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Sedimentary organic matter preservation: an assessment and speculative synthesis

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Abstract

Throughout Earth history, almost all preserved organic matter has been incorporated in marine sediments deposited under oxygenated waters along continental margins. Given modern oceanic productivity and sediment burial rates of 50×10^{15} and 0.16×10^{15} gC yr^{-1}, respectively, organic preservation in the marine environment is $< 0.5\%$ efficient. Although correlative information is often used to suggest that productivity, sediment accumulation rate, bottom water oxicity, and organic matter source are key variables, the mechanisms governing sedimentary organic matter preservation have remained unclear.

The factors which directly determine preservation vary with depositional regime, but have in common a critical interaction between organic and inorganic materials over locally variable time scales. More than 90% of total sedimentary organic matter from a wide variety of marine depositional environments cannot be physically separated from its mineral matrix. This strongly associated organic component varies directly in concentration with sediment surface area and thus appears to be sorbed to mineral grains. Sediments accumulating outside deltas along continental shelves and upper slopes characteristically exhibit mineral surface area loadings approximately equivalent to a single molecular covering. These monolayer-equivalent coatings include a fraction of reversibly bound organic molecules that are intrinsically labile, but resist appreciable mineralization as they pass rapidly through oxygenated surface sediments and are preserved within underlying anoxic deposits. The delivery of mineral surface area is the primary control on organic matter preservation within these expansive coastal margin regions where roughly 45% of all organic carbon accumulates.

Deltaic sediments account for roughly another 45% of global carbon burial, but often exhibit much less than monolayer-equivalent organic coatings. This pattern is seen in periodically oxygenated sediments off the mouth of the Amazon River, even though the component clastic minerals are discharged by the river with monolayer coatings. Comparably extensive losses of organic matter, including distinct particles such as pollen grains, occur in the surfaces of deep-sea turbidites in which long term reaction with O_2 is clearly the causative factor. Sub-monolayer organic coatings also are observed in continental rise and abyssal plain sediments where slower accumulation rates and deeper O_2 penetration depths result in increased oxygen exposure times and little ($\sim 5\%$ of the global total) organic matter preservation. A transition zone between monolayer and sub-monolayer organic coatings apparently occurs on lower continental slopes, and is marked along the Washington coast by parallel offshore decreases in total organic matter and pollen between 2000–3000 m water depth.

Sediments underlying highly productive, low-oxygen coastal waters such as off Peru and western Mexico are characteristically rich in organic matter, but account for only $\sim 5\%$ of total organic carbon burial. These sediments show a direct relationship between organic matter content and mineral surface area, but at organic loadings 2–5 times a monolayer equivalent. Organic materials sorbed in excess of a monolayer thus also may be partially protected. Such high sedimentary organic contents may result from equilibration with DOM-rich porewaters, or very brief O_2 exposure times which allow

preservation of extremely oxygen-sensitive organic materials such as pigments and unsaturated lipids. Thus organic matter preservation throughout much of the ocean may be controlled largely by competition between sorption at different protective thresholds and oxic degradation.

Future research strategies should be specifically directed at delineating the **mechanisms** for organic matter preservation in marine sediments. In particular, special effort is needed to determine the amounts and types of sorbed organic materials and the nature of their bonding to mineral surfaces. The extent and dynamics with which organic molecules are partitioned between porewaters and solid phases also should be determined, as well as the effects of these phase associations on their reactivities toward chemical and biological agents. In addition, processes for slow oxic (and suboxic) degradation of organic materials bear investigation in deep-sea sediments, as well as in other extreme environments such as oxidizing turbidites, weathering shales, and soils. Such studies should include characterizations of hydrolysis-resistant organic materials and emphasize the complementary use of biochemical compositions with readily separable particles such as pollen to calibrate and typify the mechanisms and stages of sedimentary organic degradation.

Contents

1. Introduction

This discussion paper is a speculative, and hopefully provocative, assessment of sedimentary organic matter preservation. It is neither a comprehensive review nor a conservative evaluation of data as is typical of most research papers. Rather, we have tried to critically compare published viewpoints on the preservation process with our present perceptions, which have been strongly influenced by recent findings of various research groups. Although many of the following concepts and interpretations have been previously presented, the overall geochemical scenario materializing from this synthesis often contrasts sharply with current wisdom. We will argue that the processes directly affecting sedimentary organic matter preservation act primarily via removal ("sink") control and vary systematically with the characteristic local milieu of organic and inorganic materials and the time scales over which they interact. Specifically, we will contend that: (1) continental shelves and slopes are more variable and quantitatively important repositories of organic matter than is generally appreciated and have been understudied vs. comparatively limited carbon-rich deposits, (2) organic degradation and preservation are opposites and not necessarily related in a meaningful manner, (3) many relationships between environmental characteristics and organic matter mineralization used to infer universal controls on preservation are inadequate, and (4) many observed organic distributions can be simply explained by the interplay of protective sorption onto mineral grains vs. in-situ oxic degradation. Finally, possible new techniques and directions for studying the preservation of sedimentary organic matter will be discussed.

2. Global cycles of carbon and oxygen

2.1. The carbon cycle

The global cycles of carbon (Berner, 1982, 1989) and oxygen (Berner and Canfield, 1989) offer a variety of useful perspectives on the extent and mechanisms of sedimentary organic matter burial, as well as intriguing contradictions. Inventories and stable carbon isotope mass balances indicate that

Table 1
Major reservoirs of inorganic and organic carbon

Reservoir type	Amount [a]	Reference
Sedimentary rocks		
Inorganic		
Carbonates	60,000	Berner (1989)
Organic		
Kerogen, coal, etc.	15,000	Berner (1989)
Active (surficial) pools		
Inorganic		
Marine DIC	38	Olson et al. (1985)
Soil carbonate	1.1	Olson et al. (1985)
Atmospheric CO_2	0.66	Olson et al. (1985)
Organic		
Soil humus [b]	1.6	Olson et al. (1985)
Land plant tissue [b]	0.95	Olson et al. (1985)
Seawater DOC	0.60	Williams and Druffel (1987)
Surface marine sediments	0.15	Emerson and Hedges (1988)

[a] Unit = 10^{18} g C
[b] Values corrected to levels before anthropogenic effects.

essentially all carbon is stored in sedimentary rocks where approximately one of five C atoms is organic (Table 1). About 90% of this preserved organic material ($\sim 15,000 \times 10^{18}$ g C) now resides as amorphous, highly insoluble kerogen macromolecules disseminated in shales and other sedimentary rocks. In addition to providing a molecular record of life, organic materials in sedimentary rocks include economically important coals and petroleums. Sedimentary burial of organic matter and pyrite also is essentially the only source of atmospheric oxygen, and intimately links the global cycles of C, S, and O over geologic time (Berner, 1982).

About 0.1% of the carbon in the Earth's upper crust cycles in active surface pools (Table 1). The greatest active reservoir ($\sim 40 \times 10^{15}$ g C) is inorganic carbon dissolved in seawater. Other dynamic pools are 1–2 orders of magnitude smaller (0.2–2 $\times 10^{15}$ g C) and include atmospheric CO_2, soil carbonate, soil humus, land plant biomass, dissolved organic matter (DOM) in seawater, and carbon preserved in surface marine sediments (Table 1). With the exception of terrestrial biomass, the active organic reservoirs contain complex mixtures of heavily degraded substances which are poor in recognizable biochemicals.

Rivers carry about 1% of terrestrial productivity ($\sim 60 \times 10^{15}$ g C yr^{-1}) to the ocean in comparable fluxes ($\sim 0.2 \times 10^{15}$ g C yr^{-1}) of particulate and dissolved organic materials (POM and DOM) (Hedges, 1992). Since virtually no organic matter is preserved on eroding continental platforms, and aeolian fluxes are small ($< 0.1 \times 10^{15}$ g C yr^{-1}; Romankevich, 1984), rivers provide the major conduit toward the preservation of terrigenous organic substances in marine sediments. Having been subjected to severe microbial attack in soils (Oades, 1988; Hedges et al., 1994) and aquifers (e.g. Nelson et al., 1993), riverine DOM and POM might be expected to resist extensive degradation in estuaries and at sea. However, extensive molecular and isotopic evidence indicates that most organic materials in seawater (Meyers-Schulte and Hedges, 1986; Benner et al., 1992) and marine sediments are autochthonous (Degens, 1969; Hedges and Mann, 1979; Gough et al., 1993). In addition, total OC burial in marine sediments is less than one-third of riverine OC discharge (Table 2). Thus, all indications are that riverine POM

and DOM are rapidly and extensively mineralized within seawater or surficial marine sediments.

Most marine productivity ($\sim 50 \times 10^{15}$ gC yr^{-1}) is by rapidly growing phytoplankton that are continuously grazed by protozoans and zooplankton. Little organic matter is stored in plankton biomass, and only about 20% of net primary production falls as particles (largely fecal pellets) from the lighted surface ocean. Sediment trap studies indicate exponentially decreasing fluxes of particulate organic matter down marine water columns, with 10% of surficial productivity remaining at depths of several hundred meters, and only 1% passing to an average ocean depth of 4000 m (Suess, 1980; Martin et al., 1987). Most marine primary productivity occurs in the open ocean, with the result that the global average flux of plankton remains to marine sediments is comparable to the export rate of organic matter from land to sea.

The most commonly cited preservation rate for organic matter in marine sediments is Berner's (1982) value of 0.13×10^{15} g C yr^{-1}. Berner estimated that over 80% of total OC preservation occurs in "terrig-

Table 2
Organic carbon burial rates (and percentages) in different ocean regimes

Sediment type	Deltaic	Shelf	Slope	Pelagic	Total
Data from Gershanovich et al. (1974)					
All sediment types	0 (0)	23 (10)	195 (88)	5 (2)	223 $\Sigma = 223$
Data from Berner (1989)					
Terrigenous deltaic-shelf sediments	104 (82)	0	0	0	104
Biogenous sediments (high-productivity zones)	0	0	7 (6)	3 (2)	10
Shallow-water carbonates	0	6 (5)	0	0	6
Pelagic sediments (low-productivity zones)	0	0	0	5 (4)	5
Anoxic basins (e.g. Black Sea)	0	1 (1)	0	0	1 $\Sigma = 126$
Recalculation of data from Berner (1989) [a]					
Deltaic sediments	70 (44)	0	0	0	70
Shelves and upper slopes	0	68 (42)			68
Biogenous sediments (high-productivity zones)	0	0	7 (4)	3 (2)	10
Shallow-water carbonates	0	6 (4)	0	0	6
Pelagic sediments (low-productivity zones)	0	0	0	5 (3)	5
Anoxic basins (e.g. Black Sea)	0	1 (0.5)	0	0	1 $\Sigma = 160$

Units are 10^{12} g C yr^{-1} (parenthetical units = % of total burial).

[a] Deltaic-shelf sediments were reapportioned assuming that 33% of the sediment discharge from rivers is deposited either along non-deltaic shelves or upper slopes, and assuming that those deposits have total loadings of 1.5% organic carbon rather than 0.7% as in deltaic regions. Estimates for all other regions remain the same.

enous-deltaic'' regions near river mouths (Table 2). This flux was calculated by multiplying the global rate of sediment discharge from rivers by the average carbon content of deltaic sediments, which were assumed to collect the entire input of clastic material. Biogenous sediments accumulating below highly productive coastal and open ocean zones as well as shallow-water carbonates, account for an additional 8% and 5% of OC burial, respectively. Only 4% of global OC burial occurs beneath low-productivity pelagic zones, and less than 1% of carbon preservation is accounted for by basins with anoxic bottom waters (Table 2). Berner calculated that 94% of total organic matter is preserved along continental margins and only 6% seaward of continental rises. Due to the assumption of 100% efficient removal of riverine particles by deltas, no direct account is taken of preservation of organic carbon in clastic sediments in other continental shelf or slope regions.

Different sedimentary OC burial rates have been directly calculated (Gershanovich et al., 1974) by multiplying the average carbon content of Holocene deposits by their areal size and thickness (Table 2). Gershanovich et al. also found very little preservation in open ocean sediments, but calculated that nearly 90% of all OC is preserved in continental slope and rise sediments, rather than in deltas. They obtained a total burial rate $(0.22 \times 10^{15}$ g C yr$^{-1})$ that is almost twice Berner's estimate (Table 2, Fig. 1). The difference is due in part to Berner's assumption that riverine lithogenic materials are not deposited outside deltas. The estimate of burial rate changes dramatically depending on where sedimentation occurs because slope and non-deltaic shelf deposits typically contain 2–3 times more OC than deltas (Gershanovich et al., 1974; Premuzic et al., 1982). Therefore, apportioning more lithogenic sediment to deeper coastal sites substantially increases the estimate of total OC burial. Independent sediment budgets indicate that ~ 5% of fluvial particu-
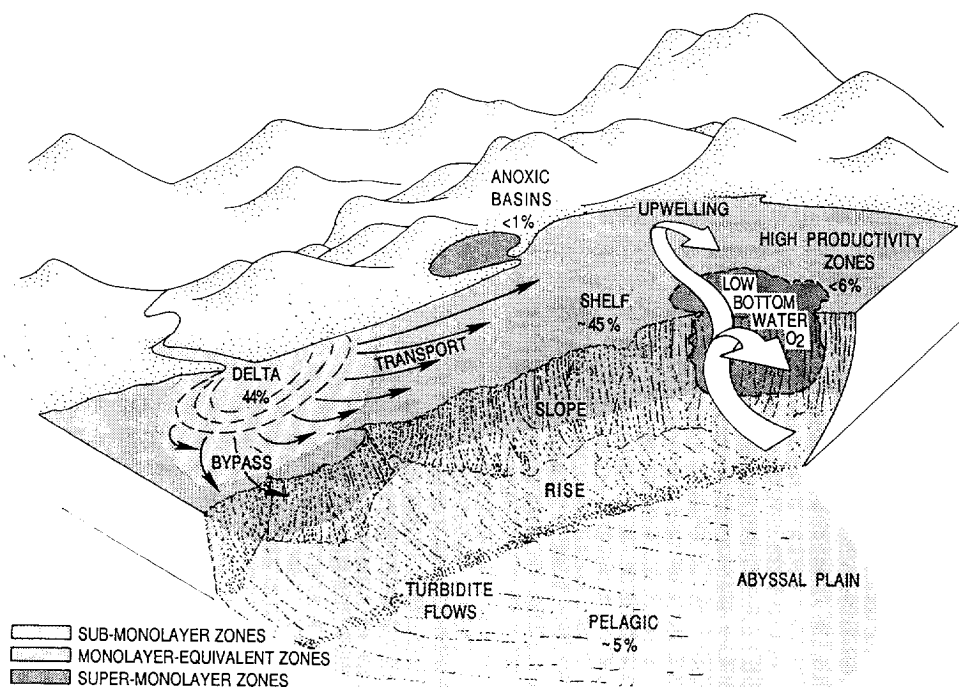

Fig. 1. Idealized diagram depicting current estimates of the percentage of total organic matter burial occurring within various marine sediment types (see Table 2). Light sections represent sediments which contain organic loadings lowe yr than a monolayer equivalent. Stippled sediments contain monolayer-equivalent loadings, and dark sediments contain loadings that are more than monolayer-equivalent.

late matter directly by-passes deltaic-shelf systems, and an additional 15–50% of the sediment initially deposited in deltas is resuspended and redeposited along shelves and slopes (Doyle and Pilkey, 1979; Einsele, 1992). A conservative estimate that 33% of the riverine suspended load is deposited outside of deltas, with twice the average OC content of deltaic sediments, would produce a global sedimentary burial rate of 0.16×10^{15} g C yr^{-1}, which is almost equally distributed between shelves and upper slopes (Fig. 1, Table 2). Although all such estimates are presently crude, organic matter preservation in offshore continental margin regions is more extensive than often assumed.

