formation of petroleum on geologic time scales (Simoneit and Lonsdale, 1982), but with important differences due to the presence of water (Seewald, 2001). In laboratory experiments, sediments heated in the presence of water typically release a large pulse of organic matter into the fluids, followed by a slow decline in overall organic concentrations, presumably due to the formation of degradation products such as CO₂ and CH₄ (Seewald et al., 1990; Lin et al., 2017). Organic acids, acetate in particular, are some of the most abundant degradation products (Eglinton et al., 1987; Fisher, 1987; Lundegard and Kharaka, 1994; Kawamura et al., 1996; Shebl and Surdam, 1996; Seewald, 2001), although reactive amino acids, polysaccharides, and small peptides have also been found to be released from Guaymas Basin sediments by heating (Martens, 1990; Lin et al., 2017). These ancient petroleum-derived substrates are further catalyzed by subsurface microbes (Pearson et al., 2005). Acetate and other low molecular weight organic compounds including formate, lactate, methanol and ethanol have been identified in Guaymas Basin sediments and were found to have a microbial rather than thermal source (Zhuang et al., 2019). Hydrothermal alteration of DOC begins at temperatures as low as 68 °C (Hawkes et al., 2016), suggesting that the hydrothermal influence may be widespread (LaRowe et al., 2017a).

3.3. Ocean basement fluids

Scientific drilling into the seafloor has revealed that the chemical constituents of fluids circulating in the ocean crust basement, such as oxygen, diffuse into overlying sediments (Orcutt et al., 2013b; Wheat et al., 2013) (see Fig. 4). The implications of this for POC degradation in sediments is only just being explored. The oceanic basement is generally considered a net sink for marine OC (Lang et al., 2006; Shah Walter et al., 2018) with both microbiological and abiotic removal mechanisms. In addition to the sediment column, deep-ocean DOC, POC and sedimentary particles enter the crust with oceanic bottom water through exposed outcrops. Most of this fluid flux occurs away from active ridge axes in older, cooler crust and is equivalent to about one fifth of the global riverine flux into the ocean (Johnson and Pruis, 2003).

Recent studies have described the concentration and isotopic composition of DIC and DOC in ocean basement fluids from naturally outflowing fluids from the Dorado Outcrop (McManus et al., 2019) and fluids recovered from IODP CORK observatories on the flank of the Juan de Fuca Ridge (Lin et al., 2019) and North Pond (Shah Walter et al., 2018) - all relatively cool settings away from mid-ocean ridge spreading centers. Although fluid chemistry is variable on the flanks of ridges, ranging from warm, anoxic fluids recovered from near the Juan de Fuca Ridge (Lang et al., 2006; Lin et al., 2019) to oxygenated fluids that resemble bottom seawater at North Pond (Meyer et al., 2016), fluid temperatures are low enough to allow for microbial activity to influence the OC reservoir (McCarthy et al., 2011; Shah Walter et al., 2018; McManus et al., 2019). Heterotrophic activity has been identified in these environments (e.g. Furnes et al., 2001; Lin et al., 2015; Robador et al., 2015; Russell et al., 2016) and DOC concentrations in circulating basement fluids are lower than in overlying bottom water. Compared to 35–45 μM in deep seawater, cool hydrothermal DOC concentrations can

be < 15 μM (Lang et al., 2006; Lin et al., 2012; Shah Walter et al., 2018; Lin et al., 2019). This DOC removal has been attributed to selective oxidation on the basis of a concurrent loss of oxygen, the ¹⁴C content of the remaining organic matter and characterization by NMR and FT-ICR-MS (LaRowe et al., 2017b; Shah Walter et al., 2018; Lin et al., 2019). The DOC removed in the crustal subsurface has a ¹⁴C age of up to 4300 years at North Pond, indicating a long residence time in the open ocean before oxidation by basement microorganisms, underscoring the importance of treating OC degradation as an ecosystem property. Chemoautotrophic DOC, isotopically and molecularly distinct from deep-ocean DOC, has also been identified in cool hydrothermal fluids, although their concentrations are lower than DOC in bottom water, implying a slow production rate (McCarthy et al., 2011; Shah Walter et al., 2018).

