Quantifying the degradation of organic matter in marine sediments: A review and synthesis

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ABSTRACT

Quantifying the rates of biogeochemical processes in marine sediments is essential for understanding global element cycles and climate change. Because organic matter degradation is the engine behind benthic dynamics, deciphering the impact that various forces have on this process is central to determining the evolution of the Earth system. Therefore, recent developments in the quantitative modeling of organic matter degradation in marine sediments are critically reviewed. The first part of the review synthesizes the main chemical, biological and physical factors that control organic matter degradation in sediments while the second part provides a general review of the mathematical formulations used to model these processes and the third part evaluates their application over different spatial and temporal scales. Key transport mechanisms in sedimentary environments are summarized and the mathematical formulation of the organic matter degradation rate law is described in detail. The roles of enzyme kinetics, bioenergetics, temperature and biomass growth in particular are highlighted. Alternative model approaches that quantify the degradation rate constant are also critically compared. In the third part of the review, the capability of different model approaches to extrapolate organic matter degradation rates over a broad range of temporal and spatial scales is assessed. In addition, the structure, functions and parameterization of more than 250 published models of organic matter degradation in marine sediments are analyzed. The large range of published model parameters illustrates the complex nature of organic matter dynamics, and, thus, the limited transferability of these parameters from one site to another. Compiled model parameters do not reveal a statistically significant correlation with single environmental characteristics such as water depth, deposition rate or organic matter flux. The lack of a generic framework that allows for model parameters to be constrained in data-poor areas seriously limits the quantification of organic matter degradation on a global scale. Therefore, we explore regional patterns that emerge from the compiled more than 250 organic matter rate constants and critically discuss them in their environmental context. This review provides an interdisciplinary view on organic matter degradation in marine sediments. It contributes to an improved understanding of global patterns in benthic organic matter degradation, and helps identify outstanding questions and future directions in the modeling of organic matter degradation in marine sediments.

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1. Introduction

Biogeochemical processes in marine sediments are essential for understanding the global carbon cycle and climate (e.g. Arthur et al., 1988; Berner and Canfield, 1989; Berner, 1990; Siegenthaler and Sarmiento, 1993; Archer and Maier-Reimer, 1994; Mackenzie, 2004; Ridgwell and Zeebe, 2005; Ridgwell and Hargreaves, 2007). Benthic biogeochemical dynamics can be traced back directly or indirectly to the degradation of organic matter. This process controls, among others, the recycling of inorganic carbon and nutrients, the dissolution of carbonates, the flux of organic carbon to the deep biosphere and, ultimately, the burial of organic carbon in the sedimentary record. As a result, organic matter degradation determines the net CO_2 removal from, and oxygen input to, the atmosphere. Consequently, numerous quantitative models have been developed to describe the fate of organic matter in marine sediments (e.g. Berner, 1978; Jørgensen, 1978; Middelburg, 1989; Boudreau and Ruddick, 1991). The purpose of this communication is to review the main physical, chemical and biological controls on organic matter degradation and analysis how they are incorporated into these models.

Almost all of the organic carbon deposited on the seafloor originates from biological photosynthetic activity in the terrestrial or marine biosphere. The photosynthetic production of this organic matter is represented by:

$$CO_2 + H_2O \overset{light}{\rightarrow} \text{“CH}_2\text{O”} + O_2. \qquad (1)$$

In this greatly simplified reaction, "CH$_2$O" is an idealized chemical formula representing the multitude of different types of organic compounds produced in variable proportions by photosynthetic organisms (e.g. de Leeuw and Largeau, 1993). For instance, plants that require structural support are composed largely of rigid polymers such as cellulose and lignin, complex carbohydrate or phenolic polymers (de Leeuw and Largeau, 1993). In contrast, the bulk of marine biomass, which is single-celled, is comparatively rich in lipids and nitrogenous compounds (Burdige, 2007). Although a large fraction of the newly produced carbon is rapidly recycled (Middelburg et al., 1993), the amount of organic matter that ultimately settles onto the sediment reveals a significant regional variability (e.g. Lutz et al., 2002). On a global scale, only a very small fraction of the organic carbon export production reaches the seafloor (e.g. Holland, 1978; Hedges and Keil, 1995; Berner, 2004). However, despite the differences in original composition and processing, detrital organic matter found in sediments typically contains similar proportions of identifiable compounds: 10–20% carbohydrates, 10% nitrogenous compounds (mostly amino acids) and 5–15% lipids (e.g. Hedges and Oades, 1997; Burdige, 2007). The remaining portion of molecularly uncharacterized organic matter (MU-OM) is a collection of chemically complex compounds that are relatively resistant to biological degradation, collectively known as humic substances (Schnitzer, 1991). The analytical difficulties associated with identifying the specific compounds that make up natural organic matter do not imply that MU-OM is biologically inactive (Burdige, 2007). For instance, kerogens, complex high molecular weight organic compounds that can give rise to fossil fuels, can be degraded by microorganisms when exposed to oxygen (Petsch et al., 2000; Henrichs, 2005; Moodley et al., 2005). The same is true of black carbon (Middelburg et al., 1999; Marschner et al., 2008) and carbon-based nanomaterials such as C_{60} fullerol (Schreiner et al., 2009).

The benthic degradation of organic matter proceeds via multiple enzymatic reactions involving different organisms and oxidants as well as a number of intermediate compounds. Organic matter oxidation is coupled to the sequential utilization of terminal electron acceptors (TEAs), typically in the order of O_2, NO_3^-, Mn(VI), Fe(III) and SO_4^{2-} followed by methanogenesis and/or fermentation. Depending

on the degradation pathway, organic matter is directly oxidized to CO_2, partly oxidized to intermediate compounds or reduced to CH_4. Ultimately only a small fraction of the deposited organic carbon escapes benthic degradation (e.g. Canfield et al., 2005; Middelburg and Meysman, 2007). Yet, compilation of field data reveals that the degradation efficiency is not constant (e.g. Canfield et al., 2005) and that organic carbon burial rates vary significantly in space (e.g. Canfield, 1994; Blair and Aller, 2012) and time (e.g. Arthur et al., 1985). Many different factors have been invoked to explain this spatial and temporal variability. They can be conveniently divided into factors that have an indirect influence on organic matter degradation, for instance deposition rate (e.g. Müller and Suess, 1979; Calvert and Pedersen, 1992; Tromp et al., 1995) or macrobenthic activity (e.g. Aller, 1982) and factors that have a direct effect on the degradation process. The latter include, but are not limited to, organic matter composition (e.g. Westrich and Berner, 1984; Hedges et al., 1988; Cowie et al., 1992; Tegelaar et al., 1989; Dauwe et al., 2001), for instance non-hydrolyzable substrates that resist fermentative breakdown (e.g. Canfield, 1994; Hedges and Keil, 1995), electron acceptor availability (e.g. Demaison and Moore, 1980; Emerson, 1985; Canfield, 1994), benthic community composition (e.g. Canfield, 1994; Arnosti, 2011), 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., 2002; van Nugteren et al., 2009a) or physical protection (e.g. Keil et al., 1994; Mayer, 1994; Kennedy et al., 2002). Consequently, disentangling the dynamic interplay between these factors remains a formidable challenge that hampers the identification of the dominant controlling factor(s) of organic matter degradation. For instance, it is commonly accepted that enhanced preservation of organic matter is related to deposition in anoxic environments (e.g. Demaison and Moore, 1980; Emerson, 1985; Wignall, 1994). Although numerous causes for this pattern have been proposed (e.g. Canfield, 1994; Hedges and Keil, 1995) anoxic degradation rates similar to oxic rates have nevertheless been frequently observed in surface sediments (e.g. Henrichs and Reeburgh, 1987; Lee, 1992; Kristensen and Holmer, 2001) and the identification of a clear relationship between water column anoxia and enhanced organic matter preservation is thus not obvious (e.g. Henrichs and Reeburgh, 1987). In addition, little is known about the controls on organic matter degradability during burial. Observations show that some organic compounds are preferentially degraded and become selectively depleted in organic matter (e.g. Cowie and Hedges, 1994; Wakeham et al., 1997a,b; Lee et al., 2000). As a result, the bulk reactivity of organic matter decreases by more than tenfold for each tenfold increase in age. Microbes living at great depths below the seafloor must therefore rely on highly refractory organic matter to sustain their metabolic needs (e.g. Parkes et al., 1994; Wellsbury et al., 1997; Jørgensen, 2006). Yet, the microorganisms responsible for the hydrolytic degradation of organic macromolecules and the fermentative pathways in anoxic sediments remain to be identified.

Research questions associated with the degradation, preservation or burial of organic matter in marine sediments are thus inherently complex and interdisciplinary. They generally concern the interplay of multiple transport and reaction processes that operate over a wide range of temporal and spatial scales. Reaction–transport models (RTMs) represent powerful tools to deal with this structural and descriptive complexity. Modeling always involves simplification and abstraction. Because modelling always involves simplification and abstraction, the modeling process provides an important platform for interdisciplinary knowledge synthesis, in which criteria of relevance, the meaning of terms and the underlying model concepts can be critically discussed. The resulting RTMs are ideal diagnostic tools for the study of the diagenetic dynamics, as they explicitly represent the coupling and interactions of the processes involved (e.g. Van Cappellen and Wang, 1996; Berg et al., 2003; Jourabchi et al., 2005; Arndt et al., 2006). They can be used, in combination with field or laboratory observations, to test hypotheses, especially with respect to the main controls on organic matter degradability. RTMs allow extracting biogeochemical reaction rates from easily obtainable pore water profiles. In addition, they can complement organic matter degradation rates determined from direct measurements or extracted from the analysis of pore water profiles. For instance, field observations primarily target shallow sediment depths and fast-decaying materials, although it is well known that the most refractory compounds may degrade over much longer distances on geological timescales (Middelburg, 1989). RTMs offer a means to bridge such a large spectrum of spatial and temporal scales and to reconstruct the sediment history in the context of a system that evolves over years to thousands or millions of years as well as over centimeters to tens of meters or kilometers (e.g. Zabel and Schulz, 2001; Riedinger et al., 2006; Arndt et al., 2009; Dale et al., 2009).

The lack of mechanistic understanding of organic matter degradation is reflected in the mathematical formulation used to represent this process in RTMs. Generally, existing organic matter degradation models do not reflect the complex interplay of factors that may control organic matter degradation on different scales. As a consequence, model parameters derived to fit observed pore water and sediment profiles implicitly account for the neglected factors. The implicit nature of model parameters thus complicates the transferability and predictive capability of existing approaches in data poor areas. Yet, the predictive capability of organic matter degradation models plays a key role for the evaluation of deep carbon cycling, the estimation of substrate fluxes to the deep biosphere (e.g. Arndt et al., 2006; Røy et al., 2012), the hindcasting and forecasting of the sediment's diagenetic history (e.g. Dale et al., 2008a; Arndt et al., 2009; Reed et al., 2011; Mogollon et al., 2012; Wehrmann et al., 2013), the prediction of methane gas hydrate inventories (e.g. Marquardt et al., 2010; Gu et al., 2011; Wadham et al., 2012) and oil reservoirs (e.g. Head et al., 2006) or the extrapolation to regional and global scales (e.g. Archer et al., 2002; Thullner et al., 2009; Krumins et al., 2013). The need for a predictive algorithm for model parameterization has led to the emergence of different global relationships that allow relating model parameters to single, readily available characteristics of the depositional environment, such as deposition rate (e.g. Toth and Lerman, 1977; Tromp et al., 1995) or organic carbon flux (Murray and Kuivila, 1990; Emerson, 1985). Nevertheless, these relationships are generally based on very limited data sets and their applicability to the global scale, as well as to the geological timescale remains uncertain. Incorporating the complex interplay of the different factors that may control organic matter degradation and proposing a consistent, predictive algorithm for parameterizing their equations that can be applied to the entire spectrum of boundary conditions encountered at the seafloor represents a major challenge for future generations of RTMs. Yet, the rapidly expanding geochemical and microbiological data sets collected in the framework of global monitoring programs, such as the Ocean Drilling Program (ODP), as well as the need for a better quantification of the past, present and future benthic carbon turnover in the Earth system calls for the prompt development of RTMs.

This review synthesizes the research conducted over the past decades in the field of organic matter degradation kinetics, with a strong emphasis on the modeling process. It focuses on marine sediments, although much of the discussion is also relevant to other aquatic systems. First, the main controls on organic matter degradation are identified. Next, we analyze the structure, forcings and parameterization of alternative organic matter degradation models and critically assess their capability to extrapolate organic matter degradation rates over a broad range of temporal and spatial scales. Finally, on the basis of 250 published modeling applications covering the entire seafloor, we evaluate the robustness of proposed global-scale relationships and identify trends between organic matter degradability and the environmental characteristics of ocean provinces.

2. Controls on organic matter degradation

The susceptibility of organic matter towards microbial degradation is defined here as its "degradability" and the terms "refractory" and "labile" are used to describe relative differences in degradability. However, it is important to note that the degradability is "*not an inherent, or absolute, property of the organic matter itself, but results from the interaction between the organic matter and its environment*" (Mayer, 1995). The benthic degradation of organic matter is thus a true reaction–transport problem that involves chemical, biological and physical processes. Fig. 1 summarizes the interconnectedness of factors that affect organic matter degradation in marine sediments, which is, first and foremost, donor controlled. In other words, the benthic consumers have little or no effect on the external supply of organic matter at the sediment water interface. Yet, the microbial community exerts an important influence on the degradability of organic matter. The degradation of the deposited material is thermodynamically and/or kinetically controlled by the different abilities of the physiological groups that compete for the common substrate. Transport processes, such as bioturbation, bioirrigation and sedimentation accumulation control the supply of substrates and terminal electron donors and, therefore, exert an additional indirect influence on the degradation process. The relative significance of these controls and the degree to which they influence each other strongly depend on the characteristics of the depositional setting and the timescale of interest. The different processes that exert an influence on organic matter degradation are discussed in the following subsections, starting with those that act most directly.

2.1. Organic matter flux, donor control

The rate of organic matter degradation in marine sediments is donor controlled and, thus, closely linked to its production, transport and alteration in the ocean (Fig. 2). Organic matter that settles in the ocean is generally derived from an initial mixture of compounds that are largely photosynthetically produced in the euphotic layer of the ocean. However, chemoautotrophy and export from terrestrial sources or near shore coastal areas also contribute to the organic matter depositional flux (e.g. Schlesinger and Melack, 1981; Ittekkot, 1988; Meybeck, 1993; Hedges and Keil, 1995; Keil, 2011; Middelburg, 2011). The flux of organic matter is mainly sustained by the gravitational settling of organic particles through the water column. Intense water circulation, transport of organic particles laterally across the shelf and down the slopes, turbidites and strong bottom water currents can also supply aged sedimentary organic matter through a succession of erosion/redeposition cycles (e.g. Jahnke et al., 1990; Ohkouchi et al., 2002; Mollenhauer et al., 2005; Mollenhauer and Eglinton, 2007; Kusch et al., 2010). In the intermediate and deep layers of the ocean, a large fraction of the sinking particles are fragmented into smaller, non-sinking particles or consumed by microbes, zooplankton and nekton. The continuous alteration of organic matter during transport leads to a consumption of the most labile organic matter components and, thus, to increasingly refractory chemical structures of the sinking material (Wakeham et al., 1997a,b; Dauwe et al., 1999). The export efficiency of the organic matter must therefore play a key role in the degradability of sedimentary organic matter. A higher vertical transport rate increases the deposition flux and influences its quality, since it reduces the degree of pelagic degradation and thus the aging of organic matter in the water column.

A compilation of deep sediment trap data reveals large regional variations in export efficiency (Fig. 3, Lutz et al., 2002; Henson et al., 2012; Wilson et al., 2012). For instance, the fraction of the organic carbon export flux that reaches depths greater than 1.5 km varies between 0.28 and 30% (5.7% average) of the export production (Fig. 3, Lutz et al., 2002). The efficiency of terrestrial organic matter export from land is even more difficult to predict, given variable controls on residence
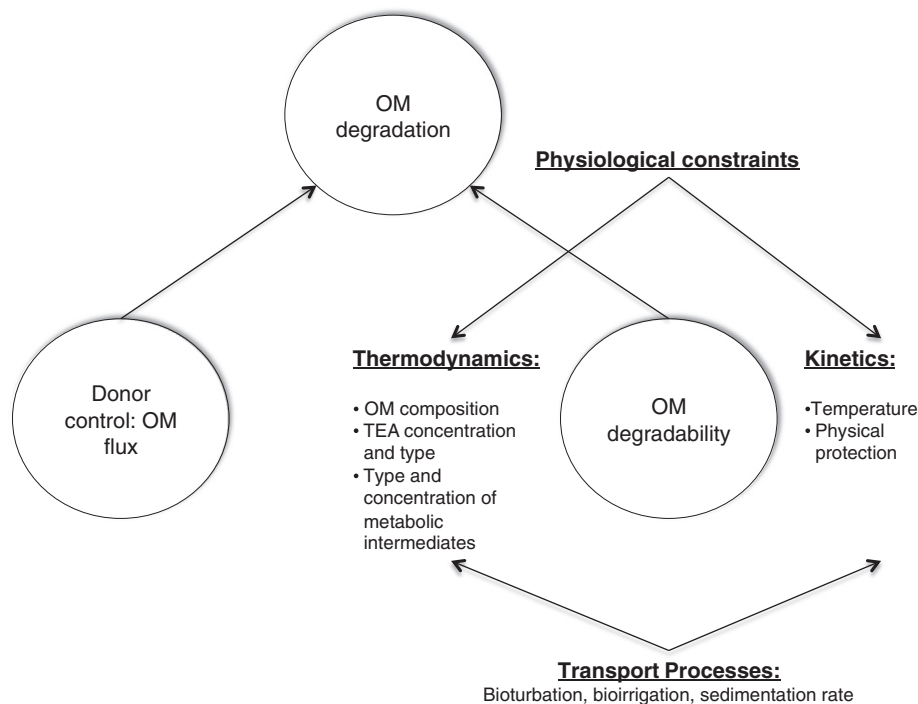
Fig. 1. Schematic illustration of the main controls of organic matter degradation in marine sediments. The degradation of organic matter (*OM*) in marine sediments is sustained by the flux of organic matter to the sediment–water interface (see Sections 2.1 and 2.2) and, therefore, donor controlled. During burial, the consumption of this flux is determined by the degradability of organic matter in the sediment. It is thus thermodynamically (see Sections 2.2, 2.3, 2.4) and/or kinetically (see Sections 2.5, 2.6) controlled through the different abilities of the physiological groups (see Section 2.3) that compete for the common substrate. In addition, transport processes, such as bioturbation, bioirrigation and sedimentation rate (see Sections 2.7, 2.8) exert an indirect control on the degradation reaction mainly through their influence on organic matter, terminal electron acceptor (TEA) and metabolic intermediate concentrations.
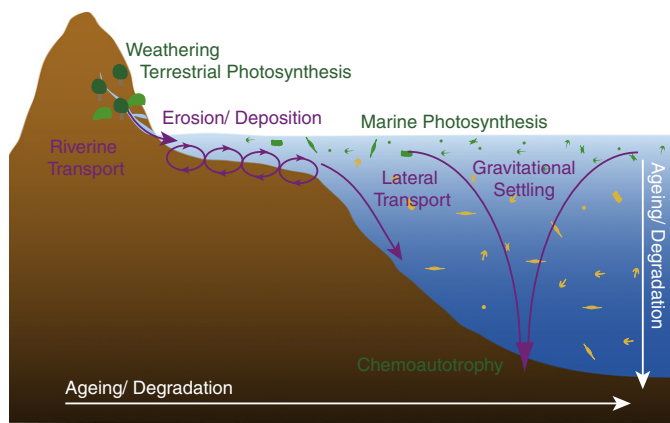
Fig. 2. Sources (green), transport (purple) and transformation (white) processes that determine the supply of organic matter to marine sediments.

times in soils, followed by widely varying degrees of alteration during transport through the riverine/estuarine/deltaic system and across the continental shelf. Capturing this variability represents a major challenge for global biogeochemical and Earth system models. These models generally apply power relationships between particulate organic carbon flux and depth. However, such relationships are derived from datasets of limited geographic and depth range coverage (e.g. Martin et al., 1987, Fig. 3). Thus, when extrapolated to the global scale, the regional variability in organic matter fluxes calls the robustness of the model predictions into question (e.g. Berelson, 2001; Lutz et al., 2002; Boyd and Trull, 2007; Buesseler et al., 2007). The incomplete understanding of particle transport efficiency between the surface ocean and sediment is among the most critical factors limiting the development of improved organic carbon export flux estimates (Buesseler et al., 2007).

The depth attenuation of carbon fluxes in the ocean interior is very critical to accurately estimating the transfer of anthropogenic carbon by biological pump into the deep ocean (Yamanaka and Tajika, 1996).
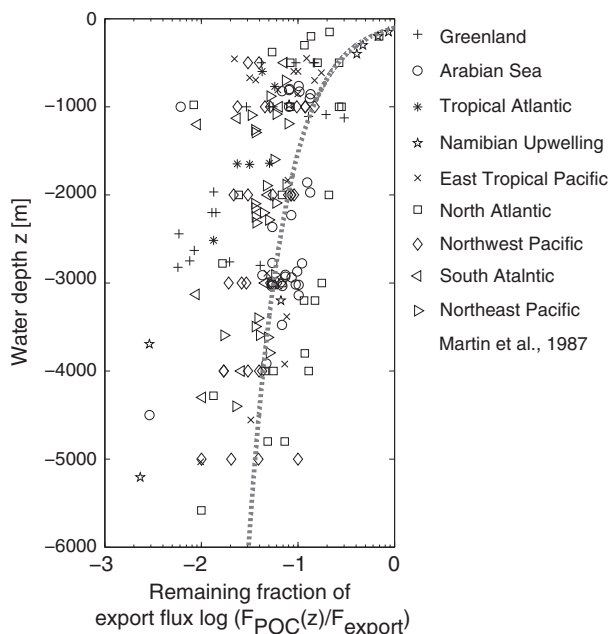

Fig. 3. Observed regional depth-distribution of particulate organic carbon fluxes, F_{POC}, normalized to the export production fluxes, F_{export}. Data redrawn from Lutz et al. (2002). The dashed line indicates the original power law relationship proposed by Martin et al. (1987) ($b = -0.858$, $z_o = 105$ m).

