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# Processes that Control Storage of Nonliving Organic Matter in Aquatic Environments

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## ABSTRACT

This article addresses processes important in the cycling of nonliving organic matter (NLOM) by focusing on storage of organic matter in sediments. It considers differences in the oxidation capacity of freshwater and marine sediments, and shows that the oxidizing capacity in marine sediments is at least 100-fold larger. The controversy surrounding the role of productivity and carbon supply versus the availability of oxygen in bottom waters as controls on organic matter storage draws information from carbon-rich rocks and contemporary sediments. Anoxic bottom water conditions and lack of bioturbation are indicated as factors preserving organic matter in carbon-rich sedimentary rocks; however, studies in contemporary environments point to productivity and sedimentation rate as the controlling factors. Contemporary studies cover a wide range of sedimentation rates and experimental conditions, but questions dealing with observation time scales and postdepositional reworking complicate a straightforward comparison with sedimentary rocks. Other processes that may also be important in carbon storage, such as stabilization and protection by sorption on mineral particles and the concept of a sediment microbial loop, have emerged during the debate and measurements suggested by them are outlined.

## INTRODUCTION

Several recent books and reviews have contributed to our understanding of the processes that control cycling of organic matter in aquatic environments. Berger et al. (1989) synthesized the current state of knowledge on ocean

productivity and loss of organic matter to sediments, and Wollast et al. (1993) reviewed interactions in the C, N, S, and P cycles and their effect on global change. Canfield (1993) summarized organic matter oxidation in sediments, Henrichs (1992) reviewed organic matter diagenesis, and Lee and Wakeham (1988, 1992) considered water column processes affecting organic matter. Hedges (1992) reviewed the role of active reservoirs in the global carbon cycle and enumerated some key questions, Holmen (1992) emphasized recent trends in the global carbon cycle, and Smith and Hollibaugh (1993) reviewed organic matter metabolism in the coastal ocean.

In this chapter I consider the processes that control cycling of organic matter by focusing on the preservation of organic matter in marine sediments. I chose this approach for several reasons: Sedimentation and storage occur at the sediment–water interface, a convenient boundary in the carbon cycle to take stock of fluxes. There is a substantial amount of data in this area as a result of the controversy surrounding controls on organic matter storage. Resolution of this controversy requires an explanation consistent with the sedimentary record, another area with a growing data base. There are pitfalls in this "inverse" approach. Organic matter decomposition is very efficient, so that the quantity of organic matter stored is the small difference between two large terms, *gross deposition* and *oxidation*, and may be sensitive to errors or small changes in either term. The range of conditions encountered in nature is large, and it is likely that several processes controlling organic matter storage are important to varying degrees over this range.

Recently, as they sought explanations for sedimentary carbon maxima in Pleistocene glacial horizons, paleoceanographers and sedimentologists have examined the processes controlling accumulation and storage of organic matter in marine sediments. These maxima and other carbon-rich sediments are generally considered to have accumulated under anoxic or low bottom water oxygen conditions (Demaison and Moore 1980; Arthur et al. 1984; Ingall et al. 1993).

Studies on contemporary systems include reviews of field data compilations from a range of environments (Henrichs and Reeburgh 1987; Canfield 1989; Betts and Holland 1991), interpretation of new data in selected high sedimentation rate environments with low-oxygen overlying water (Calvert and Pedersen 1992; Pedersen and Calvert 1990; Reimers et al. 1992; Jahnke 1990), and experimental studies of the metabolism of specific compounds under oxic and anoxic conditions (Lee 1992). These contemporary studies generally conclude that productivity and flux of organic matter to the seafloor are the principal controls on formation of organic-rich sediments.

In the following discussion I summarize the debate on organic matter storage, discuss possible explanations that have emerged during the debate, and suggest measurements that may help reconcile the conflicting observations.

