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6.07
Marine Organic Geochemistry

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S0005 ## 6.07.1 INTRODUCTION

P0005 This chapter summarizes selected aspects of our current understanding of the organic carbon (OC) cycle as it pertains to the modern ocean, including underlying surficial sediments. We briefly review present estimates of the size of OC reservoirs and the fluxes between them. We then proceed to highlight advances in our understanding that have occurred since the late 1980s, especially those which have altered our perspective of the ways organic matter is cycled in the oceans. We have focused on specific areas where substantial progress has been made, although in most cases our understanding remains far from complete. These are the fate of terrigenous OC inputs in the ocean, the composition of oceanic dissolved organic matter (DOM), the mechanisms of OC preservation, and new insights into microbial inputs and processes. In each case, we discuss prevailing hypotheses concerning the composition and fate of organic matter derived from

the different inputs, the reactivity and relationships between different organic matter pools, and to highlight current gaps in our knowledge.

P0010 The advances in our understanding of organic matter cycling and composition has stemmed largely from refinements in existing methodologies and the emergence of new analytical capabilities. Molecular-level stable carbon and nitrogen isotopic measurements have shed new light on a range of biogeochemical processes. Natural abundance of radiocarbon data has also been increasingly applied as both a tracer and source indicator in studies of organic matter cycling. As for ^{13}C, bulk ^{14}C measurements are now complemented by measurements at the molecular level, and the combination of these different isotopic approaches has proven highly informative. The application of multinuclear solid- and liquid-state nuclear magnetic resonance (NMR) has provided a more holistic means to examine the complex array of macromolecules that appears to comprise both dissolved and particulate forms of organic matter. New liquid chromatography/mass spectrometry techniques provide structural information on polar macromolecules that have previously been beyond the scope of established methods. In addition to technological advances, large multidisciplinary field programs have provided important frameworks and contexts within which to interpret organic geochemical data, while novel sampling techniques have been developed that allow for the collection of more representative samples and their detailed analytical manipulation. Two particular analytical approaches are highlighted in this chapter—NMR spectroscopy as a powerful tool for structural characterization of complex macromolecules, and compound specific carbon isotope (^{13}C and ^{14}C) analysis as probes for the cycling of organic matter in the ocean through space and time.

P0015 Finally, we outline new as well as unresolved questions which provide future challenges for marine organic biogeochemists, and discuss emerging analytical approaches that may shed new light on organic matter cycling in the oceans. For example, (i) the source of "old" dissolved organic carbon (DOC) in the deep sea have yet to be resolved; (ii) the molecular-level composition of the majority of organic matter buried in marine sediments evades elucidation; and (iii) while planktonic archaea have been found to be amongst the most abundant organisms in the ocean, the role in biogeochemical cycles and their legacy in the sedimentary record are only beginning to be considered. Such fundamental observations and questions continue to challenge us, and limit our understanding of the processes underpinning organic matter cycling in the oceans.

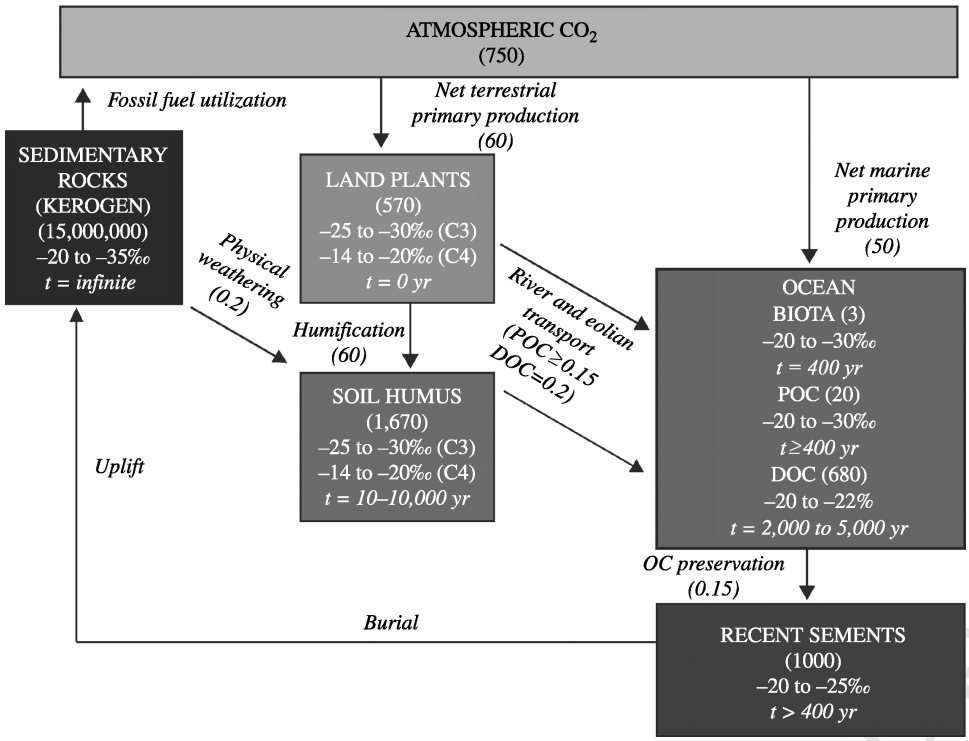
P0020 The discipline of marine organic geochemistry has expanded and evolved greatly in recent years. Hence, we have had to be selective in our coverage of new developments. This review, therefore, is by no means comprehensive and there are many important and exciting aspects of marine organic geochemistry that we have not covered. Comprehensive discussions of some of these aspects are to be found in the following review papers and chapters: soil OC (Hedges and Oades, 1997[bib62]), terrestrial OC inputs to the oceans (Hedges *et al.*, 1997; Schlunz and Schneider, 2000[bib142]), organic matter preservation (Tegelaar *et al.*, 1989[bib162]; de Leeuw and Largeau, 1993[bib27]; Hedges and Keil, 1995 [bib60]), lipid biomarkers (Volkman *et al.*, 1998 [bib170]), bacterial contributions (Sinninghe Damste and Schouten, 1997[bib150]), deep biosphere (Parkes *et al.*, 2000[bib122]), eolian inputs (Prospero *et al.*, 2003[bib130]), black carbon (BC) (Schmidt and Noack, 2000[bib143]), gas hydrates (Kvenvolden, 1995[bib89]), water column particulate organic matter (POM) (Wakeham and Lee, 1993[bib171]), carbon isotopic systematics (Hayes, 1993[bib57]), and use of ^{14}C and ^{13}C as tracers of OC input (Raymond and Bauer, 2001). Q1 Q2

P0025 In this chapter two pools of organic matter (OM) are discussed in detail. POM is manifestly heterogeneous, composed of all sorts of particles resulting from a wide range of inputs and a multitude of processes acting on them. In effect, sedimentary POM is chemically and spatially heterogeneous and much effort needs to be focused on sampling, fractionation, and bulk characterization rather than on detailed molecular-level studies. This situation contrasts sharply with the study of DOM, which, despite its largely macromolecular nature, appears to be remarkably uniform in composition throughout the oceans. Here, the prime need is for studies of the colloid processes involved and detailed molecular-level analysis of the composition and conformation of the refractory DOM in order to provide a basis for explaining its apparent lack of bioavailability, and to answer the question: why does DOM persist for years, even millennia, in the deep ocean?

6.07.2 RESERVOIRS AND FLUXES S0010

6.07.2.1 Reservoirs S0015

F1 P0030 Figure 1 depicts the major components of the OC cycle on and in the Earth's crust. Greater than 99.9% of all carbon in the Earth's crust is stored in sedimentary rocks (Berner, 1989[bib12]). About 20% of this total ($\sim 1.5 \times 10^7$ Gt) is organic, and the majority ($>90\%$) of the OC in these consolidated sediments is "kerogen," operationally defined as macromolecular material that is



F0005 **Figure 1** The global OC cycle. Numbers in yellow and in parentheses are approximate reservoir sizes (10^{15}g C = Gt) and italized in red are approximate fluxes (10^{15}g C yr^{-1}). Nonitalized numbers in white are Q61 approximate ranges for stable carbon isotopic compositions (δ^{13}C, per mil) and *italized* numbers in white are approximate radiocarbon ages (yr BP).

insoluble in common organic solvents and non-oxidizing acids (Durand, 1980[bib30]). Most kerogen is finely disseminated in sedimentary rocks (shales and limestones) which, on average, contain ~1% organic matter. Organic-rich deposits that include the World's fossil fuel reserves (coal, oil shales, and petroleum) account for less than 0.1% of total sedimentary OC (Hunt, 1996 [bib74]). Of the small fraction of organic matter that is not in the form of relict carbon sequestered in ancient sedimentary rocks, almost two-thirds resides on the continents. Approximately 25% of this "terrestrial" OC (~570 Gt) is in the form of standing biomass (plant tissue), with a further 70 Gt of plant litter on the soil surface (Post, 1993 [bib127]), and almost 1,600 Gt residing within the upper 1 m of soils and peat deposits (Eswaran *et al.*, 1993[bib35]).

P0035 Marine biota comprise only ~3 Gt of OC, and sinking and suspended particulate OC account for a further 10–20 Gt. The majority of OC in the oceans is in the form of DOC (680 Gt) and organic matter sequestered in the upper meter of marine sediments (~1,000 Gt). Concentrations of marine DOC are highest in the upper ocean, and in the coastal zone. Typical open ocean DOC concentrations in surface seawater range from 60 μM to 80 μM. In the coastal zone, concentrations may climb to in excess of 200 μM, although concentrations rapidly decrease within a few kilometers of shore (Vlahos *et al.*, 2001). The inventory of Q3 marine OC is fixed by the concentration of DOC in the deep ocean, which is relatively constant at 42 μM, although small variations of a few μM C have been reported (Hansell and Carlson, 1998 [bib53]). These variations are intriguing, in that they suggest active cycling of DOC in the deep sea. North Atlantic Deep Water, Antarctic Bottom Water, and other deep-water masses all carry the same burden of DOC, even though they are formed at different latitudinal extremes and under very different forcing conditions. Why the concentration of DOC is so constant in the deep sea is a mystery, but the narrow range of DOC values measured in the global ocean implies a very tightly controlled feedback between production and degradation.

P0040 Approximately 1,000 Gt of organic matter is sequestered in the upper meter of marine sediments. In the modern ocean, ~90% of OC burial occurs under oxygenated bottom waters along continental margins (e.g., Hedges and Keil, 1995 [bib60]). Up to 45% of OC burial occurs in deltaic sediments, which, in spite of nature as loci of

major riverine inputs, appear to include a major fraction of marine-derived organic matter (Keil *et al*., 1997[bib83]). An equivalent amount of OC is buried in nondeltaic sediments that are also proximal to land masses (Hedges and Keil, 1995 [bib60]), primarily on continental shelves and upper slopes (Premusic *et al*., 1982). Of the remainder, ~7% of OC is buried beneath highly productive regions with associated oxygen minimum zones (OMZs) and in anoxic basins. The balance (~5%) is buried pelagic abyssal sediments.

Much of the discussion in this chapter concerning sedimentary OC is centered on continental margin sediments, because this is the major locus of OC burial. In contrast, most DOM is held in the deep ocean basins, and hence discussion of the latter is largely in the context of the pelagic water column.

6.07.2.2 Fluxes

6.07.2.2.1 Terrigenous organic matter fluxes to the oceans

OC fluxes from sedimentary rock weathering on land are not well constrained but on geological timescales are believed to match OC burial in sediments (Berner, 1989[bib12]). Superimposed on this background of relict OC from sedimentary rock weathering are fluxes associated with terrestrial primary production. The global rate of net terrestrial photosynthesis is estimated to be in the range of 60 Gt y^{-1} (Post, 1993[bib127]). Approximately two-thirds of the resulting total plant litter is oxidized rapidly to CO_2 (Post, 1993[bib127]), while the remainder enters the soil cycle and is subject to further oxidation. Organic matter pools within soils exhibit different reactivities and turnover times that range from decades to millenia (Torn *et al*., 1997[bib165]). Over geologic timescales, however, the pervasive and continuous oxidative degradation and leaching and erosion processes on the continents result in little long-term storage of organic matter on the continents (Hedges *et al*., 1997). However, some fraction of this terrestrial (vascular plant-derived) OC and sedimentary rock-derived (relict) OC escapes oxidation and is delivered to the oceans. The delivery of terrigenous OC to the oceans is primarily *via* riverine or atmospheric (eolian) processes.

Riverine fluxes. Approximately 0.2 Gt each of dissolved and particulate OC are carried from land to sea annually by rivers (Ludwig *et al*., 1996 [bib92]). Much of this riverine organic matter appears to be soil derived based on its chemical characteristics (Meybeck, 1982[bib109], Hedges *et al*., 1994), although autochthonous sources may be important for the dissolved fraction (Repeta *et al*., 2002[bib139]). It is now recognized that, on a global basis, riverine discharge is dominated by low-latitude tropical rivers. This not only includes major systems such as the Amazon, and Congo, but also includes the numerous smaller rivers draining mountainous tropical regions (Nittrouer *et al*., 1995[bib117]), most notably in Papua New Guinea and other parts of Oceania, which are estimated to account for nearly 50% of the global flux of river sediment to the oceans (Milliman and Syvitski, 1992[bib113]). During the present-day high sea-level stand, much of the particulate OC associated with riverine discharge is trapped and buried on continental shelves (Berner, 1982; Hedges, 1992[bib59]). However, some rivers discharge much of their terrestrial OC load beyond the shelf due either to turbidity flows down submarine canyons (e.g., Congo, Ganges, Brahmaputra), to the presence of a narrow shelf (e.g., on the eastern flank of Papua New Guinea), or the influence of ice-rafting as an addition mode of sediment entrainment and export on polar margins (e.g., (Macdonald *et al*., 1998 [bib93]).