Although differences in export efficiencies are most likely not attributed to a single process, many authors have related the strong variability in organic carbon fluxes to variations in sinking rates (e.g. Armstrong et al., 2002; Francois et al., 2002; Klaas and Archer, 2002; Lutz et al., 2002). In general, particulate organic matter is heavy enough to sink through the water column. Nevertheless, the settling velocity of small particulate organic matter can be exceedingly slow (0.1–5.0 m/d) and only the largest particles (diameter >100 μm) contribute significantly to the organic matter flux to the sediment. Ballast materials, such as biogenic opal, biogenic calcium carbonate and lithogenic material from aerosols and riverine inputs usually increase particle sizes and densities and thus accelerate vertical transport. Particle aggregation or biological glues, such as transparent exopolymers (TEP) exert the same effect and reduce the residence time of organic matter in the water column (e.g. Alldredge and Jackson, 1995; Francois et al., 2002; Klaas and Archer, 2002; Passow, 2004). In addition, packaging and protection during settling may reduce pelagic degradation (Keil et al., 1994; Mayer, 1999) and favor deposition.

The role of ballasting on export efficiencies remains controversial. Francois et al. (2002), Berelson (2002), and Armstrong et al. (2002) argue that the ballasting effect of carbonate minerals is the main control on the transfer efficiency of aggregates. Similarly, Klaas and Archer (2002) conclude on the basis of a compilation of sediment trap data from 52 locations that most of the organic carbon rain in the deep sea is carried by calcium carbonate particles, because they are denser than opal and more abundant than terrigenous material. Yet, data from different oceanic regions did not confirm a dominant influence of ballast materials on the efficiency of the carbon pump (e.g. Lam and Bishop, 2007; Trull et al., 2008; Riley et al., 2012; Wilson et al., 2012), thereby indicating that differences in organic matter degradability may exert a first order control on the efficiency of the biological carbon pump. Antia et al. (2001) attribute the variability in export efficiency to the seasonality in export production rather than to a ballasting effect. Furthermore, the global compilation of organic matter fluxes by Lutz et al. (2002) and the observations by Buesseler et al. (2008) show that the export efficiency can be higher in diatom dominated systems. Buesseler et al. (2008) also point to the important role of the diel migration of zooplankton for carbon export. Zooplankton feed at the surface at night and subsequently carry processed organic carbon to depth where it is either excreted or released as fecal matter. A number of recent studies have confirmed the role of ecosystem structure as a master variable in determining the efficiency of the biological pump (e.g. Lam et al., 2011; Henson et al., 2012; Mayor et al., 2012). They reveal that diatom dominated, high-latitude ecosystems, which are often characterized by strong seasonal blooms export a large fraction of their primary production from the euphotic zone. However, only a very small fraction of this export flux reaches the seafloor, implying that the organic matter exported by these systems is relatively labile and is prone to degradation in the upper mesopelagic zone. Low-latitude ecosystems, in turn, are characterized by more complex ecosystem structures and an efficient microbial loop that recycles most of the produced biogenic material in the euphotic zone. However, the small fraction of primary production that is finally exported is often pre-processed, tightly packed in fecal pellets or protected by calcareous shells or mineral phases and, therefore, less susceptible to microbial degradation at mesopelagic depths. Evidence for a high variability in export efficiency is thus not in dispute, but the exact controlling mechanisms and the far-reaching implications for organic matter deposition and degradation in marine sediments remain poorly understood.

2.2. Organic matter composition

Sedimentary organic matter contains a vast range of structural motifs and functional groups, representing a range of degradabilities
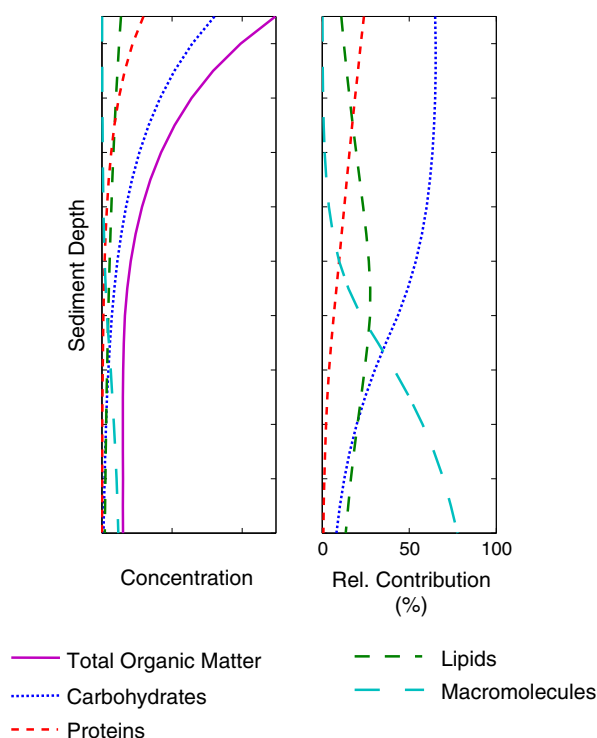
Fig. 4. Characteristic depth profiles of organic matter and organic matter compounds. The different organic matter compounds are characterized by different degradabilities. Therefore, the depths profiles of their relative contribution to the total organic matter pool reveal a complex pattern with a dominance of refractory compounds at depth.

(e.g. de Leeuw and Largeau, 1993). Capturing and defining this complexity is beyond the capacity of current sedimentary modeling, with the largest impediments being the inability to identify all chemical compounds and the very limited availability of comprehensive compound-specific kinetic data (e.g. Sun et al., 1993; Harvey and Macko, 1997; Sun et al., 2002); issues even as basic as the relative degradation rates of, for example, membrane glycolipids relative to phospholipids remain the subject of much debate (Schouten et al., 2010). Nonetheless, some general distinctions do exist and can form a guide to interpreting overall sedimentary organic matter degradability in different settings.

At the most fundamental level, it is recognized that certain biopolymers (e.g. proteins and nucleic acids) are particularly labile under a wide range of conditions, owing to a combination of relatively weak bonds between monomers (e.g. peptide bonds) or the particularly important nutrient requirements (e.g. phosphates and nitrogen) that such compounds provide. At the opposite end of the degradability spectrum are refractory biomacromolecules (e.g. algaenan and cutan) typically comprised of aliphatic moieties and cross-linked by relatively non-reactive ether bonds (Tegelaar et al., 1989; de Leeuw and Largeau, 1993). Between these two end-members lie diverse compounds: carbohydrates, including cellulose, are relatively labile, whereas others, including aliphatic ester-linked macromolecules such as cutin and suberin and the highly aromatic lignin, tend to be less degradable, with relatively few organisms having developed the specific enzymatic capacity to facilitate degradation (e.g. white rot fungi; e.g. Hattakka, 1994). Two significant consequences arise from this chemical heterogeneity. First, organic matter from different organisms is characterized by different degrees of chemical reactivity (e.g. Tegelaar et al., 1989). Although the significance of this in terms of driving overall organic matter preservation/degradation remains disputed (see below; also de Leeuw et al., 2006; Gupta et al., 2007) it does appear to be at least responsible for greater degradability of most algal biomass relative to terrestrial biomass and for the selective

preservation of some algal groups relative to others in the fossil record (e.g. Goth et al., 1988). Second, the selective preservation of refractory organic matter at the expense of labile component is perhaps one of the main reasons that organic matter becomes less degradable with burial depth.

One of the most important guideposts to the relative degradability of organic matter in different depositional contexts is the understanding that terrestrial organic matter is relatively more refractory than algal organic matter (e.g. Hedges et al., 2000), ostensibly due to a chemical composition dominated by moderately resistant (e.g. cellulose, lignin and cutin) or highly resistant (e.g. cutan) biopolymers (de Leeuw and Largeau, 1993). Alternatively, the refractory nature of terrestrial organic matter could reflect the pre-aging that it undergoes during burial in soils and subsequent transport, i.e. terrestrial organic matter in aquatic sediments that has already been extensively degraded compared to the relatively 'fresher' aquatic organic matter. Both mechanisms implicitly assume that the lower degradability of terrestrial organic matter is fundamentally due to its chemical composition. However, recent work suggests a more complex relationship between chemical structure and degradability (Bianchi, 2011). Huguet et al. (2008) compared the oxidative loss of different compound classes during sediment resuspension and redeposition cycles in turbidites in the Madeira Abyssal Plain. Branched glycerol dialkyl glycerol tetraether lipids (GDGTs) of predominantly terrestrial origin and isoprenoidal GDGTs of predominantly marine origin were both highly degraded but the latters decrease was almost an order of magnitude greater. A molecular structural explanation seems unlikely because their structures are almost identical, and instead the authors suggested that the lower degradability of the terrestrial-derived compounds was due to protection via associations with either minerals or other organic matter (i.e. encapsulation, see Section 2.6 "Physical protection").

Another aspect of the chemical composition of sedimentary organic matter that appears to directly impact its degradability is its continual alteration during transport, burial and diagenesis, all of which appear to impart decreasing degradability on the residual organic matter (Fig. 4). This may appear intuitive — the less degradable organic matter persists the longest, such that continual aerobic or anaerobic degradation will result in an increasingly refractory chemical structure (Fig. 4). In fact, such reasoning is the basis of the selective preservation model for organic matter preservation (Tegelaar et al., 1989), with sedimentary organic matter thought to primarily derive from refractory biomolecules. However, the overall importance of selective preservation remains the subject of debate (e.g. de Leeuw et al., 2006; Gupta et al., 2007), and other mechanisms, such as physical protection, temperature effects, or physiological constraints also contribute to decreasing organic matter degradability (see following sections) and may become proportionally more important with depth. Alternatively or additionally, formation of geopolymers (e.g. humification or condensation–polymerisation, forming macromolecules; Tissot and Welte, 1984) with depth (Fig. 4) likely also contributes to decreased organic matter degradability. The mechanisms by which geopolymerisation occurs remain the subject of debate but there is clear evidence for both oxidative polymerization (e.g. Gatellier et al., 1993; Riboulleau et al., 2001; Versteegh et al., 2004; Gupta et al., 2005, 2006, 2007) and sulfidization (Sinninghe Damsté et al., 1989; Sinninghe Damsté and de Leeuw, 1990) in different settings. Such reactions can render putatively labile compounds resistant to degradation, with sulfidization having been shown to facilitate the preservation of even carbohydrates (van Kaam-Peters et al., 1998; Zonneveld et al., 2010).

2.3. Microbiology

Organic matter degradation processes result from the combined effort of billions of individual microorganisms. All these microbial cells
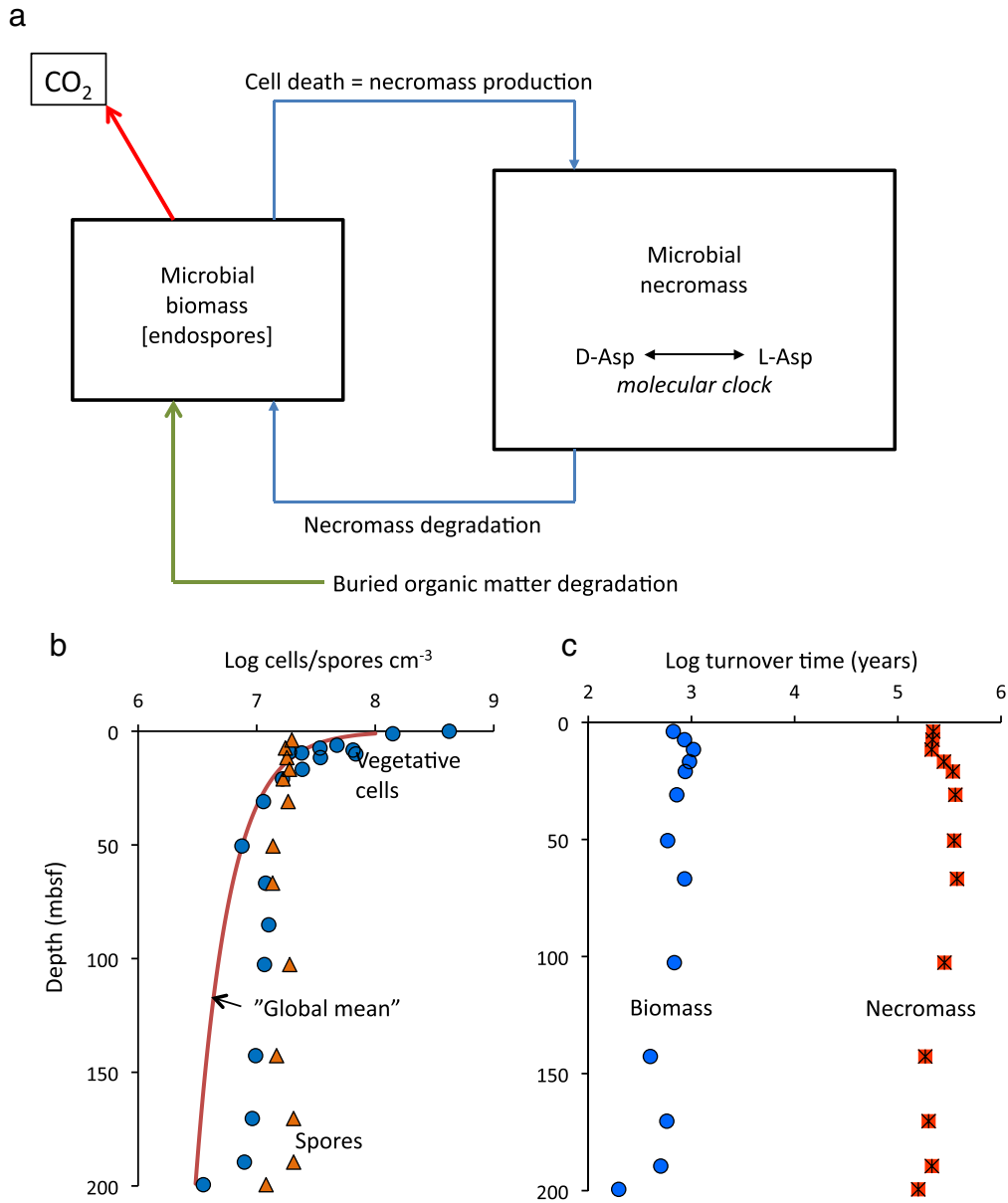
Fig. 5. A. Model of the turnover of microbial biomass and necromass (dead microbial biomass). The model is based on the built-in molecular clock of detrital amino acids driven by the slow inter-conversion (racemization) between the two stereo-isomers (L- and D-form). The model is here applied to data from a 200 m deep sediment core obtained from the Peru Trench at 5 km water depth during the IODP Expedition 201 (D'Hondt et al., 2004). B. The total number of DNA-stained cells (blue circles) is shown in comparison to the global mean curve (red) compiled by Parkes et al. (2000) and later amended. The number of bacterial endospores (orange triangles) was > 10-fold lower than the vegetative cell numbers near the sediment surface but exceeded the vegetative cells in the deeper sediment column. C. The turnover time of the total microbial necromass (red stars) calculated by the D:L racemization model was 10^5–10^6 years. The living microbial biomass (blue circles) turned over > 100-fold faster with a calculated turnover time of 200–1000 years. (Redrawn from Lomstein et al. (2012)).

have highly diverse metabolic potentials and requirements and are continuously involved in synergetic or competitive interactions that determine the outcome of their activities. The observed depth-profiles of their main substrates and products are the net result of the complex networks of these metabolic interactions. Natural organic matter deposited on the seafloor comprises a complex mixture of high molecular weight compounds that cannot be taken up directly by the cells. Therefore, extracellular hydrolysis is required to produce smaller, monomeric organic molecules such as sugars and amino acids. Aerobic organisms have the ability to mineralize organic matter completely to carbon dioxide via the tricarboxylic acid cycle. In contrast, in anoxic environments organic matter is mineralized in an anaerobic food chain. The initial breakdown occurs through extracellular and membrane-bound hydrolytic enzymes produced by certain microorganisms. The hydrolytic products are then consumed by fermenting and acetogenic bacteria

that produce compounds such as acetate and hydrogen. The terminal step in this anaerobic food chain involves the utilization of these latter compounds by microorganisms that reduce sulfate and oxidized manganese/iron or produce methane.

Although the main mineralization processes involved in the terminal degradation of organic matter are well described and their stoichiometry is well constrained, it remains highly uncertain which microorganisms are responsible for the upstream processes in the microbial food web of anoxic marine sediments, namely the hydrolytic degradation of macromolecules and the fermentative pathways. The large gaps in our knowledge of sediment microbiology have become clear from observations that archaea with no cultivated relatives and therefore of completely unknown physiology are widespread and perhaps even predominant in subsurface sediments (Biddle et al., 2006; Lipp et al., 2008; Schippers et al., 2008). This great diversity

of unknown archaea must play important roles in the complex degradation of organic matter, roles that affect the pathways and the kinetics of degradation. Yet, the overall net processes remain the same, as we know from experimental process studies, detailed sediment chemistry, and RTMs.

The main depth sequence of mineralization processes using different terminal electron acceptors follows roughly their increasing Gibbs energy yields (see Section 2.4 Thermodynamics). However, the commonly observed depth sequence also generally reflects physiological constraints of the microorganisms that use the different terminal electron acceptors in their respiratory energy metabolism. Aerobic respiration is confined to the oxic zone, which in many organic-rich shelf sediments is only a few mm to a cm deep. The bacterial community in this thin oxic skin of the seabed can account for more than half of the total organic carbon mineralization in the entire sediment column (e.g. Jørgensen and Revsbech, 1989). Their disproportionate importance stems from their relatively high cellular activity. These communities typically have a density of 10^9–10^{10} cells cm^{-3} and a respiration rate of 1–10 μmol O_2 cm^{-3} d^{-1} (Rasmussen and Jørgensen, 1992). This yields a mean respiration rate of 1 fmol O_2 cell^{-1} d^{-1} (1 fmol = 10^{-15} mol), which is 100-fold lower than for aerobic plankton bacteria under optimal substrate conditions (e.g. Warkentin et al., 2007), yet 10 to 100 times higher than the mean respiration rate of sulfate reducing bacteria a few cm deeper in the sediment (Sahm et al., 1999) and about 1000 times higher than aerobic microbes living at 10 m below the seafloor (Røy et al., 2012). Although aerobic respiration is confined to the thin surface layer, many aerobes are able to live anaerobically and subsist in the anoxic sediment, ready to respire with oxygen as soon as this becomes available through bioirrigation or bioturbation by benthic macrofauna. At the other extreme, subsurface bacterial respiration is extremely low and oxygen penetration may reach tens of meters into the sediment in central ocean regions with low plankton productivity and very low deposition rates, such as the North and South Pacific Gyres (Fischer et al., 2009; Røy et al., 2012). Many bacteria are strict anaerobes and are confined to the reducing subsurface sediment with low redox potential. The zonation of mineralization processes may thus be kinetically or energetically controlled through the different abilities of the physiological groups to compete for common substrates. A clear example of energetic control is the regulation by sulfate reducing bacteria or methanogenic archaea of the ambient H_2 at a minimum concentration that still enables these organisms to maintain the required energy yield of ≤ -10 to -20 kJ mol^{-1} (Hoehler et al., 2001). The energetic minimum concentration that can be maintained by the sulfate reducers is below the level required for the archaea to conserve energy through methane formation from H_2 and CO_2, which is the predominant methanogenic pathway in marine sediments. Acetate is another common energy substrate for both sulfate reduction and methanogenesis. Interestingly, measured pore water concentrations of acetate in marine sediments are typically on the order of 10^{-5} M, even in the sulfate zone. Such concentrations could potentially support both sulfate reduction and methanogenesis. Yet, sulfate reduction is completely dominant and net methanogenesis is not detected. The competitive and potential syntrophic relationships between these two distinct groups of microorganisms may therefore be more complex than has so far been recognized. For example, acetoclastic methanogens growing in syntrophy with sulfate reducers may shift from producing methane from acetate to feeding the sulfate reducers with H_2 (Finke et al., 2007).

In addition, processes that disturb the commonly observed vertical zonation of marine sediments may further increase the complexity of sedimentary biogeochemical dynamics. The addition of labile organic matter to deeper sediment layers may stimulate the degradation of more refractory material (e.g. Van Nugteren et al., 2009a). Different mechanisms have been proposed to explain this priming effect (e.g. Guenet et al., 2010). The availability of labile organic matter may stimulate the production of extracellular enzymes that concomitantly degrade the more refractory organic matter into simpler intermediate metabolites. The resulting intermediate metabolites can perhaps not be utilized by the enzyme-producing organisms, but are degraded by another population. Alternatively, a part of the labile organic matter degradation products may provide energy to the second population that in turn produces extracellular enzymes to degrade the refractory organic matter. However, the priming effect may also cause a homogenous community to degrade refractory organic matter when labile organic matter is available as an energy source. These three hypotheses are not exclusive, and their relative importance is currently unknown. Moreover, terminal electron acceptors may also bypass the traditional redox-sequence. For instance, although the reduction of solid-phase Mn(IV) or Fe(III) predominates in the intermediate "suboxic" zone, unreactive Fe(III) species in particular may persist for years to many thousands of years after burial into sulfidic sediment (Canfield et al., 1992). The continued reactivity of this Fe(III) may not be obvious from the pore water chemistry in the sulfate reduction zone. However, a drop in sulfide concentration deep down in the methane zone, which is often observed in continental shelf and slope sediments, reveals the continued iron reactivity. Although the reaction rate of this iron is extremely low, so is the organic carbon degradation rate at that depth. The oxidative reaction of Fe(III) with sulfide may even drive a cryptic sulfur cycle by which sulfate is produced and becomes available to the large populations of sulfate reducing bacteria that are observed in deep methanogenic sediments (Holmkvist et al., 2011).