## CARBON CYCLE IN AQUATIC SYSTEMS

Carbon is stored in a range of reservoirs that turn over and exchange with other carbon reservoirs over a range of time scales. It is crucial to place the processes and reservoirs important at various time scales in perspective. Sundquist (1985) and Walker (1993) outlined a hierarchy of interacting carbon reservoirs that controls atmospheric carbon dioxide on all time scales. These reservoirs consist of small, rapidly exchanging reservoirs (atmosphere, shallow sea, biota), which are coupled by slower transfers to the large deep-sea and sedimentary rock reservoirs. For example, at the hundred million year time scale (Berner 1992), the chemical weathering of Ca–Mg silicate rocks is the principal process for removal of $CO_2$ from the atmosphere. The weathering of kerogen in shales uplifted on continents imposes a control on the carbon cycle and atmospheric oxygen on time scales of several million years, as burial of organic carbon in modern sediments generates a continuous source of oxygen that must have a compensating sink (Hedges 1992). Studies focusing on the past million years consider changes in carbon storage on continents and continental shelves as a result of glaciation and deglaciation (Harden et al. 1992), while studies considering the effects of anthropogenic alterations with a time scale of centuries (Smith and Hollibaugh 1993) focus on metabolism in the coastal ocean. Studies in coastal sediments, which usually focus on understanding a particular environment, consider time scales of a few months to decades (Henrichs and Reeburgh 1987).

Below, I briefly describe the aquatic portion of the global carbon cycle; this description stems largely from Hedges (1992) and Emerson and Hedges (1988). Remineralization of organic matter is a very efficient process on a global basis: only $\sim 0.1\%$ ($0.1 \times 10^{15}$ gC yr$^{-1}$ ) of global primary production (terrestrial: $60 \times 10^{15}$ gC yr$^{-1}$; marine: $50 \times 10^{15}$ gC yr$^{-1}$) escapes oxidation and is ultimately buried in marine sediments. Continental reservoirs for carbon storage are small and near steady state, so that burial in ocean sediments is the ultimate fate of biosynthesized organic matter that escapes remineralization at time scales of several million years. Export to the sea is the only route for long-term preservation of significant amounts of terrestrial organic matter at this time scale. Most of the particulate fraction of this exported terrestrial organic matter, estimated to be $0.2 \times 10^{15}$ gC yr$^{-1}$, is deposited close to shore. The dissolved fraction of exported terrestrial organic carbon, estimated to $0.2 \times 10^{15}$ gC yr$^{-1}$, enters the large seawater DOC pool ($0.7 \times 10^{18}$ gC) and is apparently oxidized. Although primary productivity is higher in the coastal ocean, about 80% of the total ocean primary production occurs in the open ocean, which accounts for about 90% of the ocean area. Much of the ocean primary production is recycled in the upper 100 m of the ocean; the recycling process in the upper 100 m is more efficient in the open ocean (80–90%) than in coastal waters (50%). The portion of the particulate flux from the upper 100 m

of the ocean ($7 \times 10^{15}$ gC yr$^{-1}$) reaching the sediments is a function of water depth. Only ~1% of the primary production reaches depths of 4000 m; this decrease is accompanied by selective removal of more reactive biochemicals.

Differences in primary production, surface recycling efficiency, and oxidation of particulate organic carbon (POC) settling through varying water column depths result in deposition of a major fraction of the organic matter that reaches the seafloor in near-shore sediments. More than 80% of the preserved organic carbon is deposited in shelf and continental margin sediments. Further reworking and oxidation of deposited organic matter by diagenetic reactions occurs in shelf and pelagic sediments. The POC deposited in continental margin sediments has a marine origin as indicated by $\delta^{13}C$ measurements and consists of two components (Anderson et al. 1994; Jahnke 1990): one component is labile and is remineralized in the surface (a few millimeters of the sediments) on time scales of less than a year to several years; the other component is refractory and is derived from older material. Uniform mixed layer organic carbon distributions suggested decomposition time scales greater than mixed layer residence times; recent $^{14}C$ measurements show little accumulation of bomb $^{14}C$ and suggest a remineralization half-life for this refractory material of greater than 1000 years. The fraction of organic carbon that is oxidized on a 1000-yr time scale is higher in continental margin sediments (30–50%) than in pelagic sediments (20–40%) (Emerson et al. 1987). Despite the efficiency of organic matter remineralization, the resulting low storage rate in sediments has led to accumulation of a huge ($1.5 \times 10^{22}$ gC) reservoir of organic matter in sedimentary rocks over geologic time, and this has played a central role in modulating atmospheric oxygen concentrations.