Eolian fluxes. Eolian fluxes of organic matter from land to sea are much less well constrained than riverine inputs. They have been estimated to be <0.1 Gt yr^{-1} (Romankevich, 1984). While these flux estimates imply lesser importance of eolian inputs compared to riverine OC contributions, this mode of delivery may be significant in a regional context. In particular, marine locations downwind from major dust sources (principally in eastern Asia and western Africa) are influenced profoundly by eolian inputs of OC and other detrital components. In addition, eolian transport can deliver terrigenous materials to remote locations of the oceans, far from the influence of rivers. For such regions (e.g., central equatorial Pacific Ocean) eolian OC fluxes may be important both in terms of POMin the water column and underlying sediments (Gagosian and Peltzer, 1986[bib38]; Zafiriou *et al*., 1985 [bib183]; Prospero *et al*., 2003[bib130]; Eglinton *et al*., 2002[bib34]).

6.07.2.2.2 Water column fluxes and the burial of OC in sediments

The turnover time and fluxes of DOC into the ocean are obtained by comparing the reservoir size and radiocarbon age. The ocean inventory of DOC is ~680 Gt, and nearly all of this carbon resides in the deep sea, where concentration profiles and radiocarbon values are constant with depth. DOC ages by ~1,000 yr as deep seawater moves from the Atlantic to the Pacific Basin, but even in the Atlantic, DOC radiocarbon values are

significantly depleted relative to DIC (Druffel *et al.*, 1992[bib29]). DOC persists in seawater through several ocean mixing cycles. The average age of DOC in the deep ocean is approximately 5,000 yr. Assuming a steady-state ocean, and that all this carbon is synthesized with a radiocarbon age equivalent to atmospheric carbon dioxide via marine production, then the annual flux of DOC into and out of the deep sea reservoir is $\sim$0.1 Gt C yr^{-1}. This flux is comparable to the delivery of terrestrial DOC to the ocean by rivers, but very small compared to annual marine production (60–75 Gt C yr^{-1}). Only 0.1–0.2% of annual marine production needs to be fixed into the permanent reservoir to maintain it, making the processes that sequester and remove carbon nearly impossible to track.

P0070 Marine photosynthesis by unicellular phytoplankton produces OC at a comparable rate to land plants (Hedges, 1992[bib59]). Only $\sim$10% of the net primary production escapes the upper 100 m of the water column. This vertical export occurs in the form of sinking fecal pellets produced by zooplankton that graze upon the phytoplankton, and as aggregates of cellular debris ("marine snow") (Alldredge *et al.*, 1993[bib2]; Alldredge and Silver, 1998[bib1]). The rain of particulate organic carbon (POC) out of the surface ocean attenuates exponentially through the water column, and only $\sim$10% of the OC sinking out of the euphotic zone reaches an average seafloor depth of 4,000 m (Suess, 1980[bib159]). Subsequent to losses in organic matter through the water column, a further 90% or more of that deposited on the seafloor is degraded, leaving $\sim$0.1% of organic material originally synthesized in the surface ocean to be ultimately preserved in sediments underlying most of the open ocean (Wakeham *et al.*, 1997[bib172]). Global burial efficiencies exceed 0.1%, because a significant amount of organic matter is deposited on continental margins and in oxygen-deficient regions where burial efficiencies are considerably higher (Berner, 1989[bib12]). Estimates for the global rate of OC burial in marine sediments range from 0.1 Gt yr^{-1} to 0.6 Gt yr^{-1} (Berner, 1989 [bib12]).

P0075 In addition to vertical transport, export of OC from the margins to the ocean interior is being increasingly recognized as of significance (Bauer and Druffel, 1998[bib8]; Thomsen and Van Q9 Weering, 1998[bib163]; Ransom *et al.*, 1998). Some regions of the coastal ocean produce more OC than they respire (Smith and Hollibaugh, 1993[bib155]), suggesting that a fraction of this nonrespired, unburied OC is available for export from margins to the deep ocean (Wollast, 1991 [bib182]). Lateral transport of organic matter from margins to pelagic and abyssal environments has also been invoked to help explain carbon and oxygen imbalances in the deep ocean (Smith *et al.*, 1994; Jahnke *et al.*, 1990). Q10 Q11 Radiocarbon studies also provide evidence for basin-ward export of OM from the ocean margins. For example, Bauer and co-workers (Bauer and Druffel, 1998[bib8]; Bauer *et al.*, 2001[bib9]) observed suspended POM (SPOM) (and DOM) in Mid-Atlantic Bight slope and rise waters that are concurrently older and higher in concentration than in the adjacent North Atlantic gyres. While there are several potential origin(s) for this old, ^{14}C-depleted carbon, sediment resuspension and advection from the shelf and upper slope (Anderson *et al.*, 1994[bib5]; Churchill *et al.*, 1994[bib22]) is a likely explanation.

P0080 In addition, the chemical nature of advected particulate matter may favor its preservation over biogenic debris directly produced in surface waters. Even when vertical transport of recently produced surface ocean-derived material is rapid (e.g., seasonal thermocline breakdown, rapidly sinking POM), this fresher material may be more susceptible to degradation relative to older, margin-derived material. Thus, the ^{14}C age and concentration of suspended POC in the deep ocean may be maintained by greater relative inputs from the margins than from recent surface production, and may be partly responsible for the apparent old age of POC observed in deep North Atlantic and Pacific central gyres. It remains uncertain whether or not the presence of "old" POC and DOC in slope and rise waters (Bauer and Druffel, 1998 [bib8]) reflects pre-aged terrigenous organic matter (from continental soils or sedimentary rocks) rather than organic matter of marine origin produced on the margin and temporarily sequestered in shelf and upper slope sediments.

6.07.3 THE NATURE AND FATE OF TERRIGENOUS OC DELIVERED TO THE OCEANS S0035

6.07.3.1 Background S0040

P0085 A long-standing paradox evident from global OC flux estimates (Figure 1) is that while the combined global discharge of particulate and dissolved OC from rivers is twice the OC burial rate in marine sediments, OM in both the water column and underlying sediments is apparently dominated by autochthonous inputs (e.g., Hedges and Mann, 1979; Gough *et al.*, 1993[bib49]; Q12 Aluwihare *et al.*, 1997[bib4]). This implies that most terrigenous OM delivered to the oceans must be efficiently mineralized, and that the ocean is operating as a net heterotrophic system, accumulating less sedimentary OC than it receives via riverine discharge alone

(Smith and MacKenzie, 1987[bib156]). Potential explanations for this paradox are emerging as a result of recent studies, and our improved understanding of the composition of OM in the ocean.

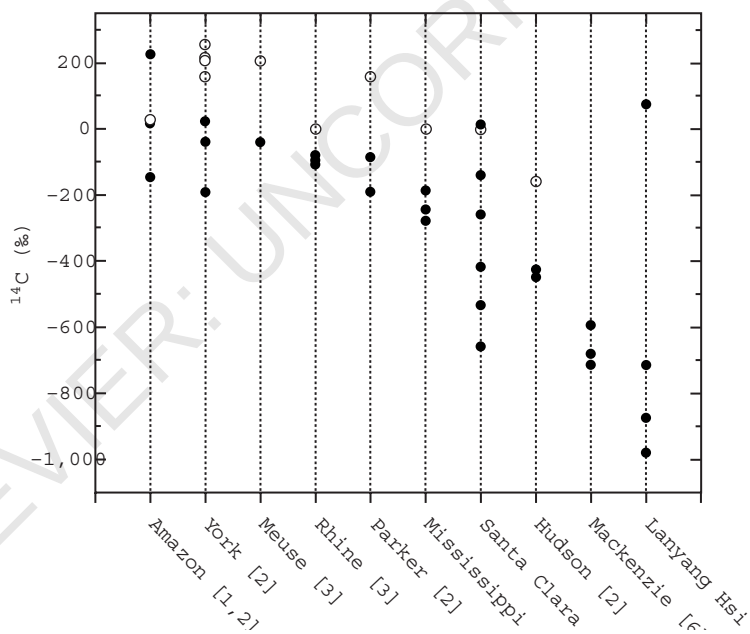
P0090 There are several unresolved issues underlying present estimates and assumptions on the abundance and fate of terrigenous organic matter in the oceans. The first is the composition and proportion of terrigenous OC that is buried in margin sediments proximal to the continental source, a second is the proportion of terrestrial OC that enters the deep ocean, and a third is the variability in input composition and flux, mode of delivery and geographic distribution.

S0045 6.07.3.2 Terrestrial Organic Matter in River Systems

P0095 One particularly intriguing question is whether a significant component of deep-sea DOC is of terrestrial origin. The annual flux of DOC through rivers is of the same magnitude as the annual flux of DOC out of and into the deep ocean reservoir, and measurements of $DO^{14}C$ in rivers show the carbon to have largely modern radiocarbon values F2 (see Figure 2). An annual flux of 0.1 Gt C with a modern radiocarbon value would support the deep-sea DOC reservoir. Lignin oxidation products, which are good biomarkers for terrestrial OC, have been measured at low concentrations in open ocean DOM, providing molecular-level confirmation of a terrestrial origin for at least some fraction of this carbon (Meyers-Schulte and Hedges, 1986[bib110]; Opsahl and Benner, 1997). Q13 Terrestrial carbon could also enter the DOC reservoir by desorption from particulate organic matter. As discussed later in this chapter, POM enters the ocean with a coating of terrestrial OC that is rapidly replaced by marine OC. The load of organic matter introduced by POM could be injected into seawater as DOM. Radiocarbon values for riverine POM are highly variable, but are often depleted relative to modern carbon. If new DOC is pre-aged in this manner, then the annual flux of DOC would be in excess of 0.1 Gt C yr^{-1}.

P0100 Marine DOC has stable carbon isotope values between −21‰ and −22‰ (Druffel *et al*., 1992 [bib29]) consistent with a largely marine source. While these data seem to exclude a significant contribution from C3 terrestrial plants, there is increasing evidence for an important contribution from C4 plants to persistent POM in marine sediments on the continental shelf and slope (see below). Desorption of C4 plant carbon and incorporation into oceanic DOC would be difficult to detect by isotopic or molecular biomarker analyses.

P0105 The sources, abundances, and compositions of SPOM carried by rivers vary significantly, depending on the characteristics of the drainage basin (Onstad *et al*., 2000[bib119]; Raymond and Bauer, 2001a[bib136]). For example, Raymond and Bauer

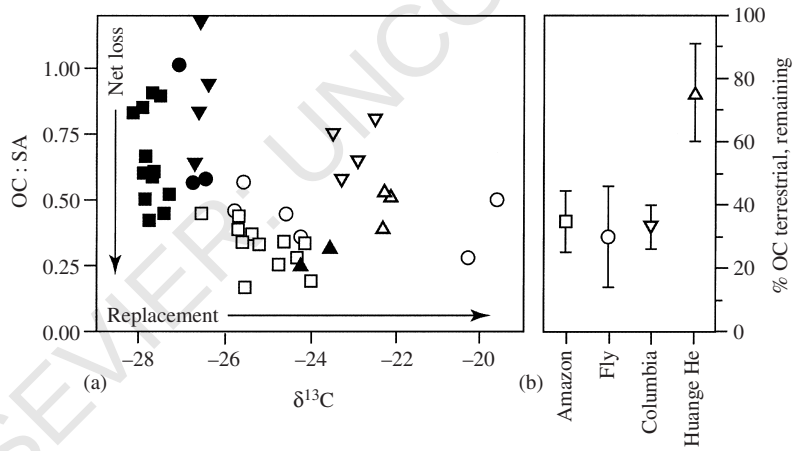


F0010 **Figure 2** Variations in the ^{14}C content, expressed as $\Delta^{14}C$ (‰) of DOC (open symbols) and suspended POC (closed symbols) from a range of river systems. Data from: [1] Hedges *et al*. (1986); [2] Raymond and Bauer (2001); [3] Megens *et al*. (2001)[bib107]; [4] Goni *et al*. (unpublished); [5] Masiello and Druffel (2001)[bib98]; [6] Eglinton *et al*. (unpubl.); [7] Kao and Lui (1996). Q64

(2001b)[bib137] demonstrate significant spatial and temporal variation in $\Delta^{14}C$ and $\delta^{13}C$ values ($\Delta^{14}C$ is the measured ^{14}C concentration normalized to pre-industrial atmospheric values following Q14 Stuiver and Pollach (1977). $\Delta^{14}C = (\%\text{modern} \times e\lambda t - 1) \times 1{,}000$, reported in per mil (‰), where $\lambda = {}^{14}C$ decay constant and $t =$ calendar age) of riverine dissolved and particulate OM, reflecting varying source and ages of terrestrial and aquatic productivity. As an example of the heterogeneity in SPOM signatures, Figure 2 shows the radiocarbon contents (expressed as $\Delta^{14}C$) of suspended OC reported for a range of river systems. Some systems transport predominantly "fresh" carbon as indicated by the presence of "bomb" ^{14}C ($\Delta^{14}C$ values greater than 0‰ reflect the atmospheric signature from aboveground nuclear weapons testing during the 1950s and early 1960s), while others carry carbon that is dominated by material older than 5×104 yr ($\Delta^{14}C$, $-1{,}000$‰). For some river systems, the ^{14}C contents of SPOM vary temporally, presumably reflecting variations in sediment provenance, mode of erosion or other characteristics of the drainage basin. Thus, contrary to earlier notions that rivers exclusively export ^{14}C-enriched OM to the ocean (Hedges Q15 *et al.*, 1986), many rivers export a significant fraction of old, ^{14}C depleted DOC and POC to the oceans (Raymond and Bauer, 2001a[bib136]). This old SPOM could reflect pre-aged, vascular plant-derived OC stored in an intermediate reservoir (e.g., soils), and/or contributions of relict OC from sedimentary rock weathering, and/or contributions from aquatic production utilizing old dissolved inorganic carbon (the "hardwater" effect).