Even given higher burial estimates, less than 10% of the organic matter reaching the ocean floor, and less than 0.5% of global productivity, is ultimately preserved in marine sediments. The small remnant of organic matter that survives degradation to be preserved in marine sediments must be highly unusual, either in its structure or circumstances of deposition. The processes that allow preservation of this small residue, however, must occur along all continental margins.

2.2. The oxygen cycle

Preservation of sedimentary OC allows a comparable amount of photosynthetically-produced oxygen to escape respiration and accumulate in the atmosphere. This resulting net influx of O_2 must be balanced by a closely matched removal process. Assuming roughly a 1:1 OC to O_2 stoichiometry, the present day burial flux of OC ($\sim 0.15 \times 10^{15}$ g C yr^{-1}) can renew the atmospheric O_2 pool ($\sim 40 \times 10^{18}$ moles) in roughly three million years. This span corresponds to less than 1% of the time over which O_2-respiring organisms have lived in the ocean and raises the question of how the delicate balance of atmospheric oxygen concentration has been poised for such long periods between appreciably lower concentrations which would drive benthic marine organisms to extinction and higher levels that would support run-away forest fires (Berner, 1989). Sufficiently sensitive and responsive negative-feed-back mechanisms have been sought by many investigators (Walker, 1974; Holland, 1984; Berner, 1989; Berner and Canfield, 1989).

The main sink for O_2 generated by modern sediment burial is thought to be oxidation of kerogen and pyrite in shales during continental weathering (Berner, 1989). This model is supported by the comparable average organic contents of shales and modern ocean sediments (Hunt, 1979) and the need for long-term mass balance between continental denudation rates and sediment accumulation rates (Mackenzie and Garrels, 1966). However, being tectonically driven and operating in physically separate O_2 source (marine sediments) and sink (continental rocks) environments, this remote feedback-control mechanism would be relatively sluggish and insensitive. Additionally, there is no a priori reason why O_2 generation by organic matter and pyrite burial should necessarily balance subaerial kerogen weathering and pyrite oxidation, especially if burial of reducing power is controlled by some process (e.g. primary productivity) other than tectonic activity. These limitations would be exacerbated if kerogen weathering is essentially complete, and thus insensitive to atmospheric O_2 concentrations (Walker, 1974).

The most extraordinary aspect of feed-back control via subaerial kerogen weathering is that it requires extensive mineralization of one of the most recalcitrant organic materials on Earth. Kerogen precursors were presumably resistant to microbial degradation when first deposited. Being subsequently encased in rock, chemically defunctionalized and structurally rearranged during burial at high temperatures (Durand, 1980), these precursors should yield mature macromolecules of monumentally poor substrate quality. Although there is evidence from ^{14}C (Benoit et al., 1979) and molecular analyses (e.g. Barrick et al., 1980; Rowland and Maxwell, 1984) for fossil organic matter in marine sediments, most kerogen must be mineralized. Modern marine sediments otherwise would consist only of recycled kerogens devoid of functionalized biochemicals and ^{14}C, as opposed actually to being composed predominantly of the remains of contemporary marine organisms (Emerson et al., 1987; Hedges, 1992).

The central conundrum of the global carbon and oxygen cycles is that extremely recalcitrant organic substances such as kerogen, soil humus, and riverine organic matter are extensively oxidized back to CO_2 in relatively short time periods on land and in the ocean, whereas seemingly reactive remains of re-

cently living marine organisms are preserved in depositing marine sediments. By what process might fossil material exhibiting the reactivity of plastic encased in brick be extensively respired and how is such severe mineralization turned off at the ocean floor along continental margins? Moreover, how could a mechanism leading to this improbable situation be the basis for sensitive feed-back control between the global oxygen and carbon cycles, and hence the geochemical intercessor for multicellular life on Earth?

3. Patterns in organic matter mineralization and preservation

3.1. Degradation vs. preservation

As pointed out by Henrichs (1992, 1993) we have a wealth of environmental factors that appear to be related to organic matter preservation, and a dearth of mechanisms to directly explain their effects. In this section we will critically evaluate some of the patterns observed during organic matter degradation and preservation. Before proceeding, it is useful to

note that degradation of organic matter and its preservation in marine sediments are often treated equivalently, many times with the assumption that the selectivity and extents of early diagenesis will be informative of preservation potential. Degradation and preservation, however, are opposite processes and information on organic matter mineralization is not necessarily useful for understanding preservation. Given that the average extent of environmental mineralization of biosynthetic products is > 99.5%, using degradation rates of organic materials in marine water columns to explain corresponding sedimentary POC distributions is a profound extrapolation into a future setting where the substrates, agents, and mechanisms involved may be completely different.

The fundamental difference between degradation- and preservation-oriented studies is illustrated in Fig. 2 (Cowie et al., 1995). A model was used to simulate the changing state of a mixture of five initially equal organic components which undergo first-order mineralization with individual rate constants varying sequentially by factors of two. The relative scale of rates and duration of degradation have been arbitrarily chosen so that 1% of the total organic matter is preserved at the final time point. The dashed curve
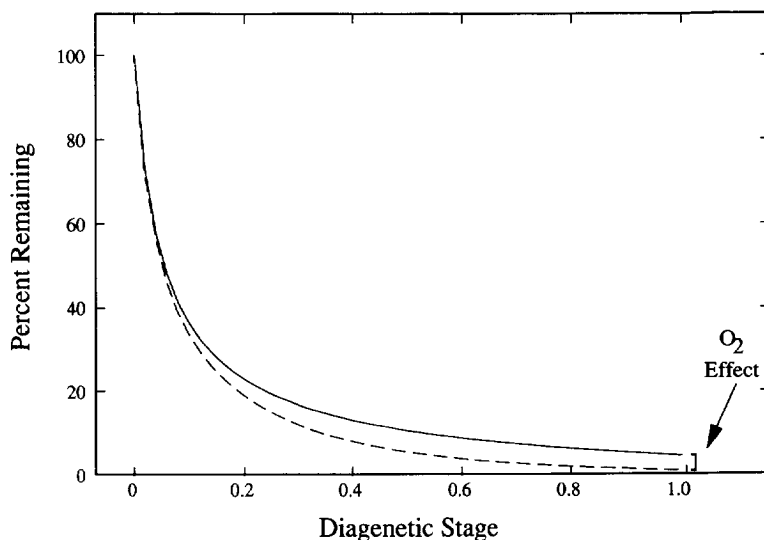

Fig. 2. Two hypothetical degradation curves for organic matter mixtures containing initially equal amounts of five different components which are mineralized with first-order rate constants that successively vary by factors of two. The only difference in the two curves is that the most stable component in Mixture A (solid line) reacts at half the rate as the most stable component in Mixture B (dashed line) (after Cowie et al., 1995).

shows the results of the model as described above, whereas the solid curve illustrates a second model run in which the mineralization rate constant for the least reactive component was decreased by an additional factor of two. The latter change makes almost no difference in the rate at which the first 50% of the total organic matter is mineralized. Halving the reactivity of the most stable component, however, substantially increases the amount of organic matter remaining at the end of the run from 1% to about 5%, a result that is not at all predicted by the early kinetics of reaction. In situations of extensive degradation, such as represented by most marine sediments, the key to characterizing and mechanistically understanding organic preservation is to focus on the types and amounts of materials that react most slowly or ultimately persist under local environmental conditions. This "slow" focus is challenging because the critical diagenetic reactions occur within the upper meter of bioturbated sediment where organic materials of widely contrasting reactivities are continually mixed, and where dynamic measurements are sensitive predominantly to the most reactive components with little or no preservation potential.

A suitable dynamic focus can be challenging in preservation studies because organic matter degrades over a range of time scales (Fig. 3) that covers ten orders of magnitude and spans from minutes for the breakdown of biochemicals in animal guts to 10^6 yr for OC mineralization in deep-sea sediments (Middelburg et al., 1993). Within this huge dynamic range the characteristic time scale of an experimental observation will narrowly predetermine the degradation rates that can be directly measured (Fig. 3). This is because organic materials degrading with half lives much shorter than the observation time span will be essentially gone before measurement progresses, whereas those with appreciably longer half lives will not measurably change in concentration. As a result, degradation rate constants measured among structurally diverse substrates will be similar for individual observations (e.g. Hamilton and Hedges, 1988), but will vary widely among studies characterized by different temporal scales. Due to the mathematical difficulty of extracting multiple components from a total organic carbon curve (e.g. Fig. 2) representing a large number of constituents with different reactivities (e.g. Van Liew, 1962), it is uncommon that more
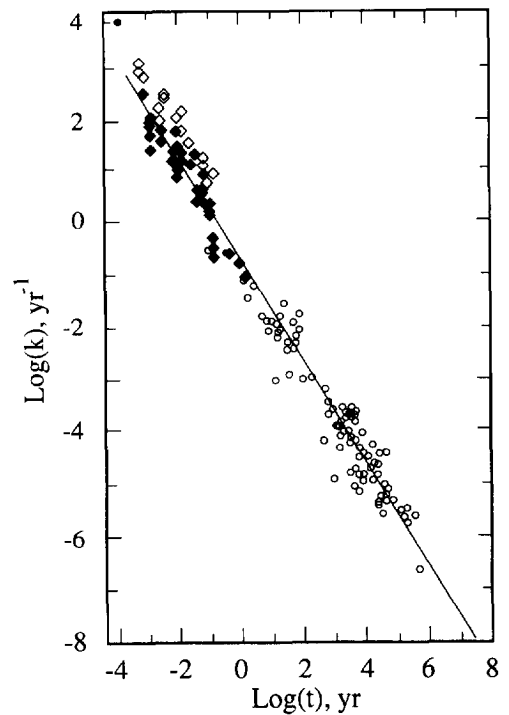

Fig. 3. Log/log plot of the measured reactivity (k) of organic carbon vs. the time interval (t) of experimental measurement. ◆ = data from laboratory studies; ◇ = data from water column measurements; ○ = data from sediment cores. The uppermost data point (●) is calculated for 75% assimilation of an algal diet by zooplankton with an average gut passage time of 1 h (Cowie and Hedges, in press) (after Middelburg et al., 1993).

than two or three dynamic classes are detected in individual studies of bulk organic matter degradation (e.g. Westrich and Berner, 1984; Goñi and Hedges, in press). The potential is great to select the wrong time scale for preservation studies, or to miss key slower reacting substrates within an experimental dynamic windows.

The extensive range of rate constants in Fig. 3 raises the more philosophical question of whether organic matter mineralization ever ceases in marine sediments. The very low weight percentages (0.1–0.2%; Premuzic et al., 1982), and almost complete lack of burial of OC in sediments underlying all but the most productive open ocean waters (Table 2, Fig. 1), clearly demonstrate the potential for essentially complete mineralization. However, OC is found at concentrations near 1 wt% in both ancient shales and

at depth in modern fine-grained continental margin sediments which represent shale precursors (Berner, 1982; Henrichs, 1993). Environmental factors apparently "turn off" mineralization at shallow sediment depths along continental margins, leading to wide-scale preservation which is unique to these environments. Though it is generally accepted that the early **rates** of organic matter degradation in marine environments are determined largely by the quality and concentrations of the available organic substrates (Westrich and Berner, 1984; Lee, 1992; Henrichs, 1992), the **ultimate extents** of preservation in the same sediments may involve very different organic matter types and processes.

3.2. Patterns in reaction and preservation

One of the most common approaches toward identifying mechanisms of sedimentary organic matter preservation has been to relate various aspects of organic matter degradation and burial to the physical or dynamic characteristics of depositional environments. While often striking, many of these empirical relationships have not been particularly useful for understanding preservation mechanisms. For example, the often cited correlation between local primary productivity and water column (or sedimentary) respiration rates is a predictable outcome of the fact that most organic matter is transferred in fast-sinking large particles that are rapidly and extensively mineralized. Direct correlations between OC rain rates to the ocean floor and associated benthic mineralization rates (Henrichs, 1992, 1993) can be similarly explained.

Sediment accumulation rate is one of the environmental variables most commonly inferred to have an effect on the reactivity and ultimate preservation of organic matter. This relationship might be expected because bacterial and animal activities are almost always highest near the sediment surface, where more potent electron acceptors also occur. Fast deposition more rapidly moves organic matter down through this diagenetically active zone, possibly with less total degradation. Rapid deposition also helps to "cap" accumulating sediments from input of dissolved oxidizing agents (O_2, NO_3^- and SO_4^{2-}) in the overlying seawater (Henrichs, 1992). The strong di-

rect correlation of average (or integrated) rates of in-situ sulfate reduction, O_2 consumption, or overall carbon oxidation (Goldhaber and Kaplan, 1975; Toth and Lerman, 1977; Berner, 1978; Canfield, 1993,1994) with average sediment accumulation rates has been viewed as a demonstration of greater preservation during faster burial, but may result largely from the ability to observe more rapid reactions only in cores representing short time intervals (Fig. 3). Finding other parameters that might relate the ultimate fate of sedimentary organic matter to accumulation rate, however, has been difficult. For example, the usually observed direct trend between the accumulation rates of OC and bulk sediment (e.g. Heath et al., 1977; Müller and Suess, 1979) is not independent because carbon burial is the product of %OC times the net sediment accumulation flux. Moreover, the observed spread in organic carbon burial fluxes is primarily driven by differences in sediment accumulation rates, which vary by factors of 10^4–10^5, vs. less than a 10^2 variation in %OC (Müller and Suess, 1979; Middelburg et al., 1993). Normalizing OC accumulation rates to local primary productivities (Calvert, 1987) before plotting the data vs. sediment accumulation rate does not remove the mathematical dependence of a common burial term.