Similar to organic matter degradation rates, the global depth distribution of microbial cell numbers in marine sediments decreases with sediment depth according to a power law (Bacteria per cm^3 = $6 \cdot 10^7 \cdot z^{-0.57}$, where z is the sediment depth in meters, Parkes et al. (2000)). However, the bacterial numbers drop off less steeply with depth and age than do the organic carbon degradation rates. Consequently, the mean carbon and energy flux per cell and time is the highest near the sediment surface and drops off with depth and age in the sediment. This has been confirmed for sulfate reducers and sulfate reduction in a continuous depth profile of a coastal sediment (Holmkvist et al., 2011) and it is evident from the extremely low rates of cellular metabolism in deep subsurface sediments (e.g. Arndt et al., 2006; D'Hondt et al., 2009; Røy et al., 2012). The observed mean rates in the deep biosphere are many orders of magnitude below the metabolism known from pure cultures, even orders of magnitude below what is considered to be maintenance metabolism in pure cultures. As a consequence of their extremely low metabolic rates, potential turnover times of deep subsurface microorganisms are hundreds to thousands of years (Jørgensen, 2011). In fact, it is not even known that they divide at such generation times since they may partly be turning over cell biomass without cell division. Consequently, living microbial biomass constitutes only a minor fraction of the total organic matter in marine sediments as the following example shows. With a typical cell density of 10^6 cells cm^{-3} (Parkes et al., 2000) in the deep subsurface and a typical dry weight per cell of $1.7 \cdot 10^{-13}$ g (Balkwill et al., 1988), the dry weight of living microbial biomass in the sediment is $1.7 \cdot 10^{-7}$ g cm^{-3}. The organic matter content of deep-sea sediment may be 1% dry weight and the total dry density 0.5 g cm^{-3}, thus yielding $5 \cdot 10^{-3}$ g cm^{-3} of the total organic dry weight. The living bacterial biomass thus accounts for only 0.003% of the total organic matter in this example.

The remains of dead microbial cells (microbial necromass) such as cell lysis products or remains of bacterial cell walls and of endospores may accumulate over time and thereby contribute to the sedimentary organic matter pool over geological time scales (Burdige, 2007). Since a considerable fraction of the organic matter becomes degraded and mineralized by microorganisms over the thousands to millions of years of burial, the total microbial biomass production integrated over time may be a significant fraction of the initially buried organic matter. How much biomass is produced depends on the effective growth yield of the microorganism, i.e. which fraction of mineralized

organic matter is assimilated into cell biomass. This in situ growth yield is currently not known and may well be lower than in laboratory cultures as the cells presumably use much of the available energy for maintenance rather than for growth. Lomstein et al. (2012) used the slow chemical racemization between D- and L- amino acids in deep marine sediments as a molecular clock to calculate the turnover of microbial necromass and of living microbial biomass. A simplified diagram of this racemization model is shown in Fig. 5a. The model uses the depth distribution of vegetative cells in the sediment column (Fig. 5b). In the example used in Fig. 5 the total cell numbers of prokaryotic cells in the deeper sediment exceeds by ca. 3-fold the global mean trend in the sub-seafloor found by R. John Parkes and Barry Cragg (updated from Parkes et al. (2000)). Dormant cells in the form of bacterial endospores are not included in the following turnover calculations although such spores may outnumber vegetative cells in the subsurface. The extent of D–L conversion in aspartic acid of dead microbial biomass is used to calculate the age of the total detrital amino acid pool and thereby its turnover time. As the necromass pool is produced by the turnover of a much smaller amino acid pool within living microbial cells, the turnover time of microbial biomass is faster by 100–1000-fold. The necromass was shown to turn over on a time scale of 10^5–10^6 years (Fig. 5c). Dead organic matter from microbial production in the subsurface is thus refractory over tens of thousands of years but is labile over millions of years. Using the same molecular clock, the turnover of living microbial biomass, i.e. the "generation time" of bacteria, was found to be 10^2–10^3 years, i.e. similar to the results above based on process rates divided by microbial cell numbers.

In summary, the organic matter degradation processes result from the combined effort of billions of individual microorganisms. The energetic and kinetic parameters used to describe the dynamic microbial food web in marine sediments therefore need to be tested against known microbial physiologies — with an open mind towards undiscovered physiologies that in the future may generate new perspectives on the pathways of organic carbon degradation. Examples of such discoveries in the past include disproportionation reactions of elemental sulfur or thiosulfate to produce sulfate and sulfide (Jørgensen, 1990; Thamdrup et al., 1993) or the anammox reaction of nitrite and ammonium to produce dinitrogen (Thamdrup and Dalsgaard, 2002). Most recently, the discovery of extracellular electron transfer as a mechanism for remote oxidation of organic carbon or sulfide with oxygen has added a novel mechanism of mineralization to the known toolbox of microorganisms (Nielsen et al., 2010).

2.4. Thermodynamics

The degradation of organic matter proceeds via multiple enzymatic reactions involving different organisms, organic compounds and oxidants, as well as a number of intermediate compounds. The net redox reaction is the sum of electron donor reaction and electron acceptor half reactions (Table 1). Yet most work on the thermodynamics of organic matter degradation by heterotrophic organisms has so far focused on the relative energy yields associated with different TEAs. The sequential utilization of TEAs (O_2, NO_2^- or NO_3^-, Mn(VI), Fe(III), SO_4^{2-}) and the onset of fermentation reactions usually follows the magnitude of the Gibbs energy yield of the electron accepting processes with a progressive decrease in energy yield down the redox ladder (Table 1; Claypool and Kaplan, 1974; Froelich et al., 1979; Stumm and Morgan, 1996). However, this sequential use of TEAs is only valid if the reactions are normalized per mole of carbon oxidized or, preferably, per electron transferred. For instance, iron reduction involves the transfer of only one electron, while sulfate reduction to sulfide involves 8 electrons. Comparing the energetics of these two reactions on a per mole basis would lead to the erroneous conclusion that iron reduction never occurs until all sulfate is exhausted (LaRowe and Van Cappellen, 2011). In addition, the order of TEA consumption (Table 1) is based on standard state calculation of

the Gibbs energy of the reactions at 25 °C and 0.1 MPa. Under non-standard state conditions, this order may no longer hold (Amend and Teske, 2005; Bethke et al., 2011; LaRowe and Van Cappellen, 2011). and sulfate may, for instance, become an energetically more favorable TEA than iron oxides (LaRowe and Van Cappellen, 2011). In addition, the energy yield also depends on the chemical structure of the oxidant source, for e.g. the specific iron mineral. Comparison of the ΔG_r values for the oxidation of glucose coupled to the reduction of goethite and 2-line ferrihydrite illustrates the significant range in energy yields associated with different Fe(III) minerals (Table 1). When 2-line ferrihydrite rather than goethite is the electron acceptor for glucose mineralization, iron reduction is nearly 20 kJ (mol e⁻ transferred)$^{-1}$ more exergonic (LaRowe and Van Cappellen, 2011).

The aforementioned thermodynamic analysis can be expanded to take into account the nature of the electron donor. Table 1 (see LaRowe and Van Cappellen (2011) for a more extensive analysis) and Fig. 6 provide an overview of standard state Gibbs energies for the oxidation half reactions, ΔG_r^0, of a number of selected organic compounds found in marine sediments. Most values are positive, indicating that organic carbon oxidation must be coupled to the reduction of a TEA or the production of a reduced carbon product in order to proceed forward. However, Gibbs energies of reaction span a range of ca. 20 kJ (mol e⁻ transferred)$^{-1}$. The observed difference in Gibbs energies between different compounds can be directly linked to the chemical structure and the oxidation state of carbon in organic matter (Fig. 6, see also Section 2.2). However, the Gibbs energy of the oxidation reaction also depends on the complex interplay between the types and numbers of bonds in these compounds and the overall molecular orbitals of their constituent electrons. For instance, oxidation of the carbon in the amino acid serine yields a higher Gibbs energy per mole of carbon and per electron transferred than that of alanine, another amino acid (see Table 1).

The average nominal oxidation state of the carbon (NOSC) represents a simple proxy that can be used to scale the bonding in organic compounds to their energetic content. The NOSC has the advantage that it does not require structural information in order to estimate the energetic potential of complex, natural organic matter. Fig. 6 relates the standard state Gibbs energies of the half reaction describing the complete oxidation of a broad array of organic compounds to the NOSC. The Gibbs energies of reaction per mole of carbon oxidized correlates inversely with the average nominal oxidation state of the carbon atom, NOSC, although values may vary by as much as 30 kJ mol C^{-1} (Fig. 6). This inverse trend is expected because more electrons can be transferred per carbon atom when a compound with a lower NOSC is oxidized. However, a similar inverse relationship between Gibbs energies of reaction and NOSC can also be observed when Gibbs energies are normalized to the number of electrons transferred (Table 1, LaRowe and Van Cappellen, 2011). Thus, on average, the removal of an electron from an organic compound becomes thermodynamically more favorable as NOSC becomes more positive. The inverse trend in Fig. 6 therefore reflects variations in both the number of electrons removed from carbon atoms during degradation and the average energy required to remove individual electrons This correlation can be used to estimate the energetics of organic matter oxidation with any TEA as long as the average NOSC, which can be directly calculated from element ratios, is known (see LaRowe and Van Cappellen, 2011).

The energetic differences between different organic matter compounds and TEAs have important implications for the degradation rates of organic matter. For instance, the oxidation of a given compound may be thermodynamically possible when coupled to a powerful terminal electron acceptor, such as oxygen, but may become thermodynamically limited when oxygen is depleted. Thermodynamic limitation may thus partly explain the difference between organic matter degradation in oxic and anoxic environments. Much controversy and confusion have revolved around the influence of oxic and anoxic conditions on organic matter degradation. Laboratory experiments have demonstrated that fresh, marine-derived organic matter is initially mineralized at

Table 1
Common terminal electron acceptor (*TEA*) and electron donor (*ED*) species, half-reactions, Gibbs energy yields and nominal oxidation state of carbon (*NOSC*).

Compound	Half reaction	ΔG_r^0(kJ (e$^-$)$^{-1}$) 25 °C	NOSC
Terminal electron acceptor (TEA) reaction			
Oxygen	$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$	−122.7	
Nitrate	$NO_3^- + 5e^- + 6H^+ \rightarrow 1/2\ N_2 + 3H_2O$	−118.3	
Pyrolusite	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	−120.0	
Goethite	$FeOOH + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	−75.9	
Hematite	$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$	−74.6	
2-line Ferrihydrite	$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	−94.7	
Sulfate	$SO_4^{2-} + 8e^- + 9H^+ \rightarrow HS^- + 4H_2O$	−24.0	
Electron donor reaction (ED)			
Amino Acids			
Serine	$C_3H_7NO_3 + 6H_2O \leftrightarrow 3HCO_3^- + 13H^+ + NH_4^+ + 10e^-$	10.18	0.67
Asparagine	$C_4H_8N_2O_3 + 9H_2O \leftrightarrow 4HCO_3^- + 14H^+ + 2NH_4^+ + 12e^-$	12.82	1.00
Alanine	$C_3H_7NO_2 + 7H_2O \leftrightarrow 3HCO_3^- + 14H^+ + NH_4^+ + 12e^-$	16.00	0.00
Tryptophan	$C_{11}H_{12}N_2O_2 + 31H_2O \leftrightarrow 11HCO_3^- + 55H^+ + 2NH_4^+ + 46e^-$	18.49	⁻0.18
Mononucleotides (x-MonoPhosphate)			
Adenosine-MP (AMP^{2-})	$C_{10}H_{12}N_5O_7P^{2-} + 27H_2O \leftrightarrow 10HCO_3^- + 35H^+ + 5NH_4^+ + 30e^- + HPO_4^{2-}$	2.85	1.00
Deoxycytidine-MP (dCMP^{2-})	$C_9H_{12}N_3O_7P^{2-} + 24H_2O \leftrightarrow 9HCO_3^- + 38H^+ + 3NH_4^+ + 32e^- + HPO_4^{2-}$	10.23	0.44
Saccharides			
Glucose	$C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 24e^- + 30H^+$	10.0	0.00
Deoxyribose	$C_5H_{10}O_4 + 11H_2O \leftrightarrow 5HCO_3^- + 22e^- + 27H^+$	12.66	⁻0.40
Membrane-type compounds			
C$_{16}$ *n*-alkane	$C_{16}H_{34} + 48H_2O \leftrightarrow 16HCO_3^- + 114H^+ + 98e^-$	19.84	⁻2.13
Hopane	$C_{30}H_{52} + 90H_2O \leftrightarrow 30HCO_3^- + 202H^+ + 172e^-$	20.61	⁻1.73
Complex organics			
Type I kerogen	$C_{415}H_{698}O_{22} + 1223H_2O \leftrightarrow 2729H^+ + 415HCO_3^- + 2314e^-$	19.95	⁻1.58
Fulvic substance	$C_{27}H_{28}O_7 + 74H_2O \leftrightarrow 149H^+ + 27HCO_3^- + 122e^-$	20.73	⁻0.52
Misc species			
Hydrogen	$H_2 \rightarrow 2H^+ + 2e^-$	⁻8.9	
Formate	$CHO_2^- + H_2O \leftrightarrow 2H^+ + HCO_3^- + 2e^-$	0.56	2.00
Ammonia	$NH_3 \rightarrow 1/2\ N_2 + 3e^- + 3H^+$	11.9	
Acetate	$C_2H_3O_2^- + 4H_2O \leftrightarrow 9H^+ + 2HCO_3^- + 8e^-$	18.02	0.00
Methane	$CH_4 + 3H_2O \rightarrow 9H^+ + HCO_3^- + 8e^-$	19.9	⁻4.00
Hydrogen sulfide	$HS^- + 4H_2O \rightarrow SO_4^{2-} + 8e^- + 9H^+$	24.0	
Ferrous Iron	$Fe^{2+} \rightarrow e^- + Fe^{3+}$	74.2	

the same rate under oxic and anoxic conditions (e.g. Westrich and Berner, 1984; Henrichs, 2005). However, this is only true for planktonic biomass, polysaccharides and proteins, and is not valid for lignins, lipids, chloropigments and other carbon-rich polymers (e.g. Henrichs, 1992, 1993). When the most labile organic compounds have been consumed, the rate of organic matter degradation in anoxic settings decreases much more rapidly than when oxygen is present (e.g. Westrich and Berner, 1984; Henrichs, 2005). It has thus been hypothesized that the enzymes catalyzing the respiration of phenolic and other terrestrial-derived organic compounds, such as lignin, cellulose and tannins, are more active in the presence of oxygen (e.g. Hedges and Oades, 1997; Freeman et al., 2001). However, the observed pattern may also be explained by the different amounts of energy released during the oxidation of different organic compounds under oxic and anoxic conditions (LaRowe and Van Cappellen, 2011). When energetic organic carbon compounds are available and degraded, the Gibbs energy yield is large in both oxic and anoxic settings. However, once these energy rich compounds are consumed, the oxic and anoxic degradation rates progressively drift apart (e.g. Canfield, 1993; Canuel and Martens, 1996; Hartnett et al., 1998; Henrichs, 2005; Jin and Bethke, 2009). Under oxic conditions, organic matter degradation rates remain high because of the very high oxidative potential and the resulting weak sensitivity towards the depletion of energy-rich organic compounds. However, in anoxic environments deprived of energy rich-organics and powerful TEAs, the degradation rate becomes thermodynamically limited.

Observations have shown that the rate of organic matter degradation is also affected by the presence of reactive intermediates or by-products (e.g. Aller and Aller, 1998). For example, the Gibbs energy yield of acetate oxidized by sulfate,

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \qquad (2)$$

at 25 °C and 0.1 MPa is −6.5 kJ (mol e$^-$)$^{-1}$ when the concentrations of acetate, sulfate, bicarbonate and sulfide are 10^{-5}, 10^{-2}, 10$^{-1.6}$ and 10$^{-4.5}$ mol l^{-1}, respectively. When the concentration of sulfide, an inhibiting species with regard to the reaction (Eq. 2), increases to 10^{-2} mol l^{-1} the thermodynamic drive for this reaction decreases to −4.7 kJ (mol e$^-$)$^{-1}$. Thus, if there is a bioenergetic threshold energy that must be overcome in order for organisms to catalyze a reaction (Schink and Thauer, 1988; Schink, 1990, 1997; Hoehler et al., 2001; Jin and Bethke, 2002; Curtis, 2003; Jin and Bethke, 2003; Hoehler, 2004; Jin and Bethke, 2005, 2009; Regnier et al., 2011; LaRowe et al., 2012), then the Gibbs energy yield of the reaction might not be sufficient for acetate oxidation by sulfate. From an energetic point of view, the rate of organic matter degradation can thus be related to the bioenergetic potential of organic matter, the specific oxidation pathway and the concentration of metabolic by-products.

2.5. Temperature effects

Temperature is an important factor regulating the rate of biogeochemical processes. In general, chemical reaction rates increase with increasing temperatures. However, the benthic degradation of organic matter cannot be reduced to a single chemical process, but proceeds via multiple enzymatic reactions resulting from the combined effort of billions of individual microorganisms and involving a number of oxidants and intermediate compounds. Therefore, factors such as physiological adaption, selective pressure and reaction path play an important role in the temperature response. As a consequence, the effect of temperature on organic matter degradation rates follows a complex pattern on both short- and long-time scales (e.g. Arnosti et al., 1998; Thamdrup and Fleischer, 1998; Ågren and Bosatta, 2002; Kirchman et al., 2005; Davidson and Janssens, 2006;
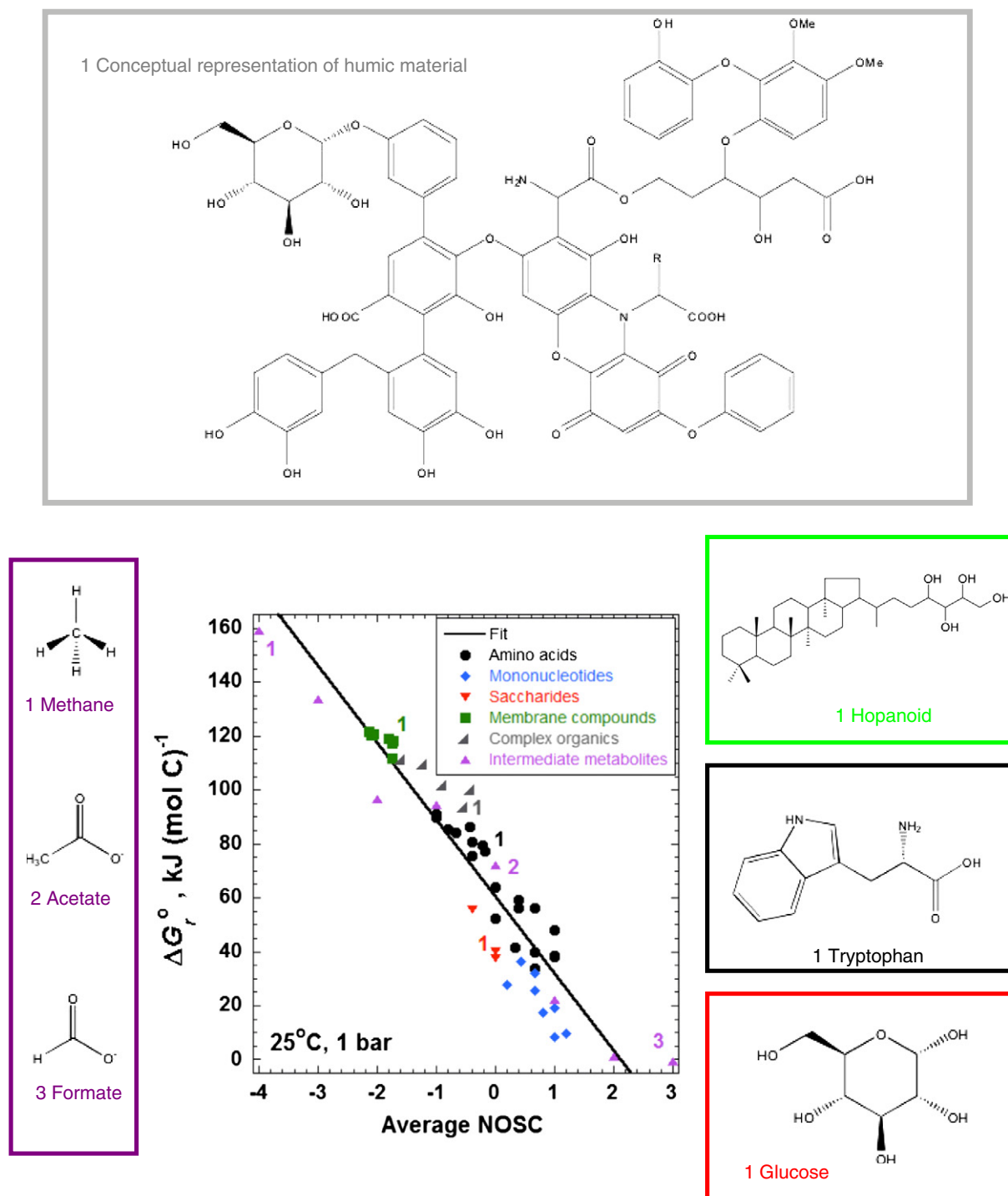
Fig. 6. Standard molal Gibbs energies of the oxidation half reactions of different organic compounds as a function of the average nominal oxidation state of carbon (*NOCS*) that serves as a proxy for the bond strength, at 25 °C and 1 bar (redrawn from LaRowe and Van Cappellen (2011)). The chemical structures of selected compounds are also shown.

Kirschbaum, 2006; Finke and Jørgensen, 2008; von Lützow and Kögel-Knabner, 2009; Robador et al., 2010).

