# Preservation of Organic Matter in Marine Sediments: Controls, Mechanisms, and an Imbalance in Sediment Organic Carbon Budgets?

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## *1. Introduction*

The burial of organic matter (OM) in marine sediments represents the major link between "active" surface pools of carbon in the oceans, atmosphere, on land, and in marine sediment, and carbon pools that cycle on much longer, geologic time scales (i.e., carbon in sedimentary rock, coal, and petroleum deposits). It also plays some role in controlling atmospheric $CO_2$ and $O_2$ on these long time scales because in a highly simplified fashion OM burial in sediments can be thought of in terms of the balance between primary production and respiration on land and in the oceans.

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2 \quad (1)$$

Burial of organic matter in sediments (i.e., $CH_2O$ in this equation) therefore leads to net $CO_2$ removal from, and oxygen input to, the atmosphere.[1,2] As a result, examining the controls on OM preservation in sediments has been an important area of research in chemical oceanography.

While the process of OM preservation in marine sediments is often thought of in an equivalent sense to OM remineralization (respiration), this view may be somewhat misleading because less than ∼0.5% of the gross production/photosynthesis on the Earth escapes remineralization; that is, for every 100 units of organic matter produced on land or in the oceans, greater than 99.5 are remineralized, and less than 0.5 are buried in marine sediments.[3] Looked at somewhat differently, the preservation efficiency of organic carbon in marine sediments with respect to production on land and in the surface ocean is less than ∼0.5%. From this perspective, one

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might conclude that information about the controls on OM remineralization will not be particularly useful in understanding the controls on OM preservation, because under these circumstances subtle changes in the extent of OM remineralization will lead to large changes in OM preservation. However, when OM preservation and remineralization are specifically examined in marine sediments, we see that the "mismatch" between these processes is generally not as severe.

Relative to that found in surface water (source) organisms, the organic matter deposited in marine sediments has decreased in absolute amount (on a weight % basis) and undergone some amount of fractionation prior to deposition[4,5] (see discussions in section 1.1 for details). As a result of these changes, OM reactivity has also decreased substantially (Figure 1). Because of these changes, OM "burial" efficiency

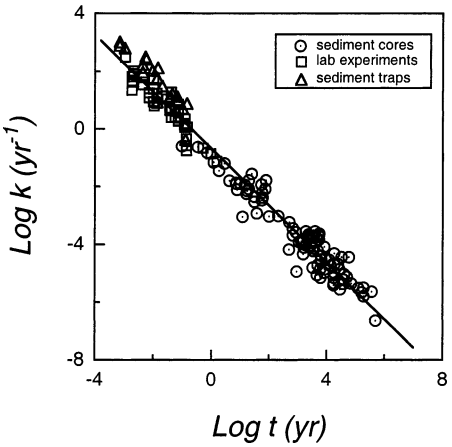


**Figure 1.** The Middelburg power model showing the inverse relationship between the reactivity of organic carbon ($k$) and the age ($t$) of the material. ■, ⊙, and △ represent, respectively, results from organic matter decomposition experiments in the lab, organic carbon depth profiles from dated sediment cores, and sediment trap organic carbon versus water column depth profiles. The original references for the data used in this compilation can be found in refs 225 and 226.

with respect to organic carbon rain rate to the sediments is generally ~10−20%, or more (Figure 2); this is particularly true in sediments that represent the major sites of OM burial in the oceans.[6−8] Thus, when the discussion is focused solely on sediment processes, it appears that the factors controlling OM preservation and remineralization could be more linked.

Because organic matter preservation is the absence of remineralization, and vice versa, preservation and remineralization are related somehow, if only mathematically (see Figure 3). However, preservation does not necessarily result simply from the absence of remineralization per se, although factors that inhibit remineralization will indirectly enhance preservation. Rather, specific factors may also more directly enhance preservation.

In this Article, I will examine OM burial and preservation in marine sediments from these two perspectives. I will then conclude with an examination of OM burial rates in marine sediments in terms of overall sediment organic carbon (OC) budgets. Through this discussion, we will see that different processes in these budgets can have very different characteristic time scales over which they operate, and I will discuss the impact that this may have on any temporal variability in these budgets.

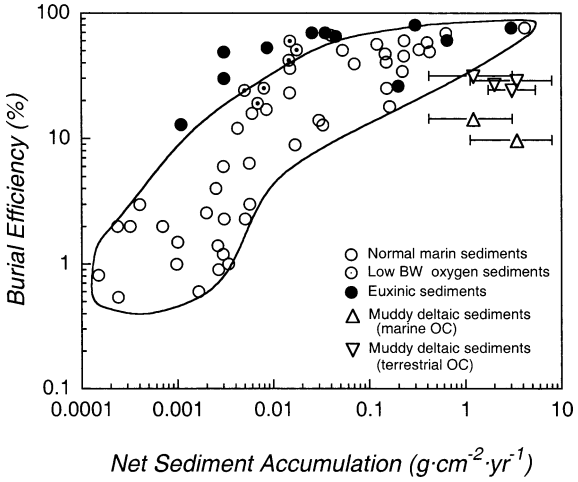


**Figure 2.** Burial efficiency of sediment organic carbon versus sedimentation rate for a range of sedimentary environments. Redrawn after refs 6 and 8 using data cited therein, and more recent results from the Southern Ocean,[227] Goban Spur (northeast Atlantic continental margin),[228] Washington state (northeast Pacific) and northwest Mexican (eastern tropical Pacific) continental margin,[229] and Skagerrak continental margin.[230] The data shown here for muddy, deltaic sediments are for the Amazon and Mississippi deltas (marine and terrestrial organic carbon) and Fly and Chiangjiang deltas (terrestrial organic carbon only).[8] Note that here and throughout the rest of this Article burial efficiency is defined as the rate of OC burial at depth (i.e., below the zone of early diagenesis) divided by the OC rain rate to the sediment surface. The envelope shown here defines the commonly observed pattern in normal marine sediments of burial efficiency increasing with increasing sedimentation rate.[6,7] This figure also illustrates three other important points: (i) sediments underlying low to zero bottom water oxygen concentrations do not show uniformly enhanced carbon preservation (high BE values) as compared to normal marine sediments, except perhaps at low sediment accumulation rates;[6] (ii) muddy, deltaic sediments generally show lower burial efficiencies than normal marine sediments at the same sedimentation rate; and (iii) marine organic carbon is more efficiently remineralized than is terrestrial organic carbon in muddy deltaic sediments.

## 1.1. Organic Geochemistry of Marine Sediments: General Considerations

The total organic carbon (TOC) content of marine sediments ranges from <2.5 mg C·$g_{dw}^{-1}$ in open ocean (pelagic) sediments to 200 mg C·$g_{dw}^{-1}$, in organic-rich coastal and continental margin sediments (i.e., those underlying oxygen-deficient bottom waters in regions of intense upwelling).[9−11] Across a similar water column gradient, the total nitrogen (TN) content of sediments ranges from <0.3 to 12 mg N·$g_{dw}^{-1}$.

In a very broad sense, we can think of organic matter in marine sediments as being derived from either marine or terrestrial sources. The "end-member" for marine organic matter is generally considered to be phytoplankton debris, or detritus, whose chemical components are predominantly proteins (amino acids), carbohydrates (sugars), and lipids (Table 1). Terrestrial organic matter consists of living biomass, plant litter, and soil organic matter, the latter being largely composed of highly altered and degraded remains of this living terrestrial biomass, for example, soil humus (see ref 12 and references therein). Terrestrial organic matter is largely brought to the oceans by rivers, in either a dissolved or a particulate form. Atmospheric inputs may be as large as 25% of the combined dissolved plus particulate river flux,[10] although other estimates suggest that the atmospheric flux is less than ~10% of the river flux.[13]

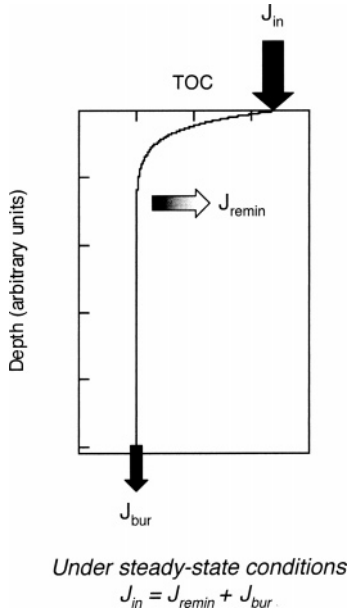


**Figure 3.** A conceptual model illustrating the steady-state relationship between OC rain ($J_{in}$), OC remineralization ($J_{remin}$), and OC burial ($J_{bur}$), based on a hypothetical TOC depth profile in a marine sediment.[45]

Lignins are a class of phenolic compounds found exclusively in vascular plants and represent important tracers of terrestrial organic matter.[14−17] They occur uniquely in vascular plant tissues and are generally associated with cellulose and hemicellulose, forming a material that is collectively referred to as lignocellulose. In contrast though to biopolymers such as proteins and carbohydrates, lignin consists of non-repeating units that are linked together in a random network by carbon−carbon and ether bonds.[18,19]

Other possible allochthonous sources of sediment organic matter include black carbon (largely the product of incomplete biomass burning; section 4.3.1) and weathered (or recycled) kerogen that has been transported back to the oceans after its uplift and weathering out of sedimentary rocks (section 4.3.2). At the same time, some fraction of the sediment OM that undergoes remineralization during early diagenesis is re-assimilated, generally at the monomer or oligomer level, and re-packaged in situ as new bacterial biomass (note that the term "bacteria" is broadly used here to describe true bacteria or eubacteria, as well as archaea and cyanobacteria). This bacterial biomass is actually better thought of as bacterially derived organic matter and is not really a new source of sediment OM in the same sense as these other primary sources. However, bacterial production of organic matter in sediments may play a role in sediment OM preservation (see section 4.2.1 for details).

Different types of biologically produced organic matter have different reactivities, and selective preservation and/or remineralization of these classes of organic matter may occur as bulk pools of organic matter undergo remineralization. This fractionation, which is also sometimes referred to as diagenetic maturity,[20,21] begins in the oceanic water column,[4] where there is a decrease in the absolute amount of organic carbon in sinking particles as they fall through the water column; this is also accompanied by a decrease in the relative amounts of presumably reactive components of the organic matter in these particles, that is, amino acids and carbohydrates.[4,11,20] This fractionation also appears to "produce" organic matter that cannot be characterized at the molecular level by conventional analytical techniques, for example, gas or liquid chromatography, and leads to an increase in what has been termed molecularly uncharacterized organic matter.[5,22]

Historically, molecularly uncharacterized organic matter (MU-OM) was thought to form through abiotic "heteropolycondensation" or geopolymerization reactions involving simple organic matter intermediates such as monomeric sugars, amino acids, or fatty acids,[23,24] producing materials that are loosely defined as humic substances. However, recent studies have indicated potential problems with this model (see section 4.1 for details). At the same time, an alternate explanation for the production of MU-OM during diagentic maturity is that the loss of reactive components is not entirely a real loss, but also occurs as a result of processes that protect reactive compounds such that they can no longer be recognized by conventional analytical techniques[5,22] (see sections 2.4 and 5.1 for further details).