Variations in %OC with sediment accumulation rate is another commonly investigated relationship with its own intrinsic limitations (Doyle and Garrels, 1985). A positive correlation in these two parameters was noted by Heath et al. (1977) for predominantly deep-water sites. Müller and Suess (1979) saw a similar pattern among a variety of sediments, mostly from open ocean and upwelling regions. As Müller and Suess (1979) acknowledged, patterns in %OC vs. sedimentation rate are subject to variations introduced by "dilution" of organic-rich debris from the upper water column with coarse minerals such as quartz sand. This effect can be seen readily in a plot (Fig. 4) which includes %OC and sediment accumulation rate data from a variety of coastal margin sediments as well as the data of Heath et al. (1977) and Müller and Suess (1979). The direct relationship over sediment burial rates of 0.1–10 mg cm^{-2} yr^{-1} described by the above authors is not universal. Carbon concentrations level off at accumulation rates near 10 mg cm^{-2} yr^{-1} and decrease for more rapidly depositing coastal marine and deltaic sedi-
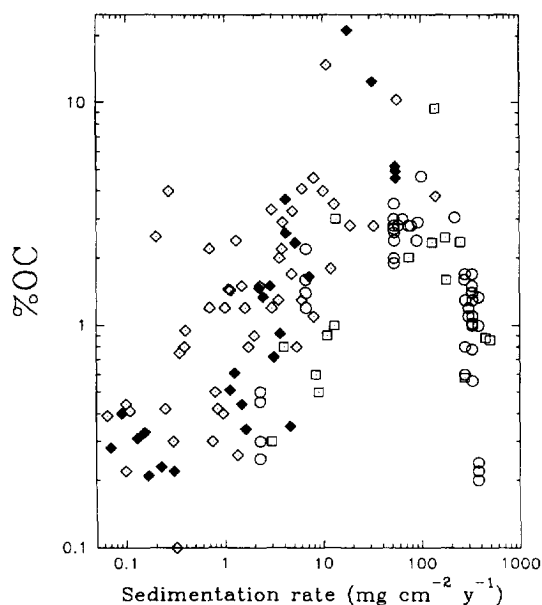
Fig. 4. Plot of weight percent of organic carbon (%OC) vs. accumulation rate for sediments from a variety of depositional environments. ♦ = data from Müller and Suess, 1979; ◇ = data compiled by Henrichs and Reeburgh, 1987; □ = data from Reimers et al. (various papers); ○ = data from the Washington Coast (Carpenter et al., 1981, 1982).

ments in which most organic matter is stored (Fig. 1). This tailing off of %OC at high deposition rates is especially pronounced in sandy deltaic sediments and is possible any time organic-poor mineral material is rapidly deposited (Doyle and Garrels, 1985). Other organic-poor diluents such as calcite or opal tests should have similar effects.

In an attempt to avoid dilution effects and mathematical interdependency, the recent trend has been toward using OC burial efficiency as a preservation indicator (Henrichs and Reeburgh, 1987; Betts and Holland, 1991; Cowie and Hedges, 1992). Organic burial efficiency is defined as the accumulation rate of organic matter below the diagenetically active surficial sediment divided by the organic flux to the sea floor. The organic input term can be (1) measured directly with deep sediment traps, (2) estimated from local primary production using an empirical function for the attenuation of POC flux down marine water columns (e.g. Suess, 1980), or (3) calculated from the sum of OC that is mineralized above and preserved below a specified sediment

horizon (Canfield, 1993). Such burial efficiencies generally range from less than 1% for slowly accumulating open ocean sediments ($10^{-4}-10^{-3}$ cm yr^{-1}) to almost 80% for some shallow-water depositional hot spots, and correlate directly with sediment accumulation rate (Fig. 5). This relationship typically is linear up to sedimentation rates of ~ 15 mg cm^{-2} yr^{-1} (~ 0.06 cm yr^{-1}; Betts and Holland, 1991) beyond which burial efficiencies begin to approach the 100% ceiling and level off (Fig. 5).

While directly applicable to the issue of organic matter preservation, burial efficiencies are mechanistically meaningful only if the preserved organic material is deposited fresh for the first time. Exclusive deposition of fresh plankton remains, however, is unlikely within continental margins where almost all organic matter burial occurs. Recycled organic materials will be, on average, more refractory than recently biosynthesized matter raining directly out of the water column and thus will increase net burial efficiencies (Hedges et al., 1988). Coastal sediments in particular can include an appreciable fraction of riverine POM, most of which already has been extensively degraded on land (Hedges et al., 1994) and **should** be relatively resistant to further mineralization at sea. In addition, resuspended sediments are common in most coastal zones (e.g. Sternberg, 1986;
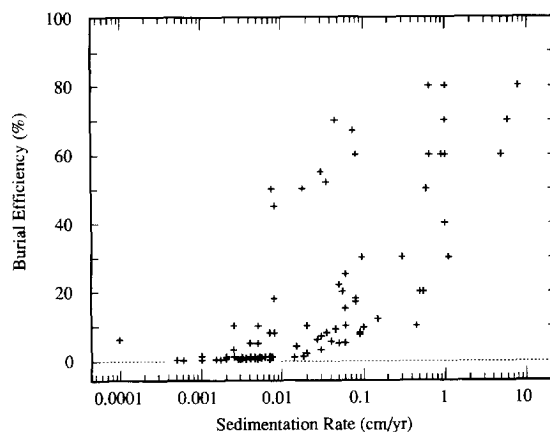

Fig. 5. Plot of percent burial efficiency of sedimentary organic carbon vs. sediment accumulation rate at different sites. Burial efficiency is defined as the organic carbon accumulation rate below the diagenetically active surface layer divided by the input rate to the sediment/water interface (data compiled from Henrichs, 1992, 1993).

Nittrouer and Demaster, 1987) and will include a large component of relatively old, reworked plankton remains with a substantially elevated preservation potential. One example of such a situation is the demonstration by Martens et al. (1992) that sediments from Cape Lookout Bight, a coastal depocenter with a sediment accumulation rate of about 10 cm yr^{-1} and a calculated burial efficiency near 80% (highest point in Fig. 5), contain a large fraction of old organic matter (500–1500 yr) that has experienced numerous deposition/resuspension cycles. A similar situation is described by Anderson et al. (1994) for the upper slope ($\sim$ 1000 m) of the Middle Atlantic Bight, indicating that redeposition is by no means confined to the inner continental margin.

A common stumbling block in using either %OC or burial efficiency as a guideline for evaluating the effects of sediment accumulation rates on preservation is that neither of these carbon-based parameters dependably reflects the source or diagenetic state ("freshness") of sedimentary organic mixtures. If preservation is controlled simply by transit time through biologically active surface sediments, then less concentrated sedimentary organic materials should be generally more degraded. There are numerous examples, however, from sediments such as those from Cape Lookout Bight of highly concentrated organic materials that are nevertheless extensively altered. To better understand the mechanisms controlling OC preservation, compositional parameters are required which reflect the degradative histories of sedimentary organic mixtures. Such indices do exist and include diagenetically decreasing fractions of total sedimentary OC and N that are comprised by biochemicals such as amino acids and carbohydrates (Cowie and Hedges, 1994, and references therein). These biochemical-based parameters, however, directly represent the diagenetic fate of only a fraction of the total sedimentary organic matter. The origins and structural features of the uncharacterized organic fraction, which is diagenetically concentrated and comprises the bulk of preserved OC, remain largely unknown.

Dissolved oxygen concentrations in ocean bottom water have long been considered by petroleum geochemists to have a critical effect on the %OC of underlying marine sediments, and hence on their

eventual source rock potential (e.g. Demaison and Moore, 1980). Organic-rich euxinic sediments, such as those accumulating beneath anoxic bottom waters of the Black Sea and Saanich Inlet, are often considered to be modern counterparts of petroleum source rocks (Tissot and Welte, 1978). Similar conclusions have been drawn for organic-rich deposits such as off Peru that form along continental margins near the depth interval where the dissolved oxygen minimum zone (typically 500–1200 m water depth) contacts the ocean floor (e.g. Richards and Redfield, 1954; Paropkari et al., 1992). Reasons given to explain the perceived pattern of increased organic matter preservation in less oxygenated sediments include (1) lower free energy yields from suboxic respiration, (2) the need to establish complex microbial consortia to stepwise degrade organic substrates, (3) the buildup of toxic waste products such as H_2S, (4) reduced sediment mixing, irrigation, and bacteria cropping by benthic animals, and (5) the presence of highly insoluble, oxygen-poor substrates which resist fermentative breakdown, but are aerobically degraded via O_2-requiring oxidative enzymes (see reviews by Emerson and Hedges, 1988; Henrichs, 1992; Lee, 1992; Aller, 1994; Aller et al., in press). Given all the variables involved, including extremely complex microbial interactions in anaerobic sediments, it has been difficult to conclusively delineate any O_2 concentration effects in modern sedimentary systems. Indeed, whether O_2 availability has any direct consequence on organic matter preservation has been an extremely controversial issue (Calvert and Pedersen, 1992; and subsequent volleys).

Arguments against an O_2 effect typically draw on both dynamic and concentration-based evidence. Dynamic evidence comes mainly from laboratory and field studies of the relative mineralization rates of bulk organic matter, or specific biochemical components, under oxic vs. anoxic conditions. Comparative studies involving relatively labile substrates such as dissolved sugars and amino acids (e.g. Lee, 1992; fresh phytoplankton (Foree and McCarty, 1970; Otsuki and Hanya, 1972a,b; Jewell and McCarty, 1971; Hansen and Blackburn, 1991) and organic material in sediments rapidly depositing in adjacent areas with oxic and anoxic bottom waters (Zsolnay, 1971; Cowie and Hedges, 1991, 1992) typically indicate little or no effect of O_2 availability on degradation
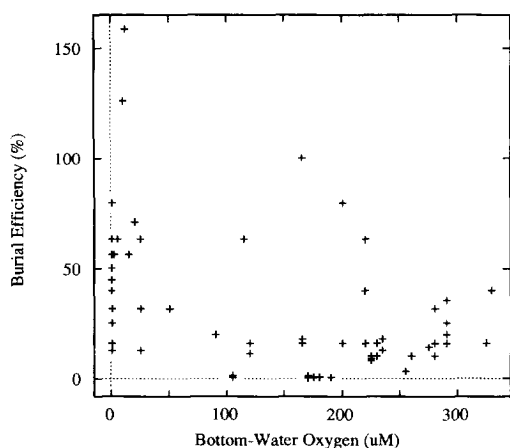
Fig. 6. Plot of percent burial efficiency vs. the corresponding bottom water oxygen concentration at different depositional sites (after Betts and Holland, 1991).

rates. The major exceptions usually are for oxygen-poor, hydrolysis-resistant material such as lignin (Benner et al., 1984; Kirk, 1984), lipids (DeLaune et al., 1980; Harvey et al., 1986) and photosynthetic pigments (Sun et al., 1993a,b). The second common line of negative evidence is the lack of a universal relationship between bottom water O_2 concentrations and sedimentary OC concentrations (Pedersen et al., 1992; Calvert and Pedersen, 1992), or burial efficiencies in modern marine sediments (Henrichs and Reeburgh, 1987; Betts and Holland, 1991). The presented field data (Fig. 6), which often include a disproportionately large fraction of OC-rich sediments from anoxic or highly productive regions, give little evidence to support the notion of a relationship between bottom water oxygen concentration and organic matter preservation. Thus, although oxygen effects have been clearly demonstrated even on short time scales (e.g. Benner et al., 1984), many exceptions exist and universal patterns are elusive.

While informative, both of these general experimental approaches have limitations. For rate-based inferences, it is highly unlikely that the degradative processes involved during rapid early organic matter turnover in the water column or laboratory are functionally equivalent to those which control long term preservation in most sediments (previous discussion; Fig. 2). All of the previously mentioned laboratory studies of the effect of oxicity on algal degradation

involved kinetic comparisons over time scales of months and ended with at least 25% of the starting material remaining (e.g. Otsuki and Hanya, 1972a,b). These simulations drew up early and far short of the degradation histories of most sedimentary organic components.

Secondly, although bottom water oxygen concentration will establish the potential for gradient-driven O_2 diffusion into surface sediments, it is only a **remote** indicator of the **potential** for oxic degradation. The actual depth limit of O_2 penetration into sediments, and hence the duration of exposure of sedimentary organic matter to O_2, is the outcome of complex interactions among a suite of variables. These additional factors include local primary productivity, organic matter composition and input to the sea floor, sediment accumulation and bioturbation rates, irrigation, and, critically, the reaction rates of the various sedimentary organic materials under both oxic and anoxic conditions (Emerson, 1985; Emerson et al., 1985). Bottom water O_2 measurements fail to represent the complex interplay of these many variables.

Other circumstances also limit the application of bottom water O_2 as a diagenetic parameter. For example, particulate organic matter fueling sedimentary respiration typically accumulates below the diffusive sublayer (~ 0.5 mm) of the sediment surface, which can have chemical properties decidedly different than the overlying bottom waters where O_2 is usually measured (Archer et al., 1989). In addition, sediments depositing at sites with active benthic communities also are subject to strong chemical gradients across the sediment surface and repeated fluctuations between oxic and anoxic conditions (Aller, 1982, 1994), which are not reflected by bottom water O_2 concentrations alone. For these reasons the potential for an oxygen effect can be more directly and meaningfully assessed from the time period that sedimentary organic matter is exposed to oxic conditions. This O_2 exposure period can be roughly estimated by dividing the mean depth of O_2 penetration into the surface sediment by the average sediment accumulation rate, and may be more closely constrained by taking bioturbation into effect.