Observational evidence from temperate environments reveals a strong increase of organic matter degradation rates with a seasonal temperature increase (e.g., Jørgensen and Sørensen, 1985; Crill and Martens, 1987; Westrich and Berner, 1988; Middelburg et al., 1996). In contrast, organic matter degradation rates measured in permanently cold Arctic sediments are not intrinsically slower than those measured in temperate or tropical sediments (Arnosti et al., 1998; Glud et al., 1998; Sagemann et al., 1998; Thamdrup and Fleischer, 1998; Knoblauch and Jørgensen, 1999; Jørgensen, 2006). This seemingly contradictory observation is the direct result of the physiological adaption of the in-situ bacterial community to the prevailing environmental conditions (e.g. Robador et al., 2009). In polar and tropical environments, bacteria generally exhibit physiological characteristics that increase their fitness to the permanently cold or warm habitat and, therefore, support high organic matter degradation rates at in-situ temperatures. In contrast, habitats with seasonally changing temperatures favor the development of psychrotolerant or mesophilic microorganisms whose combined metabolic response allow for organic matter degradation over a broad range of temperatures. This community maintains, despite a competitive disadvantage against psychrophiles in winter, a large population all year

round. However, mesophilic microorganisms are adapted to colder temperatures and organic matter degradation rates thus significantly decrease during the cold period.

These observations show that the dominant microbial populations in each environment are optimally adapted to the prevailing environmental conditions. On the one-hand, short-term changes of ambient temperatures below or above their optimal thermal range most likely result in functional constraints. On the other hand, long-term temperature changes such as those induced by geothermal gradients in sediments or climate change may result in shifts in microbial community composition and, thus, an adaptation to changing conditions (e.g. Robador et al., 2009). Incubation experiments with Arctic sediments, for instance, have shown that extreme temperatures well above in-situ temperatures may activate diverse populations of dormant mesophilic or thermophilic bacterial spores, which produce different hydrolytic enzymes that could, if not limited by substrate availability, degrade otherwise refractory organic matter (e.g. Hubert et al., 2009, 2010). The activation of bacterial spores might also be the reason for the weakening in the decrease in organic matter degradability with depth along the geothermal gradient (Parkes et al., 2007; Hubert et al., 2010).

Long- and short-term temperature changes may not only affect the microbial community composition, but also exert a direct influence on the reaction rate. Comparative studies from temperate and Arctic sediments show that, on short timescales, the balance between the rates of extracellular enzymatic hydrolysis and terminal oxidation is robust over a large temperature range (Arnosti and Holmer, 2003; Brüchert et al., 2003; Arnosti and Jørgensen, 2006). On these timescales, the increase in temperature generally is associated with an increase in the rates of both the initial and terminal step of organic matter degradation. The significance and extent of this positive effect depend on in situ temperature, the thermal tolerance of the microorganisms and on the specific metabolic process (Arnosti et al., 1998; Sagemann et al., 1998; Knoblauch and Jørgensen, 1999; Robador et al., 2010). Yet, long-term incubation experiments (24 months) of Arctic and temperate sediments reveal a different behavior (Robador et al., 2010). In these experiments, hydrolysis and terminal oxidation rates initially increase with temperature in accordance with previous findings. However, in the long-term, hydrolysis outpaced the terminal oxidation step. At the same time, degradation rates decreased by a factor of two to four relative to the initial rates. The accumulation of refractory dissolved organic carbon (DOC) compounds indicates that this observed decrease in degradation rate is associated with an increasing inability of the microbial community to ferment the hydrolytically produced DOC to smaller organic compounds (Robador et al., 2010). These results thus indicate that an increase in temperature induces a differential temperature response on the different organic degradation steps. It may limit carbon mineralization in deep anoxic sediments by triggering an increased production of refractory DOC that cannot be taken up by the anaerobic microbial communities (Weston and Joye, 2005; Robador et al., 2010).

Putting all arguments together, it currently remains difficult to assess the exact influence of temperature on organic matter degradation rates. Observations show that the response of degradation rates to temperature changes depends on numerous factors such as microbial physiology, the reaction pathway, the timescale of interest, the magnitude and duration of the temperature perturbation, the climatic zone and potentially the overall degradability of the organic matter. Observational evidence however clearly indicates that the effect of seasonal temperature variations cannot be translated to long-term temperature increases induced by e.g. slow burial of organic matter along the geothermal gradient or by climate change. Therefore, our ability to quantify the cycling of carbon in deep sediments or under changing climate conditions will strongly depend on a better mechanistic understanding of the effect of long-term temperature changes on organic matter degradation.

2.6. Physical protection

Physical protection of organic matter by interactions with the mineral matrix may inhibit the degradation of organic matter and controls organic matter degradation on the micro-scale (Fig. 7a). Sorption of organic matter to mineral surfaces has been identified as a likely mechanism to explain the observed correlation between the content of organic matter and mineral surface area (e.g. Mayer et al., 1985; Keil et al., 1994; Mayer, 1994). However, multiple mechanisms have been proposed to explain the observed physical protection of organic matter by minerals and this remains the subject of much debate. Direct sorption of organic molecules in small pores on the mineral surface that are not accessible to most of the hydrolytic enzymes could kinetically inhibit organic matter degradation (Keil et al., 1994; Mayer, 1994; Hedges and Keil, 1995; Mayer, 1999). Alternatively, the strong sorption of organic matter on mineral surfaces may sterically limit the enzymes. Sorption of organic matter to clay interlayer surfaces has been proposed as another mechanism of enhanced preservation (Keil and Hedges, 1993; Keil et al., 1994; Mayer and Xing, 2001; Kennedy et al., 2002). However, measurements of the pore volume distribution of mesopores before and after removal of organic matter show that they are mainly empty (Mayer, 2004). Furthermore, adsorption of organic molecules to mineral surfaces may favor condensation reactions and, thus, the formation of refractory macromolecules (e.g. Hedges et al., 1988; Keil and Kirchman, 1994). Recent observational evidence has shown that organic matter associated with the mineral matrix may also be present in the form of thick, discontinuous aggregates rather than continuous coatings (e.g. Mayer, 1999; Arnarson and Keil, 2001). This challenges the view of a sorption-driven, continuous coating of organic matter over mineral surfaces, and it has been postulated that the interaction occurs through the formation of organo-clay aggregates. Within the aggregates, organic matter acts as a glue, which holds the mineral fragments together (Ransom et al., 1997, 1998). At the aggregate surface, refractory organic matter or the mineral matrix probably shields organic matter from microbial attack, hence decreasing organic matter degradation. This process is effective only if the resulting aggregates are, at least partly, inaccessible to enzymatic attack and if they are stable over sufficiently long periods of time (Henrichs, 2005). The formation of organo-clay aggregates must also be correlated to the mineral surface area. In addition to the widely discussed external mineral surface area controls, Kennedy and Wagner (2011) have recently emphasized the importance of the internal surface areas of expandable clay minerals in controlling organic matter preservation under anoxic conditions. They show that an increase in expandable clay mineral content under anoxic conditions can enhance organic matter burial by up to a factor of 10. Therefore, not only the mineral surface area, but also its mineralogy may play an important role in organic matter preservation. In addition, Lalonde et al. (2012) suggested a protection of organic matter by its association with reactive iron, through a co-precipitation with iron salts or the formation of macromolecular iron-organic-carbon complexes. However, the precise mechanism of this potential "rusty carbon sink", as well as its evolution during burial remains unknown (Eglinton, 2012). Furthermore, microbiologically produced exopolymeric substances (EPS) have been promoted as a protective agent in the sorptive preservation pathway (e.g. Pacton et al., 2007a,b).

However, sorption does not always inhibit organic matter degradation. It may merely slow down (Sugai and Henrichs, 1992; Ding and Henrichs, 2002) or even enhance (Taylor, 1995) the degradation of organic matter. This wide range of behavior can be related to the nature of organic matter–mineral interactions. A thick coating leads to a weak association of bulk organic matter with the mineral surface and results in enhanced degradation, whereas, a thin coating results in a strong association, which decreases degradation rates. In addition, Henrichs (1995) pointed out that adsorption of organic matter to the mineral matrix can only decrease organic matter degradability if adsorption is strong, irreversible and if the sorbed organic matter is refractory to decay. However, despite the controversy concerning the exact mechanisms, more

Spatial Scale

a   Micro-Scale

b   Macro-Scale

Temporal Scale

c   Micro-Scale
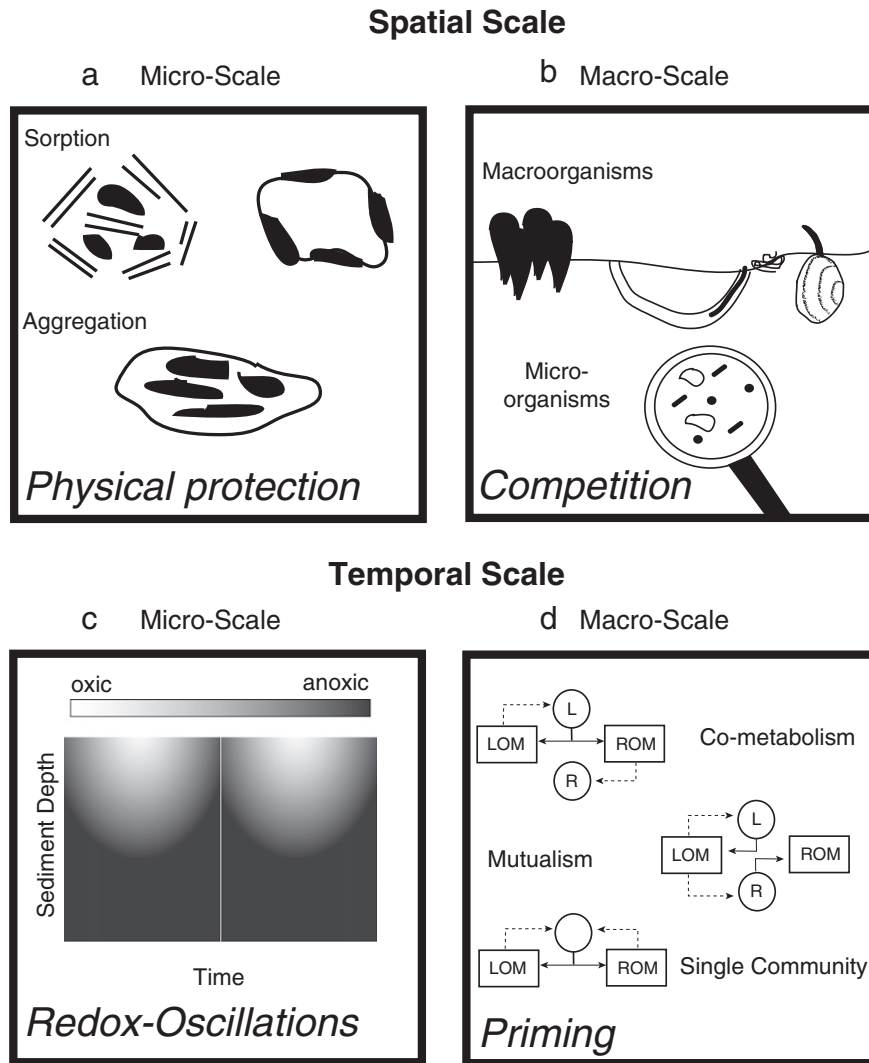
d   Macro-Scale

Fig. 7. Physical protection and macrobenthic activity control organic matter degradation on different spatial and temporal scales. In general, physical protection (a) exerts a spatial control on the micro-scale, while the competition between macroorganisms and microorganisms (b) influences degradation on a larger spatial scale. In addition, macrobenthic activity may trigger short-term oscillations of redox conditions (c). It may also mix more labile organic matter (*LOM*) into deeper sediment layers (d) that may result in a long-term enhancement of refractory organic matter degradation rates (*ROM*) through priming (see Section 2.3 for further detail; *LOM, ROM*: labile and refractory organic matter; *L,R*: community of *LOM* and *ROM* decomposers; solid arrows: enzymes; dashed arrow: energy and structural carbon; Fig. 7d modified from Guenet et al. (2010)).

than two decades of observations confirm that physical protection exerts an influence on organic matter degradation and preservation in marine sediments.

2.7. Macrobenthic activity

In oxic sediments, benthic invertebrates such as polychaetes, holothurians and bivalves extensively rework the upper centimeters of the sediment column, modifying their physical and chemical properties. A large fraction of the deposited organic matter may be decomposed within these shallow sediment horizons and, therefore, macrobenthic activity exerts an important influence on organic matter degradation on different spatial and temporal scales (Fig. 7b–d; e.g. Aller, 1980; Emerson, 1985; Aller and Yingst, 1985; Kristensen and Blackburn, 1987; Banta et al., 1995). The impact of macrobenthic activity on organic matter degradation results from particle transport through feeding and burrowing activities, bioturbation, and the ventilation of these burrows through exchange with the overlying water, bioirrigation. The magnitude of this impact depends on various factors such as sediment characteristics, supply of organic matter, as well as functional group, abundance and size of benthic macrofauna (van Duyl et al., 1992;

Banta et al., 1999; Kristensen, 2000; D'Andrea and DeWitt, 2009). Bioturbation enhances organic matter degradation rates by accelerating the supply of TEAs, preventing the accumulation of metabolic inhibitors, or by stimulating priming, i.e. the mixing of freshly deposited material into deeper sediment layers (Kristensen, 1985; Aller, 1994; Aller and Aller, 1998; Kristensen et al., 2011). Short-term redox-oscillations (Fig. 7c) have been suggested as important factors that may promote the degradation of organic matter in the bioturbated zone, while priming (Fig. 7d, see Section 2.3 "Microbiology" for further detail) exerts a long-term positive effect on organic matter degradation. Within the bioturbated zone, organic matter degradation can also be stimulated directly by bioturbation-mediated particle manipulation, grazing and excretion/secretion (e.g. Rice, 1986; Kemp, 1987). On the other hand, the production of tube linings, halophenols or body structural products, and the direct feeding on depositing organic matter could all inhibit organic matter degradation (e.g. Kristensen, 1992, 2001). Studies indicate that macrobenthic activity generally stimulates the degradation of refractory organic compounds that are not directly assimilable by most deposit-feeders (Findlay and Tenore, 1982; Kristensen and Holmer, 2001). Its impact on fresh, labile organic matter is, however, more complex. The competition between macrobenthic animals and bacteria

(Fig. 7b) for labile organic matter compounds at the sediment water interface may result in a reduction in microbial degradation rates (Kristensen et al., 1992). However, van Nugteren et al. (2009b) showed that bacteria are better adapted for the degradation of organic matter within the sediment matrix, while macrobenthic deposit feeders prefer organic matter concentrated in patches. These mechanisms may stimulate a stable co-existence through a scale-based partitioning of carbon resources (Fig. 7b).

2.8. Deposition rate

The observed correlation between average organic matter degradability and sediment accumulation rate (e.g. Heath et al., 1977; Toth and Lerman, 1977; Berner, 1978; Müller and Suess, 1979; Henrichs and Reeburgh, 1987; Canfield, 1994) has led to the hypothesis that deposition rate exerts an important influence on organic matter degradation rates. This causal relationship has often been explained by the rapid burial of freshly deposited material below the biologically active, mixed sediment layer, at depths where organic matter degradation proceeds at a slower pace (Toth and Lerman, 1977; Hartnett et al., 1998). However, the empirical relationship might also be partly explained by the correlation between organic carbon flux and total flux in the examined slope and deep ocean environments (e.g. Aller and Mackin, 1984; Hedges and Keil, 1995). Furthermore, Emerson et al. (1985) have argued that since the half-lives of labile organic compounds are generally one or two orders of magnitude shorter than typical residence times in the mixed layer, deposition rate should only exert a small effect on degradation rates. Dilution of organic matter by detritus would thus lead to a negative correlation between organic matter burial and deposition rate. Therefore, deposition rate only exerts a significant effect on organic matter degradation rates if the bulk material is refractory enough to escape degradation in the upper, mixed layer (Aller and Mackin, 1984; Mogollon et al., 2012; Røy et al., 2012). Along those lines, Blair and Aller (2012) distinguish between three distinct high deposition settings. High-energy, mobile muds with enhanced oxygen exposure and efficient metabolite exchange are generally characterized by a very low burial efficiency of both terrestrial and marine organic matter (e.g., Amazon fan, Aller and Blair, 2006). Low-energy facies that are subject to extreme accumulation rates and often high loads of fossil organic carbon reveal a high organic matter burial efficiency (e.g., Ganges-Brahmaputra, Galy et al., 2007). Finally, small, mountainous river systems that sustain average, but periodically high accumulation rates and deliver a large fraction of refractory, fossil organic matter exhibit the highest burial efficiencies (e.g. Eel River, Blair et al., 2003).

3. Model formulation

This section reviews the mathematical formulations of organic matter degradation and briefly addresses their coupling to sediment transport processes. A glossary of parameters along with their respective units is provided in Table 2.

The one-dimensional conservation equation for solid and dissolved species in porous media is given by (e.g. Berner, 1980; Boudreau, 1997):

$$\frac{\partial \sigma C_i}{\partial t} = \frac{\partial}{\partial z}\left(D_{bio,i}\sigma\frac{\partial C_i}{\partial z} + D_i\sigma\frac{\partial C_i}{\partial z}\right) - \frac{\partial \sigma \omega C_i}{\partial z} + \alpha_i\sigma(C_i(0) - C_i) + \sum_j s_i^j R^j.$$

(3)

In Eq. (3), C_i is the concentration of species i; the term σ is equal to the porosity φ for dissolved species and $(1 - \varphi)$ for solid species; $D_{bio,i}$ and D_i denote the bioturbation and effective diffusion coefficients ($D_i = 0$ for solid species), respectively; ϖ is the burial velocity, α_i is the bioirrigation coefficient ($\alpha = 0$ for solid species) and s_i^j denotes the stoichiometric coefficient of species i in reaction j, with rate R^j. The effective diffusion coefficient for solutes depends on the species-dependent molecular diffusion coefficient at a given temperature and salinity as well as on the porosity (e.g. Boudreau, 1997). Table 3 relates the controls on organic matter degradation (see Section 2) to their respective mathematical formulation (see Section 2.1).

3.1. Transport

The most important transport mechanisms that have a direct impact on organic matter degradation in marine sediments are briefly reviewed here. The interested reader is referred to the classical textbooks by Berner (1980), Boudreau (1997), or Steefel and MacQuarrie (1996) for further details.

3.1.1. Deposition rate

Sedimentation results from the net accumulation of new particles on the seafloor (Burdige, 2006), which induces a downward flux of sediment material and porewater with respect to the sediment–water interface. For solids, the advective flux in Eq. (3) results from both sedimentation and compaction upon burial. In the absence of the latter process, ϖ and φ remain constant with depth. In fine-grained sediments however, compaction is often included in the mathematical formulation, although steady state is generally assumed in this case. This approach allows determining ϖ from a given porosity profile (e.g. Berner, 1980). Apart from its direct influence on organic matter fluxes, sedimentation exerts an additional influence on organic matter degradation rates through its impact on TEA fluxes. The advective pore water flux can directly be related to sedimentation and compaction when externally impressed fluid flow is absent. If compaction is assumed negligible (as in Eq. (3)) the sediment burial velocity ϖ and the porewater velocity are equal (e.g. Boudreau, 1997; Burdige, 2006). Steady-state compaction leads not only to velocities that vary with sediment depth but also to a relative movement of the porewater with respect to a sediment matrix. However, note that the advective porewater flux is generally much smaller than the effective molecular diffusive flux.

3.1.2. Macrobenthic activity

The simplest approach to account for the complex process of bioturbation is to assume that it can be represented as a random process (e.g. Van Cappellen and Gaillard, 1996; Meysman et al., 2010). In one-dimension, the intensity of vertical sediment mixing can then be formulated as a diffusive process with a bioturbation coefficient, D_{bio}. Mixing models for bioturbation are delimited by two-end member conditions: interphase mixing, in which the solids and pore waters are assumed to intermix in the bioturbation process, and intraphase mixing, in which sediment porosity is assumed to be unaffected (Boudreau, 1986; Mulsow et al., 1998; Jourabchi et al., 2005; Meysman et al., 2005). Studies suggest that the surface sediment mixed by bioturbation is approximately 5–10 cm thick with marginal or no dependency on the sea floor depth (Van Cappellen and Gaillard, 1996; Boudreau, 1998; Teal et al., 2008). Values of the bioturbation coefficient, on the other hand, reveal a weak, yet significant correlation with seafloor depth (Middelburg et al., 1997). Bioturbation coefficients may furthermore vary within the bioturbated layer and a variety of depth distributions have thus been implemented in biodiffusion models (see, for instance Van Cappellen and Gaillard, 1996). The bioturbation coefficient profiles should ultimately reflect the vertical distribution of macrofaunal abundances, although it has been shown that the activity of some infaunal organisms may lead to transport that is inherently non-diffusive (Boudreau, 1986). For instance, particles can be transported by bioadvection, a process during which macrofauna move material in a non-diffusive manner between disconnected portions of the sediments. This non-local transport is not fully understood and, therefore, often not incorporated in diagenetic model formulations, including Eq. (3).

Table 2
Glossary.