## 2. Molecularly Uncharacterized Organic Matter

Regardless of the mechanism(s) by which MU-OM forms, this fractionation of organic matter leads to a situation in which only ~30−40% (or less) of the organic carbon in marine sediments can be partitioned, using conventional analytical techniques, into the four compound classes discussed above (Table 1). In contrast, >80% of the carbon in end-member organic matter sources, surface plankton samples, and sinking particles leaving the euphotic zone can be characterized as lipids, carbohydrates, or amino acids.[4,25] Understanding what comprises this molecularly uncharacterized organic matter (MU-OM) is of great importance and interest,[5,26] in part because of the role this material may play in OM preservation in marine sediments.

In discussing MU-OM, it is also important to recognize that its existence is ultimately inferred from specific analytical techniques that use some sort of extraction procedure (e.g., acid hydrolysis or solvent extraction) and chromatographic separation and identification of individual compounds in the extract (e.g., free amino acids or neutral sugars in an acid hydrolyzate). The summation of these individual biochemicals yields the total amount of "characterized" material, with MU-OM then being the difference between the TOC content of the sample and the carbon content of the characterized material. Based on these observations then, it appears that the majority of the organic matter in marine sediments escapes the analytical window of these techniques (also see discussions of similar problems in terms of characterizing soil organic matter[27] and dissolved organic matter in seawater[28]). However, it is also important to note here that, because MU-OM is an operational definition, advances in analytical techniques for organic geochemical analyses will also lead to the increasing characterization of this material (see section 4.2 for details).

At least three possible explanations may exist for why we observe MU-OM in marine sediments; these explanations are, however, not necessarily mutually exclusive. Also note that other possible types of MU-OM such as black carbon (section 2.1) and recycled kerogen (section 2.2) will have source histories slightly different from those discussed here.

The first explanation assumes that during the decomposition of detritial biopolymers in the sediment organic matter pool there is production of reactive intermediates (e.g., low molecular weight monomeric sugars or amino acids, or

**Table 1. Identifiable Biochemicals in Marine Sediments and End-Member Sources[a]**

| sediment type/site | amino acids | carbohydrates | lignin | total lipids | identified components |
|---|---|---|---|---|---|
| "typical" modern coastal marine sediments[b] | 0−15% | 5−10% | 3−5% | <5% | <35% |
| Cape Lookout Bight, NC sediments[c] | <8−13% | 6−8% | <1% | 5−8% | <30% |
| Namibian shelf diatomaceous ooze[d] | ∼11% | ∼22% | na | ∼5% | ∼38% |
| equatorial Pacific sediments[e] | 16−17% | 1−12% | na | <1% | <30% |
| NE Pacific sediments[f] | 11−19% | 3−18% | na | 2−3% | <40% |
| "end-member" sources | | | | | |
| marine organic matter[g] | ∼50−60% | 20−40% | 0% | 5−30% | 75−130% |
| vascular plant material[h] | ∼1−2% | ∼70% | ∼30% | ∼1−2% | ∼100% |

[a] na = not analyzed but assumed to be zero. [b] From ref 27. [c] This range is based on analyses of sediment samples from depths of 0−5 cm and 95−100 cm.[46] [d] The water depth of this site was 106 m, and the sample analyzed was from a sediment depth of 40−75 cm.[219] [e] From several sources[159,220,221] for samples collected from 0 to 12 cm sediment depth at several sites. Water depths at these sites are all >4000 m. [f] This range is based on samples collected from 0 to 14 cm sediment depth.[25] The water depth at this site is 4100 m. [g] Data from a variety of sources.[22,46,222,223] [h] From ref 12.

perhaps higher molecular weight peptides) that recombine in abiotic chemical reactions to form refractory condensates.[23,24,29] These materials are presumably too complex to be either enzymatically decomposed by organisms or chemically analyzed. In other words, these condensation reactions sufficiently transform and degrade organic matter to the point that it is biologically unavailable, and conventional analytical procedures used to analyze amino acids, carbohydrates, or lipids no longer recognize the precursor compounds in the condensates.

A second possible explanation is based on the observation that organisms produce hydrolysis-resistant, biologically refractory macromolecules.[18] Selective utilization of more reactive components of the sediment OM pool then leaves behind these refractory macromolecules, hence their preservation in sediments.[30−32] Finally, reactive organic matter may be shielded from chemical analysis (and also biological degradation) through interactions with, and/or protection by, inorganic or organic matrices.[22,33]

A related aspect of these last two explanations is that the factors controlling OM preservation versus remineralization appear to be a function of both the chemical composition of the organic matter as well as the "matrix" in which the organic matter is contained (e.g., some sort of organic matrix, or physical association with sediment particles). For example, in the coastal sediments of Cape Lookout Bight[34] and Buzzards Bay,[35] only ∼40−50% of the amino acids that are deposited in these sediments, and can be chemically analyzed, are remineralized on early diagenetic time scales. Because amino acids are presumably a relatively reactive component of the sediment OM pool, some aspect of pre- or postdepositional diagenesis may therefore protect sediment amino acids, such that their complete remineralization is impeded and/or prevented (also see discussions of this problem in refs 36 and 37). Similar factors also apparently operate on longer time scales, because the preservation of proteins/amino acids is observed in fossilized marine organisms and in early Pleistocene deep-sea sediments (∼1 million years bp[38]). Incorporation of amino acids into structural components such as peptidoglycans (section 4.2.1) or the organic matrices associated with calcareous and siliceous shells (section 5.1) may play a role in this preservation, although other factors that may be important here will be discussed in sections 4 and 5.

Studies of lipids have also shown that there is a "bound" lipid fraction that is only released from the sediments by combined saponification (base hydrolysis) and solvent extraction,[39−42] versus the more commonly studied "free" lipids that can be extracted from sediments solely by solvent extraction. The source of bound lipids is not well understood,[29,43] and they may result from strong adsorption to sediment surfaces, as well as esterification of free lipids with other forms of sedimentary organic matter. There may also be a direct bacterial contribution to the bound lipid pool, for example, lipids associated with bacterial membranes (see section 4.2.1). Studies of Madiera Abyssal Plain turbidities have shown that such bound lipids, regardless of their apparent source, are preferentially preserved relative to their free counterparts during organic matter remineralization in these sediments.[42,44] The presence of bound (versus free) lipids therefore not only enhances the overall preservation of lipids, but can also contribute to the operationally defined MU-OM pool, if the appropriate sediment extractions are not carried out.

Finally, it is important to remember that the inability to chemically characterize some amount of the organic matter in sediments or in the water column (e.g., sinking marine particles) does not necessarily imply that this material is unavailable for biological degradation.[5,45] Focusing here on sediment system, it can be shown using simple mass balance calculations that only ∼30−60% of the organic matter that is remineralized in sediments can be accounted for by downcore losses of chemically identifiable amino acids, lipids, or carbohydrates.[45,46] Thus, the remaining material is chemically uncharacterized yet is still accessible for biological degradation.

## 2.1. Black Carbon

Black carbon represents a component of the particulate and dissolved organic matter pools in both sediments and the water column that has historically been difficult to chemically characterize beyond the bulk concentration level.[47] Black carbon consists of a broad range of heterogeneous, aromatic, and refractory carbon-rich materials that can form during the incomplete combustion of fossil fuels or organic matter (biomass burning). It includes graphite (elemental carbon), soot, charcoal, and char and represents both combustion residues and condensates.[26,48] Black carbon is ubiquitous in the atmosphere, cryosphere, soils, oceans, and marine sediments (albeit at very low levels) due to its global production and apparent refractory nature.[48] Recent $\delta^{13}C$ and radiocarbon studies also suggest that a significant fraction of the black carbon in marine sediments is graphite that has been weathered from continental rocks and then reburied in sediments (also see related discussions in the next section).[49]

In marine sediments, black carbon represents from ~2% to perhaps 30% of the sediment TOC.[49−53] However, because of differences in (and potential problems with) the various methods used to determine black carbon, some caution should be placed in the interpretation of these estimates.[54] Nevertheless, while black carbon may comprise a significant fraction of the organic carbon in marine sediments, its quantification does not completely resolve the mass balance problem in Table 1 (i.e., even assuming black carbon is 30% of the TOC, roughly one-half of the sediment organic carbon still remains uncharacterized).

Black carbon is also generally thought to be extremely recalcitrant to both biological and chemical degradation and could therefore represent some component of the organic matter preserved in marine sediments. However, exposure of black carbon to oxygen in pelagic turbidites over long time periods (~10−20 kyr) can apparently lead to its significant degradation (~64%).[52]

## 2.2. Kerogen and Fossil Carbon in Marine Sediments

Most organic matter buried in marine sediments is eventually transformed into kerogen during later stages of diagenesis and catagenesis, when sediments are subject to elevated temperatures and pressures during their lithification and transformation into sedimentary rocks.[29,55] In a fashion similar to humic substances (section 4.1), kerogen is operationally defined by solubility considerations and represents amorphous, high molecular weight, insoluble organic matter in sedimentary rocks that remains after solvent, acid, and sometimes base extraction.[56,57] Kerogen is the largest repository of organic carbon on the Earth's surface[2] and is also generally thought of as being extremely refractory, in part because it derives from the very small fraction of organic matter that escapes remineralization in surface carbon cycles.

The term protokerogen is used to describe the same fraction of organic matter in unconsolidated sediments, as are terms such as "insoluble", "acid insoluble", "nonextractable", and/or "nonhydrolyzable" organic matter.[58−60] Given these definitions, protokerogen represents a pool of sedimentary organic matter that is approximately the same as MU-OM. However, given the nature of these definitions, some care should be taken with such a comparison.

Kerogen oxidation on land, after the uplift of sedimentary rocks, is generally thought to balance OM burial in marine sediments (see eq 1).[1,61] However, many of the details of how this occurs are not well understood. Despite the apparent refractory nature of kerogen, weathering profiles indicate that TOC loss from black shales on land is extensive, that is, between 60% and ~100%.[62] Such studies have not, though, unequivocally determined the extent to which this TOC loss occurs through complete kerogen oxidation to $CO_2$ or partial oxidation and/or solubilization of kerogen and subsequent loss of oxidized kerogen byproducts (e.g., oxidized fossil DOM or POM) by riverine or steam flow. Thus, some kerogen loss from sedimentary rocks may actually result in the transport of "recycled" kerogen (or fossil carbon) to the oceans, where it has the potential to escape remineralization and simply be reburied, largely in continental margin sediments.