# OXIDATION OF ORGANIC MATTER

## Oxidation Sequence

Degradation of complex organic matter is microbially mediated and generally proceeds through depolymerization reactions, which may involve digestive enzymes or exoenzymes, fermentation reactions, which produce simple compounds, and terminal metabolism of the simple compounds. Aerobic oxidizers can oxidize a wide range of substrates to $CO_2$, and are responsible for oxidation of over 90% of the organic matter in sediments. Anaerobic oxidizers have more specific substrate requirements, and can oxidize a restricted number of molecules, often incompletely. Aerobic and anaerobic organic matter degradation rates may be limited by these initial reactions. Anaerobic processes are important for their role in determining the amount of carbon preserved in sediments (Henrichs and Reeburgh 1987). One model for organic matter degradation (Froelich et al. 1979) considers that organic matter oxidation proceeds

using the available electron acceptor with the greatest free energy yield according to the sequence: $O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2$ (Table 15.1). Thus, oxidation of organic matter proceeds through a series of reactions consuming the most energetically favorable oxidant in sequence, beginning with oxygen reduction and followed by denitrification, metal oxide ($Mn^{+4}$, $Fe^{+3}$) reduction, sulfate reduction, and finally methanogenesis. This results in separation of specific microbial processes into zones of age or depth in sediments.

This sequence is generally followed in most environments; thus it serves as a reasonable framework. Yet, Canfield (1993) has demonstrated overlap of processes, i.e., anoxic processes occurring in oxic conditions, in some environments, so this sequence may be an oversimplification of the complex microbial interactions that can occur in sediments. The explanation seems to lie in competition for reduced substrates rather than free energy yield alone (Lovely and Klug 1986). Canfield (1993) emphasized the importance of focusing on rates of microbial processes rather than chemical distributions, as we have a poor understanding of how microbially reduced species interact with adjacent oxidized species as well as the overall importance of these reactions. Direct rate measurements of denitrification, sulfate reduction, and methane oxidation can be made with stable and radioisotope tracers (Reeburgh 1983); no direct rate measurements are available for oxygen, Fe oxide, or Mn oxide reduction. The rates of the latter reactions can be estimated from gradients; however, this approach may lead to underestimates for the Fe oxide and Mn oxide reduction rates (Canfield 1993). Canfield, Jørgensen et al. (1993) performed incubations on amended and unamended anoxic coastal sediments sealed in gas impermeable plastic bags to estimate metal oxide reduction rates as well as rates of interaction between oxidized and reduced species of Mn, Fe, and S. The amended experiments involved additions of $MoO_4^{2-}$ to inhibit sulfate reduction and slow interactions between Fe and Mn oxides and sulfide, and addition of Ferrozine to complex $Fe^{2+}$, reducing the possibility of Mn reduction by $Fe^{2+}$. Canfield, Thamdrup, and Hansen et al. (1993) concluded that most of the oxygen flux into these sediments was used to oxidize reduced species and that in some sediments the importance of metal oxide reduction in organic matter oxidation has been underestimated.

**Oxidation Capacity**

Composition differences between sea- and fresh waters result in large oxidation capacity differences. The above oxidation sequence is combined with typical electron acceptor concentrations and reaction stoichiometries to estimate closed sediment system oxidation capacity in Table 15.1. This oxidation capacity estimate considered a hypothetical oxygen-saturated marine sediment and estimated the amount of a hypothetical organic compound, $CH_2O$, that could