Fluids that pass through high temperature black smoker hydrothermal systems have DOC concentrations that are approximately one-third that of deep seawater (Lang et al., 2006). Abiotic removal pathways are dominant in regions of active hydrothermal venting where fluids are intensely heated and can reach temperatures of 400 °C. Thermal decomposition of OC to volatile gases, CO₂, H₂ and CH₄, has been demonstrated experimentally (Siskin and Katritzky, 1991; Seewald, 2001; McCollom and Seewald, 2003b; McCollom and Seewald, 2003a) and is known to be an important loss mechanism that “scrubs” fluids of deep-ocean DOC in high temperature reaction zones (Lang et al., 2006; Hawkes et al., 2015), although DOC sorption to crustal surfaces is also possible (Schwarzenbach et al., 2005). In subsurface regions adjacent to high temperature venting, oxygenated seawater can mix with reduced hydrothermal fluids, creating chemical disequilibria that autotrophic microorganism can use to fuel primary production (McCollom and Shock, 1997). These regions can be hot spots of organic matter production both within the fluids and within the surrounding sediments (Karl et al., 1980; Lang et al., 2006; Wankel et al., 2011). DOC is seemingly produced abiotically at vents hosted on ultramafic rocks, with elevated concentrations compared to overlying bottom water (Lang et al., 2010). Most of this increase is thought to be due to the abiotic formation of small organic acids (Lang et al., 2010; McDermott et al., 2015). A combination of microbial, abiotic and sedimentary sources likely contributes to subsurface DOC pools, which if circulated in the basement from the ridges, could diffuse into overlying sediments, potentially fueling communities.

4. Computational models

A theoretical understanding of the carbon cycle in marine sediments underpins much of the present knowledge and constraints on the burial and transformation of organic carbon in this setting, both in the present day and throughout Earth's history. Numerical models have been used for decades within this framework to quantify how POC drives sediment diagenesis at particular locations (Bernier, 1964; Lerman, 1971; Bernier, 1980; Boudreau, 1997). These models can include the role of particular electron acceptors, secondary redox reactions, sorption and desorption, and microbial dynamics while simultaneously accounting for transport processes such as sedimentation, bioturbation, bioirrigation and the diffusion of solutes. A comprehensive review of reaction transport models and their use in marine sediments is provided in (Arndt et al., 2013), covering the formulation of various reaction and transport networks, their application to natural and engineered systems across a wide range of temporal and spatial scales, and the challenges and limitations of implementing these models. The following sections highlight recent modeling advances with respect to marine sediments and new research directions that could further improve them.

4.1. Representing pools of organic molecules

It is both infeasible and ineffectual to explicitly resolve the true complexity of organic carbon in marine sediments in numerical models.

Rather, owing to its complexity and heterogeneity, OC is usually characterized by its apparent bulk reactivity. Therefore, numerical models for OC transformations in marine sediments must account for changes in both (1) concentration and (2) reactivity of the bulk substrate. If more specific information describing how the proportions of compound types are changing were available, ideally, this would be quantified as well. The concentration of organic carbon is usually defined in absolute terms as the sum of all of the various reactive fractions, and corresponds directly to conventional laboratory measurements of POC. Models of organic carbon reactivity can be broadly divided into two classes: discrete and continuum. Within discrete models, OC is attributed to either a single pool of concentration G (one-G) with a constant first-order degradation rate (Berner, 1980), or divided across a discrete number of pools representing various classes of reactivity (multi-G), where the apparent reactivity of the bulk organic matter is related to the reactivity of each class (Jørgensen, 1978). Continuum models, alternatively, assume a continuous distribution of organic matter compounds across an infinite spectrum of reactivities (Aris, 1968; Ho and Aris, 1987; Boudreau and Ruddick, 1991). The choice of model formulation is generally governed by the overarching research question, the relevant spatial- and timescales, data availability, and mathematical expedience. Since these numerical formulations are abstracted from measurements, it can be challenging to constrain reaction rate constants based on experimental data. Consequently, organic matter reactivity is traditionally constrained by inverse modeling of comprehensive sets of sediment depth profiles.