Symbol	Description
System description	
z	Sediment depth
t	Time
C	Concentration
G	Organic matter
f	Fraction of total organic matter in compound class
T	Absolute temperature
i	Species
j	Reaction number
σ	Porosity factor
Transport	
D_{bio}	Bioturbation coefficient
D_i	Diffusion coefficient of the *i*th species
ϖ	Sedimentation Rate
α	Bioirrigation parameter
Kinetics	
s^j_i	Stoichiometric coefficient of species i in the reaction j
R_j	Rate of the *j*th chemical reaction
R_G	Degradation rate of organic matter
$R_{TEA,i}$	Rate of the *i*th organic matter degradation pathway
$K_{m,G}$	Half-saturation constant for organic matter
K_{in}	Inhibition constant
$K_{m,TEA}$	Half-saturation constant for *TEA*
K_C	Half-saturation constant for the suppression of organic matter degradation by *DIC* and *CH₄*
F_{TEA}	Michaelis–Menten TEA
F_{in}	Inhibition term for
v_{max}	Maximum reaction rate
k	Degradation rate constant
$g(k,t)$	Distribution function of organic matter compounds over k
$\Gamma(v)$	Gamma distribution
a	Continuum model parameter, apparent initial age
v	Continuum model parameter, shape parameter of the gamma distribution
q	Exponent of the power model
Thermodynamics	
F_T	Thermodynamic term
ΔG_r	Gibbs energy of reaction
ΔG_{BQ}	Minimum energy for ATP synthesis
X	Average stoichiometric number of the reaction
R	Gas constant

The effect of bioturbation on the organic matter profile is twofold (e.g. Burdige, 2006). First, the concentration at the sediment–water interface decreases with increasing bioturbation intensity; second, the depth gradient decreases when, D_{bio}, increases. Thus, bioturbation ultimately leads to a higher organic matter flux to the deeper sediment layers. However, this effect is exclusively related to transport mechanisms and little is known about the influence of bioturbation on organic matter degradability, e.g. via priming. Porewater chemistry and pathways of organic matter decomposition may also be affected by the irrigation activity of benthic macrofauna. This process increases the fluxes of dissolved oxidants into the sediment (for comprehensive reviews,

see, Berner, 1980; Van Cappellen and Gaillard, 1996; Boudreau, 1997; Aller, 2001; Burdige, 2006). Following the most commonly used approach, bioirrigation is included in the mass conservation (Eq. 3) as a source or sink term analogous to a kinetic rate. It is restricted to a bio-irrigated layer which varies from site to site (e.g. Burdige, 2006) but typically falls in the range 5–50 cm. It is often calculated as the product of the irrigation intensity ($\alpha = 0$ for solids including particulate organic matter) and the difference in concentration, C_i, of the species i relative to the concentration at the sediment–water interface $C_i(0)$ (e.g. Boudreau, 1984; Emerson et al., 1984). In its simplest form, α is constant with depth within the bio-irrigated layer, but more complex functional dependencies with respect to sediment depth have also been applied in the past (Burdige, 2006), including formulations scaling the magnitude of bio-irrigation to the oxygen flux into the sediment (Meile and Van Cappellen, 2003; Thullner et al., 2009).

3.2. Reaction

3.2.1. Organic matter degradation rate law

3.2.1.1. Substrate. Organic matter degradation is a multi-step process. Generally, the initial hydrolysis of the macromolecular organic matter is considered to be the rate-limiting step (e.g. Billen, 1982; Meyer-Reil, 1990; Kristensen and Holmer, 2001). Therefore, organic matter degradation is usually described as a single-step overall reaction. Because organic matter degradation involves enzymatic reactions, the phenomenological rate law used to describe this macroscopic kinetics of the chemical reaction takes the form of Michaelis–Menten kinetics (e.g. Van Cappellen and Gaillard, 1996; Boudreau, 1997, Regnier et al., 2005; Thullner et al., 2007). This simple model of enzyme kinetics reflects the observation that the rate ultimately reaches a plateau with increasing availability of a substrate, provided that enzyme concentration is at steady state. The concentration at which the rate reduces to half its maximum value is referred to as the half-saturation constant, K_m, which is a measure of the affinity of a particular enzyme for the reactant, i.e. the lower K_m is, the stronger the affinity. Hence, the degradation rate of organic matter, R_G, can be expressed as:

$$R_G = v_{\max} \cdot \frac{G}{K_{m,G} + G} \tag{4}$$

where $v_{\max}$ denotes the maximum reaction rate and $K_{m,G}$ is the half-saturation constant for organic matter, G. In general, it is assumed that the concentration of reactive organic matter is small compared to K_m, and the rate reduces to a first-order degradation with respect to organic matter:

$$R_G = k \cdot G \tag{5}$$

with:

$$k = \frac{v_{\max}}{K_{m,G}}. \tag{6}$$

Table 3
Link between controls of organic matter degradation and the reaction–transport model formulations (see Sections 2 and 3.1 for further information).

	$\frac{\partial(1-\phi)C}{\partial t} =$	Transport — 3.1.1: $\frac{\partial}{\partial z}\left(D_{bio}(1-\phi)\frac{\partial C}{\partial z}\right) + \alpha\sigma C(C_i(0)-C_i)$	Transport — 3.1.2: $-\frac{\partial(1-\phi)\varpi C}{\partial z}$	Reaction — 3.2.3: $-k(t)$	3.2.2 — G	X	F_{TEA}	F_{IN}	F_T	F_{Tem}
2.1 Organic matter flux			●		(●)	●				
2.2 Organic matter composition					(●)				●	
2.3 Microbiology					(●)		●	●	●	●
2.4 Thermodynamics					(●)	●	●	●	●	
2.5 Temperature effects					(●)					●
2.6 Physical protection					(●)					
2.7 Macrobenthic activity		●			(●)					
2.8 Sedimentation rate			●		(●)					

Although most models represent the reaction as a single-step overall reaction with respect to the bulk organic matter, some degradation models explicitly include mass conservation equation for the intermediate species (e.g. Alperin et al., 1994; Burdige, 2002; Wirtz, 2003; Regnier et al., 2005; Thullner et al., 2007; Dale et al., 2008a). In these models, organic matter degradation is usually described as a two-step or three-step process based on the porewater size/reactivity model (Fig. 8; Burdige and Gardner, 1996). Sedimentary organic matter is degraded by extracellular hydrolysis to high-molecular-weight dissolved organic matter (HMW-DOM). This HMW-DOM is further hydrolyzed or fermented to monomeric low-molecular weight DOM (mLMW-DOC) or less reactive polymeric low-molecular-weight DOM (pLMW-DOC) that are used in the terminal respiratory process.

3.2.1.2. Terminal electron acceptor. In general, the dependence of organic matter degradation rates on TEA concentration is described by the so-called Monod kinetics (e.g. Boudreau and Westrich, 1984; Van Cappellen and Gaillard, 1996; Boudreau, 1992; Boudreau, 1997; Thullner et al., 2007). The degradation rate for the *i*th degradation pathway is then determined by:

$$R_i = k \cdot G \cdot F_{TEA,i} \tag{7}$$

with

$$F_{TEA,i} = \frac{TEA_i}{K_{m,TEA_i} + TEA_i}. \tag{8}$$

This expression reflects the observation that the rate of organic matter degradation, R_i, is essentially independent of TEA when the TEA concentration is much higher than the half-saturation constant, $K_{m,TEA}$, ($F_{TEA,i} \approx 1$) but becomes first order with respect to TEA at lower TEA concentrations ($F_{TEA,i} \approx 1/K_{m,TEAi}$). It is important to note that this relationship has been empirically derived for sulfate reduction by Westrich and Berner (1984) and Boudreau and Westrich (1984) and has been widely used for all TEAs (e.g. Rabouille and Gaillard, 1991a,b; Soetaert et al., 1996; Van Cappellen and Wang, 1996). It should not be equated to the Michaelis−Menten equation of enzyme kinetics that is based on mechanistic theory derived for a single community in a well-mixed reactor. Note that, for methanogenesis, the Michaelis−Menten term, $F_{TEA,i}$, is equal to one.

3.2.1.3. Inhibition. Inhibition terms can be introduced in the rate law to account for the suppression of a specific metabolic pathway by the presence of higher energy-yielding TEAs. The inhibition of organic matter degradation pathways is usually simulated by introducing a series of hyperbolic functions, each characterized by an inhibition constant K_{in} (e.g., Van Cappellen et al., 1993; Boudreau, 1997). For the *i*th metabolic pathway, the degradation rate becomes:

$$R_i = k \cdot G \cdot F_{TEA,i} \cdot F_{in,i} \tag{9}$$

with

$$F_{in,i} = \sum_{j=1,i-1} \frac{K_{in,j}}{K_{in,j} + TEA_j} \tag{10}$$

where $K_{in,j}$ denotes the inhibition constant for the higher energy-yielding TEA_j, whose presence inhibits the *i*th metabolic pathway. Inhibition terms similar to Eq. (10) have also been included in kinetic rate equations to match the observation that reactive intermediates, by-products or end products of the overall reaction thermodynamically limit the rate of organic matter degradation (e.g. Aller and Aller, 1998). This is nevertheless a semi-empirical approach that
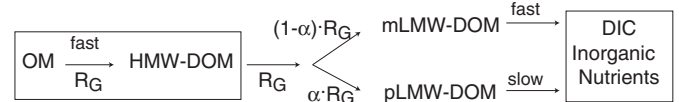
Fig. 8. Schematic representation of dissolved organic matter, *DOM*, production and consumption during the organic matter degradation process (Adapted from Burdige, 2001). Sedimentary organic matter is degraded by extracellular hydrolysis to high-molecular-weight dissolved organic matter (*HMW-DOM*) at a reaction rate R_G. A fraction, $(1-\alpha)$, of this *HMW-DOM* is further hydrolyzed or fermented to monomeric low-molecular weight *DOM* (*mLMW-DOM*) while the remainder, α, is converted to less reactive polymeric low-molecular-weight *DOM* (*pLMW-DOM*). The two fractions are characterized by different reactivities in the terminal respiratory process.

represents a special case of non-competitive enzyme inhibition. A more theoretically grounded formulation derives the competition among different organic matter degradation pathways from the relative rates of the various pathways (e.g., Watson et al., 2003; Thullner et al., 2005; Dale et al., 2006).

3.2.1.4. Bioenergetics. The kinetic model for organic matter degradation can be extended to account for bioenergetic limitations. The functional dependency of the rate on the thermodynamic driving force for the reaction is implemented through the dimensionless number F_T (e.g. Jin and Bethke, 2005; Dale et al., 2006; Steefel and Maher, 2009; LaRowe and Van Cappellen, 2011; Regnier et al., 2011). For the *i*th metabolic pathway, the degradation rate becomes:

$$R_i = k \cdot G \cdot F_{TEA,i} \cdot F_{in,i} \cdot F_{T,i} \tag{11}$$

with (Jin and Bethke, 2002, 2003, 2005):

$$F_{T,j} = 1 - \exp\left(\frac{\Delta G_{r,j} + m_j \Delta G_{ATP}}{\chi_j RT}\right) \tag{12}$$

where $\Delta G_{r,j}$ represents the Gibbs energy of the *j*th catalyzed reaction, ΔG_{ATP} stands for the Gibbs energy required to synthesize one mole of ATP from ADP and monophosphate, an endergonic reaction, m_j refers to the number of moles of ATP that are made per turnover of the *j*th reaction, χ_j denotes the average stoichiometric number for the *j*th reaction and R and T correspond to the gas constant and temperature in Kelvin, respectively. For catabolic reactions, χ is equivalent to the number of times the rate limiting step occurs per mole of ATP made multiplied by the number of electrons transferred in the *j*th reaction (Jin and Bethke, 2002, 2003, 2005).

In the case that $\Delta G_{r,j} \geq 0$ and $F_T = 0$, incorporation of the thermodynamic term, F_T, in rate equations allows accounting for the thermodynamic feasibility of the simulated reaction. Recently, LaRowe et al. (2012) proposed an alternative formulation for F_T that simplifies and extends the applicability of Eq. (12) by relying on one adjustable parameter rather than the three shown in Eq. (12) (ΔG_{ATP}, m_j and χ_j). This approach avoids the need to constrain *a-priori* the values of the minimum amount of energy required by the microorganisms to actively catalyze a given reaction ($m_j \Delta G_{ATP}$). As a result, the function described in LaRowe et al. (2012) can be used to quantify the impact of thermodynamics on reaction rates for any reaction, not just those for which values of the m_j and χ_j parameters have been determined or those which are more exergonic than some energy demand minimum, i.e. ($\Delta G_{r,j} + m_j \Delta G_{ATP} < 0$). It compares the amount of energy required to maintain a membrane potential ($\Delta G_{mp} = F\Delta\Psi$), a proxy for the minimum amount of energy that a microbe needs to be considered active:

$$F_{T,j} = \frac{1}{e^{\left(\frac{\Delta G_{r,j} + F\Delta\Psi}{RT}\right)} + 1} \tag{13}$$

where, $\Delta G_{r,j}$ denotes the Gibbs energy of the reaction per electron transferred, F corresponds to the Faraday constant and $\Delta\Psi$ indicates the electric potential across an energy transducing membrane in volts.

3.2.1.5. Temperature. Marine sediments may experience temperature changes on both temporal and spatial scales. Seasonal changes in ambient temperature affect processes in the upper sediment layers, while the temperature increase with burial may influence biogeochemical rates in the deep biosphere. The effect of temperature, T, on the degradation rate constant, $k(T)$ is typically described using an integrated version of an Arrhenius-type equation, e.g., (Middelburg et al., 1996; Davidson and Janssens, 2006; Burdige, 2011):

$$k(T) = A \cdot e^{(-E_a/RT)} \qquad (14)$$

where A refers to what is known as the pre-exponential or frequency factor and E_a denotes the activation energy of the reaction of interest, R is the gas constant and T is the absolute temperature. The activation energy is a measure of the barrier that separates a metastable equilibrium, such as organic compounds in natural settings, from a lower energy state, such as CO_2 and/or CH_4. Because values of E_a are nearly always positive, the pre-exponential factor can be thought of as a maximum rate constant that is modified by a temperature factor, F_{TEM}. For the ith metabolic pathway, the degradation rate becomes:

$$R_i = k \cdot F_{TEM} \cdot G \cdot F_{TEA,i} \cdot F_{in,i} \cdot F_{T,i} \qquad (15)$$

with:

$$F_{TEM} = e^{-(E_a/R \cdot T)}. \qquad (16)$$

It should be noted that although the Arrhenius equation is widely used to describe the temperature dependence of the complex multi-step organic matter degradation reaction, it is a semi-empirical formulation that has been derived for elementary reactions (e.g. Benson, 1976). In addition, apparent values of A and E_a are generally calculated from rate measurements, although the Arrhenius equation relates the reaction rate constant, k, and not the rate to temperature. These apparent values represent a composite of the activation energies of all the elementary reactions that comprise the overall reaction. In addition, field-determined apparent activation energies are not activation energies in the thermodynamic sense, but measures of the ecological temperature response. They thus encapsulate the temperature response of (i) the total ecosystem, (ii) the microbial community, (iii) the microbial population and (iv) the organic matter degradability/availability. As a consequence, the transferability of an apparent activation energy determined for a particular site under specific environmental conditions to other settings and, especially to the deep biosphere, is limited. Reported values span a large range between 23 to 132 kJ mol^{-1} with values clustering between 50 and 60 kJ mol^{-1} and 70 and 90 kJ mol^{-1} (e.g. Westrich and Berner, 1988; Middelburg et al., 1996; Robador et al., 2009). The observed variability is likely the result of changing substrate concentration and composition, microbial community composition, pH, temperature, TEA type and availability or reaction pathway (e.g. Tarutis, 1992; Middelburg et al., 1996). In fact, the pre-exponential factor, A, and the activation energy itself may be functions of temperature (Moore, 1964; Lasaga, 1981). Direct evidence for such temperature dependence has been reported by Crill and Martens (1987), who reported different apparent values of E_a for sulfate reduction in surface sediments from Cape Lookout Bight in winter (23 kJ mol^{-1}) and summer (114 kJ mol^{-1}). Interestingly, laboratory experiments and field observations from shallow, temperate sediments also reveal

that apparent activation energies increase as degradation rate decreases (e.g. Westrich and Berner, 1988; Middelburg et al., 1996). However, the interpretation of this qualitative correlation is not straightforward. Westrich and Berner (1988) propose a direct relationship between activation energy and organic matter degradability. Yet, a direct relationship between ΔG_r and activation energy that could explain the proposed link, has yet to be derived. Alternatively, a change in reaction path with a change in organic matter quality or a different ability of bacterial populations to respond to temperature changes may explain the observed trend. A more likely explanation for the link between apparent activation energies and degradation rates in shallow temperate sediments may be a tight coupling between temperature and organic matter input (e.g. Middelburg et al., 1996). Whatever the cause of the observed correlation may be, a direct transferability of high apparent activation energies from shallow, temperate sediments characterized by comparably high organic matter degradation rates to the deep subsurface biosphere where organic matter degradation proceeds at exceedingly low rates is, because of the above described complexity, questionable. The deep biosphere likely reveals, because of its remoteness from the strong seasonal ecosystem dynamics, the reduced variability in organic matter fluxes and the long adaption times, much lower activation energies than shallow, surface sediments.

3.2.1.6. Biomass. Models in which biomasses are explicitly included allow studying the response of a microbial community to fluctuations in environmental conditions and the competition of different microbial groups for a common substrate (e.g. Boudreau, 1999; Wirtz, 2003; Thullner et al., 2005; Thullner et al., 2007; Dale et al., 2008a; Regnier et al., 2011). Microbial rate laws explicitly account for the dependence of the microbial reaction rate on the biomass of the microorganisms. The reaction rate, R_i, of the ith metabolic pathway thus reads:

$$R_i = k \cdot F_{TEM} \cdot G \cdot F_{BIO,i} \cdot F_{TEA,i} \cdot F_{IN,i} \cdot F_{T,i} \qquad (17)$$

with:

$$F_{BIO,i} = \sum_j X_j \qquad (18)$$

where $\sum_j X_j$ denotes the biomass of the jth microbial groups mediating the rate, $R_{TEA,i}$. Growth and decay of the microorganisms are included as separate reactive processes. A standard model for the biomass dynamics is (e.g. Boudreau, 1999; Thullner et al., 2007):

$$\frac{\partial X_j}{\partial t} = Y_j \cdot R_{TEA,i,j} - \mu_{dec,j} X_j \qquad (19)$$

where μ_{dec} denotes a specific decay rate constant. The yield coefficient Y links the utilization of organic matter and TEAs, to the production of new microbial biomass. Values of Y depend on the Gibbs energy generated by the catabolic reaction, the Gibbs energy needed for the formation of a new biomass, and the efficiency with which the organisms utilize energy (Van Briesen, 2002). Some of these biomass-explicit models generally account for the contribution of dormant or dead bacterial biomass or exopolymeric substances to the sedimentary organic matter pool (e.g. Thullner et al, 2005; Dale et al., 2010; Stolpovsky et al., 2011).

3.2.1.7. Physical protection. To the best of our knowledge, organic matter degradation rate laws have not yet included an explicit description of physical protection mechanisms, although this process has been well studied and is recognized as a potentially important factor for the preservation of organic matter in marine sediments (Mayer et al., 1985; Keil et al., 1994; Mayer, 1994; Hedges and Keil, 1995). Only some metabolic models that explicitly describe the transport and reaction dynamics of dissolved organic matter, account for the

adsorption of dissolved organic matter on mineral surfaces through equilibrium, linear adsorption (e.g. Henrichs, 1995; Komada et al., 2004).

Synthesis

The total organic matter degradation rate, R_G, is thus the sum of the different metabolic pathways, i:

$$R_G = \sum_i R_i$$

with:

$$R_i = k \cdot F_{TEM} \cdot G \cdot F_{BIO,i} \cdot F_{TEA,i} \cdot F_{IN,i} \cdot F_{T,i}$$

In general, one or several terms in Eq. (20) are omitted depending on the nature of the problem, the importance of a specific process and/or the availability of data to constrain parameters. In this case, the degradation rate constant, k, implicitly accounts for the influence of these factors on organic matter degradation rates.

3.2.2. Rate constant-degradability of organic matter

The most common modeling approaches build on the idea that the organic matter degradation rate constant, k, primarily reflects the reactivity of macromolecular organic matter. The value of the rate constant can thus be interpreted as a measure of the original composition of the depositing material and its evolution during burial. However, k cannot be quantified a *priori* and empirical methods are needed to constrain its value. As a consequence, the rate constant implicitly accounts for a series of factors that are not explicitly formulated in the chosen model. For instance, the empirically derived decrease in rate constants with sediment depth not only reflects the decreasing reactivity of the remaining macromolecular components, but also encapsulates the potential effects of changes in microbial community structure, thermodynamic drive, temperature, and/or mineral protection. The resulting models can be divided into two broad classes: discrete models and continuum models (Fig. 9).

3.2.2.1. Discrete models. The first mathematical description of organic matter degradation in marine sediments led to the so-called one-G model (Berner, 1964). Here, the bulk sedimentary organic matter is attributed to a single pool of concentration, G (Fig. 9), which is degraded at a constant rate following first-order kinetics. This approach is merely a simple linear approximation for the degradation of the complex and heterogeneous mixture of different organic matter compounds. Such simplification is reasonable only if the degradability of the different compounds does not vary by more than one order of magnitude. Obviously, the one-G model cannot account for the heterogeneity of natural organic matter and the decrease in organic matter degradability from the early to late stages of degradation. Some 1G-Model applications account for the decrease in organic matter degradability by applying lower degradation rate constants in the deeper, suboxic and/or anoxic sediment layers (e.g. Heggie et al., 1987; Dhakar and Burdige, 1996; Vanderborght et al., 1977).

In an effort to account for the heterogeneity of organic matter and its evolution during burial, Jørgensen (1978) introduced the so-called multi-G model (Fig. 9). This model is based on the assumption that organic matter is composed of discrete compound classes i, each characterized by a specific degradability k_i (e.g. Jørgensen, 1978; Berner, 1980; Billen, 1982; Westrich and Berner, 1984). The apparent

reactivity, k, of the bulk organic matter and its evolution during burial is related to the reactivity of each class by:

$$R_G(t) = k(t) \cdot G(t) = \sum_i -k_i \cdot G_i(t) \tag{22}$$

and:

$$f_i(t) = \frac{G_i(t)}{\sum_i G_i(t)} \tag{23}$$

where k_i denotes the degradability of organic matter in compound class i and f_i denotes its relative concentration of organic matter in the ith compound class G_i. Similar to Eq. (21), the rate formulation in Eq. (22) can be extended to account for the influence of temperature, thermodynamics, TEA availability, inhibition or biomass on degradation rate. Two different multi-G model approaches can be distinguished based on the interactions between the different compound classes: (1) independent compound classes or a (2) feedback between compound classes (Fig. 9). The independent compound class model assumes a number of discrete compound classes that degrade independently according to first-order kinetics. Selective preservation according to the degradability of each compound class accounts for the change in organic matter degradability with burial. Westrich and Berner, 1984, for instance, identified two discrete organic matter compound classes by graphical analysis of observations from long-term degradation experiments with phytoplankton material from Long Island Sound. They divided the bulk material into a reactive fraction and a more refractory fraction, which is characterized by a rate constant, k_2, that is about one to two orders of magnitude lower than the one attributed to the most labile compounds, k_1. Although, in theory, this 2G-Model could be complemented by introducing a larger number of parallel compound classes, the difficulty to identify these compound classes from observational data generally restricts their number to a maximum of three (Jørgensen, 1978; Middelburg, 1989). The third organic matter fraction is generally characterized by a very high degradability, k_0, and is degraded right at or just beneath the sediment–water interface (Luff et al., 2000; Berg et al., 2003). Alternatively, Canfield (1994) proposed a feedback between the degradability of the organic matter compound classes to approximate the priming effect. In his "pseudo-G" model (Fig. 9), the degradability of the refractory organic matter compound class is linked to the degradation rate of the more labile organic matter. Despite its obvious simplifications, the multi-G model has been proven successful in simulating organic matter degradation in many sedimentary settings.