**Table 15.1** Sequence and capacity of organic matter oxidation processes important in freshwater and marine sediments.

| Reaction | p(e) | Eh (mV) | Energy Yield KJ/mole $CH_2O$ | Typical Oxidant Conc. (mM) | Hypothetical Sed. Conc. mmol/l$_{sed}$ | Oxidizing Capacity mmol/l$_{sed}$ | Characteristic Depth Scales (cm) Freshwater Wetland | Marine Low OM flux | Marine High OM flux |
|---|---|---|---|---|---|---|---|---|---|
| Oxygen reduction $[CH_2O + O_2 \rightarrow CO_2 + H_2O]$ | 12.1–12.5 | 720–740 | –475 | 0–0.09 | 0–0.85 | 0–0.8 | ±5 mm of water table | 0–1 | |
| Denitrification $[5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O]$ | ~12 | 710 | –448 | 0–0.04 | 0–0.037 | 0–0.03 | ? | 15 | |
| Mn-oxide reduction $[CH_2O + 3CO_2 + H_2O + MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-]$ | 8.0 | 470 | –349 | ≥1.5% (0.27 mmol/g) | 43.2 | 21.6(?) | ? | 15–30 | ≥1 m    ~1–5 cm |
| Fe-oxide reduction $[CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{3+} + 8HCO_3^- + 3H_2O]$ | 1.0 | 60 | –114 | ≥4.0% (0.7 mmol/g) | 112 | 28(?) | ? | ≥20 | |
| Sulfate reduction $[2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-]$ | –3.8 | –200 | –77 | 0–30 | 0–28.2 | 56.4 | — | — | ≥10 |
| Methane production $[CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2$ & $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O]$ or $[CH_3COOH \rightarrow CH_4 + CO_2]$ | –4.2 | –250 | –58 | | | | major process | — | ≥25 |

Adapted from Reeburgh (1983) and Canfield (1993). Hypothetical sediment has an oxygen-saturated seawater content of 85% and a density of 1.1 g cc$^{-3}$.

be oxidized under closed system conditions. This approach yields a minimum estimate, as oxygen and sulfate is supplied to sediments from the overlying water, and depending on organic matter loading, oxygen demand, and bioturbation and irrigation, can be exhausted in a matter of centimeters to meters. Nitrate is rarely present in concentrations exceeding tens of micromoles, and the role of Mn and Fe oxides remains unclear. The concentration of sulfate is the major difference between freshwaters and marine systems. Seawater sulfate concentrations are 20–30 mmol $l^{-1}$, while sulfate concentrations rarely exceed 100–200 μmol $l^{-1}$ in fresh waters. A closed-system estimate of oxidation capacity (Reeburgh 1983) shows that a marine sediment has an oxidation capacity at least 60-fold larger than an oxygen-saturated sediment containing no sulfate. The actual oxidizing capacity of a natural sediment will exceed this estimate in non-euxenic environments, because sulfide and reduced metal oxides can be reoxidized by oxygen from overlying waters added by diffusion or by irrigation processes. Thus, there appears to be unutilized oxidizing capacity in many recent marine sediments, even euxinic sediments. Dissolved oxidants are exhausted only in areas of very high organic matter settling flux, such as the Peru and Namibian margins.


## ORGANIC MATTER STORAGE

### Freshwater Aquatic Environments

Peatlands are end-member environments that illustrate the important differences in organic carbon degradation in terrestrial freshwater environments with low oxidation capacity and marine sediments with high oxidation capacity. Peatlands cover about 3% of the Earth's land surface and have been estimated to contain $180 \times 10^{15}$ gC. Seventy-five percent of the global peatland area is concentrated in two large areas: the Hudson Bay Lowlands ($3.2 \times 10^5$ km²) in Canada and the Vasuugan peatland ($5.4 \times 10^5$ km²) in Siberia. Organic matter produced in terrestrial wetland environments contains structural polymers such as lignin and cellulose, and has a relatively high C:N ratio (20–200), in contrast to marine organic matter, which consists of more labile structural polymers and has a low C:N ratio (7). Peatlands consist of two layers: the acrotelm, an oxic 10–50 cm thick surface layer where primary production by mosses and sedges and rapid decay occur, and the catotelm, which receives about 10% of the primary productivity, is usually anoxic, and has much lower decay rates. The catotelm forms the largest part of the peat mass, is waterlogged, and has low hydraulic conductivity. Since the oxidation capacity of fresh waters is low, the dominant degradation reactions in peatland catotelms are fermentation and methanogenesis, which do not result in net oxidation of carbon (Capone and Kiene 1988). Clymo (1984) emphasized

that although degradation rates in the catotelm are low, they are not zero, and that most peatlands reach a thickness, usually 5–10 m, where the net rate of accumulation is zero.