4.2. Organic molecular data

There are very few models describing the degradation of OC in sediments that use information about the molecular character of organic compounds. This is primarily because there are relatively few reports describing the chemical formulas and structures of marine sedimentary organic compounds in a way that could be parameterized in a model (see Section 2.2). The modeling studies that have used molecular information have only tangentially addressed how this information impacts rates of marine OC degradation. Reaction transport modeling (Niggemann et al., 2007; Freitas et al., 2017) and kinetic modeling studies (Schouten et al., 2010) have explored how different degradation rates of specific biomarker compounds could influence the interpretation of past sea surface temperatures. The abundance and proportion of certain types of amino acids in marine sediments has been used as an index for the degradation state of POC (Dauwe et al., 1999). In another study that evaluated the abundance of particular organic compounds, the Gibbs energy associated with the degradation of organic compounds was used to explain patterns of biomarker degradation in sediments from the Southeast Atlantic ocean (Hernández-Sánchez et al., 2014). The Gibbs energies in this study are estimated based on the oxidation state of the carbon in organic compounds, which is in turn calculated from the stoichiometry of the compounds (see LaRowe and Van Cappellen, 2011). LaRowe and Van Cappellen used this approach to argue that the rate of organic carbon degradation in anoxic marine sediments is retarded by the molecular character of the organic compounds. The rationale for this is based on the idea that the rate of microbial catabolism is proportional to the Gibbs energy of that metabolism: less exergonic reactions are catalyzed more slowly than more exergonic reactions (see Jin and Bethke, 2003; LaRowe et al., 2012).

4.3. Microorganisms in models

Although the actions of microorganisms are implicitly accounted for within models of OC degradation in marine sediments, they are rarely explicitly resolved within the mathematical formulae, i.e. as a separate state variable. This is mostly due to (a) model applications that are focused on geochemistry or biogeochemistry rather than microbiology, and (b) the uncertainties concerning microbial growth, maintenance,

death, and dormancy in marine sediments which must be resolved in order to accurately simulate microbial dynamics (Hoehler and Jørgensen, 2013; Jørgensen and Marshall, 2016; Kempes et al., 2017; Bradley et al., 2018a). Nevertheless, (Boudreau, 1999) was the first to couple microbial processes to organic carbon diagenesis, and derive a mathematical basis between previously observed microbial biomass and organic carbon concentrations in sediments (Bird and Duarte, 1989). Later work incorporated explicit mathematical representation of microbial processes into reactive transport frameworks linking sediment redox gradients and reaction rates to microbial processes (Wirtz, 2003; Thullner et al., 2005), the competition of different microbial groups for a common substrate (Thullner et al., 2007) and to assess the impact of transport processes on transient biomass distributions, anaerobic oxidation of methane rates and methane release fluxes from the sea floor (Dale et al., 2006; Regnier et al., 2011; Puglini et al., 2019). Formulations of microbial processes in sediment models have been developed further to account for the relative importance of growth versus maintenance, and variable physiological states (i.e. dormancy) (Bradley et al., 2018a, 2019).