Kerogen transport from land to continental margin sediments appears to be most important for small, steep mountainous rivers associated with active continental margins and relatively narrow continental shelves.[63−68] In these settings, there appears to be little time for kerogen remineralization because of the relatively short time between exposure in outcrops, riverine transport, and deposition in continental margin sediments. This situation contrasts with other river-continental margin settings such as the Amazon River and shelf, where extensive storage and processing of organic matter in upland soils and lowland floodplains leads to the replacement of upland organic matter, that is, kerogen, with lowland soil organic matter in riverine suspended matter.[67] Furthermore, sediments on wide and more energetic margins, such as the Amazon, are exposed to repeated resuspension/redeposition cycles that act to enhance the degradation of refractory organic matter, such as kerogen, that is deposited in these sediments (also see section 5.2.2).[8,69]

Because recycled kerogen has gone through one cycle of sedimentation (burial), uplift, and erosion, any reburial of this material in marine sediments results in no new net input of $O_2$ to the atmosphere. Consequently, any involvement kerogen reburial has in total OM burial in sediments potentially limits the strength of the feedback between sediment OM burial and atmospheric $O_2$ concentrations, and could play a role in minimizing large-scale swings in atmospheric $O_2$ levels.[1,2] Kerogen associated with marine bedrock is also likely to have heavy $\delta^{13}C$ values, consistent with that of marine organic matter, yet will be completely depleted in $^{14}C$ because of its age.[58,60,65,66] Therefore, while the input of recycled kerogen to marine sediments can potentially be masked by its marine stable carbon isotopic signature, radiocarbon analyses provide important information on its possible occurrence.

Blair et al.[67] have suggested that the riverine flux of recycled kerogen to the oceans could be as large as 40 Tg $C \cdot yr^{-1}$. When compared to results in Table 3, it can be seen that this flux is potentially a significant fraction of the present-day rate of OM burial in marine sediments (assumed here to be ~160 Tg $C \cdot yr^{-1}$; see discussions in section 7 for details). However, recent anthropogenic activity may have perturbed the balance between kerogen export to the oceans and kerogen oxidation on land, and perhaps shifted the locus of kerogen oxidation from the continents to marine sediments.[66,67] Nevertheless, based on an assumed burial rate for terrestrial organic matter in marine sediments of ~60 Tg $C \cdot yr^{-1}$ (see section 4.4), this observation suggests that the remaining ~100 Tg $C \cdot yr^{-1}$ of "presumed" marine organic matter buried in marine sediments could potentially contain a significant amount of recycled kerogen.

Evidence for the occurrence of fossil carbon/recycled kerogen in marine sediments has been presented across a wide range of sedimentary environments.[60,62,70,71] Workers have also begun to examine the quantitative importance of fossil organic carbon input to specific sedimentary environments.[58,72,73] At the same time, though, other studies suggest that recycled kerogen is not a major component of the OM matter that is buried in marine sediments.[1,3] However, given recent advances in radiocarbon dating of natural organic matter,[74,75] this problem is clearly in need of further examination. In particular, compound-specific radiocarbon analyses[72,73,75,76] as well as radiocarbon analyses of specific sediment organic matter fractions[58,60,66,67] will be useful in continuing to better quantify the role of fossil carbon in sediment organic matter cycling and burial.

## 3. Organic Matter Preservation in Marine Sediments

Understanding the factors that control OM preservation versus remineralization in marine sediments is difficult for a number of reasons. One problem here is that these effects are most apparent only for less reactive types of organic matter.[77] Thus, the ability to examine controls on preservation versus remineralization is strongly affected by the time scales of the experimental study or field observation.[45,78]

Controls on OM preservation in sediments are often examined in terms of organic carbon burial efficiency (Figure 2).[3,6,7] In general, low BE sites are low sedimentation rate sites that occur predominantly in pelagic or abyssal regions. Virtually complete remineralization of sediment OM occurs here, and as a result these sediments have extremely low TOC contents (e.g., ~0.1−0.2% in deep-sea sediments[9]). Aerobic respiration dominates in these environments,[79] and what little organic matter is preserved is of low reactivity (Figure 1).

As one moves onshore to continental margin and eventually coastal sediments, sedimentation rates increase, as does burial efficiency, the importance of sub-oxic and eventually anoxic remineralization,[45] and the preservation of more reactive sediment organic matter. Furthermore, because the vast majority of OM burial in marine sediments occurs on the continental margins (Table 3), studies in recent years have suggested that specific aspects of the biogeochemical processes occurring in continental margin sediments may play an important role in the overall controls on sediment OM preservation.[3,8,80]

Many coastal and continental margin sediments are also subject to what is referred to as mixed redox conditions or redox oscillations.[81] Here, sediment particles and pore waters are exposed to alternating oxic and anoxic condition as a result of macrofaunal activity (bioirrigation or bioturbation) or physical mixing (reworking) of the sediments.[69,82] In the simplest sense, one can think of mixed redox sediments as being periodically, or episodically, oxidized (or oxygenated), although the details of just how this occurs will vary among different sediments. The time scales over which these redox oscillations occur vary, ranging from minutes for bioirrigation[81] to longer time scales characteristic of sediment mixing (bioturbation). These redox oscillations are also generally asymmetrical in length, with anoxic conditions occurring for substantially longer times (10× or greater) than oxic conditions.[81,83]

As noted in section 1, OM preservation in marine sediments can be examined from two broad perspectives: factors that more directly enhance preservation and therefore indirectly inhibit remineralization, and factors that specifically inhibit remineralization and therefore indirectly enhance preservation (also see Figure 4). In the latter case, recent studies have more specifically focused on: (1) in situ formation of refractory OM from reactive precursors by abiotic (section 4.1) and biotic (section 4.2.1) processes, and (2) selective preservation of refractory OM of both biotic (section 4.1) and abiotic (section 4.3) origin.

In the former case, recent studies have considered: (3) the role of physical protection of reactive organic matter (section 5.1), and (4) selective concentration of redox-sensitive (i.e., $O_2$-requiring) OM during organic matter diagenetic maturity (section 5.2.1).

These preservation "mechanisms" are not necessarily mutually exclusive, and almost certainly operate together and/or in succession (see section 6 for details).[45,84,85] In the next section, I will also specifically examine the factors that control the burial of terrestrial organic matter in marine sediments (section 4.4). Here, preservation mechanisms 2 and 4 above appear to be most relevant.

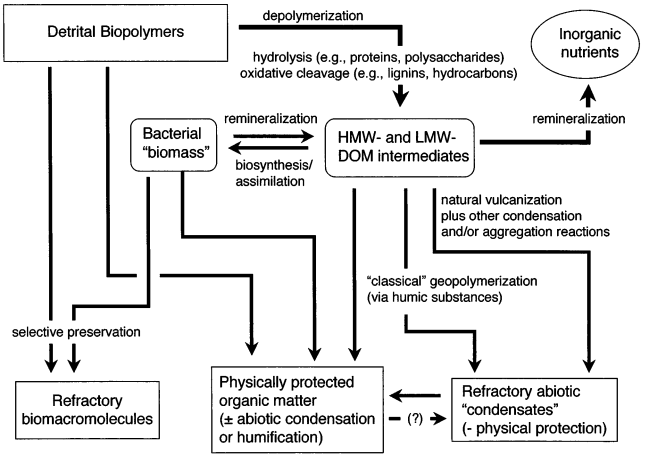


**Figure 4.** The fate of detritial biopolymers in marine sediments, including remineralization, re-incorporation into bacterial biomass, and preservation. Adapted from ref 45, Copyright 2006, with permission from Princeton University Press.

## 4. "Mechanisms" of Preservation

In this section, I will examine organic matter preservation in sediments in terms of processes that can be considered to "produce" refractory organic matter either during primary biosynthesis or as a result of subsequent reactions.

### 4.1. Geopolymerization

Geopolymerization (or humification) is a general term for the process by which humic substances form. The classical view of this process is illustrated in Figure 4. In this model, the degradation of biological polymers (biopolymers) in the sediment OM pool first leads to the production of a variety of low molecular weight biological monomers, for example, amino acids, simple sugars, or fatty acids.[45,86] While most of these monomers undergo remineralization to inorganic nutrients, in the geopolymerization model some small fraction of the monomers undergo abiotic condensation reactions, forming chemically complex materials broadly referred to as humic substances.[23] Several such condensation reactions have been proposed and are discussed in detail in earlier reviews.[26,29,55] One well-studied example is the Maillard reaction, a sugar−amino acid condensation reaction that forms compounds known as melanoidins.[87,88] Synthetic melanoidins produced in the laboratory show some similarity to marine humic substances.[24]

Humic substances are considered to be amorphous, hydrophilic materials that are refractory with respect to both chemical and biological degradation. Operationally, however, humic substances (fulvic acids, humic acids, and humen or protokerogen) are generally defined by their aqueous solubility at different pH values.[29,89]

However despite the "elegance" of the geopolymerization model, there is little direct evidence for the occurrence of geopolymerization reactions (as described here) in nature.[24,27,90,91] Under most circumstances, abiotic condensation reactions involving the monomeric reactants discussed above are likely to be quite slow in comparison to their biological

uptake or remineralization to inorganic nutrients.[92] Interestingly, however, recent papers in the literature still continue to discuss the possible occurrence of melanoidin-type condensation reactions despite these potential problems with the geopolymerization model[59,93,94] (also see discussions in sections 4.1 and 6).

The notion that humic substances form via abiotic condensation reactions is also problematic because the chemical extraction procedures used to isolate humic substance almost always co-extract known biochemicals such as lignins, carbohydrates, or proteins.[12,95,96] One interpretation of this observation is that monomers derived from these biomacromolecules are incorporated into humic substances in such a way that they still retain their chemical "signature".[29,87] However, monomers from unaltered plant fragments are also co-extracted along with humic substances,[95] suggesting that they could represent some component of sedimentary humic substances.

Along these same lines, techniques used to extract protein from marine sediments[96,97] involve methods that are very similar to those used to isolate humic substances. Furthermore, studies in Cape Lookout Bight sediments suggest that the loss of fulvic acid nitrogen and hydrolyzable amino acids both account for similar percentages (~80%) of the total nitrogen remineralization in these sediments.[34,98] While this similarity may be fortuitous, it is equally probable that reactive proteins are being co-extracted into the operationally defined fulvic acid fraction. These observations further suggest that, at least in Cape Lookout Bight sediments, fulvic acids are far from a refractory component of the sediment organic matter pool.[45]

#### *4.1.1. Other Polymerization or Condensation Reactions*

Although the geopolymerization model described above may not play a significant role in sediment organic matter preservation, other related types of condensation reactions may still be important. For example, protein in sediments may be preserved and become hydrolysis-resistant through processes such as aggregation and cross-linking, both between proteins and perhaps with carbohydrates.[99−101] Other recent studies[102] suggest that the formation of covalent linkages between peptides and other forms of macromolecular organic matter via the Michael reaction may represent another preservation pathway for peptides.