## Marine Sediments

### Intrinsic Differences in Oxic and Anoxic Rates?

Several recent studies suggest that there are no large differences in the rates of oxic and anoxic processes in degrading fresh organic matter. Laboratory microcosm experiments (reviewed in Henrichs and Reeburgh 1987) involving decomposition of added algae under oxic and anoxic conditions give similar rates of decomposition and amounts of refractory material in ~200-day experiments. Lee (1992) studied the metabolism of individual radiolabeled compounds in the oxic and anoxic portions of several stratified water columns. Her work emphasized measurements of turnover times and pool sizes of simple molecules and avoided complications due to interactions with sediments. These sediment-free systems also have the advantage that carbon incorporation as well as respiration can be measured. Lee (1992) observed no major differences in the intrinsic rates of organic matter decomposition under oxic and anoxic conditions.

Conclusions drawn from the behavior of fresh algae and simple molecules are instructive, but their applicability to interpretations of long-term organic matter storage in nature may be limited. The organic matter used in these rate determinations is representative of the labile, rapidly reacting organic matter fraction, so less information on the resistant, slowly reacting organic matter pool is obtained. Also, experiments should be designed to ensure that the amount of organic matter added does not exceed natural inputs.

### Role of Bottom Water Oxygen in Organic Matter Preservation

Emerson (1985) and Emerson and Hedges (1988) used a simple model involving sedimentation and bioturbation to examine carbon storage in deep-sea sediments. All carbon was assumed to be of plankton origin and was homogeneously degradable, i.e., one decay constant was used in the model. Oxygen was the only electron acceptor considered; all other electron acceptors were neglected. Emerson (1985) supported this assumption with correlations that showed low organic carbon contents in the presence of high bottom water oxygen concentrations. Emerson and Hedges (1988) point out that rate constants for organic matter degradation are a function of carbon age, i.e., the rates are dependent upon the observation time scales. The model results showed that bioturbation had no effect on carbon storage at high sedimentation rates but that it enhanced carbon storage at low sedimentation rates. The sedimentation rate only affected the average carbon content of sediments at

Canfield (1989) considered a similar data set and estimated the importance of sulfate reduction and oxygen reduction at given sedimentation rates with plots of depth-integrated sulfate reduction and oxygen consumption versus sediment burial rate. Data from these plots were combined to produce a plot of integrated carbon oxidation rate versus sedimentation rate. This plot showed that for sedimentation rates $> 0.1 \, g \, cm^{-2} \, yr^{-1}$, sulfate reduction and oxygen reduction are equally important in oxidizing organic carbon. For sedimentation rates below $10^{-3} \, g \, cm^{-2} \, yr^{-1}$, oxic respiration remineralized 100- to 1000-fold more organic carbon than sulfate reduction. Canfield's plot of burial efficiency versus sedimentation rate using data from euxinic and semi-euxinic environments suggested high burial efficiency at low sedimentation rates for Black Sea data not included in the Henrichs and Reeburgh (1987) analysis. Canfield concluded that anoxia could enhance carbon preservation and pointed out that small changes in depth integrated organic carbon decomposition rates could have large effects on burial efficiency. Calvert et al. (1991) pointed out that the sedimentation rates for the Black Sea data points used by Canfield were in error and overestimated carbon accumulation rates. Their work indicated that the modern anoxic Black Sea is not a site of anomalously high carbon accumulation.

Betts and Holland (1991) determined the burial efficiency of organic carbon in a data set involving 69 sites and estimated errors in the various burial efficiency estimates. As with the previous work of Henrichs and Reeburgh (1987) and Canfield (1989), they found that sedimentation rate exerts a dominant influence on burial efficiency. Although scatter in the burial efficiency data was large, Betts and Holland concluded that bottom water oxygen has, at most, a minor effect on burial efficiency of organic matter in marine sediments.