Given that organic matter is preserved predominantly in sediments accumulating on continental shelves and slopes at rates of 0.05–10 cm yr^{-1} (Fig.

1; and see Henrichs, 1992), and that most %OC gradients occur within the upper meter of sediment, the organic materials preserved in these deposits must have half lives on the order of 10–2000 yr or longer. Practical laboratory simulations of such slow natural degradation processes are difficult. Although more realistic, field studies usually are mechanistically ambiguous, dependent upon steady state assumptions, and not defined by parameters which measure diagenetic history. We are caught experimentally between the rock of insufficiently long natural observation periods to define preservation processes, and the hard place of a high probability that confusing variations will occur in source and environmental conditions during the substantial times over which sedimentary records are established. Regardless, it is evident that conditions of essentially zero organic preservation prevail throughout the open ocean (Fig. 1), landward of which some protective process must widely occur.

4. Speculative scenarios for organic matter preservation

4.1. Introduction

Degradation and preservation constitute the white and black of an intricate environmental inkblot within which each of us finds patterns that match our experiences and expectations. The rest of this article presents our current impression of mechanisms affecting organic matter preservation in marine sediments. The central premise of this model is that most organic matter preserved in marine sediments is adsorbed to mineral surfaces in protected coatings which are susceptible to appreciable degradation only under oxic to suboxic conditions. This notion is supported by a variety of evidence from many researchers and has implications for such diverse issues as microbial degradation mechanisms, organic matter distributions and dynamics, as well as control mechanisms for atmospheric CO_2 and O_2. We will first describe evidence for widespread sorptive preservation of sedimentary organic material along continental shelves and upper slopes, and then describe a specific example of slow oxic degradation that appears to produce a "redoxcline" on the lower

continental slope, below which little organic matter is buried. Possible tests of these hypotheses are then presented.

4.2. Sorptive preservation

Organic matter is usually concentrated in fine-grained sediments depositing along continental margins (Bordovskiy, 1965; Premuzic et al., 1982; Ergin et al., 1993). This phenomenon has often been attributed either to limited electron acceptor availability in less diffusive, finer-grained deposits, or to similar hydrodynamic sorting of physically separate fine minerals and low-density organic particles (e.g. Tyson, 1987). An alternate hypothesis, sorption of organic matter to mineral surfaces and its subsequent concentration in fine-grained sediments with large surface areas, has been occasionally presented since the mid-1960s (Weiler and Mills, 1965; Tanoue and Handa, 1979). In a study of shallow-water calcitic sediments, Suess (1973) demonstrated a direct correlation between the mineral surface area and the organic content of marine sedimentary particles, a relationship which is indicative of organic matter sorption. The observed loading of organic carbon per unit of surface area was comparable to the value reported by Arnold and Pak (1962) for single layers of protein associated with interfaces in aqueous systems. Suess also demonstrated that the measured surface areas of his calcite-rich sediments were an order of magnitude higher than would be calculated for smooth particles of similar size, indicating highly irregular particle surfaces.

Over the last decade, Mayer has greatly extended these earlier studies and given strong evidence that organic matter in most coastal marine sediments is sorbed to mineral surfaces. Covariation of %OC and sediment surface area within the "monolayer equivalent" range of 0.5–1.0 mg OC m^{-2} (e.g. Fig. 7) has now been found for diagenetically stabilized surface sediments from a variety of continental margin environments including intertidal zones (Mayer et al., 1985), estuaries, and continental shelves (Mayer et al., 1988; Mayer, 1994a) and slopes (Mayer, 1994b; Keil et al., 1994a). The observation that higher organic loadings in non-deltaic surficial marine sediments are reduced to a monolayer equivalent at depth suggests intrinsically reactive organic matter is
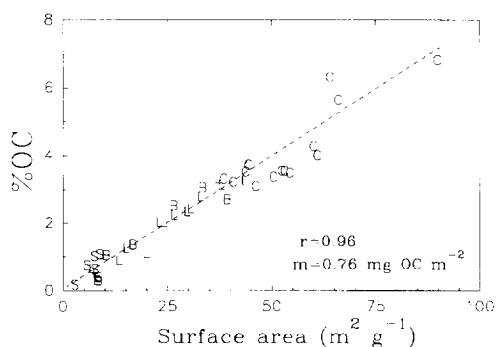
Fig. 7. Weight percent of organic carbon plotted vs. mineral surface area for bulk material (B) as well as sand- (S), silt- (L), and clay-sized (C) fractions from samples of suspended sediments in the Columbia River estuary and surface (0–5 cm) sediments from four sites along the adjacent continental shelf and slope off Washington state. This plot shows data for sediments from which discrete particles of organic matter have been removed by heavy liquid flotation. Corrections of total surface areas for a small measured component of interbasal surfaces in expandable clay minerals have also been applied (data from Keil et al., 1994a).

stabilized in association with mineral grain surfaces (Mayer, 1994a). These studies also indicate that sediment particle surfaces are highly irregular and appear to have a major portion of their total accessible areas in mesopores less than 10 nm in width (Mayer, 1994a). Exceptions to the general pattern of monolayer-equivalent loadings include lower organic concentrations in red clay regions of the open ocean and in many river deltas, and greater-than-monolayer loadings under highly productive coastal regions such as off Peru (Mayer, 1994a,b).

Our recent studies of organic and inorganic matter distributions in modern surface sediments from the Washington continental shelf and slope (Keil et al., 1994a–c) strongly support Mayer's conclusions. The Washington coast study complements Mayer's previous work in that multiple size fractions were analyzed from different sediments deposited under well-defined but contrasting conditions within the influence of a single river. Nine clay- to sand-size fractions were separated by hydrodynamic sorting and wet sieving, and the surface area, mineralogy, and elemental compositions of the inorganic materials in each fraction were determined. Sorbed organic matter and discrete organic debris (where separable in appreciable amounts) were also quantified and

analyzed for their elemental, stable carbon isotope, and major biochemical compositions.

The distributions of organic matter in the studied Washington sediments closely resemble those described by Mayer (1994a) for bulk coastal deposits from other sites (Fig. 7). Discrete organic debris accounts for < 10% of the total organic carbon in the bulk Washington sediments and most of their size fractions (Keil et al., 1994a). The major exceptions are whole diatoms in suspended particulate material from the extensively impounded lower Columbia River and woody plant debris in the two continental shelf samples. After these sand- and silt-sized particles are removed by heavy-liquid flotation, and the measured surface areas are corrected for small contributions from interbasal faces of expandable clays, the data give an excellent fit ($r = 0.96$) to a straight line with a slope of 0.76 mg OC m^{-2} (Fig. 7). This relationship holds well even though the mineralogy of the predominant particle types (e.g. smectite, chlorite, opal, and quartz) changes several times over the size spectrum, and corresponding surface areas vary by more than an order of magnitude (Keil et al., 1994a). It is unlikely that physically separate organic and mineral particles would be so proportionately distributed over such a broad textural range within contrasting depositional settings. The close agreement of sediment subsamples and the range (0.5–1.0 mg OC m^{-2}) reported by Mayer (1994a,b) for bulk coastal sediments indicates that mineral particles of all sizes carry monolayer-equivalent organic coatings. The depositional environments which have been studied to date contrast sharply in local primary production, bottom water oxygen concentration, sediment accumulation rate, water depth, and proximity to the riverine sources (Keil et al., 1994a; Mayer, 1994a,b). Surface area therefore appears to be the most important factor influencing the organic matter content of marine sediments accumulating along continental shelves and slopes.

The inference that almost all marine sedimentary organic matter is sorbed to mineral surfaces, often in monolayer-equivalent coatings, has a number of implications. One of the most fundamental is that the sorbed organic molecules were at one time dissolved. Organic particles would not spread so uniformly or thinly over the surfaces of all sedimentary minerals

(e.g. Fig. 7). Second, because most fresh organic matter is particulate, appreciable degradation likely was necessary to solubilize this material prior to sorption. Extensive and rapid dissolution of fresh organic remains also is indicated by the observation that < 10% of the total organic matter in marine sediments studied to date is present as discrete particles (Keil et al., 1994a,c). Finally, at least a portion of the sorbed organic matter appears to be reversibly bound. This is because most minerals in soils (Mayer, 1994b) and river suspensions (Keil et al., 1994a, submitted) also carry monolayer-equivalent organic coatings which, if retained after discharge, would form coastal marine sediments containing similar loadings of almost exclusively terrigenous organic matter. The commonly observed patterns of sub-monolayer organic loadings in deltaic sediments (Mayer, 1994a; Keil et al., submitted) and pronounced offshore decreases in the fraction of terrestrial organic material within the monolayer coatings of clastic sediments (Keil et al., 1994a), indicate extensive exchange of molecules both off and onto mineral surfaces. Similarly active partitioning of organic molecules between dissolved and particulate phases has been observed in laboratory experiments (Henrichs and Sugai, 1993; Wang and Lee, 1993).

Such active exchange is particularly evident for clastic minerals in surface sediment from the Amazon shelf (Keil et al., submitted). These deltaic deposits contain approximately a third of the mono-layer-equivalent organic loadings that the component particles carried when discharged by the Amazon. In addition, an average of a quarter of the remaining total organic carbon is marine in origin. The mechanisms by which approximately 2/3rds of the initial terrigenous organic matter on these particles has been removed is presently unclear, but could include both desorption by seawater and direct oxidation on the mineral surface (later discussion). Such mechanisms, if they result in eventual mineralization of the displaced molecules, could help explain the typically steep decreases in terrigenous organic materials seaward of river mouths (e.g. Hedges and Parker, 1976; Showers and Angle, 1986), as well as the remarkably low average preservation efficiency (< 30%) of riverine POC in the ocean (Hedges, 1992). Clearly, the organic loadings of deltaic sediments can be much lower than those of both their river sources

and the open continental margin sediments which they eventually form by resuspension and offshore transport.

Reversible partitioning of organic molecules between particle surfaces and ambient waters is a potentially important process because it would link sedimentary POM, DOM and minerals into an intimate network of interactions. Porewater DOM may thus act as a buffer through which a portion of dissolved organic molecules released by degrading labile particles could pass onto mineral surfaces, either replacing or displacing molecules at that interface. Because it is rapid (Wang and Lee, 1993), sorptive uptake could compete with microbial degradation for extremely labile organic molecules. If, however, porewater DOM concentrations drop, due to flushing, diffusive losses to bottom water, or mineralization in excess of labile particle dissolution, then reversibly sorbed molecules should partition back from mineral surfaces into the dissolved phase. Given typical values for surface coastal sediments of 90% porosity, 5 mg l^{-1} DOC (Martin and McCorkle, 1993), and 1 wt% POC; over 99% of the total sedimentary organic carbon is sorbed to particles. The potential of this large reservoir of surface-bound material to buffer two orders-of-magnitude less porewater DOM is immense, even if only a fraction of the organic matter is reversibly sorbed. Another implication of this interactive coupling is that DOC and POC concentrations within a sediment should be directly related, although not necessarily in a simple manner since a range of organic molecules with contrasting partitioning constants would be involved. Nevertheless, the concentrations and compositions of porewater DOM may provide a sensitive indicator of the quantity and diagenetic state of the entire sedimentary mixture. Active exchange of organic molecules between porewaters and mineral surfaces would be particularly significant for preservation if the reactivities of the same molecules in the two different phases were appreciably different.

Laboratory experiments with sediments from the Washington continental slope (Keil et al., 1994c) support previous field evidence that organic sorption to mineral surfaces is at least partially reversible and strongly protective of potentially labile organic substances. The studied sediments were from various horizons (average ages ~ 10–500 yr) within a core
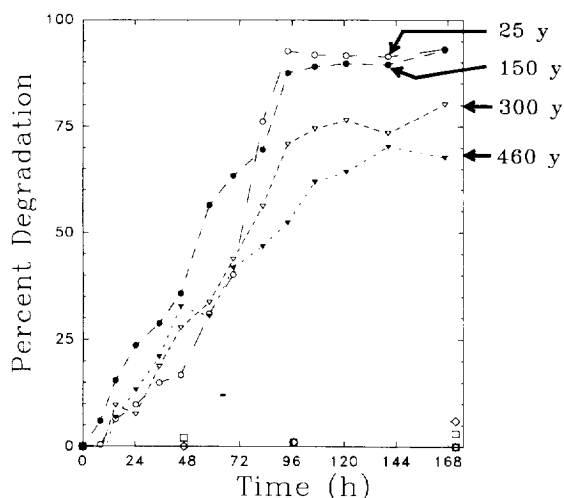
Fig. 8. Results of experiments in which organic matter was desorbed from mineral matrices and degraded (as dissolved organic matter) by aerobic heterotrophic bacteria. A 36 cm long sediment core was collected at a water depth of 647 m off the Washington Coast. At selected intervals corresponding to ^{210}Pb-estimated ages of 25, 150, 300 and 460 yr (uncertainty of about ± 50 yr), organic matter was desorbed from the sediment matrix. Overall, approximately 35% of the total organic matter was desorbed at each interval. The desorbed organic matter was diluted to ~ 6 mg OC 1^{-1} and incubated in the presence of heterotrophic bacteria collected from the overlying water. Percent degradation of the desorbed organic matter was determined from the change in DOC measured with a Shimadzu TOC-5000 carbon analyzer (Keil et al., 1994c). 48, 96 and 168 points at bottom represent controls.

and exhibited a nearly constant %OC/surface area relationship within the monolayer-equivalent range. Repeated sequential partitioning of four selected sediments with UV-oxidized seawater, 2 N KCl and distilled water solutions (5 × each) dissolved a total of 20–50% of the initial OC in these samples, indicating that at least these fractions of the total POM are reversibly sorbed. When the desorbed organic materials were inoculated with aerobic water column bacteria, 75–95% of the dissolved OC was utilized within five days (Fig. 8), during which time bacteria were observed to grow with efficiencies of 10–30% (Keil et al., 1994c). Fractions of reversibly-bound and microbially-reactive organic matter generally decreased with burial depth. Intrinsically labile organic matter in this deposit was clearly protected within the sedimentary milieu, likely as a result of sorption (Mayer, 1994a). The finding

that reactive organic matter can be preserved via sorption within sedimentary regimes suggests that in addition to organic matter "quality," sediment surface area can be a primary determinant for preservation. This is a major deviation from conventional types of Multi-G models (e.g. Westrich and Berner, 1984) in which organic reaction rates are assumed to be structurally determined. Because most sediment surface area is delivered via rivers to coastal regimes, sorptive stabilization helps explain why a higher percentage of primary productivity is preserved along coastal regions than in the open ocean (Table 2).