4.4. Application scale

Despite marine sediments comprising a significant volume of the Earth's surface (LaRowe et al., 2017a), playing a dominant role in the global carbon budget on long time scales (Arndt et al., 2013), and hosting a significant fraction of Earth's living biomass (Kallmeyer et al., 2012), their treatment in global-scale models of the Earth's climate and biogeochemistry may often be little more than a simple closure term for mass conservation (Soetaert et al., 2000; Hülse et al., 2017; Lessin et al., 2018). In case they are explicitly resolved, the interactions between marine sediments and the overlying water column, i.e. benthic-pelagic coupling, are often neglected or crudely implemented in such global-scale models (Soetaert et al., 2000; Gehlen et al., 2006; Munhoven, 2007; Hülse et al., 2017). Even relatively simple reaction-transport models are more typically applied to regional scales (Ruaidj and Van Raaphorst, 1995; Luff and Moll, 2004; Arndt and Regnier, 2007) over idealized global ocean hypsometric transects or provinces (e.g. Soetaert et al., 1996; Thullner et al., 2009; Krumins et al., 2013) and over time-spans of thousands to millions of years (e.g. Arndt et al., 2009; Krumins et al., 2013; Orcutt et al., 2013b). Only a very small number of global scale biogeochemical or Earth System models employ an explicit, vertically resolved, multi-component description of diagenetic dynamics (e.g. Heinze et al., 1999; Munhoven, 2007; Shaffer et al., 2008; Palastanga et al., 2011; Ilyina et al., 2013; Tjiputra et al., 2013; Hülse et al., 2018a). Yet, due to the need to find computationally efficient analytical solutions to the diagenetic equations these descriptions generally rely on simplifying assumptions and/or are restricted to the upper few centimeters of the sediment. However, coupled models can provide important insights into ocean biogeochemical cycling and climate feedbacks. For instance, the recent coupling of a vertically resolved benthic model to the three-dimensional Earth System Model CGENIE (Hülse et al., 2018b) has revealed that organic matter sulfuration reduces the extent and intensity of toxic euxinic conditions, and accelerates climate cooling on a scale that is globally significant during ocean anoxic event recovery (Hülse et al., 2019). Alternatively, large ensemble runs of complex one-dimensional diagenetic models have also been used to derive transfer functions for specific target outputs such as benthic fluxes or benthic methane gas hydrates that have then been applied on a regional and global scale (Gypens et al., 2008; Dale et al., 2015; Capet et al., 2016). In another large-scale effort, (LaRowe et al., 2020) have developed a global-scale model based on the analytical solution of the one-dimensional conservation equation for benthic organic carbon dynamics that reveals the 3-D distribution of marine sediment POC for Quaternary-aged sediments (< 2.6 Ma) as well as rates of its degradation. Bradley et al., n.d (in revision) have built on this model to quantitatively estimate the cell-specific power utilization of

microorganisms transforming POC in global aerobic, sulfogenic and methanogenic sediment horizons.

5. Outlook

Although it is well known that human activity is responsible for a rapid rise of atmospheric CO₂, it is unclear how this disturbance will impact the natural fluxes of carbon among major global reservoirs. In particular, it is still an open question how human-induced climate change will alter the strength of the marine sedimentary carbon sink, and therefore control of atmospheric CO₂. Recent observations and model projections suggest that the impact of climate change on marine POC is likely going to be regionally heterogeneous (Passow and Carlson, 2012), and will include warming waters, disappearing sea ice, increased DIC content, lowered pH and altered fluxes of organic carbon into and through the water column (Levin and Le Bris, 2015; Sweetman et al., 2017), particularly from terrestrial sources (Bauer et al., 2013; Regnier et al., 2013). Each of these factors have potential implications for how organic carbon is delivered to and processed within sediments. Yet, because benthic carbon dynamics are first and foremost controlled by the quantity and quality of OC that settles onto the seafloor, perhaps the most important factor in controlling the response of deep ocean (< 200 m) benthic carbon dynamics to projected environmental change is the biological carbon pump, the process by which organic carbon produced in the euphotic zone is exported into the deep ocean. In addition, coastal benthic carbon cycling, in particular in nearshore depositional environments in the vicinity of large rivers such as, among others, the Arctic shelf, the Amazon shelf or the South China Sea, will also be affected by changes in terrestrial inputs.