The age variations highlighted above are undoubtedly coupled to differences in the chemical composition and reactivity of SPOM. Onstad *et al.* (2000)[bib119] examined elemental, stable carbon isotope and lignin phenol characteristics of SPOM from rivers draining the south central US. Variations in $\delta^{13}C$ values, ranging from -18.5‰ to -26.4‰, were attributed to the contributions from C3 and C4 plants in the catchment area, and hence to temperature and hydrologic patterns in the drainage basin. Lignin–phenol compositions reflect degraded, angiosperm-rich vegetation. Results from this and other studies indicate that highly degraded soil OM is a major component of fine-grained POM transported by rivers, and that most riverine OM residing in the particulate fraction is associated with mineral phases.

In large fluvial systems, estuaries and deltas serve as the interface between the rivers and the ocean, and are sites of intensive organic matter reworking and production (Hedges and Keil, 1999 [bib61]). Recent work has revealed that extensive removal of terrestrial OC from suspended particles occurs at these locations. In one approach to quantify terrestrial OC losses, Keil *et al.* (1997) [bib83] argued that detrital mineral surface area can serve as a conservative tracer for riverine discharged POM. Accordingly, changes in OC to specific mineral surface area (OC:SA) ratios should indicate net OC exchange between upstream and downstream locations. When applied in conjunction with $\delta^{13}C$ as a source indicator of marine and terrestrial OC, this can yield estimates of the fraction of terrestrial OC entering the ocean as riverine SPOM F3 that is deposited in deltaic systems (Figure 3).



F0015 **Figure 3** Loss of terrestrial OC in deltaic systems. (a) Organic carbon to mineral surface area ratio (OC:SA) plotted against bulk stable carbon isotopic compositions for riverine suspended sediments (closed symbols) and deltaic surface sediments (open symbols). A shift to lower OC : SA values indicates net loss of organic matter, and a shift to heavier (i.e., ^{13}C-enriched) isotopic compositions indicates increasing contributions from marine organic matter. (b) The average (±1 SD) total amount of terrestrial OC persisting in deltaic sediments, based on the changes in OC:SA and $\delta^{13}C$ composition between river suspended sediments and deltaic sediments for four river systems (after Keil *et al.*, 1997[bib83]).

Using this approach, Keil *et al.* (1997)[bib83] calculate average OC loadings within the Amazon River (0.67 mg C m^{-2}) that are approximately twice those of the Amazon Delta (0.35 mg C m^{-2}), while $\delta^{13}C$ measurements suggest that approximately two-thirds of the TOC in deltaic sediment is terrestrial. Together, these data imply that >70% of the Amazon fluvial POM evades sequestration in deltaic sediments. Extrapolating losses of riverine SPOM for a range of river/delta systems (Columbia, USA; Fly, New Guinea; and Huange-He, China), Keil *et al.* (1997)[bib83] calculate a global loss of fluvial POM in delta regions of ~0.1 Gt.

P0120 The magnitude of this loss is thus substantial, and comparable to flux estimates for the delivery of terrigenous OC to the oceans (Figure 1). However, while the above studies imply low burial efficiencies for fluvial POM in deltaic environments, it is uncertain whether the apparent losses of riverine POM reflect its complete mineralization or export to the ocean interior either in dissolved or particulate form (Edmond *et al.*, 1981[bib32]). Moreover, the extent of terrestrial OC export and burial from river systems that do not form deltaic deposits is less well constrained.

S0050 #### 6.07.3.3 Quantitative Importance of Terrigenous OC in Marine Sediments

P0125 There is still much debate about the abundance and composition of terrestrial OC in both margin and pelagic sediments. Terrigenous organic matter contributions may be substantial for several reasons.

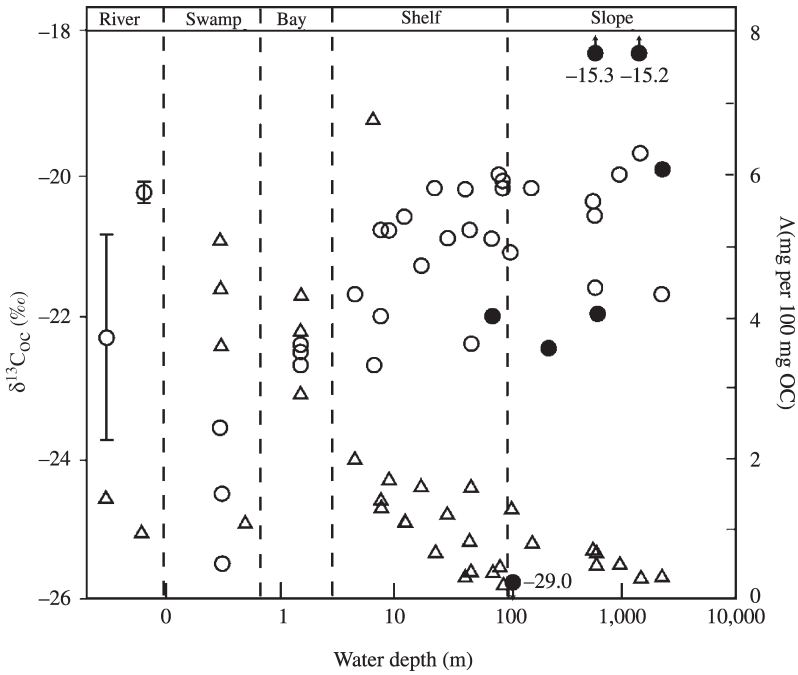
P0130 • As pointed out above, the flux of particulate OC emanating from the continents carried by rivers alone is sufficient to account for the burial of OC in marine sediments.

P0135 • Most OC burial in surface sediments occurs along continental margins, proximal to the supply of terrestrial OC.

P0140 • Much of the terrestrial OC delivered to the oceans will have been subject to extensive degradative processes in soils and rivers, implying that the fraction that survives these processes might be refractory with high potential for preservation.

P0145 Despite these considerations, terrestrial OC contributions to the marine sedimentary OM pool have generally been considered to be low. These conclusions are based on compositional studies, including bulk stable carbon isotopic ($\delta^{13}C$) and elemental (atomic $C_{organic}/N_{total}$) and biomarker compositions. Loss of terrestrial OC in deltaic systems has already been discussed (Keil Q16 *et al.*, 1997[bib83]). Hedges *et al.* (1979) also observed sharp reductions in the abundance of lignin-derived phenols (as determined by yields after CuO oxidation) in Gulf of Mexico sediments with increasing distance from riverine sources F4 (Figure 4). Compositional information stemming from the same measurements indicates that the lignin present in these samples originates from nonwoody angiosperm sources (e.g., grasses), and is highly modified. Both the terrestrial biomarker abundances and bulk stable carbon isotopic compositions (Hedges *et al.*, 1979) are in accord with the replacement of terrestrial C3 vegetation with marine OC for sediments deposited progressively further offshore (Figure 4). Thus, despite proximity of a major river system (Mississippi/Atchafalaya), an important source of terrigenous sediment to the shelf, bulk sedimentary OM composition fails to indicate the presence of significant terrestrial input. Moreover, Gough *et al.* (1993)[bib49] observed only trace quantities of lignin phenols in abyssal North Atlantic Ocean sediments.

P0150 However, some studies indicate that data of the type reported above may lead to underestimates of the proportion of terrigenous organic matter in marine sediments. For example, Onstad *et al.* (2000)[bib119] showed that the Mississippi currently discharges isotopically "heavy" ($\delta^{13}C$ ~ −20‰), lignin-poor POM that is difficult to distinguish from marine plankton remains in sediments from the Gulf of Mexico (Figure 4). Moreover, Goni *et al.* (1997[bib46], 1998[bib47]) analyzed surface sediments from two offshore transects in the northwestern Gulf of Mexico using a range of techniques, including compound-specific $\delta^{13}C$ analysis of lignin-derived phenols. Bulk OC radiocarbon analyses of core top sediments yield depleted $\Delta^{14}C$ values, indicating that a significant fraction of the sedimentary carbon is "pre-aged," and most likely of allochthonous origin. Lignin phenol $\delta^{13}C$ values for inner shelf sediments are relatively depleted (ave., −26.3‰), consistent with C3 vascular plant inputs, but are markedly enriched in ^{13}C at the slope sites (ave., −17.5‰ for the two deepest samples) (Figure 4). Goni *et al.* (1997)[bib46] interpret these molecular and isotopic compositions to indicate that a significant fraction (>50%) of the lignin, and by inference land-derived OC, in slope sediments ultimately originated from C4 plants. Consistent with Onstad *et al.* (2000)[bib119] the source of this material is likely to be soil organic matter eroded from the extensive grasslands of the Mississippi River drainage basin. The mixed C3 and C4 land plant sources, the highly degraded state of this material, and the differential transport effects (i.e., winnowing, resuspension, and lateral advection through nepheloid transport) hampers its recognition and quantification in shelf and slope sediments. These findings bear upon other river-dominated margins



F0020 **Figure 4** Variations in $\delta^{13}C$ of total OC (left axis: ‰, open circles) and the abundance of lignin-derived syringyl and vanillyl phenols (right axis: Λ, mg per 100 mg OC, triangles) in surface sediments from various water depths of the Gulf of Mexico in the vicinity of the outflow from the Mississippi River system (after Goni *et al.*, 1997[bib46]). Also shown are average values for the same parameters determined on suspended particulate matter from the upper and lower reaches of the Mississippi River (extreme left column, error bars = 1 SD; data from Onstad *et al.*, 2000[bib119]). In addition, $\delta^{13}C$ values are indicated for one lignin phenol (syringic acid filled circles), for selected shelf and slope samples (after Goni *et al.*, 1997[bib46]).

where drainage basins may include a significant proportion of C4 vegetation, and highlight the difficult in quantitatively assessing terrigenous OC inputs.

P0155 Prahl *et al.* (1994)[bib128] also concluded that terrestrial OC contributes significantly to Washington Margin sediments. These authors determined bulk elemental and stable carbon isotopic compositions and concentrations of a range of vascular plant biomarkers (epicuticular wax-derived *n*-alkanes, lignin-derived phenols and cutin-derived hydroxyalkanoic acids) for sediments from the Columbia River basin and adjacent margin. Using end-member values determined empirically by two independent means, Prahl *et al.* (1994)[bib128] estimated terrestrial OC contributions of ~60%, 30% and <15% for sediments on the shelf and slope of the Washington margin, and the adjacent Cascadia Basin, respectively.

P0160 As noted earlier, as of early 2000s, all studies have focused on only a few major river systems (e.g., Mississippi, Amazon, Columbia) that may not be representative of fluvial inputs worldwide. While our perspective on terrigenous OC inputs has been biased towards large river systems, there is a growing body of evidence that the majority of terrestrial OC delivery to the oceans occurs via numerous small rivers draining mountain regions in the tropics (Milliman and Syvitski, 1992[bib113]). The contrasting modes of OC delivery between large deltas (passive, hydrodynamic control) and small mountainous rivers (episodic, high-energy, poorly sorted particles) could have a significant influence on the proportion and location of terrestrial OC that is deposited in marine sediments (Leithold and Blair, 2001[bib91]; Masiello and Druffel, 2001[bib98]). In addition to terrestrial OC inputs at low latitudes, our knowledge of terrestrial OC inputs to the high-latitude oceans is limited. Here, ice rafting serves as another mechanism for export of terrestrial OC to the ocean basins. While some data indicates that terrestrial OC may indeed comprise a substantial fraction of the OM buried in Arctic sediments (Schubert and Stein, 1996[bib148]; Macdonald *et al.*, 1998[bib93]), traditional tools for source apportionment are not well suited to address this problem. For example, bulk stable carbon isotopes are of limited use as source indicators because of the isotopically depleted nature of phytoplankton in the polar oceans (Rau *et al.*, 1989[bib135]; Goericke and Fry, 1994[bib43]). Similarly, while eolian OC inputs to the oceans are generally considered to be minor, major dust fluxes emanating from West Africa carry a substantial

C4 plant signature (Huang *et al*., 2000[bib73]; Eglinton *et al*., 2002[bib34]), confounding estimates of marine and terrestrial OC in underlying sediments based on bulk stable carbon isotopic measurements.