While these data strongly suggest that sorption of organic matter to mineral surfaces determines organic matter loadings within continental shelf sediments, a direct cause for the stability of monolayer-equivalent amounts of the organic molecules in these coatings has not been established. Mayer (1994a,b) suggested that stability may result from localization of sorbed organic matter in small mesopores < 10 nm in length. As mesopores are the dominant microtopographic feature in marine sediments, and most enzymes are incapable of entering or operating within such a confined space, exclusion of enzymes from mesopores may prevent the degradation of sorbed organic matter. Another hypothesis is that the activity of enzymes is sterically limited by close association of substrate molecules to mineral surfaces via chemisorptive bonds, which can have strengths approaching that of covalent linkages (Clark, 1974). Similar to the mesopore hypothesis, enzymes may be sterically hindered from liberating molecules from a surface. In addition, the high concentrations of organic molecules sorbed at mineral surfaces should strongly favor condensation reactions, which would lead to larger and more refractory macromolecules (Theng, 1979; Hedges, 1988).

Despite uncertainty in the actual preservative mechanism, the strong correlation between organic matter preservation and mineral surface area may provide a useful reference point for evaluating the state of degradation of the organic component. For example, sedimentary organic matter occurring at more than a monolayer equivalent should be relatively fresh, whereas materials in sub-monolayer coatings should be unusually degraded. Porewater DOC concentrations should vary in parallel with these different particle loadings as organic molecules

actively partition between mineral surfaces and ambient water. These hypothetical relationships could be systematically tested using coupled DOC/surface loading measurements in conjunction with a variety of available biochemical-based indicators of organic freshness (Cowie and Hedges, 1994).

Protective organic sorption is consistent with many of the previously discussed patterns seen in organic matter distribution along coastal zones. For example, the low OC contents of coarse sediments likely result more from the low surface/mass ratio of the component particles than from diffusive "openness." In addition, an intimate association of organic matter with mineral surfaces will lead to a tight correlation between the rates of OC burial and sediment accumulation in texturally similar deposits, as well as to the observed reversal in trends of %OC vs. accumulation rate (Fig. 4) for sandy sediments (Aller and Mackin, 1984). The tendency for organic-rich sediments to accumulate in the proximity of oxygen-deficient bottom waters along continental slopes may also be partially explained on a textural basis. Easily transported clay-size particles often undergo repeated deposition/resuspension cycles in coastal zones until they reach deeper quiescent bottom waters, typically on the continental slope, beneath which they will deposit and efficiently bury their adsorbed organic load. These same waters will tend to be oxygen poor because they also receive minimal advective input of dissolved O_2. The resulting inverse O_2/%OC relationship may thus be traceable to largely independent processes. The lack of a direct mechanistic coupling between bottom water O_2 and sedimentary %OC along upper continental margins would help explain why these two variables do not exhibit a universal relationship (Fig. 6), and why in many coastal zones textural patterns resulting from sorting better explain sedimentary OC distributions than bottom water O_2 concentration (Premuzic et al., 1982; Calvert and Pedersen, 1992; Pedersen et al., 1992).

4.3. Oxic / suboxic degradation

Deep-sea sediments demonstrate that some degradative mechanism must consistently overpower surface area protection to produce the extremely organic-poor red clays and biogenous oozes covering abyssal plains. These open ocean sediments have
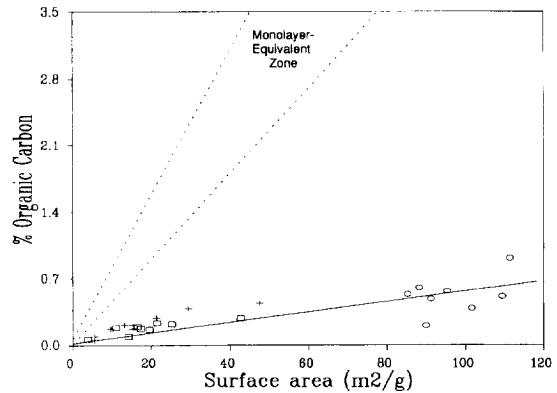

Fig. 9. Weight percentages of organic carbon plotted vs. mineral surface area for hydrodynamically-separated size fractions from surface sediments collected at 140° W and 9° (O), 5° (+), and 0° (□) N in the Equatorial Pacific (Keil, unpubl. data). For comparison, the range of monolayer-equivalent organic loadings exhibited by non-deltaic continental margin sediments is indicated by dashed lines.

surface areas in the range of 20–90 m² g⁻¹ (Weiler and Mills, 1965). At monolayer-equivalent loadings, such surface areas should correspond to %OC values in the range of 2–6 wt%. The actual organic carbon contents of most abyssal deposits are < 10% of these values (Premuzic et al., 1982). Measurements for hydrodynamically-separated fractions of clay- and carbonate-rich sediments from the Equatorial Pacific (Fig. 9) demonstrate that these extremely low organic concentrations occur across the entire textural spectrum and that the residual organic matter still exhibits a linear %OC/surface area relationship indicative of sorption. Despite low rates of organic matter delivery to deep sea sediments, inputs still exceed the amount necessary to attain monolayer loadings by 10–100 times and thus factors other than supply must be responsible for the organic deficit. The reasons offered for low OC concentrations in open ocean sediments are opposite to, but as varied as, those given for carbon preservation in continental margin deposits. Although diffusive losses of porewater DOC, deep-water columns, low sediment accumulation rates, and aeolian input of organic-poor particles from arid continental regions (Heath et al., 1977) may all contribute toward essentially no OC burial, the most direct explanation is long term exposure to oxygen and other electron acceptors (or

catalysts) such as Mn^{4+} and Fe^{3+}. For simplicity, we will generally refer to these various phenomena as an "oxygen effect," later expanding on the topic of alternate oxidizing agents and catalysts.

"Oxidation fronts" in deep-sea turbidites provide the most clear-cut evidence to date for a pronounced oxygen effect and have now been observed in deposits from a variety of settings and ages (Wilson et al., 1985; Weaver and Thomson, 1987). Formation of oxidation fronts begins with slumping of sediments from a topographic high to form a turbidity current that then flows down onto an abyssal plain. If the source of the slump is a continental slope, the particulate material forming the turbidity flow is usually fine-grained and organic-rich. Transport of such material to a distant deep-sea site typically results in a homogeneous deposit, sometimes in excess of a meter thick (Weaver and Rothwell, 1987). Once redeposited on an abyssal plain, the organic-rich material at the top of the turbidite is exposed to high concentrations of bottom water O_2 and low sedimentation rates. Under these conditions molecular O_2 diffuses into the top of the turbidite and reacts with

the organic and reduced mineral constituents at sharply defined redox fronts.

While O_2 is the primary oxidizing agent in such turbidites, redox-active metals such as iron and manganese may serve as intermediate electron carriers, much as they do in living organisms. This reaction system is largely diffusion controlled, as evidenced in active deposits by the linear gradient of porewater O_2 between the benthic boundary layer and the visually evident redox front (Thomson et al., 1987; Wallace et al., 1988). In active systems, distinct layers enriched in the oxyhydroxides of manganese, iron, and then uranium often can be seen below the oxidation front, in echelon with respect to their relative redox potentials. The reducing agents completing these couples include particulate organic matter, mineral species such as pyrite, and upwardly diffusing Fe^{2+} and Mn^{2+}. The extent of organic mineralization across turbidite oxidation fronts can be pronounced (De Lange et al., 1987), with losses sometimes in excess of 75% (Prahl et al., 1989; Thomson et al., 1993). As penetration depth increases, in-situ oxidation progresses at slower rates
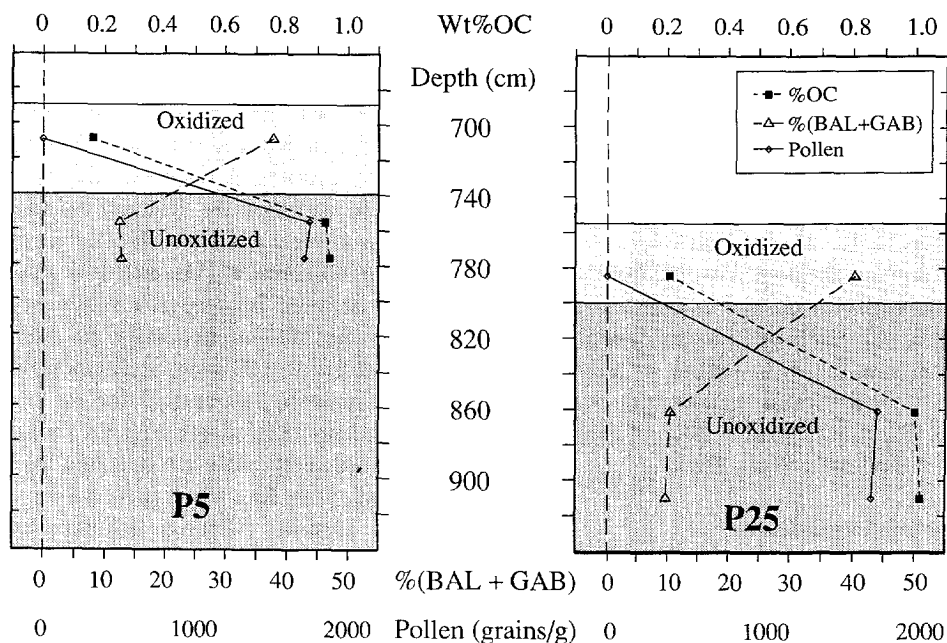

Fig. 10. Depth distributions of (a) weight percent organic carbon, (b) combined mole percent of two nonprotein amino acids (β-alanine plus γ-aminobutyric acid), and (c) total pollen abundances (grains g^{-1}) in oxidized and unoxidized sediments from two cores of the f-turbidite collected at separate sites in the Madeira Abyssal Plain (data from Cowie et al., 1995; Keil et al., 1994b).

until the active turbidite is either capped by another flow or by gradual pelagic sedimentation. Even though such deposits "relax" to suboxic conditions once cut off from the influence of oxic bottom waters, the sharp organic gradients across the redox front remain intact (De Lange et al., 1987).

Molecular-level organic analyses of only one redox front have as yet been completed (Prahl et al., 1989; Cowie et al., 1995). The studied deposit is the relict f-turbidite from the Madeira Abyssal Plain (MAP) approximately 700 km from the northwest coast of Africa. MAP sediments consist of an extensive layer cake of turbidites a few centimeters to meters in thickness, over 30 of which now have been sampled within a 30 m deep sequence (De Lange et al., 1987). The f-turbidite is one of the thickest ($\sim$ 4 m) of these deposits and extends continuously throughout the MAP region. The material comprising the f-turbidite appears to have been emplaced about 140,000 yr ago by a massive slump of fine-grained, carbonate-rich material from the continental slope off Africa (De Lange et al., 1987). The resulting distal turbidite is mineralogically and texturally uniform except for the bottom few centimeters. The upper half meter of the MAP f-turbidite was oxidized over an estimated time period of roughly 10,000 yr (Buckley and Cranston, 1988) before emplacement of the next deposit and relaxation back to suboxic conditions. The beauty of the MAP f-turbidite, and other similarly thick and initially homogeneous deposits, is that they provide well-defined "before" (continuously anoxic sediments below the redox front) and "after" (strongly oxidized material above the front) conditions for slow oxic degradation, unattended by the usual complications of varying sources, uncertain depositional conditions, and extensive bioturbation (Jarvis and Higgs, 1987).

The MAP f-turbidite exhibits a profound oxygen effect. Elemental analyses of sequences collected at sites approximately 100 km apart show that %OC decreases at both locations from 0.93–1.02% below the redox front to 0.16–0.21% in the oxidized surface zone (Fig. 10). Porewater sulfate concentrations are near seawater levels and indicate little if any in-situ sulfate reduction (De Lange et al., 1987). Thus, 80% of the same organic matter that has been stable for 140,000 yr in the presence of sulfate below the redox front, was mineralized completely within

the first $\sim$ 10,000 yr following deposition due to prolonged exposure to molecular oxygen and associated redox-active metals such as iron and manganese. In spite of this extensive mineralization, comparative analyses of the yields of individual alkenones (Prahl et al., 1989), aldoses, lignin phenols, and protein amino acids (Cowie et al., 1995) indicate unusually nonselective organic matter degradation in the oxidized surface sediments. The major observed exception to this pattern is for the nonprotein amino acids, β-alanine and γ-aminobutyric acid, whose total carbon-normalized yields are higher by about a factor of five in the surface vs. the unoxidized deep horizons of both cores (Fig. 10). Such elevated yields of nonprotein amino acids are typical of abyssal plain sediments (Whelan, 1977) and provide additional molecular-level evidence for extensive in-situ degradation.

One interesting aspect of the MAP turbidite example is that long term exposure to oxic/suboxic conditions alone was sufficient to decrease organic concentrations from values typical of coastal sediments to low concentrations characteristic of most deep ocean deposits. While many factors may contribute to the low organic matter contents of slowly depositing deep ocean sediments, the MAP turbidite indicates that prolonged exposure to O_2 (and related oxidizing agents) is sufficiently effective to be the lone direct cause of almost complete mineralization. This conclusion is supported by the laboratory observation that 14 sequential treatments with 30% H_2O_2 are necessary to remove the same amount of organic matter (Cowie et al., 1995). While slow, natural O_2 oxidation is remarkably severe.

Pollen distributions provide another dramatic indication of the extreme severity with which organic matter was degraded in the oxidized portion the f-turbidite (Keil et al., 1994b). Pollen grains, or more precisely sporopollenin exines, were quantified in the MAP samples as examples of a "super-stable" class of hydrolysis-resistant organic materials (De Leeuw and Largeau, 1993). Sporopollenins are well documented to persist for millions of years in reducing marine sediments and are important constituents of both coals and kerogens (Traverse, 1988). However, these complex organic polymers exhibit variable susceptibility to chemical oxidation and also can be appreciably altered in well-aerated soils (Elsik, 1971).