Calvert and Pederson (1992) have emphasized that increased primary productivity resulting from increased wind-driven upwelling is the likely cause of organic-rich Pleistocene sediments. Several indices of oxic conditions in Panama Basin sediments, such as size and abundance of benthic foraminifera, size and number of meiofaunal fecal pellets, no changes in the I:$C_{org}$ ratio, and the lack of Mo enrichment, are taken as evidence that the waters overlying these sediments have never been anoxic.

## Sediment Microbial Loop

Lee (1992) suggested that extending the concept of the "microbial loop" in water column environments to sediments might offer an explanation for enhanced carbon storage in anoxic sediments. The microbial loop in water column environments involves bacterial uptake of dissolved organic matter (DOM). The bacteria grow and retain the organic carbon as cellular

rates $> 10$ cm $kyr^{-1}$. Emerson suggested that it might be possible to understand the effect of bottom water oxygen with studies in California Borderland basins, where there is a fairly constant rain rate of organic carbon and a wide range of bottom water oxygen contents. Jahnke (1990) observed no correlation between burial efficiency and bottom water oxygen in sediments from the Borderland Basins of California, and Reimers et al. (1992) reported no indication that fluxes or remineralization rates in Central California slope and rise sediments were influenced by conditions in the oxygen minimum zone. Sarnthein et al. (1987) also concluded that the effect of bottom water oxygen on carbon storage was small. Isolines of carbon accumulation rate on a particulate carbon flux versus bottom water oxygen concentration plot showed sediment accumulation rate increases only at very low oxygen concentrations.

Sediments of the Oman margin of the Arabian Sea, a site of high monsoon upwelling driven production and sedimentation and one of the most intense oxygen minima, have been studied by Pedersen et al. (1992). There they found no correlation between bottom water oxygen and the abundance of sedimentary organic carbon, which was mostly of marine origin. The organic matter progressively degrades, as shown by the $C_{org}$:N ratio and the I:$C_{org}$ ratio, accompanied by reworking and winnowing as shown by correlations with Cr:Al and Zr:Al ratios, which are proxies for sediment texture. Thus the spatially variable high $C_{org}$ sediments reflect a high settling flux and postdepositional reworking.

Calvert et al. (1992) compared data from Guaymas Basin surface sediments contacting oxygenated bottom water and those contacting the oxygen minimum and concluded that bottom water oxygen levels exerted no major influence on the concentration and composition of organic matter in the sediments.

### Factors Affecting Burial Efficiency

Henrichs and Reeburgh (1987) examined the relationship between burial efficiency (the ratio of carbon buried long-term to the sediment input rate, i.e., the fraction that survives remineralization; see Blackburn 1991) and sedimentation rate in a range of environments. Burial efficiency ranged from 0.6% to 16% in pelagic sediments to 8% to 28% in slope sediments and 8% to 79% in estuarine environments. Data from environments with low or zero bottom water oxygen and thin sediment oxic layers did not cluster at the high sedimentation rate:high burial efficiency end of the data set, but were distributed along the sedimentation rate axis. The data provided no striking evidence for the importance of low oxygen conditions in preserving organic matter. Sarnthein et al. (1987) considered open ocean sediments and found a strong correlation between organic carbon accumulation rate and the carbon-free sedimentation rate.

material. Grazers (protozoans) consume the bacteria, efficiently remineralize the nutrients, and release DOM to the water column for another cycle. Lee (1992) suggested that the efficiency of grazing by protozoans in sediments may be limited by sediment compaction and oxygen concentrations in the sediments. The reduction of protozoan numbers and efficiency by compaction and anoxic conditions could result in enhanced storage of bacterial biomass and bacterial products. A number of observations are consistent with a sediment microbial loop (Lee 1992), but direct observations and experimental manipulations are needed.