S0055 #### 6.07.3.3.1 Black carbon

P0165 One group of exclusively terrestrially derived organic components found in marine sediments which has been the subject of renewed interest in recent years are the carbonaceous particles from incomplete combustion processes. These products, collectively termed "BC" (Goldberg, 1985 [bib44]), are ubiquitous in the environment, and may comprise a significant fraction of OC in contemporary marine sediments (Middleburg Q17 *et al*., 2000[bib112]; Masiello and Druffel, 1998 [bib97]; Gustafsson and Gschwend, 1998[bib51]). Schmidt and Noack (2000)[bib143] reviewed the state of knowledge of BC in soils and sediments. BC can be produced via condensation of volatiles to highly graphitized particles ("soot-BC") or by formation of solid residues through direct carbonization of particulate plant material ("char-BC"). Both forms of BC are relatively inert and are distributed globally by water (fluvial) and wind (atmospheric) transport. Although BC is directly emitted and transported during biomass burning, available radiocarbon data suggest that some BC is sequestered in soils and aquatic sediments for millennia prior to subsequent export to the oceans (Masiello and Druffel, 1998[bib97]; Eglinton *et al*., 2002[bib34]).

P0170 Limited progress has been made on standardizing techniques for the quantitation and characterization of BC. These techniques and definitions have primarily been developed with regard to BC in atmospheric particles. The problem of defining and quantifying BC in sediments adds a further layer of complexity, and hence reservoir sizes and fluxes are subject to considerable uncertainty. Current estimates of global BC production (0.05– Q18 0.27 Gt yr^{-1}; Kulbusch and Crutzen, 1995) are of the same order as those of riverine input of POC to the ocean and OC burial in marine sediments. If these flux estimates are correct, BC may represent a significant sink in the global OC cycle (Kuhlbusch, 1998[bib87]), and constitute a significant fraction of the carbon buried in soils (Skjemstad *et al*., 1996[bib154]; Schmidt *et al*., 1999[bib144]) and marine sediments (Middelburg *et al*., 2000[bib112]; Masiello and Druffel, 1998 [bib97]).

P0175 Gustafsson and Gschwend (1998)[bib51] determined concentrations and fluxes of BC in modern ocean margin sediments off northeastern USA using a thermal oxidation method (Gustafsson *et al*., 1997[bib52]). Core-top BC concentrations indicate that BC comprises a significant component of OC budgets for coastal sediments. Down-core trends were consistent with anthropogenic fossil-fuel combustion dominating BC input, while the fractional abundance of BC increased in deeper sediment sections, implying that it is resistant to degradation and may be selectively preserved (Wolbach and Anders, 1989 [bib181]). Suman *et al*. (1997)[bib160] calculated the pre-industrial global burial of BC to be ~ 10 Tg yr^{-1}, which corresponds to $\sim 11\%$ of the estimated global marine sediment burial of TOC.

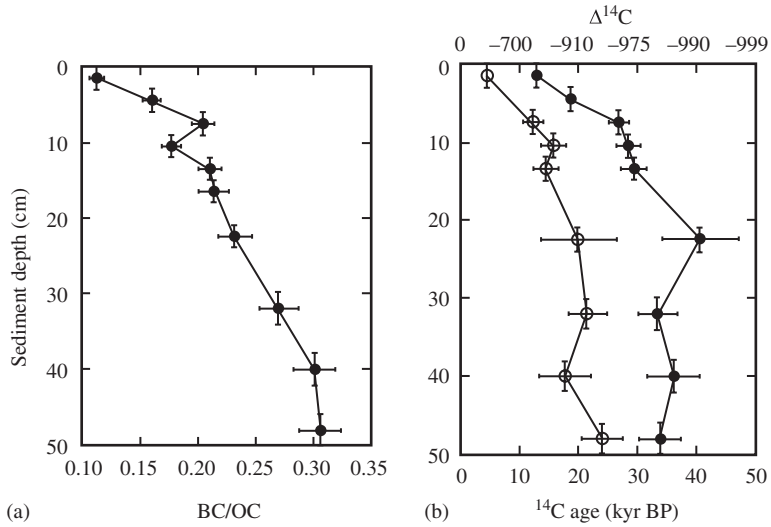
P0180 Middleburg *et al*. (1999)[bib111] compared BC determined using thermal and chemical (hot nitric acid) oxidative pre-treatments in a range of marine sediments. They found that the latter significantly overestimates combustion-derived phases. Nevertheless, the lower BC estimates obtained from the thermal oxidation method account for between 15% and 30% of total OC. Examination of BC concentrations across a relict oxidation front in a Madeira Abyssal Plain turbidite provided evidence for significant BC degradation under prolonged exposure to oxygenated bottom waters.

P0185 Masiello and Druffel (1998)[bib97] measured the abundance and radiocarbon content of BC (isolated by wet chemical oxidation) in sediment cores from two deep Pacific Ocean sites. They found BC comprises 12–31% of the total sedimentary OC, and was between 2,400 ^{14}C yr and 13,000 ^{14}C yr older than non-BC sedimentary F5 OC (Figure 5). For sediment intervals deposited prior to the Industrial era (i.e., free of BC inputs from fossil fuel utilization), the authors argue that the older ages for BC must be due to storage in an intermediate reservoir before deposition. Possible intermediate pools are oceanic DOC and terrestrial soils. They conclude that if DOC is the intermediate reservoir, then BC comprises 4–22% of the DOC pool. If soils are the intermediate reservoir, then the importance of riverine OC has been underestimated.

S0060 ## 6.07.4 A BIOPOLYMERIC ORIGIN FOR OCEANIC DOM

S0065 ### 6.07.4.1 Background

P0190 As deep water upwells to the surface, some 30–40 μM carbon is added to the dissolved phase (Peltzer and Hayward, 1995[bib126]). Although the mechanisms that fix carbon into DOC are not known, it has long been recognized that this new carbon represents water-soluble byproducts of algal photosynthesis (Duursma, 1963 [bib31]; Menzel, 1974[bib108]). Phytoplankton in laboratory culture and in seawater have been shown to exude OC (Hellebust, 1965; Iturriaga Q19 and Zsolnay, 1983[bib75]), and the release of



F0025 **Figure 5** Abundance of radiocarbon age of BC in slowly accumulating (~2.5 cm kyr^{-1}) deep-sea sediments from the Southern Ocean (54°S 176° 40′W): (a) a plot of the ratio of BC to total organic carbon (BC/OC) with sediment depth and (b) $\Delta^{14}C$ (per mil) and ^{14}C age (kyr BP) of BC (solid symbols) and non-BC sedimentary OC (open symbols) as a function of depth (after Masiello and Druffel, 1998[bib97]).

dissolved OC through exudation, grazing, cell lysis, or other processes fuels much of the microbial growth and respiration in the marine environment (Hellebust, 1967[bib66]; Nagata and Kirchman, 1992[bib115]). Stable isotope measurements of carbon standing stocks throughout the entire water column confirm an autochthonous origin for marine DOC, with values identical to marine particulate matter (−21‰ to −22‰) (Druffel *et al.*, 1992[bib29]). As DOC cycles through the water column, new carbon is somehow altered and sequestered into the more permanent, deep ocean carbon reservoir.

P0195 Although DOC production is a function of primary production, DOC accumulation is not. There are a few reports of transient, localized increases in DOC inventory following algal blooms (Holmes *et al.*, 1967[bib72]), and annual cycles of DOC inventory in the upper ocean share features in common with annual cycles of primary production (Duursma, 1963[bib31]; Holmes *et al.*, 1967[bib72]; Carlson *et al.*, 1994[bib19]). However, DOC concentrations are not well correlated with either phytoplankton biomass or primary productivity (Carlson *et al.*, 1994[bib19]; Chen *et al.*, 1995[bib20]). The accumulation of DOC in surface seawater results from a decoupling of production and removal processes over annual to decadal timescales, and it is convenient to subdivide DOC into at least three distinct reservoirs of differing reactivity (Carlson and Ducklow, 1995[bib18]). The largest reservoir in terms of production is very reactive, and supports most secondary production in the ocean. This fraction of DOC consists of a few μM C of soluble biochemicals (proteins, carbohydrates, lipids, etc.), which has a turnover time of hours to days, and may equal 10–30% of total primary production (Vaccaro *et al.*, 1968[bib166]; Mague *et al.*, 1980[bib94]; Jørgensen *et al.*, 1993[bib76]). The largest fraction of DOC in terms of total inventory is the nonreactive fraction. Nearly all the DOC in the deep ocean, and half the DOC in the surface ocean, is considered to be nonreactive based on radiocarbon measurements, which show this fraction to be 4,000–6,000 yr old (Williams *et al.*, 1969[bib180]; Druffel *et al.*, 1992[bib29]). This nonreactive component of DOC persists through several ocean-mixing cycles before remineralization or sequestration as particulate OC. Finally, the 30–40 μM DOC equal to the difference between deep and surface seawater DOC concentration values is considered to be reactive DOC, and cycles on seasonal to decadal timescales. Reactive DOC is produced in the surface ocean, and largely consumed as surface water is subducted into the deep ocean. The composition, cycling, and fate of reactive DOC has been the focus of much of the research on DOC completed since the 1990s.

6.07.4.2 High Molecular Weight DOM: Biopolymers or Geopolymers? S0070

P0200 The very old radiocarbon age of DOC was originally attributed to the structural complexity of the organic constituents that make up this fraction of marine organic matter. Simple biochemicals produced by marine bacteria,

algae, and animals were thought to react through abiotic or geochemically mediated reactions to form more complex humic-like substances that are metabolically unavailable to marine microorganisms (Gagosian and Stuermer, 1977[bib39]). The concept of organic matter humification in seawater follows earlier models of humification reactions in soils, and early studies on marine DOC sought to characterize and compare marine humic substances with humic substances extracted from terrestrial and freshwater environments in an attempt to better understand the reactions in each environment (Hatcher *et al*., 1980[bib56]; François, 1990[bib37]) These studies show marine DOM to have a low average molecular weight (< 1,000 Da), to be relatively rich in nitrogen and aliphatic carbon, and poor in aromatic carbon (Stuermer and Harvey, 1974[bib157]; Stuermer and Payne, 1976[bib158]). Chemical differences between marine and terrestrially derived humic substances could be attributed directly to the nature of biochemicals prevalent in each environment, and the differences in reaction conditions (e.g. light, presence of catalytic surfaces) (François, 1990[bib37]; Malcolm, 1990[bib95]). Marine and terrestrial humic substances represent two, chemically distinct, carbon reservoirs.

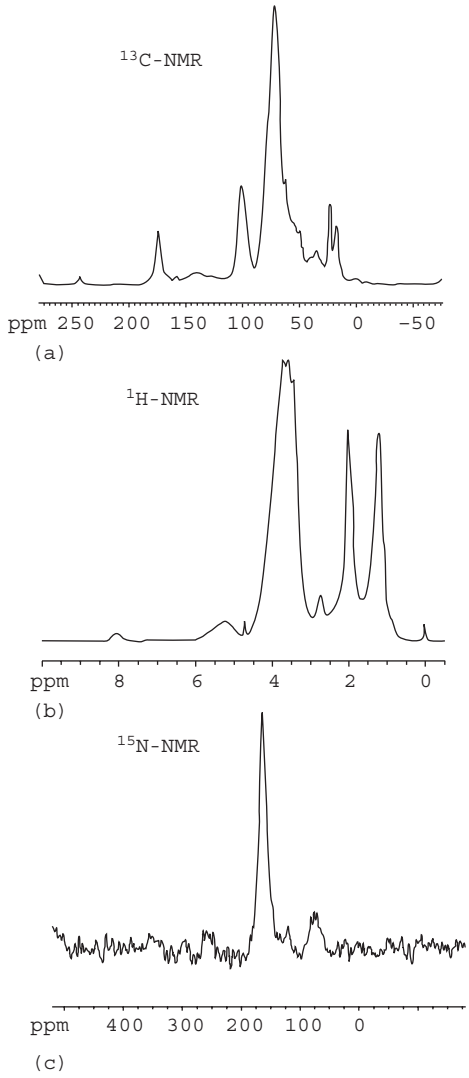
P0205 Marine humic substances are isolated by adsorption onto hydrophilic resins and contribute only a small fraction (10% or less) of total marine DOC. The difficulty in sampling DOC in the presence of much more abundant inorganic salts significantly slowed progress in marine DOM research for over a decade. Application of ultrafiltration, and especially large volume ultrafiltration made a much larger fraction (up to 40%) of DOC available for study (Buesseler *et al*., 1996 [bib16]). Ultrafiltration does not select strongly for the chemical characteristics of the organic matter as does resin adsorption, but selects on the basis of molecular size instead, and therefore preferentially isolates the high molecular weight (HMW) fraction of DOM. Initial studies of HMW DOM composition showed this fraction to be chemically distinct from humic substances (Benner *et al*., 1992[bib10]).

P0210 Our understanding of DOM composition and cycling has undergone a rapid change since the 1990s. Chemical studies of HMW DOM now show a composition that is rich in specific polysaccharides and proteins and remarkably uniform across diverse environments. These discoveries led Aluwihare *et al*. (1997)[bib4] to propose that a major fraction of HMW DOM arises directly from biosynthesis. The concept that marine DOM has a large component of metabolically resistant bioploymers is a sharp departure from earlier ideas that described DOM as a mixture of simple biomolecules that had experienced abiotic transformation (geopolymerization) into HMW substances (fulvic and humic substances). Support for the directly formed biopolymer hypothesis comes from the chemical composition of HMW DOM itself.