The total assemblage of microscopic, hydrolysis-re-sistant organic materials (or "palynomorphs" - Tyson, 1987) in the unoxidized horizon of the f-turbidite included an average of about 1600 grains of pollen g^{-1} (Fig. 10). Also recovered with the pollen were lesser numbers of dinoflagellate cysts (~ 30

grains g^{-1}) and a predominant background of amorphous organic matter (Fig. 11), which, given the harsh isolation procedure, must be highly resistant to acid hydrolysis. In sharp contrast, recognizable pollen grains are entirely absent from the surface oxidized horizon of the f-turbidite (Fig. 10). Although the
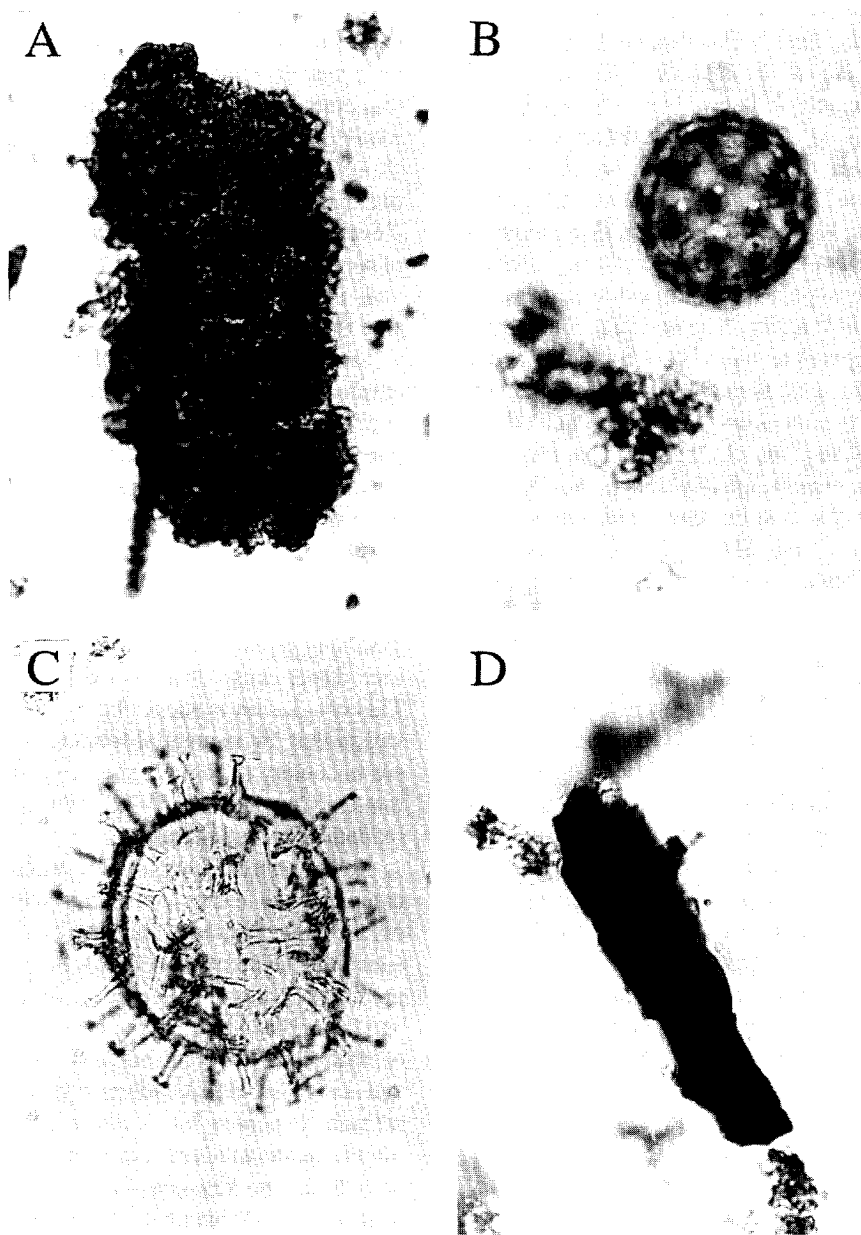

Fig. 11. Photomicrographs of various forms of sedimentary organic matter isolated from the MAP unoxidized f-turbidite. All $\times \sim 200$. (A) Non-hydrolyzable amorphous organic matter. (B) Pollen grain. (C) Dinoflagellate cyst. (D) Charcoal fragment.

isolates from the oxidized segments are also essentially free of hydrolysis-resistant amorphous organic materials, they contain dinoflagellate cysts in reduced numbers ($\sim$ 35% loss) and small amounts of charcoal (Fig. 11), one of the most oxidation-resistant forms of reduced carbon (Wolbach and Anders, 1989). Thus pollen, some dinoflagellate cysts, amorphous hydrolysis-resistant materials, and 80% of the bulk sedimentary organic matter exhibit high susceptibilities to oxic degradation on hundred- to thousand-year time scales. The complete absence of intact pollen grains in the oxidized MAP horizons is mechanistically informative because it indicates organic matter was destroyed in situ, and not simply stripped away by diffusion of porewater DOM and reversibly sorbed POM into the overlying bottom water.

A *transition zone* from sorptive protection along coastal margins to oxic degradation within deep-sea sediments should be expected somewhere on the lower continental margins if the inferred competition between these opposing processes actually exists (Fig. 1). Is there evidence for such a boundary in modern depositional settings and how does the transition correspond to oxygen exposure histories? Support for a transition can be drawn from the data compilation of Premuzic et al. (1982), who noted a strong correlation between organic carbon content and sediment grain size along upper slopes and shelves, but observed lower carbon contents and no correlation in deep slope and rise sediments. Further support comes from data for the Washington coastal region where sands and coarse silts delivered from the Columbia River accumulate along the shelf, but give way to fine silts and clays on the upper slope and rise. This textural change corresponds to a gradual increase then leveling off of mineral surface area at greater water depths. Over the same region, sediment accumulation rates decrease from about 0.3 cm yr^{-1} on the continental shelf, to 0.03 cm yr^{-1} on the continental slope ($\sim$ 1000 m) and 0.01 cm yr^{-1} in Cascadia Basin and the nearby abyssal plain (Carson, 1971; Carpenter et al., 1981, 1982). These accumulation rates are largely based on ^{210}Pb measurements and therefore should be considered maximal values due to the possible effects of sediment mixing (Carpenter et al., 1982). Corresponding depths of O_2

penetration into surficial sediments average about 0.3 cm over the 100–600 m interval (Archer, 1990), and by analogy with the California margin (Reimers et al., 1992), likely reach 1–3 cm at water depths > 2000 m. Division of these penetration depths by corresponding sediment accumulation rates give minimal estimates of oxygen exposure times (disregarding bioturbation and irrigation) on the order of 1, 30 and > 300 yr for these continental shelf, slope and basin environments, respectively (Keil et al., 1994b).

These trends are accompanied by distinct patterns in organic matter and pollen distributions. Given measured mineral surface areas, and assuming monolayer-equivalent organic loadings (Fig. 7), Washington margin sediments are expected to attain maximal stable loadings of $\sim$ 3.0% OC at a water depth of $\sim$ 500 m and greater (Fig. 12A). Within the shelf and upper slope, the predicted and actual organic matter loadings agree quite well (Fig. 12A). Actual loadings of organic matter along the lower slope, however, gradually diminish from monolayer-equivalent amounts ($\sim$ 3.0%) to typical open ocean levels ($\sim$ 0.2%; Fig. 12A). Strikingly parallel distributions of pollen (Fig. 12B) occur throughout this region of widely contrasting texture and sedimentary oxygen exposure. Inshore of about 2000 m this similarity probably arises because pollen grains and organic-rich silts exhibit comparable hydrodynamic properties (Keil et al., 1994b) and are equally subject to extensive dilution by sand (Fig. 12B). This inference is supported by the nearly constant pollen/silt ratios (silt defined as the clastic 3–38 μm size class) throughout this texturally variable region (Fig. 12C) and previously presented evidence for monolayer-equivalent organic coatings across the particle size spectrum within these shallow-water deposits (Figs. 7 and 12A). In contrast, sediments accumulating seaward of 2000 m water depth contain steadily decreasing OC and pollen concentrations (Fig. 12A,B). Since both pollen and silt have a terrestrial source and are hydrodynamically equivalent, their ratios in coastal sediments should remain fairly constant unless one component is preferentially removed. The steady decline in pollen/silt ratios (Fig. 12C) among these uniformly fine-grained lower slope and rise deposits is unlikely to result from either differential sorting or simple dilution of these two terrigenous particle types. This drop off, however,
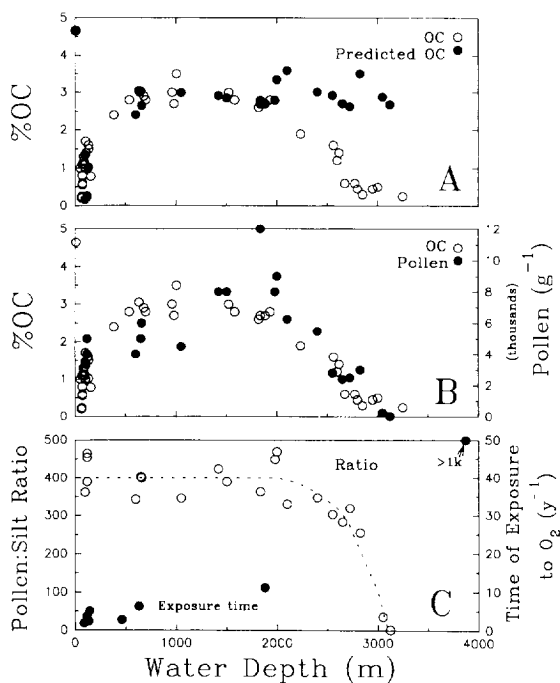
Fig. 12. Trends in organic matter preservation along the Washington coast. (A) ● = Weight percentages of organic carbon predicted from mineral size and surface area measurements (Carson, 1971; Walker, 1974) and converted into expected carbon loadings using a relationship of 0.76 mg OC m^{-2} (Keil et al., 1994a). ○ = Actual carbon loadings measured by various researchers (Hedges and Mann, 1979; Prahl, 1985; Carpenter and Peterson, 1989; Keil et al., 1994a). (B) Parallel distributions of %OC (○) and pollen concentrations (●) in Washington coastal sediments. (C) Ratio of pollen abundance (from B) to weight percent silts (3–38 μm size range) for the same sediments (○). ● = Estimated exposure times of sedimentary organic matter to molecular oxygen dissolved in sediment porewaters, calculated as the oxygen penetration depth divided by the sedimentation rate. No data for oxygen exposure is presently available for depths greater than 2000 m off the Washington coast and the > 1000 yr value is given as a reference point for deep ocean environments (Keil et al., 1994b).

does coincide with the water depth interval on the lower slope where O_2 exposure times can be expected to increase sharply toward deep ocean values. A broad transition from sorptive preservation to oxic degradation thus appears to occur on the lower slope of this region.

The coincident decrease in %OC and pollen abundance over this interval is similar to that observed across the redox boundary of the MAP turbidite (Fig.

10), suggesting that total organic matter and its pollen component are oxygen sensitive in modern depositional environments as well. Given these gradual decreases, various types of pollen and other palynomorphs such as dinoflagellate cysts, which are known to have varying resistances to degradation (Elsik, 1971; Dale, 1976), may disappear at different stages of O_2 degradation. If so, the changing abundances of these uniform and easily counted bodies might be used to directly calibrate an absolute scale of oxic exposure history, without complications from diffusive losses. Moreover, positions along this diagenetic scale might be delineated in detail by characteristic changes in the chemistry or appearance (e.g. surface erosion patterns) of the various palynomorphs, either of which may be indicative of oxic degradation mechanisms. The potential to combine microscopic and chemical characterization would be greatly enhanced by development of techniques for physically recovering different palynomorph types without the harsh chemical treatments typically used in pollen isolations.

A model for oxic degradation of sedimentary organic matter illustrates the potential for a sensitive response of organic matter preservation to O_2 exposure times such as may occur in the transition zone off the Washington coast (Fig. 13). For simplicity, we will assume that all sediments receive only three components: (1) totally refractory organic matter, (2) oxygen-sensitive organic matter (OSOM) that degrades slowly in the presence of O_2 (and/or metal oxides), but not at all under anoxic conditions, and (3) hydrolyzable organic matter that is completely mineralized regardless of conditions. In deeply oxygenated sediments that deposit slowly, OSOM will have ample time to degrade completely at its intrinsic rate until only refractory organic materials such as charcoal remain. Such conditions may well be approximated by the surface of the MAP f-turbidite and most open ocean sediments. As more rapid sediment accumulation and shallower O_2 penetration depths contribute to briefer O_2 exposure times at more landward sites, OSOM mineralization will be effectively "turned off" at progressively shallower depths (Fig. 13).

Because OSOM decreases exponentially with depth under oxic conditions, decreases in O_2 exposure times lead to pronounced increases in organic matter
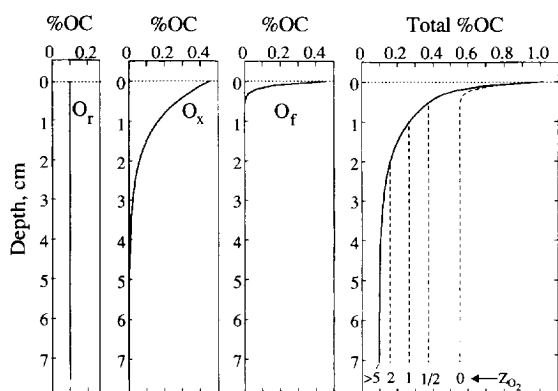
Fig. 13. Model-derived %OC profiles for three different organic fractions and for total organic carbon in a hypothetical continental slope sediment. The three individual profiles at the left correspond to refractory (O_r), oxygen-sensitive (O_x) and fermentable (O_f) organic matter components that were assigned initial concentrations of 0.10, 0.45 and 0.45 wt%, respectively. These three fractions were assumed to have first-order decay constants of 0, 0.03 (only reactive under oxic conditions) and 0.30 yr^{-1}, respectively, and to be present within a sediment that has accumulated without mixing at a constant rate of 0.03 cm yr^{-1}. The three profiles to the left and the total profile to the extreme right are for conditions of deep (> 5 cm) O_2 penetration. The dashed vertical lines in the plot to the right correspond to total %OC profiles obtained when the oxygen penetration depth (Z_{O_2}) decreases from > 5 to 2, 1, 1/2 and 0 cm below the sediment surface.

preservation (Fig. 13). Under these conditions, preservation could vary inversely with bottom water O_2 concentration and directly with sedimentation rate, but in an imperfect manner. Only at deeper water sites would surface area control give way to the slower dynamics of erosive oxic degradation. Bioturbation should not appreciably affect average oxygen exposure times. Deep physical mixing, however, would lengthen OSOM profiles and could increase OSOM preservation by randomly passing a small fraction of this material rapidly through the surface oxic zone. Although hydrolyzable organic matter would never be preserved in this situation, its rate of input is critical for controlling diffusive O_2 penetration, and thus the extent of degradation of the coexisting OSOM. In this case again, the kinetics of total organic matter reaction would be much less informative of mechanisms affecting preservation than the ultimate extents of reaction. The most definitive approach to studying oxic effects and the

mechanisms involved would be to directly characterize and quantify the OSOM component(s) remaining at depth.