The geologic record includes numerous examples of such climate change induced perturbations in the functioning of the biological carbon pump (Arthur et al., 1985; Kohfeld et al., 2005; Ridgwell, 2011; John et al., 2014; Hülse et al., 2019). For instance, abundant black shales in the sedimentary record speak to periods when much or all of the world's bottom ocean waters were devoid of free O₂ (Jenkyns, 2010), likely due to a warmer climate, the paleogeography, enhanced nutrient supply and elevated marine primary productivity that in turn might have been maintained by benthic nutrient cycles perturbed by this bottom water anoxia (Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994). Ultimately, the widespread anoxic and euxinic depositional conditions enhanced organic carbon preservation such that atmospheric CO₂ and, therefore, temperatures decreased and O₂ eventually returned to bottom waters, a process lasting tens to hundreds of thousands of years (Arthur et al., 1988; Kolonic et al., 2005; Jarvis et al., 2011; Hülse et al., 2019; Raven et al., 2019). Though there is a consensus that it is not currently possible to gauge how the biological pump will be altered in the next several decades (Pörtner et al., 2014), a number of studies are hinting at how climate change will impact the flux of carbon to marine sediments.

As a master variable for biogeochemical reactions, temperature will have likely have a significant impact on the reactivity of organic carbon in marine sediments. Ocean warming has already led to the expansion of oxygen minimum zones in the water column over the last 50 years (Schmidtko et al., 2017; Bertagnolli and Stewart, 2018; Breitburg et al., 2018), disrupting the role of bioturbation on POC reactivity. Warmer water seems to select for smaller plankton altering the export flux of POC to the seafloor (Morán et al., 2010) since smaller particles tend to have longer transit times to the seafloor. In high latitudes, the disappearance of sea ice, an increase in the length of the growing season, fundamental changes to regional circulation (e.g. Atlantification) resulting in changing salinity, temperature and nutrient conditions will exert important, yet poorly known impacts on ecosystem structure. In general, temperature changes are known to influence the structure and function of marine microbial communities (Sunagawa et al., 2015), and, in addition to other environmental forces, virus-host relationships (Danovaro et al., 2008; Danovaro et al., 2011), which in turn can alter

patterns of carbon sequestration (Guidi et al., 2016) in sediments. The combination of warming, acidification, eutrophication and human activities such as bottom trawling (Hiddink et al., 2017) and seafloor mining (Orcutt et al., 2020) might lead to ecosystem destruction and/or many areas of the seafloor to become covered in microbial mats (de Bakker et al., 2017; Ford et al., 2018), rather than bioturbated sediments. In addition, lower than normal pH cause some marine bacterioplankton to express genes for maintenance rather than growth (Bunse et al., 2016), thus slowing the flux of C to sediments. Although it is difficult to predict how it will impact the reactivity of organic carbon in sediments, e.g. (Isla and DeMaster, 2018), it is clear that climate change is altering the physiochemical variables that govern microbial behavior. Therefore, attempts to better understand how carbon fluxes will respond to projected climate change and also how carbon fluxes have responded to past extreme climate and carbon cycle perturbations will require an ecosystem approach that includes the role of microorganisms (Cavicchioli et al., 2019).

The information summarized in this contribution supports the emerging view that organic matter reactivity in marine sediments is a complex function of biological, geochemical and physical forces that vary from one part of the seafloor to another. Given the large variety of organic compounds, minerals, organisms, and environmental conditions found in marine sediments, it is undoubtedly true that all of the mechanistic hypotheses described in this review contribute in some way to the long-term preservation of organic carbon, with the relative importance of each changing with both time and space. Going forward, it will be critical that studies examining sedimentary organic carbon account for the whole array of biophysiochemical factors that impact reactivity, thus providing the much needed interdisciplinary data sets required to advance our quantitative understanding and predictive capabilities. Disentangling which mechanism operates under what set of environmental conditions is a complicated task requiring integration of measurements, laboratory experiments, quantitative modeling and an open mind. A community effort will be required to understand not only what determines organic carbon reactivity in marine sediments now, but how this will change in the future. Moreover, integrated approaches considering marine sediments in relation to the terrestrial and water column settings is needed to gain a truly global and comprehensive understanding of the carbon cycle.

Declaration of Competing Interest

The authors of this manuscript declare that they do not have any conflicts of interest that would impact the information in the manuscript or improperly benefit from its publication.

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