Another related process that may be important here is the sulfurization of lipids and carbohydrates (sometimes referred to as natural vulcanization reactions).[30] A wide range of organic sulfur compounds have been found in recent marine sediments and crude oils,[103] and evidence-to-date suggests that most are likely not directly biosynthesized (although also see discussions in ref 104). Rather, these organosulfur compounds appear to form through the incorporation of inorganic sulfur (sulfide or polysulfides) into functionalized lipids and carbohydrates.[93,105−107] These sulfurization reactions may therefore play some role in carbon preservation in certain environments.[30] They may also help preserve structural information in reactive biomarkers by protecting sulfurized biolipids from diagenetic transformations or remineralization.[108]

In contrast though, studies in the highly sulfidic, permanently anoxic sediments of the Cariaco Trench,[93] where such natural sulfurization reactions would be expected to be of greatest importance, suggest that these processes are slow in comparison to other degradation−recondensation reactions that may be more similar to "traditional" geopolymerization reactions (also see results in ref 59). However, whether these processes involve the "complete" degradation of detrital biopolymers to low molecular weight monomers such as amino acids and sugars, as opposed to partial degradation to higher molecular weight materials such as small peptides or oligosaccharides, is not clear from these results.

A third process that could be of importance here is one that is analogous to the sulfurization reaction. Here, reactions between ammonium and reactive functional groups in non-nitrogen containing organic compounds (e.g., carbonyl groups) are followed by autopolymerization to form new heterocyclic nitrogen compounds.[109−111] Given the large amounts of ammonium produced in anoxic sediments during organic matter remineralization,[45] such reactions might be of most importance in such sediments, if indeed they do occur in marine sediments. Furthermore, while most nitrogen in fossil fuels and coal exists as heterocyclic nitrogen,[112,113] it presumably begins as amide nitrogen (i.e., amino acids) in source organisms. Therefore, the occurrence of this reaction could help explain the change in nitrogen functionality that occurs during organic matter preservation and late stage diagenesis.

### 4.2. Selective Preservation of Refractory Biomacromolecules

A large number of organisms produce highly aliphatic, macromolecular material that is insoluble, nonhydrolyzable, and resistant to biological degradation.[18] These refractory molecules tend to be produced by vascular plants and algae[18,114] and include algaenans (algal cell wall components consisting of long-chain aliphatic compounds with hydroxyl or ester functional groups) and cutans (a nonhydrolyzable component of the cuticles of higher plants). Because these compounds are nonhydrolyzable, they fall outside the conventional analytical window used to determine biomacromolecules such as proteins and polysaccharides (i.e., they would historically be considered MU-OM). However, techniques such as analytical pyrolysis,[56] Curie point pyrolysis,[114] and solid-state $^{13}C$ NMR with cross polarization/magic angle spinning[115,116] have proven useful in examining the structure and composition of these refractory biomacromolecules. These same techniques, along with TMAH thermochemolysis,[117−119] have also been used to examine insoluble, nonhydrolyzable organic matter (again ~MU-OM) in marine sediments.

Refractory biomacromolecules likely represent a very small fraction of the initial biomass produced by marine and terrestrial organisms. However, they have the potential to make up a major fraction of the organic matter that is preserved in sediments and soils because of their extreme recalcitrance (i.e., they will be selectively preserved and therefore concentrated in the OM pool during diagenetic maturity).[30] Consistent with this, kerogens in ancient rocks have also been shown to resemble, both chemically and morphologically, these types of refractory biomacromolecules from ancient plant and bacteria.[18]

#### *4.2.1. Production of Bacterial Biomass in Marine Sediments*

During OM remineralization in sediments, some fraction of the sediment organic matter that undergoes mineralization is re-assimilated at the monomer or oligomer level, and repackaged as new in situ bacterial biomass (Figure 4). The

importance of this bacterially derived material as a component of the sediment OM pool, and particularly that which is preserved, has been discussed by numerous authors, and a variety of techniques (e.g., lipid biomarkers, molecular-level isotopic studies, diagenetic, and mass balance modeling) all suggest that production of bacterially derived organic matter is important during early diagenesis in sediments[11,120−126] (also see ref 127 for discussions of earlier organic geochemical studies). The majority of this bacterially derived organic matter in sediments is not intact cells, either alive or dead, but rather is organic matter derived from living cells, for example, cell exudates, cell lysis products, or remnants of bacterial cell walls. This material is therefore sometimes referred to as bacterial "necromass", and it has been suggested that it can make up a significant component of the molecularly uncharacterized organic matter in marine sediments.[123] While most studies assume that this bacterial necromass is derived from sediment bacteria, some of this material may actually be input to sediments from the overlying water column on sinking particles.[37]

Bacterial necromass may be more or less reactive than the original sediment organic matter (see the references cited above as well as discussions in ref 81). However, much of the interest in studying this material stems from its possible role in OM preservation in sediments. The mechanisms by which this may occur are not well understood and may include production of inherently refractory materials such as bacterial membrane lipids (see section 2) or peptidoglycan (the primary structural component of bacterial cell walls that is generally presumed to be more resistant to degradation than other non-structural proteins[128−131]). Bacterially derived organic matter may also be preserved as a result of physical protection (e.g., encapsulation; see section 5.1).

Lee[127] has suggested that bacterially derived organic matter can be preserved in anoxic sediments due to the effective exclusion of all organisms other than bacteria in such sediments (i.e., microbial grazers such as benthic macrofauna). In the absence of grazers who feed on bacterially derived OM, this material may be less efficiently remineralized and therefore be preferentially preserved. At the same time, recent studies[80,81,132] also suggest that bacterially derived OM matter could be an important component of the sediment carbon that is buried and preserved in anoxic sediments not simply because of this lack of grazing by higher organisms. Rather, it may occur because oxic or mixed redox conditions in sediments promote the more efficient remineralization of total sediment organic matter in general, and (potentially refractory) bacterial necromass in particular. This possibility will be discussed further in section 5.2.

### 4.3. Other Types of Refractory Organic Matter in Marine Sediments

Some amount of the refractory OM deposited in marine sediments may not have a recent biological origin. Black carbon and recycled kerogen represent two such types of this material. The extent to which these materials are truely "inert" (as appears to be the case for refractory biomacromolecules) may be a question of time scales of degradation versus burial (see the discussions in sections 2.1, 2.2, and 6). However, these materials may be buried through the zone of early diagenesis in surface sediment with little or no degradation and will therefore largely be preserved in sediments.

### 4.4. Burial of Terrestrial Organic Matter in Marine Sediments

Understanding the fate of terrestrial organic matter (TOM) in marine sediments is strongly related to questions associated with OM burial in marine sediments in general. In part, this stems from the observation that marine organic matter (MOM) is broadly considered to be more reactive than terrestrial organic matter.[133−137] Therefore, one might suppose that marine organic matter that is deposited in sediments should be preferentially remineralized, and thus subject to less efficient burial. Similarly, terrestrial organic matter deposited in marine sediments might then be expected to undergo less efficient remineralization and therefore be preferentially buried.

However, an examination of the carbon budget for the oceans suggests that roughly 2−3 times as much organic carbon is transported to the oceans from land by rivers than is buried in marine sediments.[2,3] Therefore, the preservation efficiency of TOM in marine sediments must ∼33−50% or less, depending on the amount of TOM (versus marine organic matter, or MOM) that escapes remineralization in the oceans (water column and sediments) and is buried in the sediments (note that, in contrast to the term burial efficiency, as defined in the caption to Figure 3, preservation efficiency is defined here as the ratio of OM burial in sediments divided by the rate of its ultimate input to the oceans, i.e., riverine input for TOM and primary productivity for MOM). In fact, TOM preservation efficiency is indeed relatively low, suggesting that the oceans are fairly efficient in remineralizing refractory terrestrial organic matter (see discussions below for details). Furthermore, given a low TOM preservation efficiency, marine sediments must also bury, or preserve, marine organic matter that is presumably more reactive. In an earlier review article, Hedges et al.[12] referred to this as a geochemical "conundrum" and noted that its resolution has important implications in terms of understanding carbon cycling in the oceans and the controls on sediment OM burial and preservation.

Interest in TOM burial in marine sediments also stems from the fact that only a small fraction (∼20% or less) of riverine suspended matter is deposited in deep-sea sediments.[69,138] As a result, much of the particulate TOM transported by rivers to the oceans should therefore be deposited in continental margin sediments. Because continental margin sediments are the major sites of sediment OM burial and remineralization,[2,3] this further suggests that there could be a linkage between TOM burial and remineralization in sediments and sediment OM preservation in general.

In recent years, a number of studies have examined different aspects of TOM input, burial, and preservation in marine sediments.[8,12,14,17,73,139−142] Other studies have examined more general sediment−organic matter interactions as they relate to overall carbon preservation in sediments (also see section 5).[3,143,144] Recent calculations based on results from these studies[145] have yielded the following observations about TOM burial in marine sediments.

First, the estimated rate of TOM burial in continental margin sediments is 58 (±17) Tg C·yr$^{-1}$ (Table 2), with the majority of this burial occurring in deltaic sediments associated with large river systems such as the Amazon or the Mississippi Rivers. Assuming that TOM burial is insignificant in other sediment regimes, for example, deep-sea sediments,[78,146−148] this observation implies that ∼$^1/_3$ of the organic matter buried in marine sediments is of terrestrial

**Table 2. Burial of Terrestrial Organic Matter in Marine Sediments**

| sites | TOM/$\sum$OM$_{bur}$ | TOM burial[a] |
|---|---|---|
| deltaic continental margin sediments[b] | 67 ± 24% | 47 ± 17 |
| inner continental shelf sediments of the northern Gulf of Mexico near the Atchafalaya River (0−20 m water depth)[c] | ~70−80% | |
| non-deltaic continental margin sediments[b] | 16 ± 4% | 11 ± 3 |
| Washington (U.S.) outer shelf/continental slope (~200−2000 m water depth)[d] | ~10−30% | |
| total TOM burial | | 58 ± 17 |

[a] Units are Tg C·yr$^{-1}$. [b] Based on surface area, and TOC concentration and stable isotope ($\delta^{13}$C) measurements reported in the literature.[145] [c] Based on biomarker, stable carbon, and radiocarbon measurements.[73] [d] Based on biomarker, stable carbon, and radiocarbon measurements.[139−141]

origin, again assuming a total OM burial rate in marine sediments of ~160 Tg C·yr$^{-1}$ (value from ref 3).