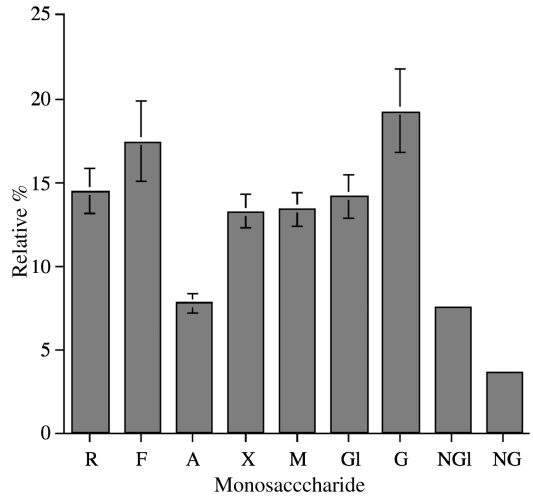
6.07.4.2.1 *Acylpolysaccharides in HMW DOM* S0075

P0215 NMR spectroscopy has proven to be the most effective technique for characterizing carbon functional groups in HMW DOM. The ^{13}C-NMR spectrum of HMW DOM collected at 15 m in the North Pacific Ocean surface is given F6 in Figure 6(a). Nearly identical spectra have been collected from the Atlantic Ocean, as well as from some lakes and rivers (McKnight *et al*., 1997 [bib106]; Repeta *et al*., 2002[bib139]). All ^{13}C-NMR spectra display a rather simple pattern of broad resonance from carboxyl (CO–(OH or NH); 175 ppm), alkene/aromatic (C=C;140 ppm), anomeric (O–C–O,100 ppm), alcoholic (H–C–OH; 70 ppm), and alkyl (CH_x;10–40 ppm) carbon (Figure 6(a)). From these spectra we can quantify the relative amounts of carbon associated with each class of functional group, and by inference, identify the major biochemical units in DOM. Carbon-13 NMR shows HMW DOM to be especially rich in carbohydrate (100 ppm (O–C–O), and 70 ppm (H–C–OH), which accounts for 76% of the carbon in the spectrum. The ratio of alcohol to anomeric carbon (70–100 ppm) is 4.5, within the expected range for most sugars (4–5). The importance of carbohydrate is confirmed through molecular-level analyses of monosaccharides which show neutral sugars to be abundant in HMW DOM (Sakugawa and Honda, 1985[bib140]; McCarthy *et al*., 1994[bib102]; Q20 Aluwihare *et al*., 1997[bib4]; Biesmith and Benner, 1998; Borch and Kirchman, 1998 Q21 [bib15]). However, the amount of carbohydrate determined by NMR is much higher than that measured by molecular-level techniques (76% versus 20%, respectively for Figure 6(a)). Reconciling NMR data and molecular-level techniques is currently a major challenge in understanding the composition of HMW DOM.

P0220 Sugar distributions are dominated by six neutral sugars—fructose, galactose, glucose, mannose, rhamnose, and xylose—which occur in approximately equimolar amounts. A seventh neutral sugar (arabinose), and two amino sugars (*N*-acetyl glucosamine and *N*-acetyl galactosamine) are also abundant, but occur at only half to one quarter the concentrations of other sugars. The relative amounts of these nine sugars, and their contribution to surface water HMW DOC vary remark-F7 ably little in fresh and marine waters (Figure 7). The uniformity in molecular and spectroscopic properties of many HMW DOM samples suggests that the fraction of HMW DOM enriched in



F0030 **Figure 6** NMR spectra of HMW DOM from surface seawater. (a) ^{13}C-NMR spectra can be used to quantitatively determine the functional groups, and by inference, the relative importance of different biochemical classes in HMW DOM. The spectra highlight the importance of carbohydrates (100 ppm and 70 ppm), carboxylic acids (175 ppm), and alkyl carbon (10–30 ppm). (b) ^{1}H-NMR also show the importance of carbohydrates (4 ppm) and alkyl carbon (1 ppm), but additionally show that acetyl groups most likely bound to carbohydrate are an important components. ^{15}N-NMR show that 80–90% of HMW DON is amide, while 10–20% is free amine. Quantitative analyses for acetate and nitrogen suggest that most amide in surface seawater is bound as *N*-acetyl amino sugars and protein residues. In the deep ocean HMW DOM however, most amide is nonhydrolyzable, and is of unknown molecular environment.



F0035 **Figure 7** The distribution of neutral and basic monosaccharides in HMW DOM. Hydrolysis of HMW DOM followed by monosaccharide analysis show a remarkably uniform distribution of sugars in samples from surface and deep ocean waters in all ocean basins. Important neutral sugars include rhamnose (R), fucose (F), arabinose (A), xylose (X), mannose (M), glucose (Gl), and galactose(G). Error bars show 1 SD in relative abundance of 12 HMW DOM samples collected from the Atlantic Ocean and Pacific Ocean between 1994 and 2001. Little change in the relative abundance of sugars is observed between ocean basins. Important amino sugars include *N*-acetyl glucosamine (NGl) and *N*-acety lgalactosamine (NG), which are less abundant than the neutral sugars. If all acetate is bound as *N*-acetyl amino sugars, then monosaccharide analyses significantly under-recover the amount of amino sugars in HMW DOM.

carbohydrate, acetate, and lipids is a well-defined family of biopolymers synthesized by marine algae (Aluwihare *et al.*, 1997[bib4]; Aluwihare and Repeta, 1999[bib3]). These polymers, referred to as acylpolysaccharide (APS) are ubiquitous in natural waters (Repeta *et al.*, 2002 [bib139]).

P0225 The ^{13}C-NMR spectrum of HMW DOM also includes contributions from carboxyl (CO–(OH or NH), 5% of total carbon), and alkyl (CH_x, 14% total carbon) functional groups, which may derive from proteins, lipids, or carbohydrates(deoxy- and methyl sugars). Hydrolysis of HMW DOM followed by extraction with organic solvent yields 4–8% of the total carbon in HMW DOM as acetic acid. Acetyl is easily recognized in the ^{1}H-NMR spectra of HMW DOM, where it appears as a broad singlet centered at 2 ppm (Figure 6(b)). Free acetic acid and its derivatives are not retained by ultrafiltration, and the acetyl in HMW DOM must be covalently bound to macromolecular material, most likely as an *N*-acetyl amino sugar. Acetyl contributes up to half the carboxyl carbon in the ^{13}C-NMR spectrum.

P0230 Elemental C/N and C/P ratios of HMW DOM lie between 13–16 and 300–800, respectively (McCarthy *et al.*, 1996[bib103]; Karl and Bjorkman, 2002[bib78]). Although C/P ratios are so

high that they prohibit a major contribution from organophosphorous compounds to HMW DOC, C/N ratios are sufficiently low that N-containing biochemicals must contribute an important fraction of DOM carbon. Natural abundance ^{15}N-NMR measurements show that 80–90% of HMW DON is amide (R-CON; Figure 6(c)) (McCarthy *et al.*, 1997[bib104]). Free amine groups contribute the remaining 10–20% of HMW DON that can be observed by NMR. Small amounts of other components, such as aromatic *N*-containing compounds, may also be present but are below the limit of detection by this technique. The amount of nitrogen in HMW DON is approximately equal to the amount of carboxylic carbon. If nearly all *N* is amide, then conversely nearly all carboxyl carbon must be amide as well, and in agreement with molecular-level analyses which show only trace amounts of biomarker lipids (<0.1% total carbon), little carboxyl carbon can be components of other organic acids (fatty acids, etc.; Mannino and Harvey, 2000[bib96]).

P0235 Several important biochemicals are amides, of which proteins and *N*-acetyl amino sugars are the most abundant in marine organisms, where proteins contribute up to 80%, and amino sugars up to 10% or the total nitrogen. Molecular-level analyses show both these biochemical classes to be present in HMW DON, but only at low concentrations. For most samples, amino acids account for <15–20% of HMW DON, and aminosugars <1% of the HMW DON (McCarthy *et al.*, 1996[bib103]; Kaiser and Benner, 2000 [bib77]; Mannino and Harvey, 2000[bib96]). Either HMW DON amide is derived from some other component, or the analytical protocols used in molecular-level analyses are not appropriate for measuring these biochemicals in HMW DON.

P0240 The discrepancy between molecular-level and NMR measurements of amide nitrogen can best be resolved by using the two techniques interactively. Proteins and *N*-acetyl amino sugars both yield amino compounds (free amino acids and amino sugars, respectively) on treatment with acid (Figure 8). Therefore, acid hydrolysis of HMW DON should be accompanied by a change in the ^{15}N-NMR chemical shift from amide to amine (Figure 9). *N*-acetyl amino sugars will also yield free acetic acid with hydrolysis, and the high concentrations of acetate in HMW DOM along with pyrolysis MS measurements of acetamide suggest that much of HMW DON is *N*-acetyl amino sugars (Boon *et al.*, 1998[bib14]). The amount of acetate bound as amide can be quantified by comparing the amount of free acetic acid released by hydrolysis with the hydrolytic yield of free amine observed by ^{15}N-NMR. Treatment of HMW DOM with mild acid converts ~60–70% of amide to free amine. This amount equals the molar sum of free amino acids (10–20% total N, from protein hydrolysis) and acetic acid (90–50% total N, from *N*-acetyl amino sugars) measured by molecular-level techniques after HMW DON hydrolysis. The agreement between NMR and molecular-level analyses indicates that 40–50% of HMW DON is derived from N-acetyl amino sugars and that molecular-level analyses underestimate the amount of amino sugars in HMW DON by at least an order of magnitude.

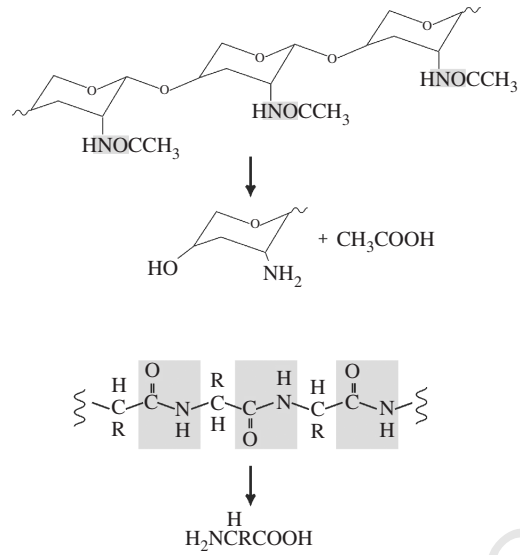
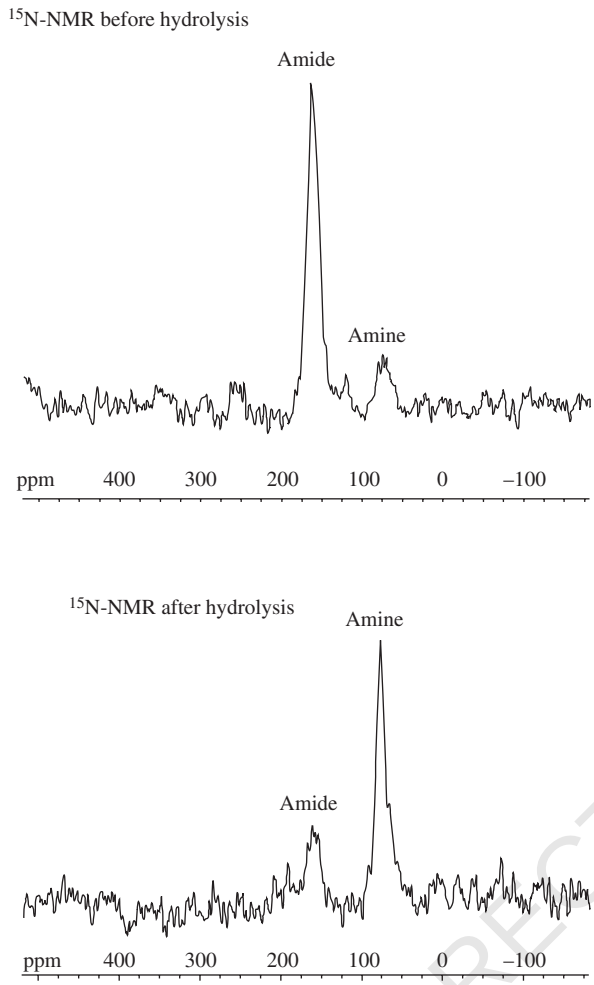


Figure 8 The effect of mild acid hydrolysis on amides in HMW DOM. Two potentially important classes of biochemicals that likely contribute to HMW DOM are (poly)-*N*-acetyl amino sugars (top) and proteins (bottom). Mild acid hydrolysis of (poly)-*N*-acetyl amino sugars will yield free acetic acid, but will not depolymerize the polysaccharide. The generation of acetic acid will be accompanied by a shift in the ^{15}N-NMR from amide to amine. In contrast, mild acid hydrolysis of proteins does not yield acetic acid, but may depolymerize the protein macromolecular segments to yield free amino acids. Free amino acids can be quantified by chromatographic techniques and compared to the shift from amide (protein) to amine (free amino acid) in ^{15}N-NMR.