Continuum models. Continuum models assume a continuous distribution of organic matter reactivities and provide an alternative to discrete multi-G models. They assume a continuous distribution of organic matter compounds, thus avoiding the need to partition the bulk material into a limited number of discrete compound classes (Fig. 9):

$$R_{(t)} = -\int_0^\infty k \cdot g(k, t) \quad dk \tag{24}$$

where g(k,t) denotes a function that determines the concentration of organic matter having a degradability between k and k + dk at time t (Fig. 9). Similar to Eq. (21), the rate formulation in Eq. (24) can be extended to account for the influence of temperature, thermodynamics, *TEA* availability, inhibition or biomass on degradation rate. Assuming that each compound is degraded according to first-order kinetics, Eq. (24) becomes:

$$R_{(t)} = -\int_0^\infty k \cdot g(k, 0) \cdot e^{-kt} dk \tag{25}$$
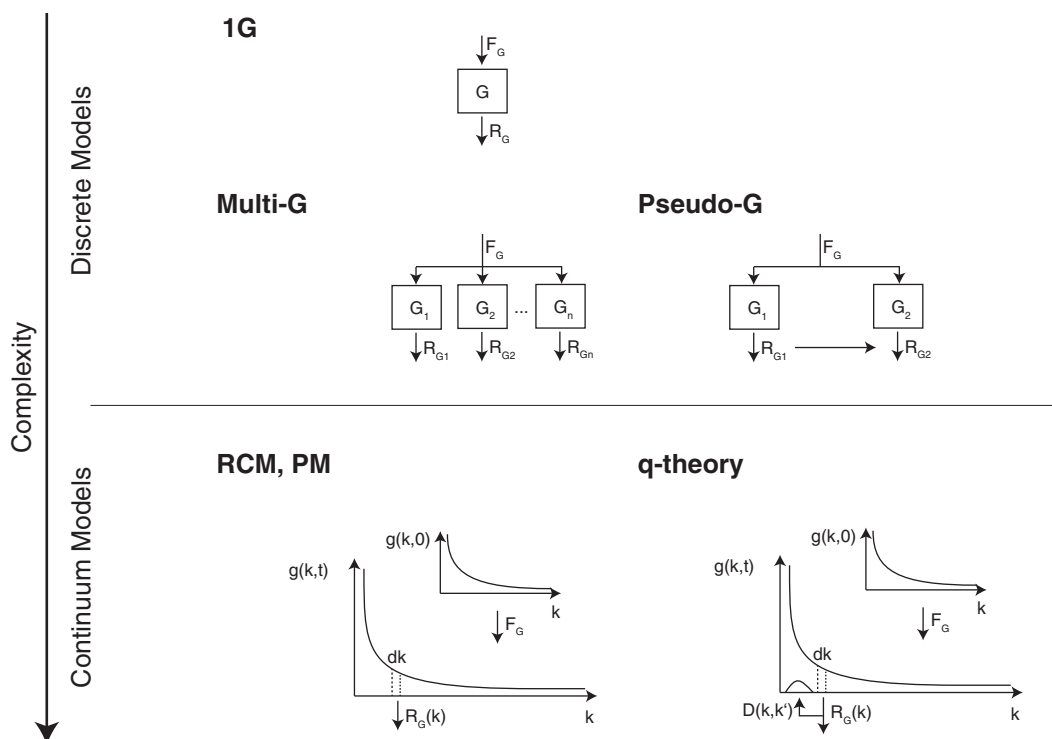
Fig. 9. Schematic illustration of organic matter degradation model structures. The common approaches can be broadly divided into discrete models that divide the bulk organic matter into discrete fractions, *G*, and continuum models that are based on a distribution of organic matter over reactive types, *g(k,t)*. The size of the organic matter pool is determined by the input flux, F_G, and the bulk degradation rate R_G.

where $g(k,0)$ denotes the initial distribution (Fig. 9). The initial distribution, $g(k,0)$, may take different mathematical forms, but cannot be inferred by observations. In their reactive continuum model (RCM), Boudreau and Ruddick (1991), following Aris (1968) and Ho and Aris (1987), proposed to assign the Gamma distribution to $g(k,0)$ due to its flexibility and desirable mathematical properties. Although their choice was partly guided by expedience, the Gamma function has the advantage of capturing the organic matter degradation dynamics observed in nature:

$$g(k,0) = \frac{g_0 \cdot k^{v-1} \cdot e^{-a \cdot k}}{\Gamma(v)} \qquad (26)$$

where the rate constant k is treated as a continuous variable and $\Gamma(v)$ is the Gamma function (e.g. Abramowitz and Stegun, 1972). The free, positive parameters a and v completely determine the shape of the initial distribution of organic matter compounds over the range of k values. In the RCM, the apparent rate of organic matter degradation is greater than the rate of a first-order law (Boudreau and Ruddick, 1991). However, for the gamma-based RCM, the rate can be formulated as a first-order degradation rate law by expressing the mean degradability of the organic matter mixture $g(k,t)$ as a function of time (Tarutis, 1993):

$$R_{(t)} = k(t) \cdot G_{(t)} \qquad (27)$$

with:

$$k(t) = v \cdot (a+t)^{-1} \qquad (28)$$

where a denotes the apparent initial age of the initial organic matter mixture and v indicates the shape parameter of the organic compound distribution. Fig. 10 illustrates the effect of different a and v values on the temporal evolution of the probability density, $g(k,t)/g_0$, and the degradability sediment depth profile as degradation progresses. High v and low a values indicate that the organic matter mixture is dominated by

labile organic matter compounds and, therefore, a higher degradability, k (Fig. 10a,c and d). Low v and high a values, on the other hand, indicate a dominance of refractory compounds and a low degradability (Fig. 10b,c and d). The parameter a controls the lifetime of the most reactive compounds (Fig. 10a and b). Low a values result in a rapid loss of the most reactive types, as illustrated by a rapid shift of the probability to less reactive types (Fig. 10a). Therefore, for a constant v value, low a values result in a higher degradability at the sediment–water interface and a faster decrease with depth (Fig. 10d). High a values, on the other hand, reflect a longer lifetime of the most reactive types and lead to a slower shift of the probability to less reactive types as degradation proceeds (Fig. 10d). For a constant v value, high a values lead to a lower degradability at the sediment–water interface, but a slower decrease of degradability with sediment depth (Fig. 10d). Drawing upon a large body of organic carbon depth profiles of well-dated cores and laboratory measurements, Middelburg (1989), statistically derived a formulation that is mathematically equivalent to Eq. (28), the power model (PM):

$$k(t) = v \cdot (a+t)^q. \qquad (29)$$

Rothman and Forney (2007) derived a similar functional relationship from a theoretical exploration of the effect of physical protection on organic matter degradability. However, Boudreau et al. (2008) criticized their assumptions and parameter choice. In addition, they point out that the model fails to explain the similarity between experimentally determined degradation rate constants of fresh organic matter in sedimentary and non-sedimentary environments. Wallmann et al. (2006) extended the power model to account for the accumulation of the reaction products methane and dissolved inorganic carbon (DIC) on anaerobic organic matter degradation:

$$k(t) = \frac{K_C}{K_C + DIC + CH_4} \cdot v \cdot (a+t)^{-q} \qquad (30)$$

where K_C denotes a half-saturation constant for the suppression of organic matter degradation when DIC and CH_4 build up in the porewaters.
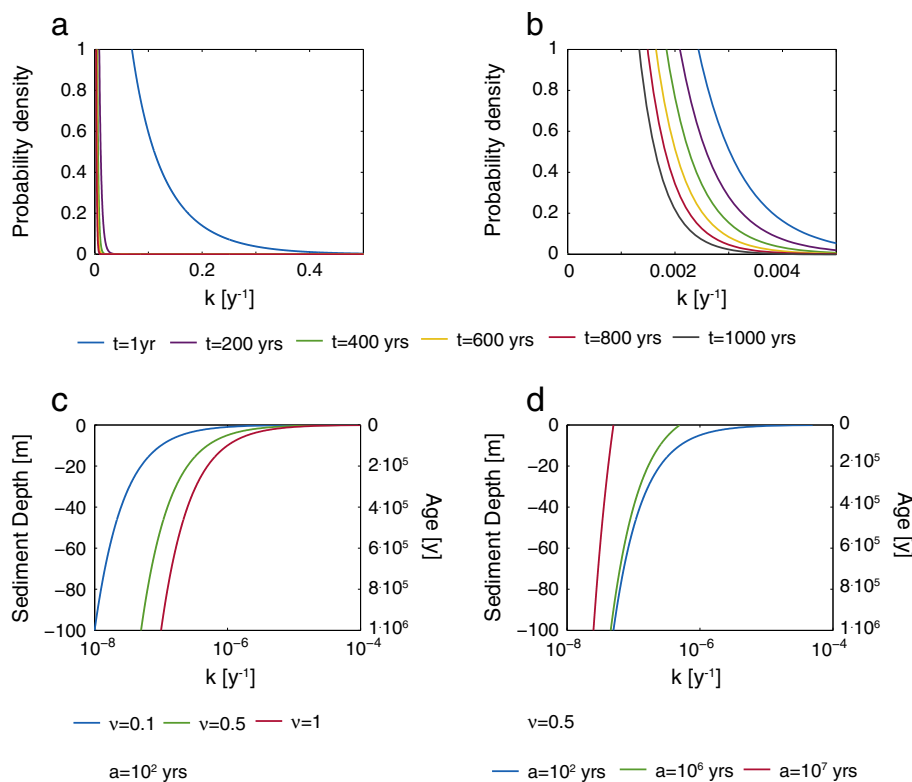
Fig. 10. Temporal evolution of the shape of the gamma distribution of organic matter reactive types for a) $v = 0.5$, $a = 10$ yr and b) $v = 0.5$, $a = 1000$ yr over 1000 yr of degradation. The preferential degradation of more reactive types results in a shift of the probability, $g(k,t)/g_0$, towards less reactive types with increasing time/degradation. The velocity of this shift depends on the magnitude of the parameter a. Dependence of the sediment depth profile of organic matter degradability, k, on c) different v values and d) a values. Sediment depth profiles are calculated assuming a sedimentation rate $\omega = 1 \cdot 10^{-4}$ m yr^{-1}.

Note that the PM (Eq. (29)) is only equivalent to a gamma distribution based RCM (Eq. (28)) if the exponent q in Eq. (29) is equal to -1. In addition, distributions other than the gamma-type initial distribution could be used in the RCM (Boudreau and Ruddick, 1991) and, therefore, all RCM models are not necessarily equivalent to the PM. For instance, Vähätalo et al. (2010) use a beta distribution to provide a probabilistic representation of degradation dynamics. In addition, both models are conceptually very different. While the power model uses a single time-dependent reaction rate coefficient, the reactive continuum model explicitly integrates the effect of compound-specific degradability on organic matter degradation. Based on isotopic evidence Aller and Blair (2004) have argued that the RCM is conceptually more satisfying to represent organic matter degradation in marine sediments; it is also in agreement with theoretical qualitative understanding of the degradation process (see Section 2). In the RCM, a and v are free parameters. Middelburg (1989) suggested that v is constant ($v \approx 0.16$) for a large number of organic matter mixtures from a wide array of benthic and pelagic environments. Based on the fit of the PM to field data, an exponent, q, close to -1 was derived. Recently, Jørgensen and Parkes (2010) found, however, that the degradation constant for buried organic matter determined by experimental sulfate reduction rate measurements leads to a more negative exponent q (-1.4 to -2). Their results suggest that the exponent can thus be variable and call for further investigation, especially in deeper and older sediments where methanogenesis is a dominant degradation pathway.

A noteworthy alternative to the PM and RCM is the q-theory (Fig. 9; e.g. Bossata and Ågren, 1985; Bossata and Ågren, 1991). Although the q-theory has never been directly applied to marine sediments, it is a popular choice in soil organic matter modeling (e.g. Manzoni et al., 2009). In the q-theory, the continuous distribution of organic matter compounds over the spectrum of degradabilities does not only change according to the respiratory loss of organic matter compounds, but also in response to a transfer of organic matter

between reactive types, $D(k,k')$ (Fig. 9). Such a transfer could be induced, for instance, by microbial assimilation and the production of by-products and dead microbial biomass (Ågren and Bosatta, 1996). Bossata and Ågren (1995) show that the PM and the RCM are particular cases of the q-theory. The q-theory reduces to the RCM if transfer of organic matter between compound classes is neglected. The PM is obtained from q-theory if specific functions are used for the microbial growth rate and growth efficiency (Bossata and Ågren, 1995).

4. Model applications: a synthesis

A comparative synthesis of organic matter degradation formulations used in 60 published diagenetic modeling studies at 251 different sites (Table 4a–e) covering a wide range of different environments (Fig. 11) provides insights into the criteria that have guided model choice.

Among all formulations, the 1G-Model is not only the oldest, but it is also the most popular (29 publications, 124 sites, Fig. 12a). Its popularity mainly stems from its mathematical properties that allow the derivation of analytical solutions for the diagenetic equation (Eq. (3)). Fig. 12a reveals nevertheless an increase in 2G-Model applications since the mid-1990s (16 publications, 72 sites), following the rapid increase in computing power that triggered the emergence of transient, coupled, multi-component diagenetic models (e.g. Soetaert et al., 1996; Van Cappellen and Wang, 1996). Most of the reviewed 1G and 2G-Model applications investigate shallow subsurface processes (<1 m) assuming steady-state conditions in the sediment-porewater system (Fig. 12b and c). Over the past decade, however, an increasing availability of comprehensive porewater data sets that resolve temporal variability (seasonal, annual) or large spatial scales (10–100's of m) has increased the need for model formulations that address organic matter degradation dynamics on these scales. As a consequence, the 3G-Model is currently experiencing an increased popularity in short-term
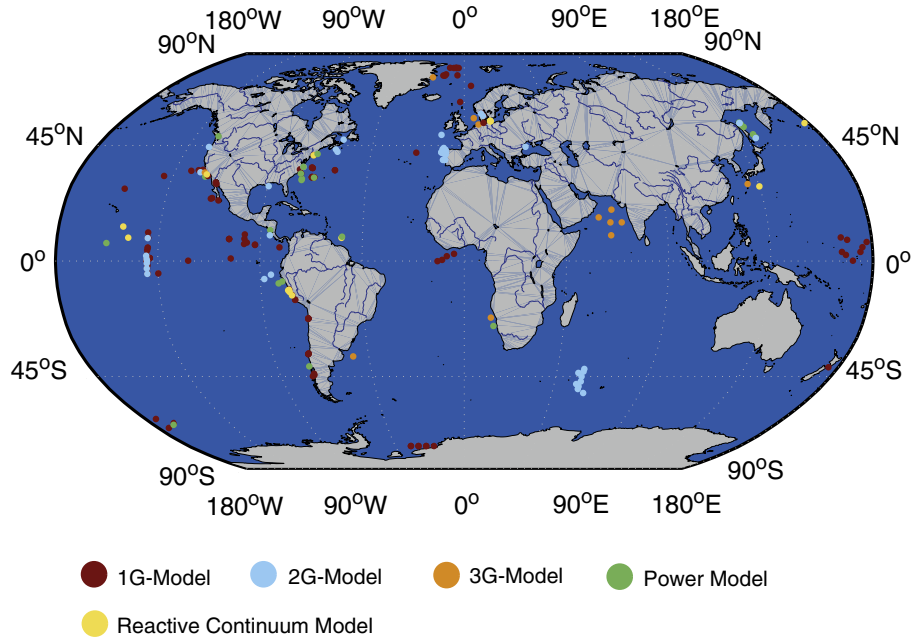
Fig. 11. Site locations of published model applications summarized in Table 4a–e.

transient model studies (9 publications, 14 sites, Fig. 12a and b). Nevertheless, it is important to note that G-type models converge to a constant apparent organic matter degradability at depth. They thus fail to reproduce the widely observed, continuous decrease in organic matter degradability with sediment depth (e.g. Middelburg and Meysman, 2007) and, therefore, their application should be limited to the maximum depth of observation. Continuum models, on the other hand, are better suited to investigate organic matter degradation dynamics at
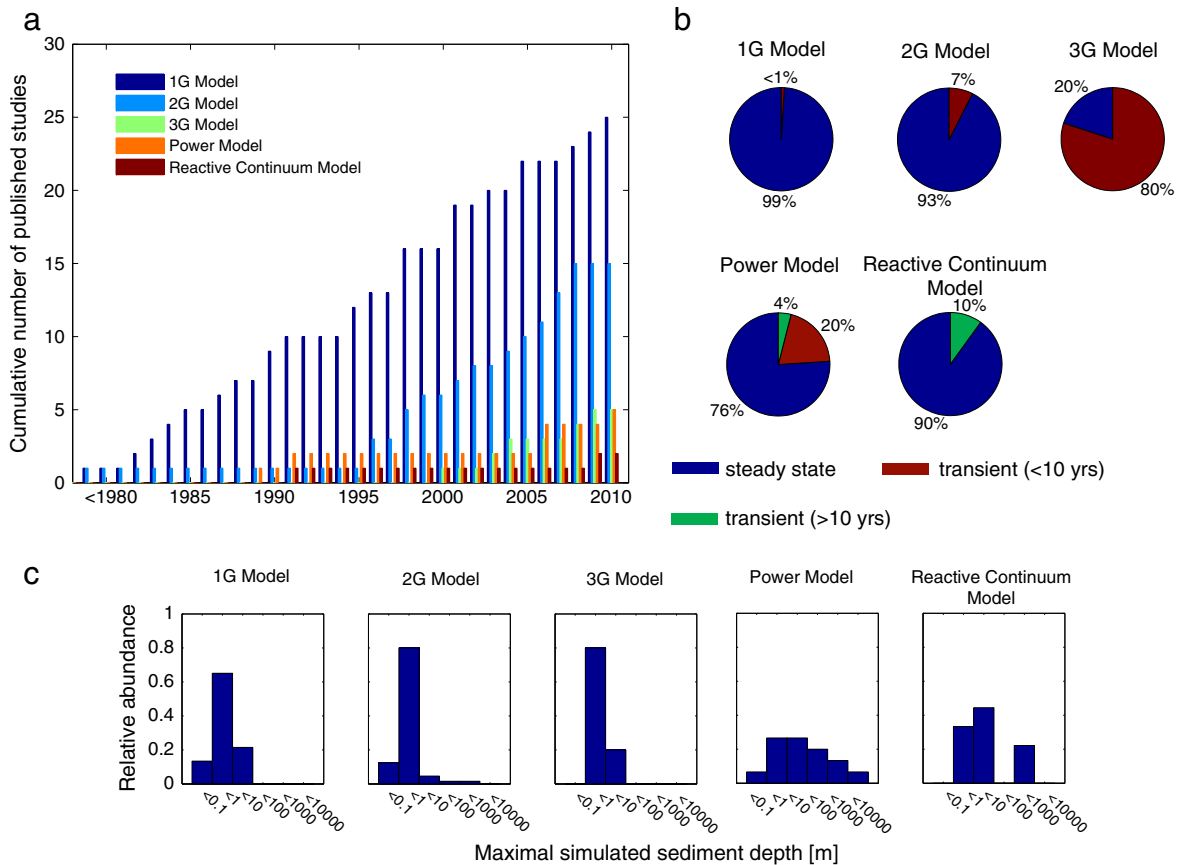
Fig. 12. a) Cumulative number of model studies using specific organic matter degradation models over the period 1979–2012. b) Relative abundance of steady state, short-term and long-term transient published model applications for specific organic matter degradation models. c) Relative abundance of maximum simulated sediment depths for each of the model approaches.

spatial and temporal scales that are not directly accessible by observation only. Therefore, both power (5 publications, 26 sites) and reactive continuum models (4 publications, 15 sites) are increasingly applied to simulate organic matter degradation (Fig. 12a,b and c), in particular in deep sediments (Arndt et al., 2006; Marquardt et al., 2010; Wadham et al., 2012) or over millennial and geological time scales (Arndt et al., 2009; Mogollon et al., 2012; Wehrmann et al., 2013). However, their predictive capability remains limited by our poor mechanistic understanding of the controls on organic matter degradation in the deep biosphere. Both, the popularity of the respective organic matter degradation models, as well as their mode of application illustrate the need for more sophisticated organic matter degradation models that directly results from the increased availability comprehensive observational data sets, as well as the increase in computing power.

5. Model structure and parameterization

In general, model parameters can be constrained on the basis of theoretical considerations or through site-specific field and laboratory observations. It has been commonly believed that the parameters of organic matter degradation models are related to the chemical composition of the organic matter. Yet, rate constants of different organic matter compounds at a single site may show a higher degree of similarity than rate constants of a specific organic compound at different sites (Middelburg et al., 1993), emphasizing the importance of other controlling factors, such as microbial community structure and abundance, bioenergetics, enzyme kinetics, macrobenthic activity, and/or adsorption by mineral surfaces that are not explicit included in most models (Table 4a–e). For instance, except for the controversial theoretical study of Rothman and Forney (2007), physical protection of organic matter has so far been ignored in model design. Thermodynamic constrains, metabolic inhibition or microbial dynamics are rarely included in the model design.