Second, these calculations suggest that TOM as a percentage of total organic matter buried in marine sediments (TOM/$\sum$OM$_{bur}$) is ~70% in deltaic, continental margin sediments and ~16% in non-deltaic, continental margin sediments (Table 2). These calculations are, however, based largely on stable isotope results and organic carbon:surface area measurements. Therefore, given the uncertainties in this approach,[145] these estimates of relative TOM burial can be compared to similar estimates that are based on lipid biomarkers, lignin oxidation products, and/or compound-specific stable isotope and radiocarbon measurements used in conjunction with bulk tracers such as the $\delta^{13}$C of TOC.[139−141,148,149] Such a comparison suggests that these two different approaches to estimate TOM/$\sum$OM$_{bur}$ in continental margin sediments yield very similar results (Table 2). In contrast though, studies of sediments from the Mexican continental margin show that that there is essentially no burial of TOM in these sediments.[139,150] This is not necessarily surprising, given the absence of major rivers in close proximity to the Mexican margin. However, this observation reinforces the fact that future studies aimed at more accurately quantifying the input and burial of TOM in continental margin sediments will require multi-tracer approaches similar to those discussed here (see related discussions in refs 69 and 145).

Finally, when the TOM burial rate calculated here is compared to the global rate of organic carbon burial in marine sediments (assumed to be ~160 Tg C·yr$^{-1}$), it suggests that the majority of the organic matter buried in marine sediments (~100 Tg C·yr$^{-1}$) is of marine origin. In an absolute sense then, the burial of marine organic matter (MOM) is roughly twice that of TOM. However, based on earlier discussions, MOM is (in general) presumed to be more reactive than TOM. This apparently counter-intuitive observation can be reconciled, though, when looked at in terms of the overall preservation efficiency of MOM with regards to its ultimate source, primary production in the water column. When this is done, estimates of MOM preservation efficiency (0.25% to <1.3%) are significantly smaller than those for TOM (~9−17%; see ref 145 for details). Thus, from this perspective, it is clear that marine organic matter is remineralized much more efficiently in the oceans than is terrestrial organic matter, despite the observed trends in the composition of OM buried in marine sediments. Looked at another way, because of the shear magnitude of marine productivity versus riverine input of TOM (~40 000 Tg C·yr$^{-1}$ vs ~400 Tg C ·yr$^{-1}$ [12,142,151]), more marine organic matter is buried in marine sediments despite these differences in MOM versus TOM preservation efficiency.

When the problem of TOM reactivity in the oceans and burial of marine sediments is re-examined in the context of results presented here, the geochemical conundrum described earlier[12] may not be as severe as once thought. Nevertheless, a number of key problems still exist that will require further study to verify the calculations presented here, and therefore better constrain the rate of TOM burial in marine sediments.[145]

## *5. Preservation as a Result of the Inhibition of Remineralization*

### 5.1. Physical Protection of Organic Matter

Physical protection of organic matter by both organic and/or inorganic matrices may play a role in OM preservation in marine sediments. Under some circumstances, this may involve protection of labile compounds such as reactive proteins, in a way that shields these compounds from chemical attack (e.g., abiotic acid hydrolysis) or enzymatic degradation. Physical protection may also allow for the subsequent chemical modification of the organic matter that then further enhances its protection from both degradation and analysis (see section 6 for details).

In thinking here about the role of physical protection, it is important to recognize that factors that impede OM degradation do not necessarily also render the material unrecognizable (i.e., contribute to the "formation" of MU-OM). For example, carbohydrate- and protein-rich material associated with calcareous or siliceous plankton shells may be protected from biological degradation, yet will still be susceptible to acid hydrolysis and subsequent chemical analysis.[36,37]

One mechanism by which physical protection of organic matter may occur is through encapsulation of reactive OM within insoluble, hydrolysis-resistant organic matrices such as algaenans.[33,111] While encapsulation may protect reactive proteins from acid hydrolysis or biological degradation, $^{15}$N NMR or pyrolysis GC/MS techniques can still detect the occurrence of such proteinaceous compounds in hydrolysis-resistant fractions of sediment organic matter.[109,118,152]

Much of the work examining encapsulation has been carried out either in organic-rich sapropel sediments with very low (<10%) mineral content or in "short-term" algal degradation studies, that is, generally less than ~1 yr. Studies of more typical marine sediments from the northwest African upwelling region also show that what appears to be protein-derived material is similarly found in a hydrolysis-resistant fractions of these sediments.[59] However, these authors suggest that here this occurs by melanoidin-type condensation reactions (i.e., more "traditional" geopolymerization reac-

tions). Similar conclusions were reached in studies of recent sediments from the Cariaco Trench.[93]

Interest in the role that inorganic matrices might play in OM preservation began with observations that the vast majority of the organic matter in marine sediments is intimately associated with fine-grained sediment particles.[9,140,143,144,153] Subsequent studies have further examined these organic matter−mineral interactions as they relate to organic matter dynamics, and ultimately preservation, in marine sediments.[3,154−157]

Based on observations from these works, these interactions appear to involve physical protection of organic matter in small mespores either on mineral surfaces or in-between mineral grains. This led Mayer[143] to propose the "surface adsorption/mesopore protection" hypothesis for OM preservation in marine sediments. In this model, organic matter−mineral interactions may protect organic matter from bacterial exoenzymes (and therefore remineralization) in at least two ways. First, these pores are likely to be too small to allow entry of these enzymes, thus preventing the direct contact needed by most of these enzymes to carry out their activity. Second, steric constraints within the pores may further reduce the effectiveness of an enzyme even if it is able to enter a pore. This hypothesis may also provide a mechanistic explanation for the possible role of anoxia in enhancing carbon preservation, or conversely, for the enhanced remineralization of some types of organic matter when exposed to oxygen (see section 5.2.1 for details).[3,80,81,132]

For mesopore protection to contribute to organic matter being preserved in sediments, the attachment of OM to mineral surfaces must be sufficiently strong, for example, near irreversible adsorption, such that there is effectively no detachment/desorption of this organic matter, particularly during acid or base hydrolysis, or solvent extraction.[143,158] Subsequent chemical changes in the organic material after its initial attachment/adsorption to sediment particles may also play a role here, in that this could render this attached organic matter chemically non-recognizable and/or increase the strength of its attachment (see section 6 for further details).

However, $^{13}C$ NMR studies of organic matter in sinking marine particles[22] and in a range of marine sediments[50] (e.g., organic-rich coastal sediments to organic-poor pelagic sediments) suggest that there is a gross similarity between the biochemical composition of characterized and uncharacterized (∼nonhydrolyzable) natural organic matter. These results therefore appear to argue against the occurrence of substantive chemical changes in organic matter that is physically protected by either organic or inorganic matrices. At the same time though, more recent work[85] using direct-temperature resolved mass spectrometry (DT-MS) suggests that physical protection may show some amount of selective preservation that could be difficult to detect using $^{13}C$ NMR. It is also possible that slight alteration of natural biochemicals occurs during physical protection such that these compounds are "missed" by standard chromatographic techniques but can still be detected by $^{13}C$ NMR.[5,159] Thus physical protection in association with some form of chemical modification, and some amount of selective preservation, cannot be unequivocally ruled out.[85]

Finally, Burdige[45] provides an independent line of evidence in support of the model of physical protection of reactive organic matter during diagenetic maturity. Using organic geochemical data and inorganic pore water nutrient data from coastal to deep-sea sediments, it can be shown that the composition of the organic matter that is remineralized in all of these sediments exhibits little variation over a range in remineralization rates that spans more than 3 orders of magnitude; this material appears to be ∼30−60% amino acids, ∼20−50% carbohydrates, and ∼10−30% lipids, and therefore largely looks like marine organic matter (compare with results in Table 1). One possible explanation of this remineralization "constancy" is that during diagenetic maturity some inherently reactive material escapes remineralization and becomes protected by an organic matrix that can only be decomposed by $O_2$, or by activated oxygen species such as the hydroxyl radical (also see discussions in section 5.2.1).[77,160] An analogous effect is also to be expected if this reactive organic matter is associated with, and protected by, mineral surfaces as discussed above.

## 5.2. Role of Oxygen

Historically, the role of oxygen in carbon preservation has been examined in terms of the role of bottom water oxygen concentration in controlling the organic carbon content of marine sediments. In part, this has occurred because petroleum geochemists have generally considered organic-rich sediments underlying anoxic bottom waters (e.g., the Black Sea) as modern counterparts of petroleum source rocks.[55,161,162] However, studies of recent marine sediments have not shown any clear-cut and systematic relationships between bottom water $O_2$ concentration and either sediment TOC content, organic carbon BE, or the preservation of type II "oil-prone" kerogen.[6,7,150,163,164] At the same time, these observations do not imply that oxygen per se has no effect on carbon preservation or remineralization (e.g., see results in ref 77). Rather, it suggests that bottom water $O_2$ concentrations are not necessarily the correct metric with which to examine these effects.

### *5.2.1. Inherent Reactivity of Sediment Organic Matter in the Presence or Absence of $O_2$*

In examining the role of oxygen in controlling sediment organic matter remineralization, several broad conclusions can be reached. The first is that the effective remineralization of relatively fresh, that is, labile, organic matter occurs under both oxic and anoxic conditions,[127,165−167] although not necessarily always at the same rates.[168] A second broad conclusion is that "aged" or refractory organic matter is degraded much more slowly, if at all, under anoxic versus oxic conditions.[77,169,170] While some caution must be applied to subjective terms such as "labile", "refractory", or "aged" as they are applied here,[45] these results suggest that oxygen-sensitive organic matter (i.e., organic matter requiring $O_2$, in some way, for degradation) is selectively concentrated with increasing organic matter diagenetic maturity.

One possible explanation for this observation involves potential controls on remineralization processes by the initial depolymerization of sedimentary organic matter to form lower molecular weight (and eventually dissolved) intermediates. Here, in the presence of $O_2$ the oxygen molecule is used both as an electron acceptor in aerobic respiration and as a cofactor by enzymes such as oxygenases or peroxidases to cleave nonhydrolyzable bonds in materials such as lignins, hydrocarbons, and other more refractory organic compounds. Often times, this oxidative cleavage occurs through the production of strong oxidants such as peroxide ($H_2O_2$) and other reactive oxygen-containing radicals.[6,171,172] Because

many of these enzymes are nonspecific, that is, they do not target specific compounds or types of bonds, they are useful in degrading materials such as lignins, which are randomly polymerized upon formation. Such oxidants may also play a role in decomposing refractory (i.e., nonhydrolyzable) biopolymers or geopolymers in the sediment organic matter pool.