### Sorption by Particles

Recent determinations of organic carbon concentration and specific surface area on a range of marine sediments from a variety of environments (Mayer 1994b) show that in most cases organic matter is present at monolayer equivalent (ME) concentrations on mineral surfaces. The organic matter appears to be associated with the high density or mineral phase. The topography of these natural mineral grains is such that ~80% of the surface area is inside pores of <8 nm width (Mayer 1994a). Mayer hypothesizes that organic matter is stabilized and protected by its incorporation into pores and slits in the mineral surfaces too small to allow functioning of hydrolytic enzymes involved in the initial stages of degradation. This hypothesis offers an explanation for the "refractory background" level of organic carbon observed in shelf sediments and also provides a plausible mechanism for the carbon burial:sedimentation rate relationship discussed earlier. Exceptions to this relationship are areas with high riverine sediment input (deltas), which have lower than possible ME concentrations, and areas with organic pollution and low oxygen water columns, which have greater than possible ME concentrations. The lack of ME levels of organic carbon in high sedimentation rate deltaic sediments suggests that a finite time is necessary to accumulate organic carbon concentrations to ME levels, as in soils. Interactions between adsorption and slower processes like condensation reactions may also be important in the slow accumulation to ME concentration levels.

## SUMMARY

The preceding discussion presents a number of puzzling and apparently conflicting observations. The studies on carbon-rich marine shales point to anoxic conditions and lack of bioturbation as important in formation of laminated organic-rich shales (Ingall et al. 1993), and differences between the organic C:P

ratio in laminated and bioturbated shales offer additional support. Studies on contemporary sediments overlain by anoxic and low oxygen waters, however, show no differences in storage that cannot be explained by higher productivity and organic matter deposition when compared to nearby sediments in contact with oxic bottom waters. Field studies in a range of environments show that the major control on sediment burial efficiency appears to be primary production and the supply of organic matter. Differences in the intrinsic rates of oxic and anoxic degradation reactions on fresh organic matter appear to be small; however, small changes in sediment degradation rates can result in large changes in burial efficiency.

The controversy surrounding carbon storage has polarized into two camps, and although information is being added to the debate, it consists of similar information from different environments. Can these conflicting observations be reconciled? What additional information is needed? Since the controversy has drawn on data from a range of water depths, the following points should be carefully considered when drawing comparisons:

- the $10^4$- to $10^6$-fold range of sedimentation and organic matter supply rates,
- the range of reactivity of organic matter,
- questions relating to observation time scales, time since deposition, and organic matter age.

Emerson and Hedges (1988) observed that decomposition rates are a function of carbon age and observation time scale; this suggests that rate measurements from short-term field and microcosm experiments on fresh organic matter may be inapplicable to explanations of long-term storage. Van Capellen and Canfield (1993) point out that the surface sediments studied in high deposition rate areas have been subjected to diagenetic processing for only a decade or more and that the organic matter remaining in sediments after extensive microbial degradation is another end member that should be studied. They argue that the degree of preservation of organic matter in the surface 1–5 cm of sediments only set limits on how long diagenetic processing must take place before effects can be distinguished. The refractory organic matter concentrated by reworking and redeposition is another important component of this carbon age-observation time scale range. The work of Anderson et al. (1994) shows that about half of the organic matter deposited in the Middle Atlantic Bight (U.S. East coast) margin is refractory and originated from older deposits. The amount deposited and the nature and age of this refractory sediment organic matter is very important to a general explanation of controls on organic matter storage.

## INFORMATION NEEDED TO FOCUS THE DEBATE

*1. What is the role of sediment texture and mineralogy in organic matter transport and storage?*

Recent work (Mayer 1994a, b; Keil et al. 1994) indicates that organic material is present as monolayer equivalent coatings on sediments and that organic matter loadings increase linearly as a function of sediment specific surface area. This hypothesis offers an explanation for the "refractory background" level of organic carbon observed in shelf sediments and provides a plausible mechanism for the carbon burial:sedimentation rate relationship. It should be considered one of the strongest possibilities for resolving the carbon storage controversy. Separation by SPLITT (split flow, thin cell, lateral flow) fractionation (Giddings 1985) permits sorting sediment samples into size/density fractions under conditions that mimic natural winnowing processes with little loss of organic material. Quantities of particular sediment fractions large enough to permit more extensive analyses can be isolated with this technique. Fractions collected with this technique would provide a starting point for long-term reactivity and kinetic (Canfield 1994) experiments on intact sediment-organic associations under oxic and anoxic conditions. Collection of large quantities of selected fractions would permit more complete studies of the composition, structure, and possible origin of sorbed organic matter, including compound specific isotope ratio measurements (Hayes et al. 1990; Freeman and Hayes 1992).