P0245 Our knowledge of APS structure and composition is still evolving; however, Aluwihare and Repeta (1999)[bib3] suggest that APS is a biopolymer that is largely, perhaps exclusively, composed of carbohydrate units. This biopolymer is approximately half neutral sugar and half *N*-acetyl amino sugar (Figure 10). Together these two components contribute 40–50% of the total carbon, 60–70% of the total carbohydrate, and an equal amount of the total new (or modern) carbon in HWM DOC (Druffel *et al.*, 1992[bib29]; Guo *et al.*, 1994[bib50]). Further work is needed to establish, on a molecular level, the abundance of *N*-acetyl amino sugars in APS. Are the neutral sugars



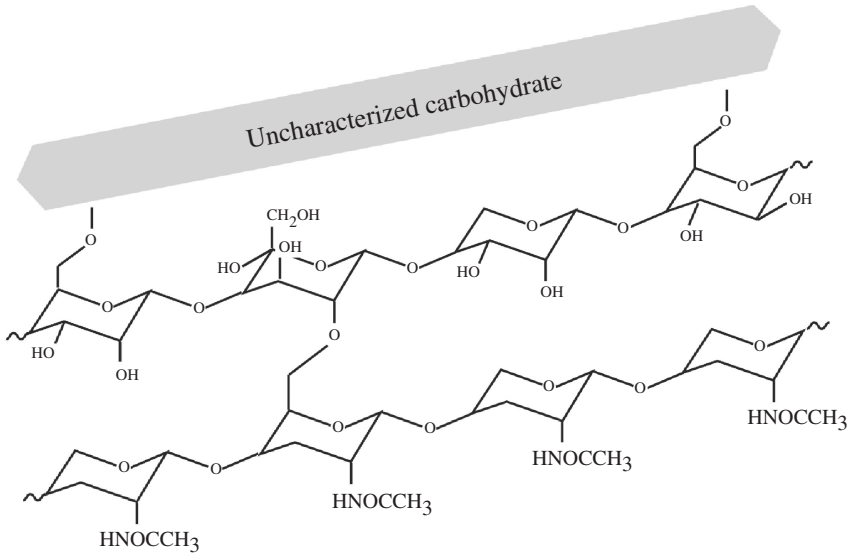
F0045 **Figure 9** The effect of mild acid hydrolysis on ^{15}N-NMR of HMW DOM. Nitrogen in HMW DOM is primarily amide (180 ppm), with smaller amounts of free amine (90 ppm). Treatment of HMW DOM with dilute hydrochloric acid increases the amount of amine and decreases the amount of amide. The decrease in amide equals the amount of acetic acid and amino acids released by hydrolysis of poly-*N* acetyl amino sugars and proteins. The relative amount of protein and amino sugar can be determined by the ratio of acetic acid to amino acids in the hydrolysis product.

and amino sugars covalently linked into a common macromolecule, and if so, what is the full structure of this polysaccharide?

S0080 ***6.07.4.2.2 Proteins in HMW DOM***

P0250 A small fraction of the carbon, and a larger fraction of the nitrogen in HMW DOM, is protein. Tanoue *et al*. (1995)[bib161] analyzed HMW DOM by gel electrophoresis and found a complex mixture of proteins with masses between 14 kDa and 66 kDa. Two major components were noted at 48 kDa and ~34–39 kDa. The 48 kDa protein was purified for *N*-terminal sequencing and shown to have significant homology with porin-P from the gram negative bacterium *Pseudomonas aeruginosa*. Tanoue's data are the most direct evidence to date that resistant biopolymers selectively survive degradation and accumulate as oceanic DOM.

P0255 Additional evidence for a bacterial contribution to HMW DOM proteins comes from molecular-level analyses of dissolved amino acids. Hydrolysis of HMW DON releases 11–29% of the nitrogen as amino acids (McCarthy *et al*., 1996 [bib103]). Specific amino acids include common protein amino acids, as well as β-alanine and γ-aminobutyric acid which are nonprotein amino acid degradation products. The distribution of amino acids is similar to that of fresh plankton cells, suspended particulate matter, and total dissolved amino acids. However, stereochemical analyses show HMW DOM amino acids to be elevated in the D-enantiomer, with D/L ratios for



F0050 **Figure 10** Hypothetical structure of APS in HMW DOM. Spectroscopic and molecular-level analyses suggest that approximately one-third of APS is neutral sugars, one-third amino sugars, and one-third unidentified carbohydrate. The consistency in monosaccharide distribution, and the fixed relative amount of acetate to total carbohydrate suggests these portions of HMW DOM are coupled into the same macromolecular structure. Further work needs to be done to establish the coupling of neutral and amino sugars directly, and to identify the unknown component of APS to bring molecular-level and spectroscopic measurements into better agreement.

alanine, aspartic acid, glutamic acids, and serine ranging from 0.1 to 0.5 (McCarthy *et al.*, 1998 [bib105]). Racemization of phytoplankton-derived L-amino acids is too slow at ocean temperatures to yield such high D/L ratios, but bacteria can synthesize D-amino acids, and it is likely that the D-amino acids in HMW DOM result from bacterial bioploymers rich in these particular amino acids. The high D/L ratios of some amino acids and the abundance of amide nitrogen in HMW DOM ^{15}N-NMR spectra led McCarthy *et al.* (1998)[bib105] to postulate that peptidoglycan may be one such biopolymer that is significantly enriched in HMW DOM. Most gram-negative bacteria produce peptidoglycan as part of their cell membrane and, like porin-P discussed above, are therefore a potential source for HMW DON in the ocean.

P0260 Further chemical characterization of HMW DOM is needed to verify this hypothesis. Peptidoglycan is a polymer of *N*-acetyl glucosamine, muramic acid, and amino acids. *N*-acetyl glucosamine has already been identified by molecular-level techniques in HMW DOM. The concentration of *N*-acetyl glucosamine is low, but consistent with the amounts of D-amino acids in samples, assuming all D-amino acids are part of a peptidoglycan biopolymer. However, muramic acid has not been detected in HMW DOM samples, and the absence of muramic acid suggests pepidoglycan is not present (Repeta, unpublished). Lactic acid, a component of muramic acid, is recovered from HMW DOM in amounts of ~0.5% of total carbon, or again at levels consistent with peptidoglycan. The analytical protocols used to release lactic acid from HMW DOM are nonspecific, and it is not known whether lactic acid comes from muramic acid, or from the degradation of another polymer. Molecular-level techniques used to quantify muramic acid may suffer from the same uncertainties as those discussed previously for *N*-acetyl amino sugars, e.g., current techniques may be inappropriate for the degradation resistant biopolymers in HMW DOM, and therefore they may not as yet provide accurate data on the distributions of molecular constitutents in HMW DOM. Assuming all alanine, serine, aspartic, and glutamic acid in HMW DOM is bound as peptidoglycan, then this bacterial polymer could contribute up to a maximum of 9% of the total HMW DOC. However, if these amino acids are assumed to occur only in porin-P or other bacterial proteins, then the contribution of bacterial carbon to HMW DOC would be much lower.

6.07.4.3 Gel Polymers and the Cycling of HMW DOM S0085

P0265 HMW biopolymers are part of the colloid-sized fraction of marine organic matter that can be visualized and enumerated with transmission electron microscopy (TEM) (Wells and Goldberg, 1991[bib176], 1993[bib177]). Colloids range in size from a few nanometers up to ~1 μm in size.

Very small colloids (<30 nm) are irregular in shape, while larger colloids (~30–60 nm) are more spherical assemblies of 2–5 nm sized subparticles. Concentrations of small colloids (<200 nm) range from nondetectable (<104 colloids per ml) to $>9 \times 10^9$ per ml, making them the most abundant particles in seawater. Vertical profiles of colloids show a highly variable distribution throughout the water column, characteristic of a dynamic reservoir that is rapidly cycling (Wells and Goldberg, 1994[bib178]). Colloids have low electron opacity by TEM, consistent with a largely organic composition, and slight enrichments of some trace metals (iron, cobalt, chromium, nickel, and vanadium) and other elements (silicon, aluminum, and calcium). Santschi *et al.* (1998)[bib141] examined colloids using atomic force microscopy (AFM), which gives comparable results to TEM but has a greater resolving power for small colloids. Visualization of colloids by AFM shows fibrils, elongated particles ≈1 nm in cross-section by 100–200 nm long, to be ubiquitous and a major component of colloidal material. Chemical analyses of samples artificially enriched with fibrils (through laboratory manipulation) show a parallel enrichment in carbohydrate, which may be the biochemical component of fibril material.

P0270 Colloids have been described as classic polymer gels, and their dynamics in seawater may be understood in terms of polymer gel theory (Chin *et al.*, 1998[bib21]). Polymer gels are stable, three-dimensional networks of polymers and F11 seawater (Figure 11). Gels assemble spontaneously from DOM to form nanometer to micrometer sized particles. The kinetics of polyF12 mer gel assembly has been monitored by flow cytometry and dynamic laser scattering, which show a rapid formation of particles in filtered seawater. In less than 30 min DOM can assemble into micometer-sized particles that continue to grow as long as free polymers remain in solution (Chin *et al.*, 1998[bib21]). Gels are stabilized by the presence of divalent cations, particularly Ca^{+2} and Mg^{+2}, and will disassemble in the presence of EDTA which out competes natural polymers for these cations. The composition of the gels is unknown, but the polymers that form the gels are F13 presumed to be organic. Gels stain positively for a number of biochemicals, including carbohydrates, proteins, and lipids. The picture of colloid formation that emerges from these experiments is consistent with observations of natural colloids in seawater. Dissolved organic polymers, 1–10 nm in size, spontaneously assemble in seawater due to the relatively high concentrations of calcium ions present. Assembly is rapid and reversible, and the gel particles will grow to at least several microns in size. Particles may continue to grow until they sink out of the water column, or are removed by other processes. Polymer gel assembly couples the dissolved and particulate reservoirs of OC through the rapid exchange of colloids (Figure 12).

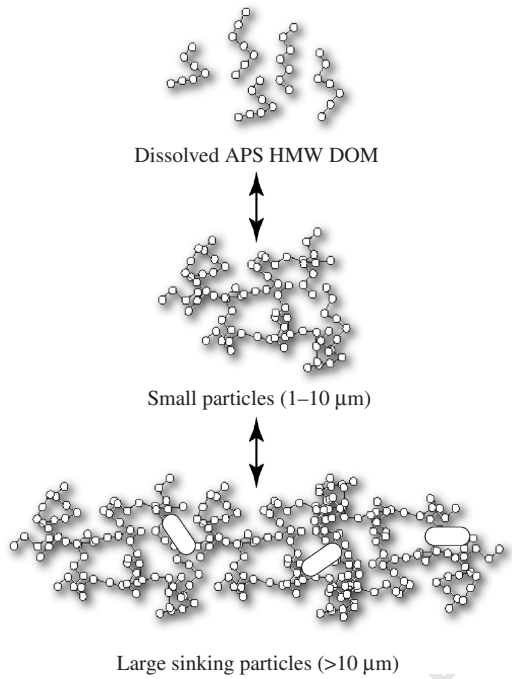
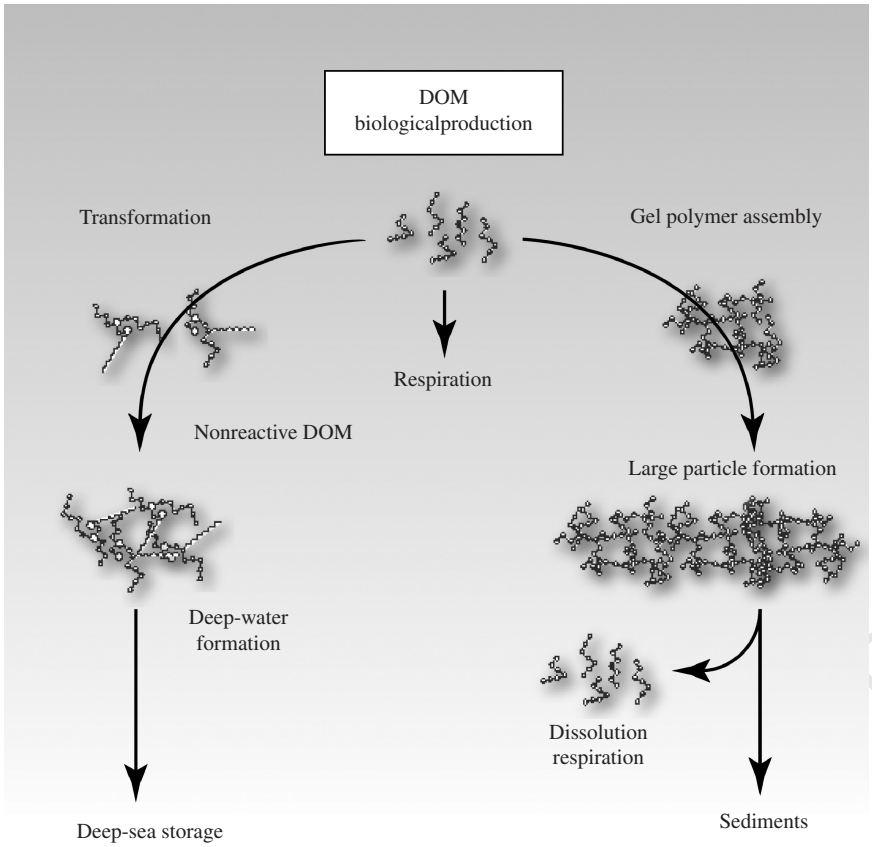


Figure 11 Formation of gel polymers by APS. The APS fraction of HMW DOM may entangle and spontaneously assemble into small particles. Further assembly will increase particle size and be accompanied by colonization by bacteria or incorporation into large, rapidly sinking particles. F0055

P0275 The polymers active in gel polymer assembly may be aged polysaccharides. Santschi *et al.* (1998)[bib141] noted that fibril enriched samples of HMW DOM were rich in carbohydrate and radiocarbon. APSs are also rich in carbohydrate, and isotopic analyses of monosaccharides show this fraction to be enriched in radiocarbon relative to total DOC. APSs have a size distribution consistent with polymers that assemble into polymer gels, and are recovered from seawater as isolates rich in calcium. NMR spectra (Figure 13) and molecular-level analyses of 3 kDa, 10 kDa, and 100 kDa HMW DOM show the same major resonances and the same distribution of neutral sugars as1 kDa HMW DOM (Figure 7). It has not been established if these size fractions represent true APS polymers of increasing molecular weight, or assemblies of smaller (1–3 kDa) sized APS.