In contrast, other biopolymers such as proteins or carbohydrates can undergo hydrolysis in the presence or absence of oxygen. Thus, the preferential remineralization of reactive proteins and carbohydrates may occur under either oxic or anoxic conditions during early stages of diagenetic maturity. This may then concentrate in the remaining organic matter hydrolysis-resistant materials, or carbon-rich substrates such as lignin or some lipids, which can only be effectively degraded when $O_2$ is present. Consistent with this suggestion are, for example, discussions in section 4.4 that marine organic matter, for example, proteins and carbohydrates, can be preferentially degraded over terrestrial organic matter, such as lignins or perhaps soil organic matter. Similarly, results in Figure 2 also show that terrestrial organic matter has a higher burial efficiency than does marine organic matter in muddy deltaic sediments subject to mixed redox conditions by physical reworking.[8,82]

### 5.2.2. Redox Oscillations and Organic Matter Remineralization

A related "oxygen" effect may occur as a result of the sediment redox oscillations described in section 3. These oscillations have the potential to greatly enhance organic carbon remineralization in sediments over that which might occur under more strict anoxic conditions, despite the general asymmetry between cycles or "times" of anoxic versus oxic conditions.[82,173,174]

The specific mechanisms by which enhanced organic matter remineralization occurs under mixed redox conditions are not well characterized, although there are at least four likely possibilities. First, physical processes that cause redox oscillations (i.e., resuspension/deposition cycles) can also add fresh/reactive organic matter to the sediments,[136,175] and the oxidation of refractory components of the sediment OM pool may then be catalyzed through a process referred to as co-metabolism or co-oxidation.[6,81,176] In this situation, the reactive OM input "primes" the sediments, and the resulting microbial decomposition stimulated by the addition of this reactive organic matter also catalyzes the degradation of more refractory material.

Second, the periodic introduction of oxygen into these sediments may initiate the subsequent anaerobic microbial decomposition of certain types of organic matter that would otherwise be refractory under continuous anaerobic conditions.[81] This may occur, for example, as a result of the initial depolymerization (oxidative cleavage) of these compounds by $O_2$-requiring enzymes or reactive $O_2$ products (e.g., $H_2O_2$; see section 5.2.1). Third, the more direct activity of benthic macrofauna in some mixed redox sediments plays an important role in the dynamics of carbon remineralization in these sediments (see the next section for details).

Finally, oxygen input to mixed redox sediments also leads to extensive Mn and Fe redox cycling in these sediments.[82,177,178] Several aspects of this metal redox cycling may facilitate the oxidation of a wide range of refractory organic compounds, including many aromatic compounds.[3,45,179−181] The processes could therefore play a role similar to that which oxygen and associated enzymes play in depolymerizing refractory, and nonhydrolyzable, organic compounds. Some of these same refractory organic compounds can apparently be used by metal oxide reducing organisms,[182] although these organisms may simply take advantage of abiotic reactions between metal oxides and refractory organic compounds, and then utilize the end-products of these reactions.

### 5.2.3. Role of Benthic Macrofuanal Processes

The role of benthic macrofaunal processes in affecting sediment OM preservation is often thought of in terms of their role in adding oxygen to marine sediments. While in many sediments this may indeed be important, the role of benthic macrofauna in affecting sediment OM preservation is actually more complex.[45,134,173,174,183−187] In general, it appears that macrofaunal processes impact the rates of sediment OM matter degradation, along with the overall efficiency of remineralization. The enhancement of OM remineralization by benthic macrofauna then translates into a decrease in OM burial efficiency.

Although benthic macrofauna are aerobic organisms, they are also able to live in mixed redox sediments and can also physically rework (bioturbate) sub-oxic sediments (i.e., those found below the oxygen penetration depth[188]). This therefore implies that they must also maintain "metabolic contact" with either oxic surface sediments or oxygen-containing bottom waters. As a result, macrofaunal effects on OM preservation/remineralization are sometimes viewed broadly in the context of an "oxygen" effect.

### 5.2.4. Oxygen Exposure Time as a Determinant of Organic Carbon Preservation in Sediments

Previous discussions have strongly suggested some role for oxygen in controlling carbon preservation in sediments; recent results further suggest that this may somehow be related to the average time that sediment organic matter is exposed to "oxic" conditions.[1,8,80,132] In the simplest sense, organic matter oxygen exposure time (OET) can be viewed as the average time organic matter is exposed to oxic conditions in sediments before being permanently buried into deeper sediments that are devoid of oxygen. It can be determined from pore-water $O_2$ profiles and rates of sediment accumulation, although estimates of OET may also be obtained using benthic $O_2$ flux measurements and simple diagenetic models.[132] For reasons that will become apparent later in this discussion, such estimates of sediment organic matter OET will be referred to as the "steady-state" OET.

To begin to quantitatively examine the role of oxygen exposure on OM preservation, Hartnett et al.[132] examined the relationship between sediment OET and organic carbon burial efficiency for sediments along the western Pacific continental margin. Results from this study indicated that organic carbon BE varies inversely with log(OET), over more than 3 orders of magnitude of OET; specifically, values of OET range from essentially zero for sediments deposited under the anoxic bottom waters of the intense oxygen minimum zone on the Mexican continental slope, to values of ~1000 yr for sediments on the lower slope of the California and Washington margins. Organic carbon BE values at these sites ranged from ~50−60% to <5%, that is, within the broad range of BE values seen in Figure 3.

Follow-up studies examining this problem[80] led to the more general observation that oxidant availability plays a role in

sediment OM burial and preservation for some types of organic matter as one moves offshore across the continental margin (also see additional discussions in refs 1 and 173). As a result, the extent of OM preservation, particularly after some degree of organic matter diagenetic maturity, appears to involve a set of processes that are somehow associated with exposure of sediment organic matter to oxygen and/or oxygen input to the sediments. In contrast, rates of OM remineralization for relatively "fresh" OM (and hence its extent of preservation) are largely controlled by the quality and the quantity of available organic matter[77,90,165] and are also largely independent of sediment redox conditions (e.g., see section 5.2.1). The oxygen effects described here are also broadly consistent with the mesopore protection hypothesis (section 5.1),[143] particularly if reactive oxygen species such as peroxide or the superoxide radical are required for the degradation of certain types of refractory sediment organic matter.

Many aspects of the previous discussion have been presented in terms of the specific role of OM exposure to molecular $O_2$ on preservation versus remineralization. However, the specific mechanisms by which this occurs may not necessarily directly involve $O_2$ itself. Rather, oxygen exposure may actually lead to other processes or conditions that enhance remineralization over that which occurs under more strict anoxic conditions.[1,81,189] Earlier discussions have indicated several possibilities for how this might occur, including a number of effects associated with redox oscillations (i.e., Fe and Mn redox cycling), physical reworking of sediments, or benthic macrofaunal processes. Under some circumstances then, oxygen exposure time may therefore simply be a reasonable proxy, in some way, for these effects.

These considerations also suggest that the processes leading to sediment OM oxygen exposure occur in a complex, and often non-steady-state, fashion that is not always easily characterized by the steady-state OET calculations discussed above.[82,183] Similarly, lateral (versus vertical) sediment transport implies that organic matter deposited in a given sediment may have undergone varying (and stochastic) amounts of degradation and oxygen exposure as a result of numerous deposition/resuspension cycles prior to its most recent deposition.[3,46,190]

Taken together then, all of these observations appear to suggest that in a more broad sense sediment OM oxygen exposure (and perhaps other co-related processes or phenomena) is the more important general controlling parameter, as opposed to steady-state oxygen exposure time (specifically as calculated above). Examining these issues will be important in the further development of a more complete mechanistic understanding of OM preservation in marine sediments, and in developing more robust predictors of sediment OM preservation than the steady-state estimate of OET.

## 6. Relationship between Physical Protection, Oxygen Exposure, and Abiotic Condensation Reactions in Sediment Carbon Preservation

Past interest in abiotic condensation reactions such as geopolymerization has stemmed from the possible role that these processes might play in both the formation of molecularly uncharacterized organic matter and the preservation of OM in marine sediments. Although the "classical" mechanism of humification (Figure 5) does not appear to adequately explain the formation of MU-OM in sediments, related

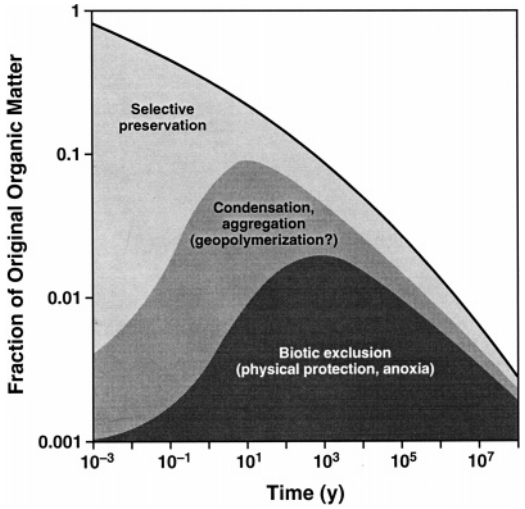


**Figure 5.** A schematic diagram indicating one possible way in which the succession and overlaying of OM protection mechanisms may occur (Adapted from ref 84, Copyright 2004, with permission from Elsevier). To give some sense of the relevant time scales here, the relative amount of organic matter remaining as a function of time was calculated with eq 11 from ref 224 assuming $a = 0.09d$. In the scheme shown here, early stages of OM preservation are dominated by selective preservation/remineralization with some amount of abiotic condensation or aggregation (geopolymerization?). With time, however, there is an increase in the relative importance of physical protection and anoxia as preservation mechanisms. As Mayer[84] notes, this diagram does not account for all preservation pathways, and the relative contributions that different pathways have on overall preservation may differ from that which is shown here. However, this diagram is meant to illustrate that different OM preservation/protection mechanisms operate over different time scales, and likely proceed through some sort of sucessional overlaying of processes.

abiotic reactions, perhaps in association with inorganic or organic matrix protection, may play a role in affording the material some degree of protection from biological degradation, and therefore enhancing its preservation in sediments.

Collins et al.[191] have suggested that organic matter adsorption and protection in sediment particle mesopores could promote the occurrence of geopolymerization reactions by either steric- or concentration-related phenomena (also see similar discussions in refs 3 and 143). If these or other types of condensation reactions occur in association with adsorption, and also operate in concert, then this could lead to a positive feedback in which adsorption promotes condensation, which might then enhance the strength of adsorption of the resulting condensate. This mechanism also requires that increased condensation lead to an increase in the number of adsorption binding sites within the condensate. Calculations[158] support this suggestion and show that the strength of adsorption (i.e., the adsorption coefficient) increases with the number of attachment points between a molecule and a particle surface.