Factors contributing toward extensive mineralization in oxic vs. anoxic (sulfidic) sediments may be varied and interrelated. One possibility is that a major portion of the sedimentary organic matter in marine sediments may be non-hydrolyzable. Such material would be highly resistant to fermentative break down (McInerney, 1988), which is a prerequisite for sulfate reduction (Widdel, 1988). We have crudely calculated that pollen accounts for about 0.2% of the total OC in the unoxidized segment of the MAP f-turbidite (Keil et al., 1994b). Although it is difficult to precisely quantify by optical methods the amount of coexisting hydrolysis-resistant amorphous material, it is clearly orders of magnitude greater than pollen (Fig. 11A), and thus a major component of the total sedimentary OC. This conclusion is similar to that obtained by direct treatment of modern sediments from the Peru margin where approximately 80% of the sedimentary organic matter resists hydrolytic solubilization (Reimers and Suess, 1983). The fact that hydrolysis-resistant organic matter would, like lignin, have to be chemically eroded by exoenzymes, is consistent with previously discussed field evidence that this mode of mineralization is characteristically slow.

Second, by analogy with lignin, molecular oxygen may be necessary for extensive degradation of pollen and other forms of insoluble or carbon-rich organic materials in these sediments. Such organic substances, including olefins, dimethyl amines and saturated hydrocarbons, are biologically degraded by O_2-requiring enzymes (Sawyer, 1991). These enzymes include (1) oxygenases that catalyze electron transfer from organic matter to O_2, (2) dehydrogenases that remove hydrogen from organic matter producing peroxides and water, and (3) mono- or dioxygenases that insert one or two atoms from O_2 directly into organic molecules (Sawyer, 1991). A variety of examples of selective preservation of lignin (Hedges et al., 1985), aliphatic polymers (Hatcher et al., 1983), chloropigments (Sun et al., 1993a) microbial lipids (Harvey et al., 1986) and other hydrophobic compounds (Atlas et al., 1981) under anoxic conditions are known. Geochemists have long recog-

nized that anoxic conditions are tightly associated with the formation of petroleum source rocks (Tissot and Welte, 1978) and that the penetration of molecular oxygen into petroleum reservoirs leads to extensive biodegradation not observed in the presence of sulfate-rich brines alone (Connan, 1984; Palmer, 1993).

Direct enzymatic oxidation, however, may not be necessary for oxic degradation of resistant organic substances. Aerobic organisms give off small amounts of superoxide ion ($O_2^- \cdot$) as a metabolic by-product, and thus indirectly generate H_2O_2 (Sawyer, 1991). For example, white-rot fungi involved in the aerobic degradation of lignin are thought to release diffusive activated oxygen species such as H_2O_2 and its reaction product, hydroxyl radical (Kirk and Farrell, 1987). Such high-energy oxidative species may be responsible for the characteristically nonspecific oxidative erosion of structurally complex lignin polymers and might explain the similarly extensive degradation of very different biochemicals and total organic matter in the oxidized MAP sediments (Cowie et al., 1995). Moreover, oxidative agents such as H_2O_2 are sufficiently small to diffuse into nanometer-size pores on mineral surfaces where sorbed organic materials may be preserved because microbial exoenzymes are too large to function (Mayer, 1994a). If so, then the sorptive protection and slow oxic degradation hypotheses are logically more consistent competing reactions.

While the role of molecular oxygen is often emphasized, redox-active metals such as iron and manganese may play a direct role in organic matter degradation. Redox couples involving iron, Fe(III)–Fe(II), and manganese, Mn(IV)–Mn(II), are intermediates in the transition from oxygen- to sulfate-based biodegradation (Stumm and Morgan, 1981) and can act as potent redox agents or catalysts in both microbial and abiotic systems. In the presence of O_2 these metals can be oxidized both spontaneously and by bacteria (Fenchel and Blackburn, 1979; Stumm and Sulzberger, 1992). Contrary to sulfate reducers, which are strict anaerobes and utilize only a small variety of fermentatively-produced compounds for growth (Widdel, 1988), metal reducers typically are facultative anaerobes capable of growing on a vast array of organic molecules (Nealson and Myers, 1992). Such microorganisms may also strip re-

versibly sorbed organic matter from particle surfaces by driving down porewater DOM concentrations.

Abiotic reactions involving redox metals may be equally important. For example, manganese oxides are reported to spontaneously oxidize recalcitrant humic substances to products such as acetaldehyde and pyruvate (Sunda and Kieber, 1994). Fe(III) is known to be an effective electron acceptor in suboxic systems where it can oxidize a variety of organic substances (including aromatic compounds) with and without microbial mediation (Lovely et al., 1989,1991). Spontaneous oxidation of Fe(II) and other metal ions (Mn, Cu) by O_2 at the surface of oxide minerals generates superoxide radical, which decomposes to H_2O_2 (Sawyer, 1991). Ferrous iron combines with H_2O_2 to form Fenton's reagent (Fenton, 1894), a source of hydroxide radical and one of the most powerful oxidizing systems known for organic substances. The rates of the above reactions are proportional to surface area and the concentrations of dissolved O_2 and redox active metal ions (Stumm and Sulzberger, 1992). Sediment surfaces, many of which comprise oxide layers, can thus be sources of activated oxidizing agents, as well as physically protective microenvironments for organic substances.

The potential importance of metals as diagenetic agents is also suggested by the previously discussed evidence for extensive mineralization of refractory riverine organic matter in suboxic deltaic sediments, such as those on the Amazon shelf where iron and manganese reduction strongly prevail (Aller et al., 1986; Aller, 1994). In such environments a complex variety of "dark" oxygen activation mechanisms may come into play and explain extensive and nonselective organic degradation patterns characteristic of these and other such oxic and suboxic environments (Cowie et al., 1995). Partitioning of porewater DOM and reversibly sorbed organic molecules into seawater during sediment resuspension events may also contribute toward extensive organic matter losses. Introduction of greater amounts of labile marine organic matter could push the delicately poised redox environments of deltaic and slope sediments on to sulfate reduction, which would halt iron- and manganese-based degradation when these metals are precipitated as insoluble, reduced sulfides. The relative concentrations of nutrients, organic matter, and

metal oxides discharged by rivers might therefore predispose their deltaic regions toward different redox regimes, and consequently toward contrasting carbon preservation efficiencies.

4.4. Organic-rich sediments

Less than 8% of sedimentary organic matter presently is being deposited under regions of high productivity and low bottom water oxygen (Table 2, Fig. 1). However, these organic-rich sediments often occur in disproportionately high abundance in data compilations such as Figs. 4–6. Much of this focus stems from the idea that modern organic-rich sediments may be mechanistically informative analogs for petroleum source rocks, and the extrapolation that the mechanisms governing carbon preservation in these sediments may also function in more typical environments. Carbon-rich deposits tend to be the focal point of the debate between proponents of anoxia- vs. productivity-induced preservation of organic matter (e.g. Pedersen et al., 1992), and represent a relatively well-studied extreme of the preservation spectrum.

Monolayer-equivalent sorption of organic matter to sedimentary mineral grains cannot easily explain the high %OC values ($>5\%$) characterizing these deposits. This is because particles less than 1 μm in
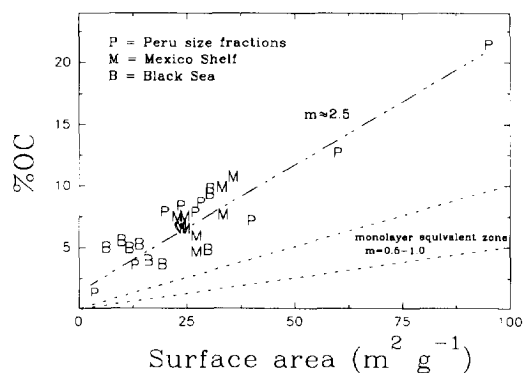

Fig. 14. Weight percent of organic carbon plotted vs. mineral surface area for surficial sediments from productive regions with low bottom water oxygen concentrations such as the Black Sea (bulk material), Mexico shelf (bulk material), and Peru margin (SPLITT size fractions). The typical data range for continental margin sediments exhibiting monolayer-equivalent organic loadings is given for comparison (e.g. Keil et al., 1994a).

size required to carry such high surface coating are well below the textural norm for such deposits (Krissek and Scheidegger, 1983). Such sediments must therefore contain either high abundances of discrete organic debris or multilayer coating of organic material. Analysis of bulk sediments from the coast of Mexico and hydrodynamic fractions from the Peru upwelling region suggest that the preserved organic matter is still intimately associated with minerals, as indicated by a direct OC/SA relationship (Fig. 14). As with other sediments, very little ($<15\%$) organic matter can be separated from the mineral matrix via either hydrodynamic or density separation. Both bulk sediments and hydrodynamic fractions contain similar amounts of organic coatings that fall in the range of 2–5 organic layers thick (Fig. 14). This could reflect either true multiple layering, or a change in the conformation of the sorbed organic matter (e.g. with less direct interaction as more of the sorbed molecules move away from the mineral surface; Taylor et al., 1994).

In either case a protective mechanism in addition to monolayer sorption typical of most coastal deposits may be involved. As noted by Mayer (1994b), the deposits which exhibit stable super-monolayer coatings all underlie waters with very low oxygen contents. Some regions, such as Skan Bay, AK or Saanich Inlet, BC, contain sediments with high carbon loadings at the surface but monolayer-equivalent loadings at depth, and are not considered to represent high carbon depocenters. Others, such as the Mexican Shelf, the Black Sea, and the Peru upwelling region do appear to maintain diagenetically stable multilayer-equivalent loadings at depth, although few cores have been analyzed. Current work along the Mexican Shelf (Hartnett et al., submitted) indicates that sediments inshore of a strong oxygen minimum have monolayer-equivalent OC/SA ratios, and that the ratio increases dramatically once bottom water oxygen concentrations fall below a threshold of approximately 20 μm l^{-1}. This change in OC/SA ratio is not accompanied by a change in mean sediment grain size or in carbon flux to the sediments, and occurs within an extremely narrow distance of <20 km. Thus, it appears that diagenetically stable coatings equivalent to 2–5 times a monolayer may be reached in sediments underlying waters with very low (<20 μm l^{-1}) bottom water oxygen contents,

at least along the Mexican margin. This result would not be easily reflected in traditional plots of either %OC or burial efficiency vs. bottom water oxygen (e.g. Fig. 6).

The mechanisms that might lead to super-monolayer organic loadings are many. In particular, sediments under highly productive, low-oxygen waters exhibit elevated porewater DOC concentrations (e.g. Lyons et al., 1979) which, by reversible partitioning, could cause increased organic sorption onto the component minerals. Possible reasons for such high DOC concentrations include reduced irrigation by benthic organisms and hence attenuated exchange of O_2 into, and DOC out of, surficial sediments. Parkes et al. (1993) suggested that sediments depositing under the Peru upwelling region contain high amounts of bacterial exopolymers, which presumably would build up as multiple layerings on mineral grains. An explanation of why the exopolymers are not degraded under anaerobic conditions has been lacking. Another hypothesis is that in-situ degradation of sorbed multilayers is retarded by extremely high concentrations of sulfide or other metabolic products in diagenetically reactive, but iron-poor deposits. Alternatively, under such circumstances extremely reactive substances such as polyunsaturated fatty acids and carotenoid pigments may persist for sufficiently long time periods to come in contact with high concentrations of porewater H_2S and polysulfides. As a result, natural vulcanization reactions may form carbon-rich organosulfides (Kohnen et al., 1989; Sinninghe Damsté et al., 1989) that resist fermentative degradation.

In addition, high concentrations of partially degraded biochemicals that accumulate in porewaters or within multilayer mineral coatings may subsequently combine via Maillard- or polyphenol-type reactions to form heteropolycondensates (Hedges, 1988; Keil and Kirchman, 1994). These larger geopolymers could be expected to have lowered susceptibilities to microbial degradation (Henrichs and Doyle, 1986) and increased affinities for mineral surfaces (Theng, 1979), two trends which were observed at greater depths in the coastal sediment studied by Keil et al. (1994c). Higher-order condensation reactions might be particularly favored within greatly concentrated surface coatings where at least a foundation of directly sorbed organic molecules

should be strongly protected (see Keil et al., 1994c) and available as a template for condensation. Whether increased preservation might be due to a protective environmental factor vs. in-situ formation of less reactive combination products could be tested by evaluating the relative freshness and reactivities of these organic materials with chemical (Cowie and Hedges, 1994) or culture (Keil et al., 1994c) techniques.

4.5. Implications for global carbon and oxygen cycles

An important aspect of both the proposed sorptive protection and oxic degradation processes is that each would directly affect global carbon and oxygen cycles. Sorptive preservation, for example, would directly link kerogen weathering on the continents to OC preservation in depositing coastal marine sediments via the continuity of mineral surface area (see also Mayer, 1994a,b). Presently, about 80% of all continental weathering products are derived from sedimentary rocks deposited during previous geologic eras (Garrels and Mackenzie, 1971). The kerogen contents of these rocks are similar to the concentrations of organic matter now being preserved below the diagenetic active surface zones of texturally equivalent coastal marine sediments. Because seawater cannot store appreciable amounts of most continental weathering products (Mackenzie and Garrels, 1966), which presumably weather to the same grain sizes as the clastic minerals from which they were originally formed, total surface area should be conserved. Sorptive preservation thus provides a direct, wide reaching, and essentially immediate mechanism for balancing kerogen mineralization with the burial of newly formed organic matter. Although working by mass balance, and not via negative feed-back control, sorptive preservation would greatly help stabilize the sensitive cycle of atmospheric oxygen over million-year time scales.