P0280 One promising approach that may help to establish APS as the fraction of HMW DOM that assembles into particulate matter is to compare the chemical composition of polymer gel assemblies with HMW DOM. In one such



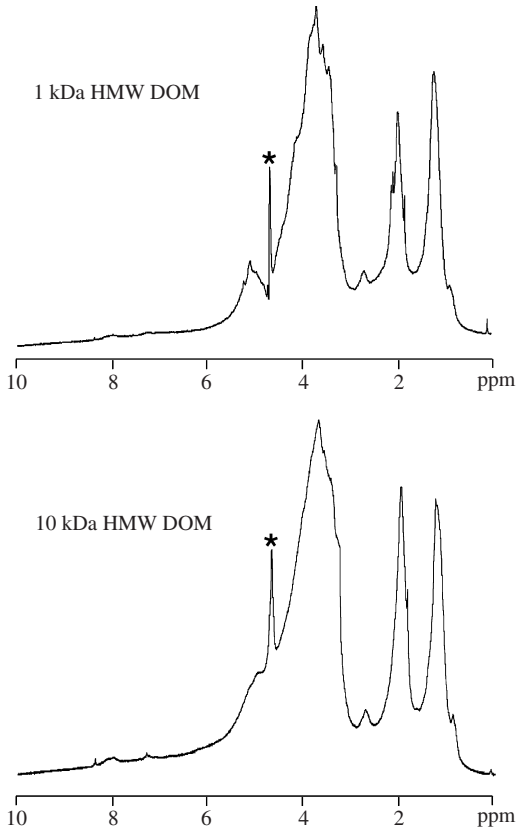
F0060 **Figure 12** DOM cycling in the ocean. DOM is initially produced as a by-product of marine production in the mixed layer. Carbon stable isotope data suggests that some fraction of this organic matter becomes incorporated into the longer-term reservoir of rather refractory DOM to be subducted into the deep ocean. Newly produced DOM may also assemble into particles to enter the POMcycle. POMis oxidized, or transported into the deep ocean on large, rapidly sinking particles where biological activity may cause further oxidation, or drive re-dissolution to HMW DOM.

experiment, HMWDOM recovered by ultrafiltration of seawater or spent culture media was redissolved in seawater and agitated by bubbling to produce particles which collect at the top of a bubble tower (Gogou and Repeta, unpublished). Particles formed by bubbling have the same neutral sugars in approximately the same proportions as APS. NMR data likewise show particles to be rich in carbohydrate and have the same major resonances as APS, although the relative amount of major biochemicals differs between the two samples. This and other similar approaches further support the hypothesis that APS is the reactive fraction of HMW DOM that undergoes spontaneous assembly into polymer gels and larger particles.

S0090 ## 6.07.5 EMERGING PERSPECTIVES ON OM PRESERVATION

S0095 ### 6.07.5.1 Background

P0285 The vast majority of POM that sinks from the surface ocean is recycled during passage through the water column and burial in the upper sediment layers. The portion that escapes recycling to be sequestered in the underlying sediments serves to modulate atmospheric carbon dioxide concentrations over geological timescales, and provides a valuable archive of past ocean and climate conditions. The mechanisms by which OM survives degradation in the water column and in sediments, and the composition of the residual material are questions that have challenged marine organic chemists for many years. These processes have remained unclear, partly due to the difficulty of resolving the composition of the residual organic matter at depth using traditional wet chemical procedures and chromatographic and/or mass spectrometric techniques. In general, even for organic matter residing in the surface ocean, and in material that has recently exited the photic zone, there is a significant fraction of the OM that is no longer recognizable as biochemicals using traditional assays (Wakeham *et al.*, 1997 [bib172]). For example, a recent molecular-level survey of over 100 amino acids, sugars, and lipids in the water column of the central Pacific Ocean



F0065 **Figure 13** NMR spectra showing the similar spectral characteristics of 1 kDa and 10 kDa HMW DOM. Spectroscopic and chemical analyses of different-sized fractions of HWM DOM show each fraction to have essentially the same spectroscopic and elemental properties, and the same distribution of neutral sugars. The very HMW DOM (>10kDa) may be made up of either assemblies of 1–10 kDa APS, or true polymers of increasing molecular weight that spontaneously assemble in seawater. Further work is needed to establish if APS is the component of HMW DOM that forms gel polymer assemblies.

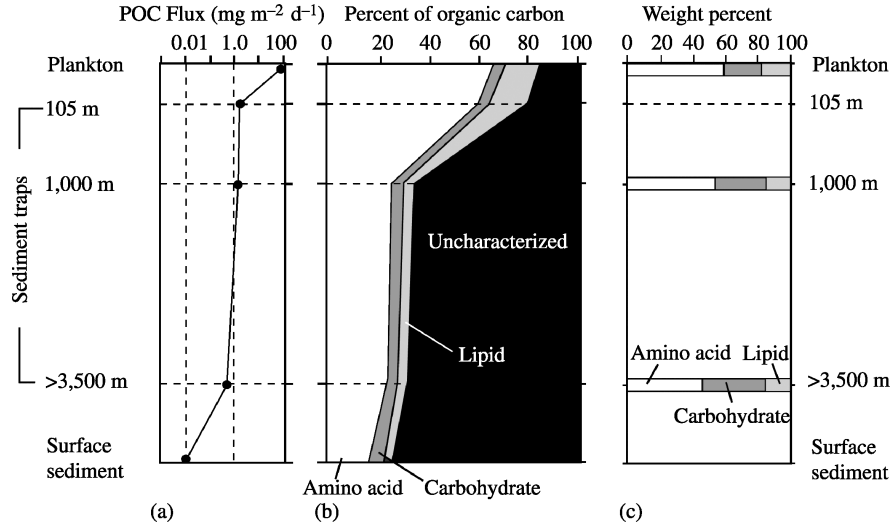
(Wakeham *et al*., 1997[bib172]) failed to account for ~15% of the molecules composing "plankton" and missed greater than 75% of the organic molecules in particulate debris raining in a matter F14 of days to the ocean floor (Figure 14). Our assessment of the degree of diagenetic alteration undergone by organic matter using the abundance and compositional parameters based on the minor fraction of identifiable biochemicals is thus subject to major uncertainty.

P0290 The processes of signal attenuation and modification continue to varying extents on material after deposition and vary, depending on burial conditions. Moreover, our ability to structurally identify organic matter decreases as it becomes further removed from its biological source(s). Thus, we can account for less of the sedimentary organic debris leaving the photic zone derived from primary production compared to that in the original phytoplankton biomass, and organic matter in the underlying sediments contains less recognizeable biological constituents than that in sinking particles. Indeed, often >80% of organic matter in surficial marine sediments remains unaccounted for in terms of readily distinguishable organic molecules (Hedges *et al*., 2000 [bib64]). Broad structural features of this "molecularly uncharacterized component" have been gleaned from bulk elemental and spectral analyses. However, without detailed molecular-level information the origins, reactions, and fates of this fraction are likely to remain obscure. To quote Hedges *et al*. (2000)[bib64], "biogeochemists of today are playing with an extremely incomplete deck of surviving molecules, among which most of the trump cards that molecular knowledge would supply remain masked."

6.07.5.2 Compositional Transformations Associated with Sedimentation and Burial of Organic Matter S0100

P0295 By virtue of where, when, and how the various organic matter inputs were formed and transported to the underlying sediments, it is possible to exploit specific chemical and isotopic characteristics to make inferences about the sources and composition of sedimentary organic matter. Much of this information is inaccessible at the bulk level. For example, bulk elemental compositions and stable carbon isotopic compositions are often insufficiently unique to distinguish and quantify sedimentary inputs. Abundances and distributions of source-specific organic compounds ("biomarkers") can help to identify specific inputs. However, this molecular marker approach suffers from the fact that the source diagnostic marker compounds are typically present as trace components, and extrapolation of abundances to infer overall organic matter contributions is therefore subject to considerable uncertainty. Isotopic measurements at the molecular level have provided a means to bridge the information gap between bulk and biomarker composition.

P0300 New insights into composition and transformation in sinking and SPOM have been gleaned from isotopic analyses performed in conjunction with compositional studies (e.g., Wang *et al*., 1996, Wang *et al*., 1998[bib175]; Megens *et al*., Q23 2001[bib107]). For example, Druffel *et al*. (1992) [bib29] measured ^{14}C, ^{13}C, bulk carbon, and biochemical constituents in dissolved and particulate carbon pools from the North Central Pacific Ocean and subtropical North Atlantic (Sargasso Sea). The decrease in $\Delta^{14}C$ values of suspended



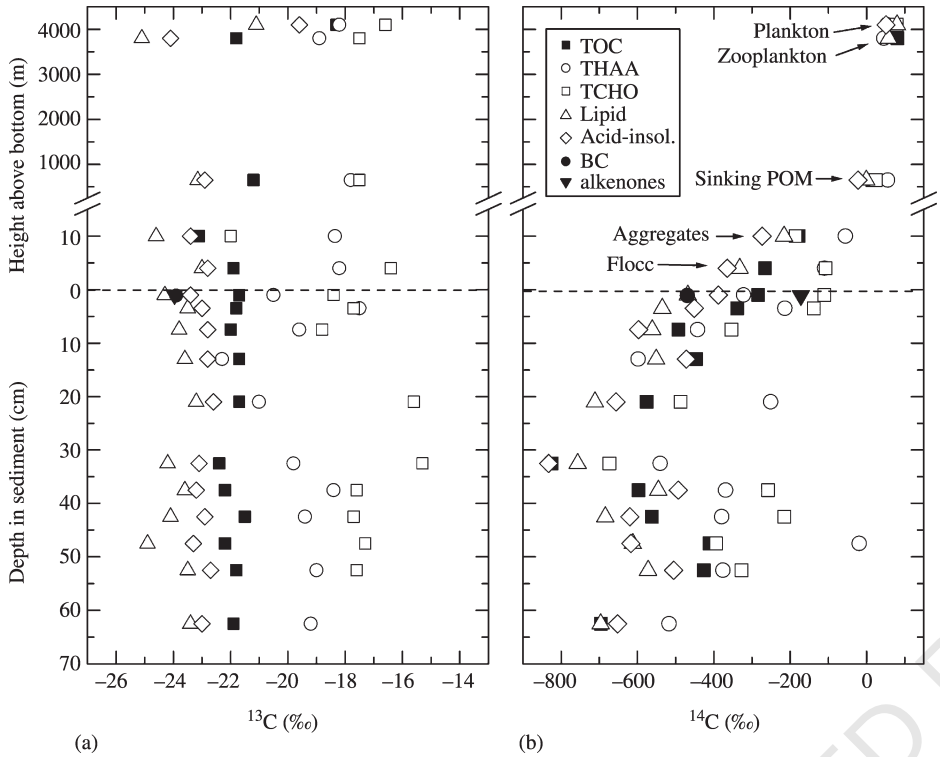
F0070 **Figure 14** Fluxes and composition of particulate organic carbon in the equatorial Pacific Ocean equatorial Pacific Ocean. (a) POC fluxes (mg m^{-2} d^{-1}). (b) Corresponding fractions of amino acid, carbohydrate, lipid, and molecularly uncharacterized carbon (biochemical class-carbon as a percentage of total OC) in plankton, sediment Q66 traps (105 m, ~1,000m, >3,500 m) and surface sediment samples from the The fraction of molecular uncharacterized organic carbon (calculated as the difference between total OC and the sum of amino acid + carbohydrate + lipid) increases with more extensive degradation to become the major constituent in deeper POC samples (after Wakeham *et al.*, 1997[bib172]). (c) Calculated weight percentages of amino acid, carbohydrate, and lipid in plankton and in sinking (sediment trap) particles in the upper and lower water column as determined by solid-state ^{13}C-NMR spectroscopy (source Hedges *et al.*, 2001[bib65]).

and sinking POC with depth has been interpreted in terms of incorporation of low-reactivity OM into the POC pool, possibly via DOC sorption or heterotrophy (Druffel *et al.*, 1992[bib29]). Carbon-14 and carbon-13 measurements on different classes of biochemical revealed that lipids were much "older" than corresponding amino acid and carbohydrate fractions in detrital aggregates, sediment floc, and sediments. These data indicate differences in decomposition and chemical behavior for different classes of biochemical in the F15 deep ocean (Figure 15; Wang *et al.*, 1998 [bib175]).

P0305 Similar trends in organic matter reactivity and isotopic composition are evident in sediments. For example, Wang and co-workers (Wang *et al.*, 1996; Wang and Druffel, 2001[bib174]) measured ^{14}C and ^{13}C compositions of total hydrolysable amino acids (THAAs), total carbohydrates (TCHO), and total lipids in deep-sea sediment profiles (Figure 15). Based on sedimentary concentration profiles, and using a "multi-G" model considering both labile and refractory organic fractions, Wang *et al.* (1998)[bib175] calculated that degradation rate constants were in the order THAA ≈ TCHO > TOC ≈ TN > Total Lipid, indicating their relative reactivities in the sediment during early diagenesis. This is in good agreement with the order of average Δ^{14}C values in the sediment (THAA, −275‰; TCHO, −262‰; TOC, −371‰; lipid, −506‰), indicating that differential decomposition of organic matter may be a major process controlling the observed Δ^{14}C signatures. Alternatively, these results may indicate sorption and/or biological incorporation of "old" DOC into POC pool.