*2. What is the composition of the "resistant when anaerobic" and recalcitrant fractions of sediment organic matter? What is the age and origin of this material?*

Many studies have suggested that a fraction of sediment organic matter is refractory under anoxic but not oxic conditions, while others have demonstrated a fraction that is recalcitrant, even under oxic conditions. Henrichs (1992) cautions that a small fraction of this "resistant when anaerobic" material cannot explain the entire range of burial efficiencies, as a large fraction of the incoming organic matter is buried in the most rapidly depositing sediments. More information on the composition of the organic matter that is deposited and survives burial below the oxygenated sediment layers is needed to understand its susceptibility to microbial remineralization. Henrichs (1992) points out that complete characterization of the composition of sediment organic matter is not a realistic goal, but that identification of differences in structure between the remineralized and preserved fraction of organic matter buried at high and low preservation sites would be valuable as a starting point for understanding reactivity as a control on storage. These studies could be conducted by either examining down-core differences in sediments from selected sites or by fractionating quantities of sediments, as in Question 1 above, to

determine age and reactivity as a function of grain size and mineralogy. Organic matter $^{14}C$ measurements from all of the contemporary environments discussed in this chapter, particularly the environments with the highest sedimentation rates where bomb $^{14}C$ is detectable, are needed to determine how much of the deposited material has been recycled.

## 3. What is the role of metal oxides in organic matter remineralization?

Metal oxides are capable of serving as electron acceptors in biologically mediated organic matter remineralization (Lovely and Phillips 1983; Sørensen 1982; Wilson et al. 1986), and have high oxidizing potential and capacity. Canfield et al. (1993a, b) showed that metal oxides in coastal sediments are more important as electron acceptors than previously believed. Sediment environments where metal oxides are important in organic matter remineralization should be identified and estimates of their global importance should be made. Metal oxide surfaces are important organic matter adsorption sites; does organic matter adsorption affect oxidizing capacity?

## 4. What is the role of the "microbial loop" in storage of sediment organic matter?

The role of the microbial loop promises to be more difficult to observe in sediments than in water column environments, but it could be clarified by several approaches. Studies of the distribution of bacterial biomarkers (Lee 1992) with depth may give some indication of the depth at which grazing becomes unimportant. It may be possible to develop hybridization probes for protozoan grazers and assess their numbers and depth distributions directly.

## 5. What is the role of animals and bioturbation/bioirrigation processes in the preservation of sediment organic carbon, reoxidation of reduced metal and sulfur species, and the effectiveness of storage of microbial organic matter?

Lee (1992) and Emerson and Hedges (1988) pointed out that animals deserve attention as an explanation for the differences in organic carbon preservation in oxic and anoxic systems. Animals play an important role in remineralization of organic matter by fragmentation and digestion of organic matter or by direct uptake or further degradation of polymers by intra- or extra-cellular enzymes. These processes provide new surfaces and substrates that stimulate further microbial degradation. Protozoan grazers can help maintain microbial populations in a state of high growth rate, and their absence may be important in storage of microbial organic matter. Sediment irrigators and bioturbators appear to enhance degradation of POC and PON (Kristensen and Blackburn 1987) and may be important in the reoxidation of metal oxides and reduced sulfur compounds (Stone and Morgan 1987). Emerson's (1985) model showed

that bioturbation played an important role in enhancing storage of carbon in pelagic sediments, but that it was of less importance in high deposition rate coastal sediments. The work of Ingall et al. (1993) shows striking differences in the organic matter content between bioturbated and laminated (unbioturbated) shales.

## ACKNOWLEDGEMENTS

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