Adsorption studies of monomeric amino acids, small peptides, and proteins to sediments show that some of this adsorption is not readily reversible and that adsorbed amino acids may undergo what appears to be melanoidin-type condensation reactions.[94,192] Protein degradation in seawater also appears to occur more slowly when proteins are associated with either sub-micrometer particles or bacterial membranes.[193−195] Such decreased rates of protein degradation may then enhance the occurrence of other condensation reactions that ultimately lead to protein preservation (also see section 4.1.1).[196]

**Table 3. Sediment Organic Carbon Budgets in the Oceans (All Values Are Tg C·yr$^{-1}$)[a]**

| | MK[b] | J[c] | Ag[d] | Ab[d] | Mg[e] | Ma[e] | SH[f] | MMK[g] | BR[h] | BRS[i] | HK[j] | G[k] | S[l] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| All Marine Sediments | | | | | | | | | | | | | |
| rain rate | 930 | | | | 2374* | 5739* | | 930 | 2628 | 2300 | | | |
| remineralization | 775 | | | | 1784 | 3127 | 2616 | 702 | 1991 | 1991 | | | |
| burial | 155 | | | 2520 | 590 | 2612 | | 228 | 637 | 309 | 160 | 223 | |
| Deep-Sea[m] | | | | | | | | | | | | | |
| rain rate | 310 | 411* | 1029* | | 351* | 693* | | 310 | 616 | 616 | | | 500−600 |
| BE | 0.3 | 0.04* | 0.07 | | | | | 0.05 | | | | | |
| remineralization | 217 | 396 | 957* | | 321 | 563 | 816 | 295 | 555 | 555 | | | |
| burial | 93 | 15 | 72 | 302 | 30 | 130 | | 15 | 61 | 61 | 15 | 5 | 2−120 |
| Continental Margin[m] | | | | | | | | | | | | | |
| rain rate | 620 | | | | 2130* | 5233* | | 620 | 2013 | 1684 | | | |
| BE | 0.1 | | | | | | | 0.25 | | | | | |
| remineralization | 558 | | | | 1570 | 2752 | 1800 | 407 | 1436 | 1436 | | | |
| burial | 62 | | | 2218 | 561 | 2481 | | 213 | 577 | 248 | 145 | 218 | |

[a] In this table, starred values (*) were calculated here with the "primary" results reported in the original paper. Also note that the way results are presented in these papers, it is not possible here to report or estimate all of the terms in each budget. [b] From ref 199. Satellite data were used to estimate net primary production, which was attenuated with water column depth using standard models. This was then applied to a global bathymetry database to determine OC rain rates to these two ocean regions. Using assumed BE values, OC burial rates and remineralization rates were estimated. [c] From ref 200 based on a global extrapolation of deep-sea sediment oxygen uptake measurements, sediment OC concentrations, and sedimentation rates. [d] From ref 79. The Ag calculation is based on results from a sediment diagenesis model (MUDS) applied to a gridded map of OC rain rates to the seafloor below 1 km water depths.[200] The Ab calculation uses the same MUDS model and a depth/bottom water oxygen hypsometry of the whole ocean.[79] [e] From ref 198. These calculations use empirical relationships between rates of remineralization processes and water depth combined with hypsometry data to estimate globally integrated rates. The two sets of values shown here differ depending on whether arithmetic (Ma) or geometric (Mg) means are used when the logarithmic empirical relationships are back-transformed to linear depth units. [f] From ref 224. [g] Modified from ref 199. The OC rain rate from this work was assumed to be the rate of marine organic matter input to sediments, and BE values taken from Figure 2 were applied to these rain rates to estimate burial rates of marine organic matter. The burial of terrestrial organic matter[145] was also included in the OC burial rate in continental margin sediments. [h] From Table 4. [i] From Table 5. [j] From ref 3, recalculated from data originally presented in ref 2. [k] From ref 215 as reported in ref 3. This calculation is based on the average TOC content of Holocene sediments multiplied by their areal size and thickness. [l] From ref 197, based on regional correlations between benthic $O_2$ uptake, surface sediment TOC content, and bottom water $O_2$ concentrations. [m] The boundary between deep-sea sediments and continental margin sediments is taken to be at a water depth of 2000 m for all calculations except the J, Ag, and Ab budget calculations, in which this transition was assumed to occur at 1000 m.

These observations along with others discussed throughout this Article therefore suggest the following scenario. During early stages of diagenetic maturity, selective utilization of reactive organic matter occurs, leading to an enrichment of more refractory, and $O_2$-sensitive (?), material. Associated with these trends may be processes such as physical protection or adsorption that then decrease the rate of biological degradation of some types of sedimentary organic matter. This may then increase the probability that this organic matter becomes involved in abiotic aggregation or condensation reactions. If such processes occur, they have the potential to operate in a positive feedback mode, leading to at least some sedimentary organic mater that becomes increasingly more refractory as well as increasingly physically protected from degradation. The net result is that this material is preserved in sediments, and either operationally or in actuality falls into the category of MU-OM. Mayer[84] discusses many of these same concepts, and Figure 5 (modified from this work) illustrates a potential timeline for the succession and overlayering of different processes associated with OM preservation.

The occurrence of abiotic condensation reactions in concert with physical protection could also play a role in explaining the oxygen effects associated with the remineralization of some diagenetically mature fractions of sediment organic matter (see section 5.2.1). As discussed in this section, nonspecific, $O_2$-requiring enzymes or strong chemical oxidants, such as $H_2O_2$, are very effective at cleaving a wide range of nonhydrolyzable bonds. Such enzymes and oxidants could therefore play a role in decomposing not only refractory biopolymers (i.e., those that are nonhydrolyzable and/or are randomly polymerized), but also abiotic condensates that have an analogous random structure. This could then help explain why aged organic matter is degraded more slowly, if at all, in the absence of oxygen.

Other discussions (section 5.2.2) have further suggested that Mn and Fe redox cycling may actually be responsible, to some degree, for these oxic effects on OM degradation. Specifically, Mn and Fe redox cycling in mixed redox sediments could play a role similar to that which oxygen and associated enzymes may play in depolymerizing refractory and nonhydrolyzable organic matter. Again, this recalcitrant organic matter may be natural biopolymers or abiotic condensates that form in situ during sediment diagenesis.

## *7. Organic Matter Preservation in Marine Sediments and Sediment Organic Carbon Budgets*

In recent years, several studies have made regional and global estimates of sediment OC remineralization and burial.[3,79,145,197−200] Table 3 summarizes the results of these studies. Also shown in this table are three new sediment OC budget estimates. The first (labeled MMK) uses OC rain rates from the MK budget[199] and applies BE values to these rain rates that are based on Figure 2, rather than those used in the original MK budget. Furthermore, because of the way OC rain rates are derived in the MK budget, they are largely marine organic matter fluxes, and so the MMK calculation also takes into account the recently estimated[145] burial of terrestrial organic matter in continental margin sediments (58 Tg·yr$^{-1}$; note however that this calculation does not take into account the amount of terrestrial organic matter that is remineralized in marine sediments).

The second of these estimates (labeled BR) is based on the summary of sediment OM remineralization rates versus

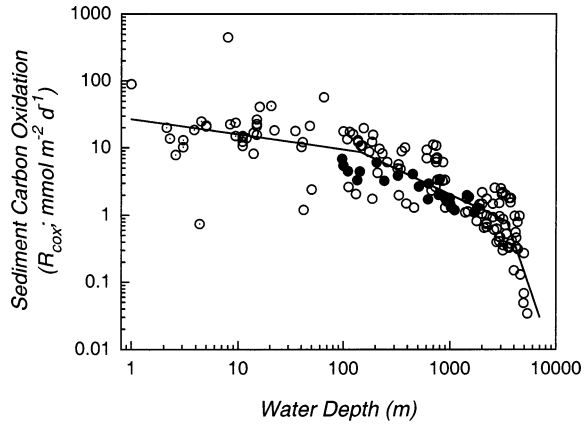


**Figure 6.** The depth-integrated rate of sediment carbon oxidation ($R_{cox}$) in marine sediments as a function of water column depth of the sediment (see the original references cited below for details on how these rates were calculated). ○ represent results from "normal" marine sediments (largely siliciclastic sediments from the Atlantic, Pacific, Arctic, and Southern Oceans), ● represent continental margin sites in the Eastern Pacific (from the Washington coast to the Mexican margin) underlying low (<50 $\mu$M) bottom water oxygen concentrations, and ⊙ represent results from sandy (high permeability) continental margin sediments. The log−log transformation of these data was fit to three straight lines in the depth regions 0−200 m, 100−4000 m, and >3000 m, and with this approach there are then two crossover points for this set of three curves, at 146 and 3415 m. These curves were used to calculate the aerially integrated rates of carbon oxidation for different ocean regions (Table 4) using the first curve for water depths 1−146 m, the second curve for water depths 146−3415 m, and the third curve for water depths >3415 m. Sample locations and references: Equatorial Pacific between 2° S and 2° N;[231] MANOP sites M, H, S, and C and eastern Equatorial Atlantic;[232] eastern North Atlantic;[233] Goban Spur (northeast Atlantic continental margin);[228] Iberian margin (northeast Atlantic continental margin);[130] northwest Atlantic continental margin;[234] California Borderlands;[235,236] Santa Barabara Basin;[237,238] Patton Escarpment;[236] central California (northeast Pacific) continental margin;[239] Washington state (northeast Pacific) and northwest Mexican (eastern tropical Pacific) continental margin;[229] northwest Atlantic continental margin;[240] North Carolina (U.S.) upper continental slope and rise;[241] Skagerrak continental margin;[230,242] North Sea continental margin;[243] western Arctic continental shelf sediments;[244,245] Danish coastal sediments;[246] Aarhus Bay, Denmark;[247] Arctic coastal sediments;[248,249] coastal sediments of the Northern Adriatic Sea;[250] Long Island Sound;[251] Skan Bay, AK;[252] Tomales Bay, CA;[253] mesohaline Chesapeake Bay;[254,255] Cape Lookout Bight, NC;[46,256] Buzzards Bay;[257] sandy sediments in the South Atlantic Bight off Georgia (USA);[206] and shallow water, sandy (i.e., high permeability) carbonate sediments on the Bahamas Bank (Burdige et al., unpublished data; rates derived from pore water models).

water depth that is shown in Figure 6. The log−log transformation of these data was fit to three straight lines, and using ocean hypsometry results[201] these remineralization rates were integrated regionally and globally (Table 4). Using BE values based on those in Figure 2, these remineralization rates were then used to calculate OC rain rates and burial rates.