In general, 1G model applications are limited to the upper, oxic and biologically active sediment layer. Most of them only simulate organic matter and oxygen dynamics and, therefore, do not include Michaelis–Menten kinetics for TEA consumption or inhibition terms (Table 4a). Multi-G and continuum models, on the other hand, usually resolve at least a part of the redox sequence and thus generally integrate Michaelis–Menten and inhibition terms (Table 4b–e). Because early diagenetic modeling theory emerged from the field of geochemistry, the vast majority of models do not provide an explicit description of microbial dynamics (Meysman et al., 2005). Exceptions include models that have addressed the influence of microbial growth on redox dynamics (Boudreau, 1999; Wirtz, 2003; Thullner et al., 2005), the transient response of microbial communities to abrupt or periodic shifts in transport regimes (Wirtz, 2003; Dale et al., 2008a,b) and food–web interactions at a methane seep (Dale et al., 2008a, 2010). Thullner et al. (2005) and Dale et al. (2008a) showed that microbial growth kinetics might result in a lagged response to changing environmental conditions, thus highlighting the potential benefits of geomicrobial models for the transient case. The applications by Dale et al. (2008a,c, 2010) also account for bioenergetic limitations, an approach that is well-suited to simulate carbon turnover in energy-limited environments, such as the deep subsurface biosphere. Model predictions remain, however, partly theoretical because laboratory and field data required for calibration or validation are scarce or even missing. Yet, they highlight the limited predictive capabilities of simplified modeling approaches.

A comparative analysis of the model-derived degradation parameters for the 251 sedimentary settings (1G Model: 124; 2G-Model: 72, 3G-Model: 14; power model: 26; RCM: 15) provides further insights into the transferability of alternative model parameterizations. Reported parameter values generally span several orders of magnitude (Fig. 13). While for the continuum models, parameters are essentially randomly distributed, the distribution of k values for the G-models reveal distinct maxima around 10^{-3} yr^{-1} for k_2, 10^0–10^1 yr^{-1} for k_1 and around 10^1 yr^{-1} for k_0. Furthermore, the maximum in k_1 values from published 1G-Model applications is systematically lower than the k_1 maximum from 2G-Model applications. This result is consistent
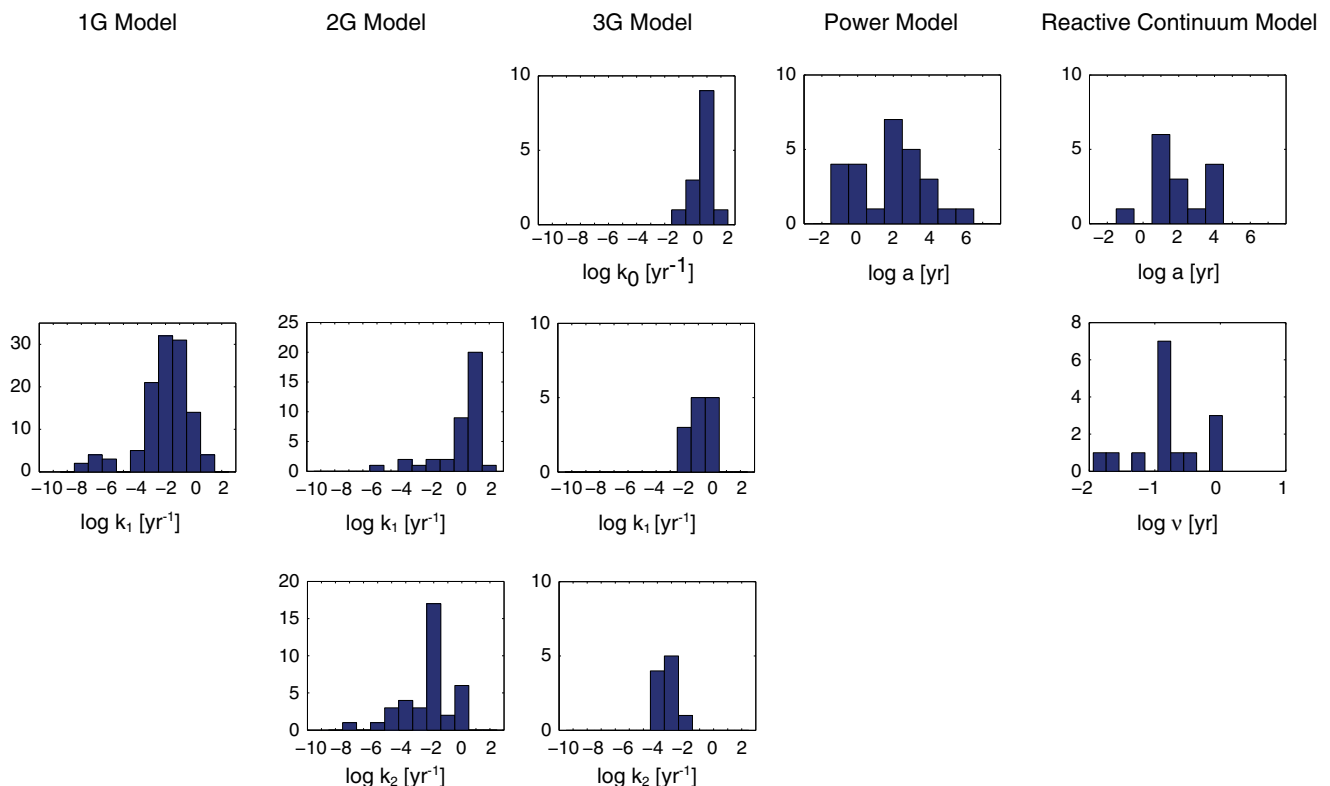
Fig. 13. Distribution of organic matter degradation model parameters reported in the literature.

with the idea that the first order degradation rate constant in the 1G-Model represents the average degradability of the bulk organic matter over the specified model domain. It should thus be lower than the k_1 values of multi-G model applications that only represent the degradability of the most labile organic matter fraction. In addition, multi-G model approaches are usually applied to either resolve the subsurface dynamics near the SWI or the slower dynamics in deep sediment layers. In the former case, organic matter degradation rate constants (k_1/k_2 or k_0/k_1) typically fall into the higher end of the reported range, while in the latter case they plot at the lower end of the spectrum.

The comparative analysis reveals that parameter values are model-specific and should thus be compared with caution. It also reflects the lack of a mechanistic foundation of the organic matter degradation models and the site-specific nature of parameter values. Both the distribution of organic matter among different fractions and the degradability of each fraction will depend on the timescale of observation and the characteristics of the site (e.g. Burdige, 2006). In addition, the limited number of studied sites and the sampling bias towards geochemically more interesting sites or "hot spots" (e.g. Henrichs, 1993) further complicates the comparison of model results and their transferability.

6. Regional and global upscaling

Diagenetic models have proven extremely useful in quantifying organic matter degradation dynamics at specific sites for which comprehensive observational data sets are available to constrain the model parameters. However, these models are of limited value in the context of global modeling unless a mechanistic framework for model parameterization can be specified for the entire spectrum of boundary conditions encountered at the seafloor.

6.1. A review of global relationships

The need for a general framework that allows constraining model parameters in data-poor areas has been recognized since the formative days of diagenetic modeling and, consequently, different approaches have been proposed in the literature. The most common strategy has been to relate the rate constant to easily observable quantities that characterize the depositional environment. Based on the rationale that the degree of organic matter degradation in the water column controls its degradability in the sediment, it has been argued that the degradation rate constant should correlate with water depth. Although no global empirical relationship between these two variables has been proposed, model-determined rate constants from depth transects along continental slopes (e.g. Epping et al., 2002) indeed reveal a decrease with increasing water depth. More quantitative approaches relate degradation rate constants to deposition rates or organic matter fluxes. For instance, a positive correlation between the rate constant (of sulfate reduction) k, and the deposition rate, ω was first identified by Toth and Lerman (1977). Drawing on a larger dataset of first order rate constants, their relationship was then revised by Tromp et al.
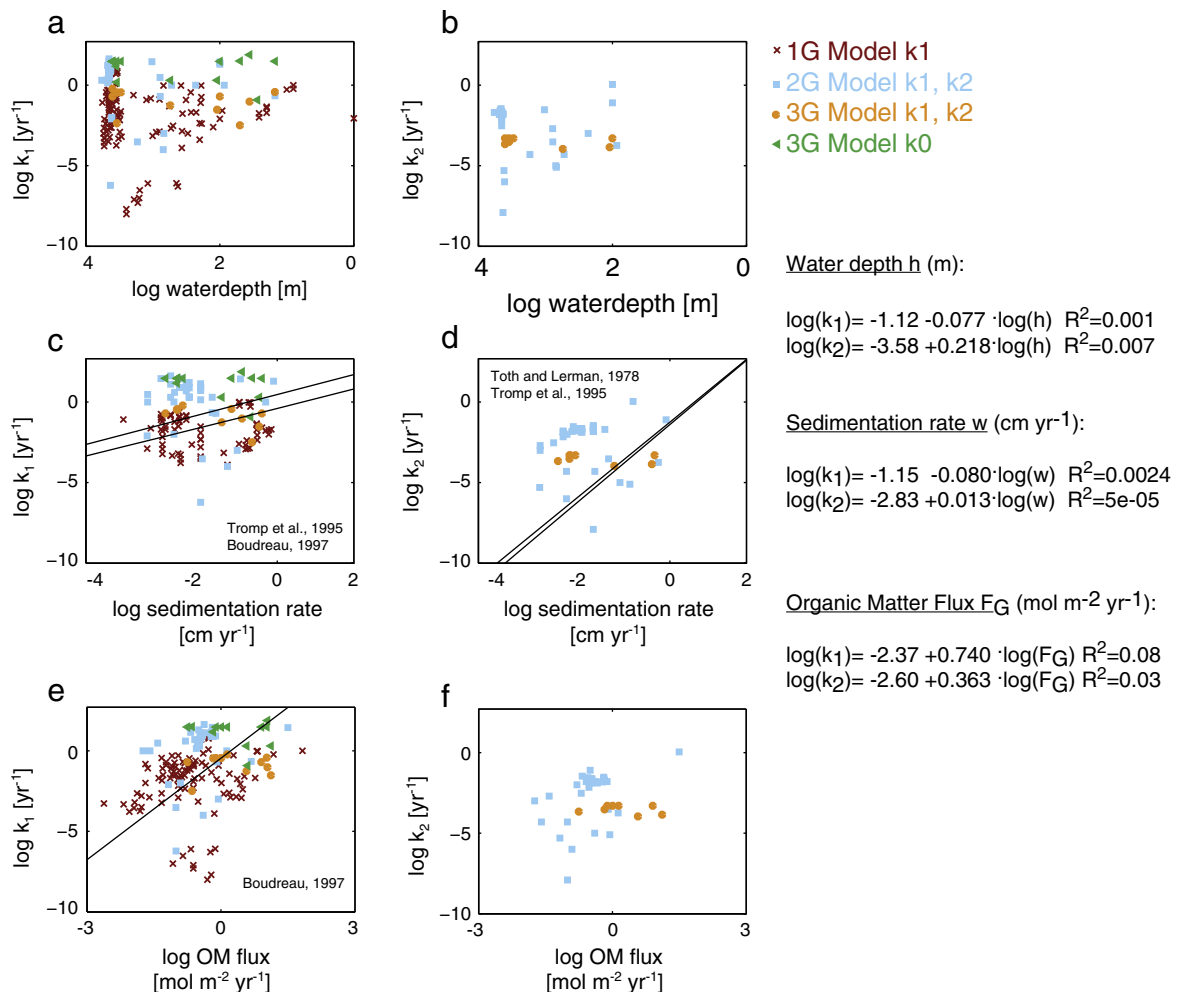
Fig. 14. Distribution of organic matter degradation rate constants over water depth (a, b), sedimentation rate (c, d) and organic matter deposition flux (e, f). Black lines indicate published relationships. The results of a linear regression analysis are provided with Coefficients of Determination R^2.

(1995) and further complemented with a k–w relationship for aerobic degradation rate constants (see also Boudreau, 1997). Emerson (1985) and Murray and Kuivila (1990) argued however that aerobic rate constants may correlate better with organic matter fluxes than deposition rate following a power law relationship. These global relationships are nevertheless drawn from a limited number of observations. As already emphasized at the time of their publication, they might thus not be representative of the wide diversity of seafloor conditions. The synthesis carried out here (n = 251; Fig. 11, Table 5) allows revisiting these global relationships.

The distribution of compiled k_0, k_1 and k_2 values over corresponding water depths, deposition rates and organic matter fluxes are reported in Fig. 14. Model-determined rate constants for the highly reactive pool, k_0, are shown alongside the k_1 values and, altogether, the k_i values span almost 10 orders of magnitude. Although the distribution of rate constants might show a very weak trend with water depth (Fig. 14b), deposition rates (Fig. 14d) and organic matter flux (Fig. 14e and f), no statistically significant relationship can be established ($R^2 \ll 0.1$). Similarly, the parameters of the continuum models show little or no correlation with water depth or deposition rate (Fig. 14). While the PM applies a fixed pre-factor of 0.16, model-constrained v-parameters of the RCM vary between 0.01 and 1.08. Based on their analysis of 8 sediment cores from very different environments, Boudreau and Ruddick (1991) argued that the v-parameters could be divided into two groups. The majority of the cores are dominated by refractory components, as reflected by low v-parameters between 0.1 and 0.2. The remaining cores are characterized by higher v-parameters between 0.8 and 1.0. Nevertheless, the authors point out that more data would be needed to confirm such a trend and to determine its underlying causes.

The a parameters in continuum models is conceptually related to the average age of the organic matter at the sediment water interface. Its value should thus correlate with factors that control the transit time of organic matter from the euphotic layer to the seafloor (Middelburg, 1989; Boudreau and Ruddick, 1991). Middelburg (1989) showed that a increases with increasing water depths and decreasing deposition

rates. The compilation by Boudreau and Ruddick (1991) also reveals the inverse trend between a and deposition rate. The analysis performed here confirms the weak correlation with water-depth and deposition rates (Fig. 15c and d), although it should be emphasized again that the dataset is still limited while the variability remains significant, especially at low deposition rates (Fig. 15d).

The difficulty to identify statistically significant relationships between organic matter degradation rate constants and individual factors such as water depth, deposition rate, or organic matter flux is, in the light of the complexity of the problem, not surprising. None of these master variables comprehensively include the different chemical, physical and biological factors that control organic matter degradation. For instance, although water depth may be used to evaluate organic matter degradability along a given transect through a particular depositional environment (e.g. Epping et al., 2002) it is not a sufficiently robust proxy to constrain the degradability on the global scale. Furthermore, even if the deposition rate and thus the residence time of organic matter in the oxic, biologically active surface layer is an important control on organic matter degradability, a global scale analysis cannot be reduced to this factor only.

6.2. Diagenetic models at regional and global scales

Over the past decades, the increased availability of observational data, the increased computational power, as well as the development of coupled biogeochemical and Earth system models has fostered the emergence of diagenetic models suited for global and regional scale applications (Table 6). The research efforts have broadly followed two distinct paths. First, generic models tackling the full complexity of the coupled diagenetic processes have been developed (OMEXDIA, Soetaert et al., 1996; STEADYSED, Van Cappellen and Wang, 1996; CANDI, Boudreau, 1996; BRNS, Regnier et al., 2002; Aguilera et al., 2005; ISM, Wirtz, 2003; MUDS, Archer et al., 2002; MEDIA, Meysman et al., 2003). These models are not designed for a site-specific problem, but rather aim for a high degree of transferability. Yet, they are generally constructed using a multi-G approach. Degradation rate constants and organic matter fractions are

Sedimentation rate w (cm yr^{-1}):

$\log(a) = 3.35 - 14.81 \cdot w$ $R^2 = 0.46$

- Reactive Continuum Model
- Power Model
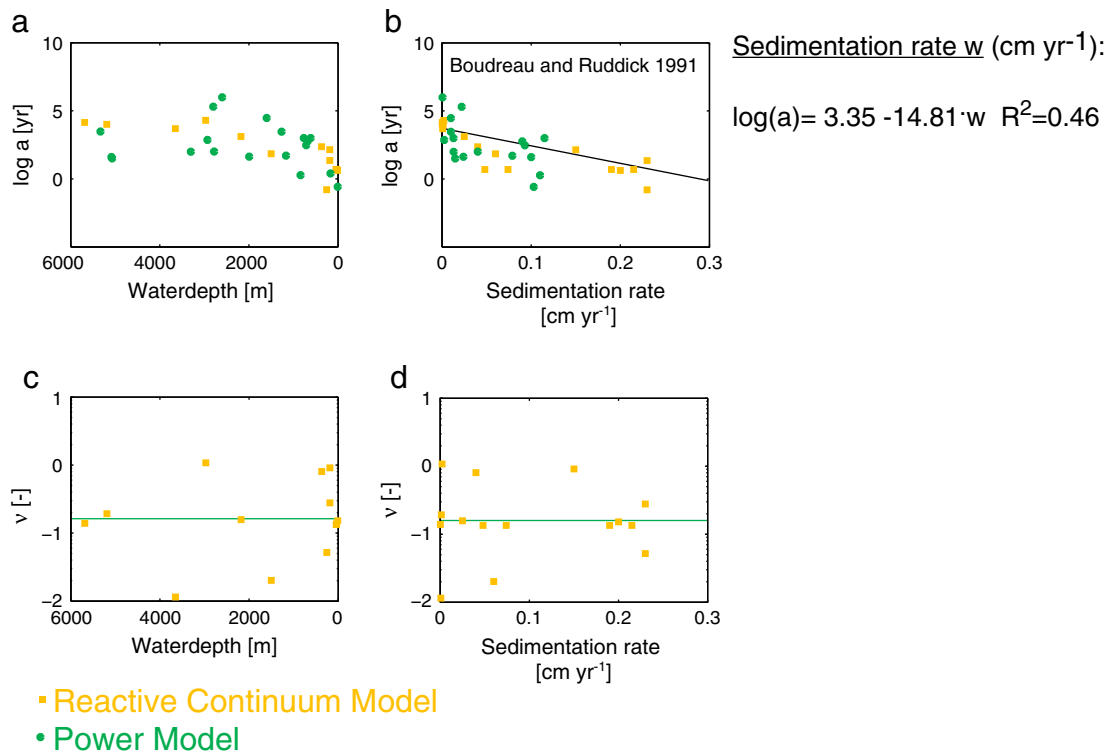
Fig. 15. Distribution of continuum model parameters over water depth and sedimentation rate. The black line indicates the published a-w relationships (Boudreau and Ruddick, 1991). The result of a linear regression analysis is provided with the Coefficient of Determination R^2.

Table 6
Summary of parameterizations used in generic diagenetic models or diagenetic submodules.