Slow oxic degradation of sedimentary organic matter seaward of mid-continental slopes (e.g. Figs. 1, 12A), and possibly in deltaic regions, could modulate both the carbon and oxygen cycles by sensitive negative feedback control. The key aspect of the feedback loop is that given a constant sedimentation rate, O_2 penetration into sediments (and thus oxygen

exposure time) is ultimately diffusion controlled and broadly proportional to the concentration of dissolved oxygen in ocean bottom waters (Emerson, 1985). Dissolved oxygen concentrations in the deep ocean will directly reflect the partial pressure of atmospheric O_2, with which these water masses equilibrated before downwelling. Although a host of environmental variables conspire to determine oxygen exposure times at different ocean sites, increases in atmospheric O_2 will lead on average to elevated oxygen gradients across the water/sediment interface, greater O_2 penetration, and hence to more complete degradation of oxygen-sensitive organic matter within surficial marine sediments (Keil et al., 1994b). This type of kinetic control on sedimentary organic matter burial resembles in many ways the mechanism by which the calcium carbonate compensation depth is established in the deep ocean. It appears for example that the "organic carbon compensation depth", below which appreciable OC burial does not occur, is poised presently near 3000 m water depth in sediments depositing off the Washington coast (Fig. 12A). This interval is dependent on local sediment accumulation rates and will vary regionally. The first quantitative effects of slow oxic degradation, equivalent to a carbonate lysocline, appear seaward of about 2000 m water depth in the Washington coastal region (Fig. 12A). The depth interval of apparent O_2 effect (the transition zone), is thus relatively broad ($\sim$ 1000 m), possibly corresponding to a wide range of susceptibilities of different sedimentary materials to slow oxic degradation. Different types of pollen grains, dinoflagellate cysts, and other palynomorphs likely will exhibit narrower individual "lysocline" (incipient surface erosion) and "compensation" (effective disappearance) depths within this broad interval. Negative feedback control on atmospheric O_2 concentrations would be effected by movement of this composite interval up or down along the slope and rise, thereby decreasing (response to higher O_2) or increasing (response to lower O_2) the area landward of this boundary where OC preservation can occur.

Similar processes may take place in deltaic sediments where higher atmospheric O_2 concentrations could lead to increased organic mineralization directly, or via more effective oxidation of redox active metals during sediment resuspension and mix-

ing events. Profound organic matter losses such as those occurring off the Amazon river could be extremely important in the global carbon cycle because roughly half or more of all OC is preserved presently by deposition within or near deltaic regions (Table 2). During glacial low sea-level stands, however, rivers discharged their loads directly onto slopes and cones, from where turbidity currents carried huge volumes of sediment for immediate burial at deep ocean sites (Weaver and Thomson, 1987). Effective by-passing of heterotrophic estuaries and deltas may have resulted in extensive organic carbon preservation in rapidly accumulating deep sea turbidites during glacial periods (e.g. Newman et al., 1973).

Finally, surface area may provide a direct link between the preservation of organic matter and pyritic sulfur in continental margin sediments. Berner and Raiswell (1983) demonstrated a direct relationship between the weight percentages of total sulfur (predominantly in pyrite) and OC in modern, non-euxinic marine sediments accumulating below the diagenetically active surface horizon. The OC/S weight ratio in these deposits ranges from about 1.5 to 5.0, with a mean near 2.8 (Berner, 1984). This direct relationship has been ascribed either to (1) constant proportions of reactive (sulfide generating) and refractory (eventually preserved) organic materials fortuitously deposited at different sites (Berner and Raiswell, 1983), or (2) the concentration of sorbed hydrous ferric oxides and organic compounds on fine-grained sedimentary minerals (Berner, 1984). Iron is key in diagenetic sulfur immobilization because under anoxic conditions sedimentary iron oxyhydroxides (e.g. lepidocrocite, goethite and hematite) react rapidly with dissolved H_2S released by sulfate reduction to form insoluble iron monosulfides and eventually, pyrite (Berner, 1984; Canfield et al., 1992). Without precipitation by reactive iron, most of the sulfide generated by in-situ organic matter breakdown diffuses upward into O_2-bearing waters and is subsequently oxidized to sulfate and lost (Berner, 1984).

The second explanation, proportional introduction of surface-associated iron and organic matter, is directly compatible with the sorptive preservation hypothesis. Sorption of a constant loading of reactive iron oxyhydroxides per unit surface area, along with a monolayer equivalent of protected organic matter

(Day et al., 1994), would strongly favor ultimate burial of sedimentary mixtures with nearly constant OC/S ratios. In this case the capacity of mineral grains to ultimately preserve both organic matter and pyrite would be predetermined by the relative magnitudes of their surface areas and the reactive iron coatings they carry at the time of burial. The only additional requirement is that labile organic materials be introduced in total quantities sufficient to generate at least two moles of sulfide (via in-situ sulfate reduction) per mole of reactive iron. In fact, under these conditions all OC in excess of a monolayer-equivalent coating, and all sulfide in excess of the amount trapped to form iron minerals, must eventually be lost in order to maintain a constant C/S burial ratio.

Using the data set from the Washington Coast, we have made a crude estimate of the potential relationship between reactive iron and carbon preservation at this site. Total iron was measured by neutron activation and reactive iron was estimated as the amount of excess iron after accounting for mineral matrix iron (e.g. sediments composed largely of smectite were expected to have iron contents of $\sim 4.5\%$, and the excess was considered reactive; Newman, 1987). As with total iron (Keil et al., 1994a), reactive iron and mineral surface area exhibit a significant linear relationship with a correlation coefficient of 0.79 ($p >$ 0.95) and a slope of 0.26 ± 4 mg Fe m^{-2} (Fig. 15). Estimated this way, reactive iron comprises 15–50% of the total Fe in the samples, in good agreement
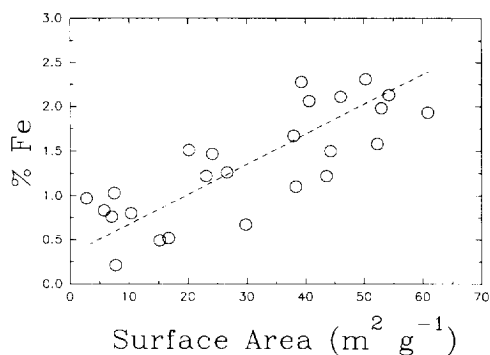
with chemically-derived estimates of reactive iron in other fine grain marine sediments (Aller et al., 1986; Canfield, 1989). Reactive iron loadings of 0.26 mg m^{-2} have the capability to immobilize 0.30 mg pyrite sulfur m^{-2}. This corresponds to a C/S mass ratio of 2.5 (0.76 mg OC m^{-2}/0.30 mg S m^{-2}). This estimate indicates that Washington coastal sediments have the potential to preserve OC and pyrite sulfur at a ratio similar to the global mean C/S of 2.8 for modern marine deposits (Berner and Raiswell, 1983). Of course, this ratio will only be obtained if sufficient labile organic matter is introduced to generate the needed sulfide, which we have not tested for Washington coast sediments. While as yet circumstantial, this mechanism for trapping reduced carbon and sulfur on sedimentary mineral surfaces is straightforward and readily tested. If in fact clastic minerals are predestined to preserve OC and pyrite sulfur at ratios near 3 in coastal marine sediments, then surface-associated organic matter and iron could intricately and responsively link the global cycles of sulfur, carbon, and oxygen over geologic time.

5. Major problems and research directions

5.1. Inconsistencies and unresolved problems

Many questions and uncertainties remain concerning organic matter preservation, particularly the mechanisms involved. It is not known, for example, to what degree monolayer-equivalent organic coatings typify upper continental margin sediments throughout the world, and how these loadings might change toward river sources and the open ocean. The conditions leading to sub-monolayer organic concentrations in some deltaic deposits and to organic loadings equivalent to multiple layers beneath productive coastal waters also are unclear, as are the reasons why in both extreme settings sedimentary OM still appears to be largely sorbed. Could the inference that the OM in all these sediments is predominantly sorbed be wrong, due either to experimental or logical inconsistencies? Both the association mechanisms of organic molecules with inorganic particles, and the resulting distribution patterns of the sorbed molecules over sediment mineral surfaces (spread in monolayers or pocketed?) are poorly

Fig. 15. Weight percentage of total iron (%Fe) vs. total exterior surface area (m^2 g^{-1}) for size fractions of modern sediments from the Washington continental shelf and upper slope (see Fig. 7). The equation of the best least-squares fit ($r = 0.77$) of a straight line to these data is %Fe = $0.026 \times$ SA $+ 0.40$.

defined. It is not evident presently how intrinsically labile organic molecules might be protected from biodegradation when sorbed to mineral surfaces, or why these molecules are not stripped away via reversible partitioning into more susceptible dissolved forms (Lee, 1994). To what extent does sorption favor in-situ condensation reactions among closely packed organic molecules on mineral surfaces and what are the relationships of these materials to conventionally defined humic substances and protokerogens? Are dissolved organic molecules released by rapid degradation of fresh organic particles exchanged via porewater with counterparts on sediment mineral surfaces, and if so, what are the biological and geochemical implications of this highly interactive system?

Oxic degradation is even more hypothetical and requires testing in a variety of field settings where the duration of O_2 exposure can be determined. In the course of such studies it is critical to define the structural or physical factors that might characterize oxygen-sensitive organic matter. Mechanistically, the fundamental question of whether oxic degradation is spontaneous or biologically mediated must be addressed. The importance of macrobenthos, bioturbation and irrigation on the extent of oxic degradation deserves specific attention. It is also important to establish whether the immediate electron acceptor is O_2, H_2O_2, $O_2^-\cdot$, or a metal species, and what conditions apparently shut down this mechanism in anoxic sediments. Are sub-monolayer organic loadings in open ocean and some deltaic sediments due to similar oxidative mechanisms, and is diffusive OC loss also important? Where and how is kerogen mineralized so that weathered clastic minerals can "reload" with fresh organic matter during successive deposition cycles? To tie together the two key hypotheses presented here it is necessary to explain how and why organic matter sorbed to mineral grains apparently resists anaerobic degradation, yet seemingly succumbs to slow oxic degradation.

5.2. Promising research directions

The above questions can be addressed by a variety of approaches, including tests of the fundamental issue of whether sorptive protection and oxic degradation are the root controls for organic matter preser-

vation. With respect to sorptive processes, studies of %OC/SA relationships are needed for a wider variety of ocean margin environments which represent well-defined contrasts in sediment accumulation rates and oxygen penetration depths. These studies should also incorporate measurements of reactive iron and reduced sulfur compounds so that the interactions of Fe, S, C and O_2 can be assessed and linked to mineral surface properties. Although "hot spots" such as the Peru shelf might be mechanistically informative, attention should be focused on more typical, and quantitatively important, continental shelf and slope environments to see how broadly the sorptive stabilization model applies. These studies should particularly emphasize the often ignored lower boundary of the oxygen minimum zone and the lower continental slope where slow sedimentation rates may emphasize oxygen effects. There also is a need to study deltaic regions and adjacent continental shelves where the bulk of organic matter is deposited (Table 2), and where large variations in the extent of surface coating can occur. Natural environments, such as glacial fjords or volcanic ash fall regions, where mineral surfaces initially devoid of organic coatings are introduced, should provide useful information about the mechanisms and rates of monolayer development. Emphasis on tropical deltaic systems is warranted because of the large volumes of iron-rich sediment delivered to the oceans by low-latitude rivers. Such field studies could be complemented by laboratory investigations of the mechanisms controlling organic/mineral interactions and the distributions of different types of molecules over various microenvironments on mineral surfaces. The relationship between mineral–organic interactions and the reactivity of sorbed organic substances to microorganisms, macrobenthos, and their enzymes and chemical agents warrants detailed study. A key requirement for both field and lab studies will be equally intensive characterizations of the mineral phases as well as both the dissolved and particulate organic components, which can no longer be treated as functionally separate entities. To approach these goals, a variety of preparative methods for gently separating different sizes and types of sedimentary particles are needed, as well as analytical methods that sensitively reflect different types and mechanisms of organic molecule/mineral surface interac-

tions. A better understanding of the remineralization of kerogens will be necessary if we are to understand how sediment can be "recharged" with recent organic matter.

The question of slow oxic degradation can be addressed by an equally broad variety of approaches. Related field studies should also focus on deep continental slope and rise environments where slow oxic degradation may exhibit a gradient of profound effects (Fig. 12). Such investigations will need to include precise measurements of oxygen penetration depths, POM and DOM concentrations, the extents of suboxic zones, and redox-reactive metals, as well as sediment accumulation and mixing rates. When considering preservation, organic characterizations should concentrate more on the types and amounts of organic materials that are preserved below a diagenetically active surface layer, rather than on the rates of reaction of more labile substances in the surface horizon. In such studies, surface area loadings, porewater DOC concentration, and compositional parameters indicative of the diagenetic history of the sedimentary organic mixture should be measured in addition to more ambiguous bulk POC concentrations and fluxes. Similar approaches should be taken in studying quantitatively key deltaic sediments, with an eye toward defining the effective redox couples and the relative turnover rates of marine and riverine organic materials. Other possible extreme environments for mechanistically informative investigations of oxic degradation might include active deep ocean oxidation fronts, soils, weathering subaerial shales and coals, and organic matter dissolved in the deep ocean. Chemical simulations of these systems in the laboratory with oxidizing agents of different severity and size may be informative. Such studies should include microscopic and direct chemical characterizations of pollen grains, dinoflagellate cysts and other palynomorphs which may serve as calibrants for oxidation mechanisms and histories. A challenge in all these efforts will be to characterize a major fraction of the oxygen-sensitive organic material, much of which likely will be intimately associated with mineral surfaces and resistant to conventional methods of solvolytic breakdown and chromatographic analysis. Pyrolytic and thermogravimetric analyses may prove helpful for such substances, as well as spectral characterizations that can be applied

to bulk sediment. Continued effort also should be made to develop methods to gently separate and concentrate bulk organic components for conventional CHNS, NMR, pyrolysis and solvolysis characterizations without often troublesome mineral matrix effects. The fundamental challenge in these initiatives will be to relate molecular-scale interactions among the various organic and inorganic constituents of marine sediments to the gross characteristics and intrinsic dynamics of different depositional settings.

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