Focusing first on OC remineralization rates, I note that the different estimates for either the whole ocean, continental margin, or deep-sea sediments vary by only a factor of ∼4−5; estimates of OC rain rate show a similar range (∼3−8; also note that given the way many of these calculations are presented in the literature it is not possible to report or estimate all quantities in all budgets). In contrast though, OC burial rates vary by more than an order of magnitude among the different budget calculations (i.e., ∼160−2600 Tg C·yr$^{-1}$ for all marine sediments, ∼60−2500 Tg C·yr$^{-1}$ for continental margin sediments, and ∼2−300 Tg C·yr$^{-1}$ for deep-sea sediments). In particular, many of these burial estimates are significantly larger than the commonly cited[2,3] whole ocean OC burial rate of ∼120−160 Tg C·yr$^{-1}$.

The reasons for these differences are not well understood, although it has been suggested that a bias toward sampling "hotspots" of sediment biogeochemical processes could play a role in explaining this discrepancy.[198,202] This is certainly a possibility, and, in particular, an important point may be the fact that ∼70% of all continental shelf sediments (defined here as sediments in water depths <200 m) are non-accumulating, relict sands with a very low TOC content.[203] These sediments are therefore likely to be insignificant sites of OC burial despite the importance of continental margins in general as sites of sediment OC burial.[2,3] At the same time, recent studies have demonstrated that sandy continental shelf sediments may be much more important sites for sediment organic matter remineralization than previously thought.[204−206] Therefore, the low TOC content of these sediments may be the result of rapid degradation of reactive organic matter deposited in these sediments, coupled with the lack of dilution of this material by either less reactive (or "aged") organic matter or reactive organic matter that is protected from degradation by any of the mechanisms described earlier in this Article. As a part of this explanation, it has been observed that advective processes in high permeability, sandy sediments lead to far greater sediment oxygen penetration than is seen in more fine-grained, muddy sediments.[207−209] Therefore, the greater oxygen exposure these sediments experience may enhance OM remineralization and thus minimize OM preservation.

Rates of OM remineralization in sandy, continental shelf sediments are not as well-represented in summaries such as those in Figures 6 as compared to more "muddy" sediments. However, the few results from sandy sediments that are shown here appear to be consistent with the general trends illustrated in this figure. More importantly though, because of the nature of these sandy sediments, BE values for these sediments are almost certainly much lower (close to ∼0?) than the BE value of 30% used in Table 4 for continental shelf sediments. This observation will therefore lead to an overestimation of OC burial in continental shelf sediments (and hence all sediments globally), if the presence of these relict sands is not taken into account.

This can be seen in budget calculation BRS (Tables 3 and 5) in which results in Emery[203] are used to divide the continental shelf into "sands" (70%) and "muds" (30%), and it is further assumed that these sediments have the same average $R_{cox}$ values but very different BE values (1% [as an extreme (?) upper limit] and 30%, respectively). As expected, the OC burial rate in continental margin sediments and in all oceanic sediments decreases in this calculation, and, in particular, the whole ocean OC burial rate estimated here differs from the Hedges and Keil[3] value by only a factor of ∼2. While these results suggest one possible explanation for the disagreement in OC burial rates in Table 3, more work is needed to verify this possibility.

In addition, I would also like to suggest another possible explanation for these budget imbalances. I first note that all of the budgets shown here essentially use three types of data: OC rain rates, OC burial rates, and OC remineralization rates. In specific sedimentary environments (e.g., Cape Lookout Bight, NC[46,210]), it is possible to independently

**Table 4. Marine Sediment Organic Carbon Budget Based on a Global Compilation of Organic Matter Remineralization Rates**

| depth range (km) | area ($10^{12}$ m$^2$)[a] | avg. $R_{cox}$[b] | int. $R_{cox}$[c] | BE (%)[d] | OC burial rate[e] |
|---|---|---|---|---|---|
| 0−0.2 | 27.1 | 9.4 | 1121 | 30 | 480 |
| 0.2−1 | 16.0 | 3.0 | 210 | 25 | 70 |
| 1−2 | 15.8 | 1.5 | 104 | 20 | 26 |
| 2−3 | 30.7 | 1.0 | 138 | 15 | 24 |
| 3−4 | 76.8 | 0.8 | 269 | 10 | 30 |
| 4−5 | 114.7 | 0.2 | 116 | 5 | 6 |
| 5−6 | 76.8 | 0.09 | 31 | 1 | 0.3 |
| >6 | 4.4 | 0.04 | 1 | 0.5 | 0.004 |
| continental margin sediments (0−2 km) | | | 1436 | | 577 |
| deep-sea sediments (>2 km) | | | 555 | | 61 |
| all marine sediments | | | 1991 | | 637 |

[a] From ref 201. [b] The average depth-integrated rates of organic carbon oxidation ($R_{cox}$; units of mmol C m$^{-2}$ d$^{-1}$) for each depth range. This was determined using the curves shown in Figure 6 and the arithmetic mid-point of each region (see the caption to Figure 6 for more details). [c] Units of Tg C·yr$^{-1}$. Obtained by multiplying the area in the second column by the average $R_{cox}$ in the third column. [d] Burial efficiency (BE) values were obtained from Figure 2. [e] BE was estimated as $(R_{cox}\cdot(BE/100))/(1 - (BE/100))$ on the basis of the definition of BE ($=100\cdot(OC_{bur}/OC_{rain})$) and the assumption of a steady-state sediment OC budget (i.e., $OC_{rain} = R_{cox} + OC_{bur}$).

**Table 5. Modified Marine Sediment Organic Carbon Budget Taking Account of Relict Sands on the Continental Shelf**

| depth range (km) | area ($10^{12}$ m$^2$)[a] | avg. $R_{cox}$[b] | int. $R_{cox}$[c] | BE (%)[d] | OC burial rate[e] |
|---|---|---|---|---|---|
| 0−0.2[f] | 27.1 | 9.4 | | | |
| sand (70%) | 19.0 | | 785 | 1 | 8 |
| mud (30%) | 8.1 | | 336 | 30 | 144 |
| 0.2−1 | 16.0 | 3.0 | 210 | 25 | 70 |
| 1−2 | 15.8 | 1.5 | 104 | 20 | 26 |
| 2−3 | 30.7 | 1.0 | 138 | 15 | 24 |
| 3−4 | 76.8 | 0.8 | 269 | 10 | 30 |
| 4−5 | 114.7 | 0.2 | 116 | 5 | 6 |
| 5−6 | 76.8 | 0.1 | 31 | 1 | 0.3 |
| >6 | 4.4 | 0.04 | 1 | 0.5 | 0.004 |
| continental margin sediments (0−2 km) | | | 1436 | | 248 |
| deep-sea sediments (>2 km) | | | 535 | | 61 |
| all marine sediments | | | 1991 | | 309 |

[a] From ref 201. [b] The average depth-integrated rates of organic carbon oxidation ($R_{cox}$; units of mmol C m$^{-2}$ d$^{-1}$) for each depth range. See footnote *b* in Table 4 for details. [c] Units of Tg C·yr$^{-1}$. Obtained by multiplying the area in the second column by the average $R_{cox}$ in the third column. [d] With the exception of sandy continental shelf sediments (0−0.2 km), burial efficiency values were obtained from Figure 2. [e] See footnote *e* in Table 4. [f] In this calculation, it is assumed that 70% of the continental shelf is low TOC relict sands (see the text and ref 203 for details). Although these sediments are non-accumulating, I have assumed here that 1% of the TOC that rains on these sediments is retained by the sediments.

constrain all three quantities over similar time scales and obtain a sediment OC budget that is internally consistent. In contrast, the calculations shown in Table 3 generally estimate only two of these three quantities with the third obtained by assuming steady-state,

$$\text{OC rain} = \text{OC burial} + \text{OC remineralization} \quad (2)$$

(also see Figure 3). Burial efficiencies are also often calculated using a similar steady-state approach.

Given these observations, potential problems can arise because measures of these three processes integrate over very different time scales ($\tau$) such that

$$\tau_{\text{OC rain rate}} < \tau_{\text{OC remineralization}} < \tau_{\text{OC burial}} \quad (3)$$

While measured OC rain rates generally integrate over time scales as short as annual cycles, OC burial in some sediments integrates over times scales as long as tens of thousands of years (i.e., glacial−interglacial time scales). Under some circumstances then, this "mixing" (or mismatch) of measurements that integrate over different time scales can lead to apparent discrepancies in sediment OC budget calculations that may not necessarily be real. For example, failure to appreciate this point can lead to the appearance of non-steady-state conditions in calculated budgets for sediment systems that may actually be in steady-state, if all of the terms in the budget are examined over more appropriate, and consistent, time scales.[45,211]

Changes in sea-level on glacial−interglacial time scales also impact deep-sea versus continental margin sedimentation patterns, and may therefore bias certain OC burial rate estimates toward higher values.[198,212] Similarly, recent human activity, along with more general changes in the global OC cycle on glacial−interglacial time scales, will both affect estimates of sediment OC burial.[2,213,214] However, an examination of the studies cited here suggests that these considerations might lead to a factor of ~2 change (at most) in sediment OC burial rates; they therefore do not appear to explain the ~15-fold range in OC burial rates listed in Table 3.

All of these observations therefore lead to the following question: is the present-day sediment OC budget in non-steady-state, or are the observations in Table 3 simply the result of attempting to calculate sediment OC budgets using measurements that integrate over different time scales? A resolution of this problem is clearly beyond the scope of the discussion here, although these observations do suggest that this problem should be carefully re-examined, with attention specifically paid to matching observations and time scales. This is particularly true when comparing "bottom-up" estimates of OC burial (based on, for example, particulate river discharge rates or aerially averaged sediment accumulation rates and sediment TOC concentrations[2,3,198,215]), and

"top-down" estimates of OC burial (Tables 4 or 5 or ref 79, based on sediment OC remineralization rates and rain rates, and burial efficiencies that are estimated or derived as discussed above, e.g., using eq 2).

Finally, setting aside these issues, these results demonstrate that continental margins are major sites of OC remineralization and burial despite the fact that they are a small fraction of the whole ocean (~10−20% depending on how they are defined). At the same time, we have also observed that organic carbon dynamics in continental margin sediments can be particularly complex, and not necessarily well quantified in budget calculations such as those discussed here. In particular, important questions still remain regarding: the role of sandy, continental margin sediments as efficient sites of OM remineralization despite the fact that they are non-accumulating sedimentary environments;[205,206,208,216] the role of small, mountainous rivers as sources of recycled kerogen (fossil carbon) to continental margin sediments, as well as the magnitude and non-steady-state nature of their organic carbon transport to the oceans;[60,63,68,218] the spatial and temporal variability of biogeochemical processes in fluid muds associated with river-dominated margin sediments (e.g., the Amazon Shelf), and the role these systems play in the remineralization of terrestrial (and marine) organic matter.[69,82]

Work in these areas will not only address questions associated with the budget calculations discussed here, but will also greatly improve our understanding of carbon cycling in continental margin settings, its role in the global carbon cycle, and its linkages to past and future climate change.[2,145,198,199]

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