Model	Approach	Parameterization	Master variable	Reference
Generic diagenetic models				
EDGE Global early diagenetic model	1G	$k_{ox} = 1.5e-9\ s^{-1}$ $k_{NO3} = 5e-10s^{-1}$ $k_{MnO2} = 5e-16\ l\ \mu mol^{-1}\ s^{-1}$	–	Rabouille and Gaillard (1991a,b)
OMEXDIA Carbon and nutrient cycling in marine sediments	3G-Model	$F_0 = 0.74 \cdot F_{POC}$ $k_0 = 26\ yrs^{-1}$ $F_1 = 0.26 \cdot F_{POC}$ $k_1 = 0.26\ yrs^{-1}$ $F_2 = 1.9 \cdot w^{1.31}$ $k_2 = 0\ yrs^{-1}$	F_{POC} implicitly h and T	Soetaert et al. (1996)
STEADYSED Fe-Mn cycling	1G-Model or imposed profile	User defined	–	Van Cappellen and Wang (1996); Wang and Van Cappellen (1996)
CANDI Carbon and nutrient cycling in continental margin	2G-Model	User defined or $F_1 = 1$ $k_1 = 2.2 \cdot 10^{-5} \cdot F_{POC}\ (k < 1)$ $k_1 = 1.0\ (k > 1)$ (Boudreau, 1998)	F_{POC} implicit w	Boudreau (1996)
BRNS Flexible reaction–transport code for porous media	User-defined, applications include 1-G Model, multi-G model and RCM	Local applications: user defined global application (Thullner et al., 2009): k–w relationship (Tromp et al., 1995)	– w implicitly h	Regnier et al., (2002); Aguilera et al. (2005)
MEDIA Flexible reaction–transport code for porous media	Multi-G	User defined	–	Meysman et al. (2003)
ISM Biogeochemical dynamics in near-shore sediments	3G-Model	User defined	–	Wirtz (2003); Holstein and Wirtz (2009)
MUDS Oxic and anoxic diagenesis of shallow and deep sea sediments	2G-Model (TEA-dependent k)	$F_1 = 0.5\ F_{POC}$ $F_2 = 0.5\ F_{POC}$ $k_{1O_2} = D_{B0}/z^2_{scale,1}$ $k_{2O2} = D_{B0}/z^2_{scale,2}$ $k_{1O_2} = 0.3\ k_{1O2}$ $k_{1Mn} = 1.9 \cdot 1.0753 \cdot 10^{-16}\ F_{POC}^{1.75}$ $k_{1Fe} = 0.4 \cdot 1.0753 \cdot 10^{-16}\ F_{POC}^{1.75}$ $k_{1SO4} = 1.3 \cdot 1.0753 \cdot 10^{-16}\ F_{POC}^{1.75}$ $k_{2,i} = k_{1,i}$ $k_{2O_2}/k_{1O_2}\ i = Mn, Fe, SO_4$ Toth and Lerman (1977), tuned to global data	D_{B0}, z_{scale} for oxic pathways, F_{POC} for anoxic pathways Implicit F_{POC} for oxic pathway	Archer et al. (2002)
Diagenetic submodules within coupled system scale models				
HAMOOC sediment Sediment model for longterm climate studies	1G-Model	$k_{ox} = 0.05\ yr^{-1}$ $k_{ox} = 0.01\ yr^{-1}\ (h < 2000\ m)$ $k_{ox} = 0.005\ yr^{-1}\ (h < 2000\ m)$ $k_{ax} = n.d.$	Tunable fit to Seiter et al. (2004)	Heinze et al. (1999); Palastanga et al. (2011)
DCESS sediment Sediment model for longterm coupled climate studies	1G-Model	$k_{O2} = k_0 D_B/D_{B0}$ $k_{anox} = \beta_0(F_{POC}/F^0_{POC})^\gamma \cdot k_{O2}$ $F^0_{POC}: 10^{-12}\ mol\ cm^{-2}\ s^{-1}$ $D_{B0}: 10^{-8}\ cm^2\ s^{-1}$ $k_0: 0.093$ (tuned to data) $\beta_0: 0.897$ (tuned to data)	D_B for oxic pathway, F_{POC} for anoxic pathway	Shafer et al. (2008)
MEDUSA Sediment model for longterm coupled climate studies	1G-Model	$k_1 = 0.024\ yr^{-1}$	tuned to match global burial rate of 0.02Gt C/yr (Berner, 1982)	Munhoven (2007)
Benthic submodel in ERSEM Sediment model for ecosystem model ERSEM	1G-Model	Degradation coupled to benthic foodweb model		Ebenhöh et al. (1995)
Benthos6 Sediment model for ecosystem model PROWQM	1G-Model	$k_1 = 0.02d^{-1}$	–	Lee et al. (2002)
MIRO sediment Sediment model for ecosystem model MIRO	2G-Model	$k_1 = 78.84 - 0.0876\ yr^{-1}$ $k_2 = 43.8 - 0.0876\ yr^{-1}$	T	Gypens et al. (2008)

F_1: Flux of first POC fraction, F_2: Flux of second POC fraction, F_3: Flux of third POC fraction, $k_{1,TEA}$ degradation rate first POC fraction using TEA (k independent of TEA if no TEA is provided), $k_{2m,TEA}$: degradation rate second POC fraction using TEA, $k_{3,TEA}$: degradation rate third POC fraction using TEA, D_b: bioturbation coefficient, T: Temperature, h: water depth, w: sedimentation rate, z_{scale}: oxygen consumption scale depth (see Hales and Emerson, 1996, 1997 for more details), k_0 oxic remineralization rate scale; F^0_{POC}: organic carbon rain rate scale, D_{B0}: bioturbation rate scale.

either defined by the user or specified on the basis of published empirical relationships. Notable exceptions are the MEDIA and BRNS environments that offer full flexibility in the choice of model components and

biogeochemical reactions, including the formulation of organic matter degradation kinetics. A second group of models has emerged out of the need for realistic descriptions of the benthic–pelagic coupling at regional

(ERSEM, PRWQM, MIRO) or global scales (HAMOOC, DCESS, MEDUSA). Although generic diagenetic models, such as, MUDS (e.g. Ridgwell, 2007; Ridgwell and Hargreaves, 2007; Archer et al., 2009) or CANDI (e.g. Luff and Moll, 2004) have addressed diagenetic processes at large scales, their application remains limited by the high computational requirements for the simulation of the coupled redox and equilibrium reactions at an adequate resolution. Therefore, the applied model structure and formulation is generally less sophisticated and comprehensive than in state-of-the art diagenetic models. In particular, most coupled models rely on the 1G approach with a constant degradation rate constant, often tuned to match existing estimates of the organic carbon burial rate at the global scale (Table 6).

6.3. Identification of regional trends

The emergence of sophisticated, global biogeochemical or Earth system models has sparked the desire for more generic diagenetic models that could provide robust estimates of diagenetic processes on the global or regional scale. Such an approach inevitably has to account for the regional variability in controlling factors. The identification of an environmental vector that unambiguously characterizes the depositional environment with respect to the most dominant controlling factors could provide a promising route towards a generic algorithm for the parameterization of organic matter degradation models. Seiter et al. (2005) used a large dataset of total organic carbon (TOC) and diffusive oxygen uptake (DOU) to subdivide the global ocean (water depth >1000 m) into ten different groups of oceanic provinces, each with a specific TOC/DOU signature. Because oceanic regions within one group are generally characterized by similar organic matter sources and export efficiencies, Seiter et al. (2005) argued that differences between the ten groups are mainly related to the environmental characteristics of the depositional environment. The compilation of POC flux data by Lutz et al. (2002) (Fig. 3) also revealed a regional difference in the efficiency of the biological pump in transferring organic carbon from surface waters to the ocean's interior.

Fig. 16 synthesizes the values of apparent first order degradation rate constants, k_{ap} ($k_{ap} = \sum k_i \cdot G_i/G$), derived from model parameters reported in Table 5a–e, as well as published radiocarbon (^{14}C)

ages of sedimentary organic carbon from the respective regions (Griffith et al., 2010). The use of apparent constants allows for a direct comparison between different G models of organic matter degradation. However, it should be noted that the degradation rate constants extracted from 1G-Model applications provide an integrative measure for the degradability of both labile and refractory organic matter compound classes and may thus underestimate the degradability of organic matter at the sediment–water interface. Therefore, they are generally lower than the apparent rate constants of the multi-G applications. Fig. 16 reveals general trends in organic matter degradability for different depositional environments.

6.3.1. Arabian Sea, Greenland Sea, Antarctic Polar Front, Eastern Tropical Pacific

Sediments from the Arabian Sea, the Greenland Sea, the Antarctic Polar Front as well as from the eastern Tropical Pacific are characterized by a high organic matter degradability (highest k, Fig. 16a). These findings are in agreement with the steep gradients in TOC/DOU data reported by Seiter et al. (2005), which indicate high benthic mineralization rates and high degradability of the depositing organic matter. Young ^{14}C ages translate into high F_m values (Fig. 16b) and point to a dominantly marine organic matter source and a strong coupling between the photic zone and the sediment. Model-determined rate constants of the most labile fraction in the Greenland Sea ($k_0 = 75.68$ yr^{-1}; Berg et al., 2003), the Arabian Sea ($k_0 = 15$–30 yr^{-1}; Luff et al., 2000), the Tropical Pacific ($k_1 = 2$–43 yr^{-1}; Hammond et al., 1996) and the Antarctic Polar Front ($k_1 = 1.4$–16.4 yr^{-1}; Rabouille et al., 1998) are comparable to degradation rate constants attributed to fresh phytoplankton ($k = 7$–26 yr^{-1}; Westrich and Berner, 1984). Thus, they support the idea of a very efficient vertical transfer of freshly produced marine organic matter from the surface ocean to the sediment (Lutz et al., 2002; Seiter et al., 2005). In the Arabian Sea, the vertical transport is stimulated by intense eolian dust input from the Arabian Peninsula and other Asian sources (e.g. Haake et al., 1993; Ittekkot, 1993; Schnetger et al., 2000; Armstrong et al., 2002). In the productive high-latitude oceans and the eastern equatorial Pacific, carbon export is accelerated by aggregation and the presence of ballast minerals such as calcite and silicates (Armstrong et al., 2002; Berelson, 2002; Klaas and Archer, 2002). A steady balance between diatom and coccolithophore production dramatically accelerates particle export in the Equatorial Pacific, as witnessed by the presence of chlorophyll containing organic matter in the underlying sediment (Smith et al., 1996). In the Polar and Subantarctic Fronts (Rabouille et al., 1998), small and spiny spore forming *Chaetoceros* species or other phytodetritus aggregate in the form of fast-sinking particles. These aggregates support high deposition fluxes, equivalent to 70–100% of the local export production (Smetacek, 1985, 1999; Abelmann et al., 2006). Aggregate formation during bloom conditions is also responsible for the high export efficiencies in the basin area of the Greenland–Norwegian–Iceland Sea (Ritzrau et al., 2001). TOC and DOU data from this area indicate that the overall degradation of organic matter is as high as in the Arabian Sea (Seiter et al., 2005).

6.3.2. Continental margins

Continental margins are the transition zones between the coastal (water depth <200 m) and the deep ocean and comprise the continental shelf (waterdepth >200 m), the continental rise and the continental slope. They are important, but extremely complex components of the global carbon cycle that are influenced by a variety of organic matter sources, by intensive lateral transport and large river plumes and by abrupt relocation of sediment through successive erosion/deposition cycles. They also reveal a strong temporal variability and a marked seasonality in energy, organic matter fluxes and redox conditions. The heterogeneous nature of margins is reflected in the large number of provinces used by Seiter et al. (2004, 2005)
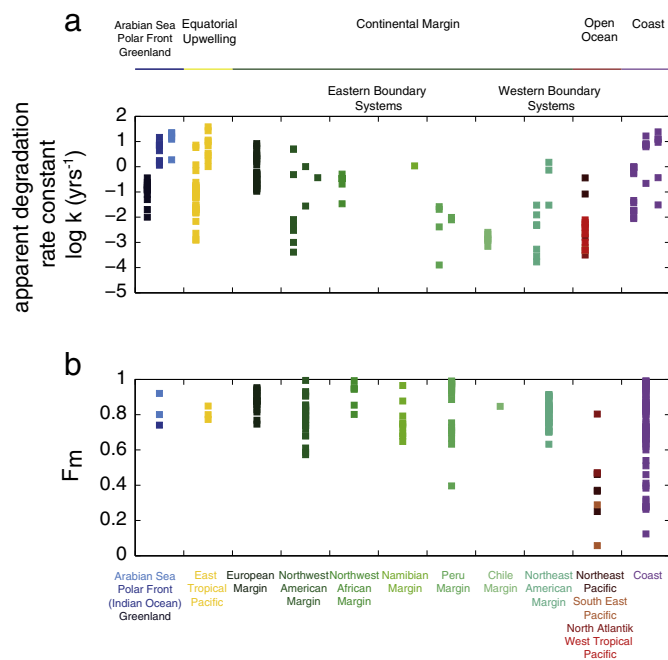

Fig. 16. Regional distribution of a) apparent degradation rate constants (Table 5a–c) and b) radiocarbon (^{14}C) contents of total organic carbon as fraction of modern, F_m (Griffith et al., 2010).

to regionalize this area. Our compilation also highlights the large variability in k_{ap} and F_m values (Fig. 16a,b), for both western and eastern boundary systems.

6.3.3. Western boundary systems

Western boundary systems are characterized by poleward flowing intensified surface currents and are often subject to intermittent coastal upwelling. The North American continental margin region is strongly influenced by the Gulf Stream, but also receives sediments from the Canadian margin off Nova Scotia. Apparent degradation rates and F_m values are variable and reflect a mixture of in-situ produced organic matter and allochtonous organic matter that is supplied by variable processes such as lateral advection or focusing of fine-grained sediment and entrainment in the deep recirculation gyre. The contribution of this pre-processed material results in comparably low apparent degradation rate constants.

6.3.4. Eastern boundary systems

Eastern boundary systems are generally characterized by equatorward flowing surface currents and associated with coastal upwelling, which fuels high primary productivity. The Iberian Upwelling system, the Pacific Ocean off western North America and the various coastal upwelling cells on the equatorial Western African Margin are classic eastern boundary systems. Primary productivity and thus benthic deposition of organic matter reveals a strong temporal variability. Apparent degradation rate constants are representative of partially mineralized, fresh phytodetritus and decrease with increasing distance from the shore (Epping et al., 2002; Table 5b). Comparably high F_m values indicate that the sedimentary organic matter is relatively young. However, the large variability in F_m values and apparent degradation rate constants suggests that, in particular at offshore locations, resuspension and degradation in the benthic boundary layer may exert an important influence on organic matter degradability and age. In addition, the supply of terrestrial or fossil organic carbon by large rivers may result in even lower degradation rate constants and F_m values (Fig. 16).

The Humboldt (Chile, Peru) and Benguela (Namibia) eastern boundary upwelling systems are among the most productive areas of the world. Yet, these regions are characterized by apparent rate constants of intermediate values (Fig. 16). Although these systems are dominated by marine organic matter and generally reveal exceptionally high primary production rates, factors such as high deposition rates, low water column oxygen concentrations, intense mineral protection or high sediment reworking rates associated with strong bottom currents may reduce organic matter degradability (e.g. Mollenhauer et al., 2003; Inthorn et al., 2006; Mollenhauer and Eglinton, 2007). The wide range of F_m values support these observations (Fig. 16). They generally reveal a rapidly decreasing trend with increasing water depth suggesting that a significant fraction of the benthic organic matter is pre-aged (Griffith et al., 2010). Observed discrepancies between the ^{14}C age of specific algal biomarkers (alkenones) with co-occurring planktonic foraminiferal carbonate confirm the important influence of pre-depositional processes on organic matter ages and, thus, degradability (e.g. Mollenhauer et al., 2003, 2005; Griffith et al., 2010). At these highly productive continental margin sites, the dominance of slowly sinking fluffy aggregates and the continuous resuspension by strong bottom water currents that maintain organic matter for an extended period in extensive bottom nepheloid layers and, thus, disperse material laterally across the margin. For example, Mollenhauer et al. (2003) showed that the radiocarbon age of alkenons in sediments from slope depocenters underlying the Benguela upwelling zone is as much as 4000 yr older than the radiocarbon age of foraminifera from the same sediments. This result reveals that degradation within the nepheloid layer consumes most of the labile organic matter compounds and the depositing benthic organic matter is thus comparably old, degraded and unreactive. In addition, the presence of *Thiomargarita namibiensis*,

Beggiatoa or *Thioploca sp.* mats (e.g. Vairavamurthy et al., 1995) as well as the occurrence of periodical outgassing events in these areas (e.g. Brüchert et al., 2003; Weeks et al., 2004; Brüchert et al., 2006) indicate that sediments are predominantly anoxic and sulfide-rich. The euxinic conditions promote the sulfurization of organic matter during the early diagenetic stages (<1000 yr) and may significantly reduce the degradability of organic matter (e.g. Van Kaam-Peters et al., 1998; Moodley et al., 2005). High concentrations of organic sulfur are found in sediments from all coastal upwelling areas (e.g. Mossmann et al., 1991; Vairavamurthy et al., 1995; Suits and Arthur, 2000). Thus, the reduced degradability of the sulfurized organic matter enhances, in combination with high deposition rates and anoxic environmental conditions, organic matter preservation and burial (e.g. van Kaam-Peters et al., 1998; Zonneveld et al., 2010).

6.3.5. Central Gyres, Western Tropical Pacific

The central, deep ocean gyres and the western tropical Pacific generally reveal low apparent degradation rate constants and radiocarbon ages ($F_m < 0.5$). Enriched δ^{13}C values indicate a predominantly marine origin of organic matter deposited in these regions. Open ocean provinces are characterized by low accumulation rates (e.g. Jahnke, 1996; Seiter et al., 2005; Røy et al., 2012) and low export efficiencies due to the intense degradation of organic matter in the water column (e.g. Lutz et al., 2002; Henson et al., 2012). As a result, the depositing organic matter is refractory and benthic oxygen uptake is low (Seiter et al., 2005; Fischer et al., 2009; Røy et al., 2012). The lowest apparent degradation rate constants are determined for sediments in the Northern Atlantic Hatteras Abyssal Plain (Heggie et al., 1987) and the South Eastern Pacific Ocean (Reimers and Suess, 1983). The highest values are recorder in deep-sea sediments of the North Eastern Pacific (Murray and Kuivila, 1990), but the DOU/TOC data for the North East Pacific reveals that this region is in fact closely related to the adjacent Northwest American Continental Margin (Fig. 16). The reasons for the comparably high degradability in this oligotrophic ocean province remain elusive but may be related to a strong seasonality in organic matter fluxes (Smith and Baldwin, 1984) or a lateral transport of organic matter from the continental slope (e.g. Jahnke et al., 1990; Mollenhauer et al., 2005; Mollenhauer and Eglinton, 2007).

6.3.6. Coastal ocean

Sediments underlying the shallow coastal ocean (water depth <200 m) show a significant heterogeneity in k_{ap} and F_m values (Fig. 16). These shallow systems receive highly variable organic matter loads from different sources and are subject of erosion/deposition cycles, as well as a strong temporal variability and a marked seasonality. They also receive high loads of pre-processed terrestrial or fossil organic matter that may result in extremely low F_m values. Coping with this high degree of variability is currently not achievable with the existing set of model-derived values.

6.3.7. Regional synthesis

Fig. 16 reveals general trends in organic matter degradability for different depositional environments. These trends can be broadly related to important characteristics of the depositional environment, such as the main organic matter source or the transport efficiency of organic matter through the water column and, thus, its age. Fig. 16 nevertheless also shows that organic matter degradability inherent to each environment remains highly heterogeneous. The use of different sampling techniques may lead to variability in model-determined rate constants. For instance, the loss of the top sediment in gravity cores as opposed to multi-cores may result in variations in k_1 and k_0. Furthermore, primary driving factors such as organic matter fluxes and sources, deposition rates, lateral transport processes, water depth or benthic and pelagic redox conditions may reveal strong gradients within one province that translate into differences in organic matter degradability. For instance, Moodley et al. (2011) found low

degradation rate constants for sedimentary organic matter from the oxygen minimum zone (OMZ) of the Arabian Sea. The reduced degradability of the organic matter in an environment that is otherwise dominated by highly reactive organic matter is supported by relatively low biomass in sediment below the OMZ zone on the Pakistan margin and western Indian continental margin of the Arabian Sea (Woulds et al., 2009; Ingole et al., 2010). Nevertheless, the emergence of a global patterns indicates that, despite the observed inter-regional variability, a global characterization of depositional environments could facilitate the search for global and regionalize patterns that would ultimately allow a better quantification of organic matter degradation dynamics in data-poor areas.

7. Challenges

Despite the increasing number of reactive-transport model studies, the increasing demand for prognostic diagenetic modeling tools and the considerable progress made in understanding the dynamics of organic matter degradation, organic matter degradation models have not significantly evolved for over two decades. The mathematical formulations of organic matter degradation are still highly simplified and thus of limited transferability across time and space. One of the biggest challenges facing the next generation of reaction-transport models will be the development of generalized biogeochemical reaction networks that apply to the entire spectrum of boundary conditions encountered at the seafloor. Our ability to understand the global biogeochemical cycling and to assess past and future global change will critically depend on the development of such prognostic tools. Future progress will strongly depend on an increased availability of observations from different marine environments, as well as on more efforts to relate the models to the observed complexity, rather than to overly simplified global relationships. The following paragraphs identify some of the outstanding challenges and open questions that should help direct future research:

7.1. Comparative Studies

The need for regionalization is evident in the recognition that the degradability of organic matter varies geographically. Local studies form the basis for the identification of global and regional patterns. The reliability of these patterns improves with the number of single studies and their spatial resolution. However, the imbalance in geographical coverage and in particular the paucity of observations and model studies from deep ocean environments remains evident. In addition, the strong dependence of model parameters on model structure limits the comparability of model-determined degradability. Furthermore, diversification of observational methods, different degrees of model validation/calibration or seasonal variability may further complicate the problem. Therefore, more comparative model studies are needed. These studies should aim at quantifying the biogeochemical transformations and fluxes in different benthic environments by applying an identical model structure and using similar sets of validation/calibration data. Model results should be compared with direct experimental rate measurements of organic matter mineralization where possible. Ideally, the geographical coverage should be guided by a minimum set of locations that cover the lower and upper bounds of important environmental boundary conditions and, therefore, could help relate organic matter degradability to an environmental vector. In addition, comparative interregional or intra-seasonal studies could provide important insights into the importance of spatial and temporal variability within each benthic region. Such comparative studies would help identify the most important drivers of organic matter degradation within each region and could ultimately provide the basis for a better quantification of biogeochemical cycling on the global scale, as well as for more generic parameter algorithms.

7.2. Model transferability

There is a strong need to couple diagenetic models with regional and global scale general circulation models of the coupled carbon-climate system. However, the lack of a generalized approach that provides objective means to constrain model parameters and that can be applied to the entire spectrum of boundary conditions encountered at the seafloor seriously compromises the application of diagenetic models on the regional and global scale, as well as for past and future projections. Much work remains to be done to adequately represent the fundamental controls on organic matter degradation dynamics. Yet, our ability to evaluate past, present and future global change will strongly depend on the development of such a mechanistic understanding as well as global upscaling strategies.

7.3. Predictive capability

The simplified theoretical framework underlying existing model approaches and the lack of a generic algorithm for their parameterization limit their predictive capability. In particular bioenergetic and microbial aspects of the carbon cycling in low energy environments, such as the deep biosphere remain poorly understood. Nevertheless, the reconstruction of past environmental conditions and climate change critically depend on our ability to hindcast organic matter degradation dynamics over geological timescales spanning all sediment depths. In addition, the evaluation of biogeochemical cycling in the deep biosphere, as well as the prediction of gas hydrate inventories and oil reservoirs depends on the model's ability to not only interpolate, but also extrapolate observational data. A better mechanistic understanding of organic matter degradation dynamics in extreme environments and under changing environmental conditions can help improve existing models. Recent attempts to quantify organic matter quality, e.g. the amino acid based degradation index, might help to further constrain and improve predictability of organic matter degradation constants (Dauwe et al., 1999).

7.4. Mechanistic model

A better mechanistic understanding of organic matter degradation could ultimately lead to the development of more mechanistic models. Comprehensive, multi-disciplinary studies that address organic matter degradation from an interdisciplinary point of view could advance our understanding of the process. Such studies would ideally integrate an organic geochemical characterization of the depositing organic matter and its diagenetic evolution, investigation of microbial populations and rates, porewater analysis, theoretical calculations of bioenergetic aspects, as well as diagenetic modeling. This approach would provide insights into different aspects of the organic matter dynamics and would help link drivers to observed patterns. More mechanistic models could then be developed on the analysis of molecular structure and degradation mechanisms. Such a bottom-up approach could help extrapolate knowledge from the micro- to the macroscale. The detailed mechanistic understanding can be used to develop common, comprehensive and conceptual approaches that facilitate the extrapolation to the global scale. In addition, it guides meaningful simplifications and thus provides an important basis for the construction of Earth system models, which are used to study the past and future evolution of the climate system.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.earscirev.2013.02.008.

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