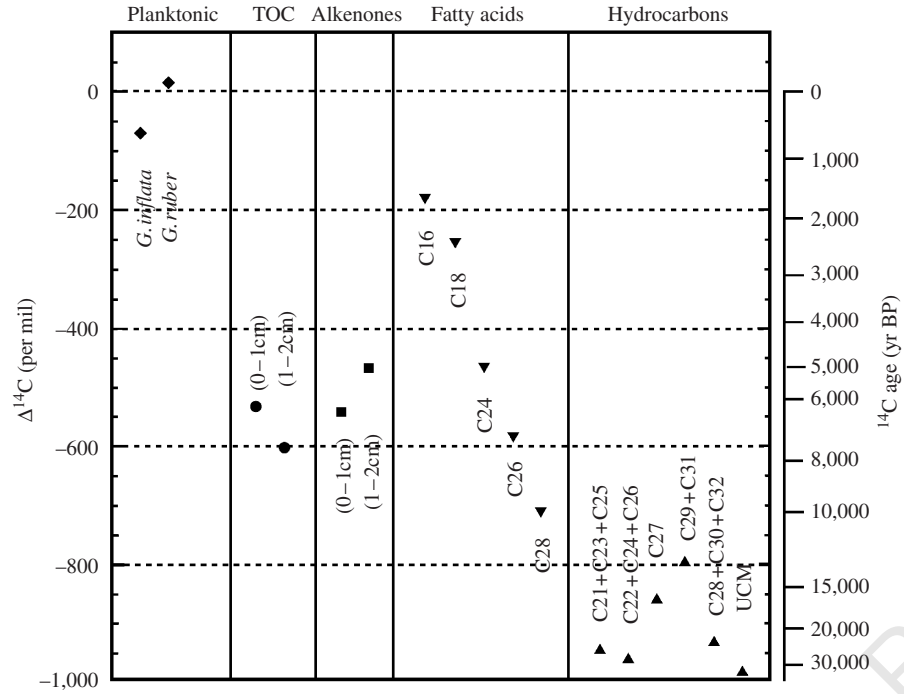
P0310 ^{14}C age differences observed between biochemical classes are both expressed and magnified at the level of individual organic compounds (e.g., Eglinton *et al.*, 1997[bib33]; Pearson *et al.*, 2001[bib124]). This is because compound class measurements integrate molecular species derived from potentially diverse sources, whereas the full range of isotopic variability is retained in source-specific molecules. Intermolecular isotopic variability is most evident in the lipids, a biochemical class common to all organisms, but with specific compounds that may be unique to a subgroup of organisms, or even individual species.

P0315 The diversity in stable carbon isotopic compositions evident at the molecular level became apparent with the advent of gas chromatography coupled to isotope ratio mass spectrometry (irm-GC-MS; e.g. Hayes *et al.*, 1990[bib58]). More recently, ^{14}C age variations among different biomarkers have been investigated (e.g., Eglinton *et al.*, 1997[bib33]; Pearson *et al.*, 2001[bib124]). Substantial variability has been observed where inputs from diverse sources are encountered, even within depth horizons representing short periods of sediment accumulation. For example, surficial



F0075 Q67 **Figure 15** Variations in: (a) stable carbon isotopic composition (δ^{13}C, ‰) and (b) radiocarbon content (Δ^{14}C, ‰)of water column and sedimentary organic matter in the northeastern Pacific Ocean (Stn M, 34° 50′N, 123° 00′W; 4,100 m water depth). Samples: phytoplankton (1 m), zooplankton (100 m), sinking particulate material collected in a sediment trap 650 m above the seafloor, detrital aggregates, and surface flocc material isolated from the sediment surface and sediment core samples. Fractions measured: Total organic carbon (solid squares), total hydrolyzable amino acids (THAA, pen circles), total carbohydrates (TCHO, open squares), lipids (open triangles), acid insoluble organic matter (open diamond), BC (solid circles),and alkenones (solid triangles). With the exception of BC (Masiello and Druffel, 1998[bib97]) and alkenone (Ohkouchi and Eglinton, unpublished) data, all measurements are from Wang *et al.* (1996, jk175%1998), or Wang and Druffel (2001)[bib174].

sediments from the Bermuda Rise in the northern Sargasso Sea deposited over a time span of less than 300 yr yield over a 3×10^4 yr spread in ^{14}C ages for different organic compounds (Figure 16). These different organic compounds that can be confidently assigned to marine photoautotrophs (alkenones), vascular plant waxes (long-chain fatty acids), and fossil (mainly thermogenic) organic matter (even carbon-numbered long chain *n*-alkanes). Their ^{14}C contents can provide valuable information on the relative importance and mode of delivery of these different inputs. In this particular example, substantial age variations are evident within a single compound class (e.g., fatty acids), highlighting the isotopic heterogeneity evident at the molecular level. Distinct ^{14}C age differences are also revealed between phytoplankton markers (alkenones) and planktonic forams—nominally both tracers of surface ocean dissolved inorganic carbon (Pearson *et al.*, 2000). These variations are potentially interpretable in terms of the provenance, modes, and timescales of delivery of different sedimentary constituents. However, even at this molecular level, it is important to recognize that ^{14}C data for a specific compound still reflect a population of otherwise identical molecules which will likely have different origins and have experienced diverse histories. For example, in the case of the alkenones from the Bermuda Rise (Figure 16), the ^{14}C age of the C37–C39 compounds isolated from a single sediment sample undoubtedly reflects two major populations: alkenone molecules input directly from the overlying water column (and therefore presumably of similar age to the planktonic forams) and alkenone molecules which had been biosynthesized several millennia ago, stored on the margins, and subsequently transported to this location *via* lateral advection in deep currents or turbidity layers (Ohkouchi *et al.*, 2002[bib118]). Although such studies are revealing the extraordinary complexity of organic matter in marine sediments, there is the exciting potential for these molecular-level age variations to provide invaluable novel insights into oceanic processes.



F0080 **Figure 16** Bulk and molecular-level radiocarbon variations (expressed as $\Delta^{14}C$, ‰, and ^{14}C age, yr BP) in surface (0–3 cm) sediment from the northeastern Bermuda Rise in the subtropical North Atlantic (33° 41′N, 57° 36′W, ~4,500 m): planktonic foraminiferal calcite (diamonds), total OC (circles), C37–C39 alkenones (squares), fatty acids (down triangles), and hydrocarbons (up triangles). Carbon numbers of fatty acids and hydrocarbons are adjacent next to the symbols (UCM = unresolved complex mixture of hydrocarbons). The sedimentation rate at this site during the Holocene averages 10–20 cm kyr^{-1} (source Ohkouchi and Eglinton, unpublished).

S0105 ### 6.07.5.3 Controls on OM Preservation

P0320 Compositional and isotopic studies have shown that a wide range of organic materials are sequestered in marine sediments. These include direct or indirect products of marine photoautotrophy, vascular plant debris, and relict OC derived from sedimentary rock weathering.

P0325 The survival of any organic matter in the sedimentary record seems remarkable, given the efficiency of OM recycling in the water column and surface sediments. The means by which organic matter escapes degradation has been the subject of much debate and research. While the processes and mechanisms have remained elusive, it is evident that there are several principal factors that contribute to OM preservation in sediments, including organic matter source/provenance, the time interval over which sedimenting materials are exposed to oxic degradation, and the availability of (and physical associations with) detrital mineral phases. It seems likely that all of these factors play a role to some extent, and that their relative importance will depend on the specific depositional circumstances. Distinguishing between these factors is difficult, because they often vary in concert, and we have limited ability to recognize compositional features resulting from a given input or depositional characteristic. For example, higher burial efficiencies are encountered in many continental margin sediments yet it is unclear whether this result reflects greater inputs of recalcitrant terrigenous carbon, higher OC fluxes stemming from high primary production in coastal waters, or shorter oxygen exposure times (OETs) due to the elevated fluxes of OC and other materials. We summarize prevailing concepts and supporting evidence in the following sections.

6.07.5.3.1 Physical protection S0110

P0330 One major determinant in organic matter preservation appears to be the interaction of organic molecules with inorganic materials (Mayer, 1994[bib99], 1999[bib100]; Keil *et al*., 1994a[bib81], b[bib82]; Hedges and Keil, 1995 [bib60]). These interactions provide a means of physically protecting labile biochemicals from degradation in the water column and underlying sediments.

P0335 Recently, Hedges *et al*. (2001)[bib65] analyzed organic matter in both surface plankton and sinking particulate matter using solid-state ^{13}C-NMR spectroscopy. They observed that, despite

extensive signal attenuation, minimal changes in bulk organic composition occurred, with apparently labile biochemicals such as amino-acid-like material and carbohydrates dominating organic matter content throughout the entire water column (Figure 14). These NMR measurements do not exclude the possibility of subtle modifications to these biopolymers. Nevertheless, the compositional similarity between phytoplankton biomass and the small remnant of organic matter reaching the ocean interior does imply that the formation of "unusual" macromolecules, either by chemical recombination (e.g., melanoidin formation (Tissot and Welte, 1984[bib164])) or microbial biosynthesis is not a major process controlling the preservation of POMin pelagic waters. Instead, Hedges *et al*. (2001)[bib65] suggest that OM might be shielded from degradation through association with the inorganic matrix (e.g., opal, coccoliths, and detrital aluminosilicates). This mineral matter makes up most (>80%) of the mass of sinking particles and, in addition to their protective role, also serves as ballast, expediting OM transport through the water column. Moreover, most sedimentary organic matter cannot be physically separated from its mineral matrix, indicating that the majority of OM is in intimate association with mineral phases.

P0340 Observations of organic-carbon-to-mineral surface area (OC:SA) ratios by Mayer (1994)[bib99] and others have revealed that sediments accumulating along continental shelves and upper slopes (excluding deltas) characteristically exhibit surface area loadings approximately equivalent to a single molecular covering on detrital mineral grains, the so-called "monolayer-equivalent" F17 coating (Figure 17). Experiments have shown that a fraction of this organic matter is bound reversibly, and is intrinsically labile (Keil *et al*., Q25 1994), but apparently escapes mineralization through association with minerals. This appears to hold true for situations where the OM passes relatively rapidly through oxygenated bottom and pore waters prior to sequestration in the underlying anoxic sediments.

P0345 In summary, the above observations and relationships indicate that the supply and availability of mineral surface area may be a primary control on OM preservation, particularly in open continental shelf and upper slope sediments where ~45% of all carbon burial takes place in the contemporary ocean. However, while a clear first-order relationship between mineral surface area and OC loading has been apparent for some time, the exact mode of this association remained unclear. Specifically, it was uncertain whether adsorbed organic matter is dispersed over all mineral surfaces or is more localized in occurrence. Theoretical considerations and empirical relationships have suggested the former to be

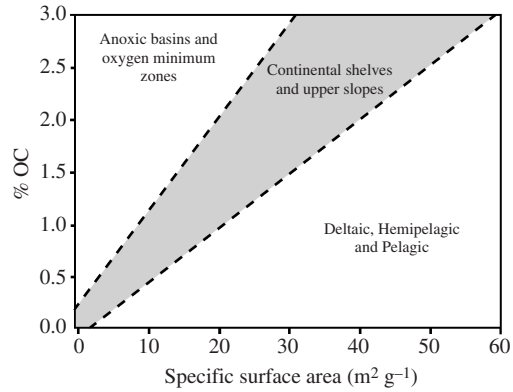


Figure 17 Generalized relationship between weight percent OC (% OC) and specific mineral surface area (SA) for marine sediments. The shaded area represents the boundaries (OC : SA ratio of 0.5–1.1 mg C m^{-2}), within which most continental shelf and upper slope sediments (outside the direct influence of rivers) fall. Sediments underlying anoxic basins and OMZs associated with high productivity (upwelling) margins tend to exhibit OC : SA ratios greater than 1.1 mg C m^{-2} whereas deltaic and abyssal sediments exhibit OC:SA ratios of less than 0.5 mg C m^{-2} (after Mayer, 1994[bib99]; Hedges and Keil, 1995[bib60]). F0085

the case (Keil *et al*., 1994), but recent work has not supported this paradigm. Transmission electron microscopic examination of sedimentary mineral grains (e.g., Ransom *et al*., 1997[bib132], 1998) has revealed that OM is not uniformly distributed across all mineral surfaces, but instead is preferentially associated with minerals of high surface area, particularly smectite-rich clays. Ransom *et al*. (1998) have concluded that the association is a function of differences in the site density and chemistry of the clays, as well as differences in their flocculation behavior. Similarly, studies of gas adsorption in model systems and marine aluminosilicate sediments (Mayer, 1999[bib100]) have shown that the sediments with low to moderate loading of OM (<3 mg OC m^{-2}) have generally less than 15% of their surface coated. These data imply that the abundance of non-spherical, high surface area-to-volume particles—such as clays, oxyhydroxides, and inorganic biogenic debris (e.g., diatom frustules)—controls specific surface area in most continental margin sediments. Thus, although OM is associated with mineral grains (Mayer *et al*., 1993[bib101], Mayer, 1994a[bib99]; Keil *et al*., 1994), it is not adsorbed as a monolayer (Mayer, 1999[bib100]), but must instead be locally concentrated on certain surfaces. Mayer (1999)[bib100] argued that the term "monolayer equivalent" should, therefore, be removed from usage, and there appears good justification for so doing. Hence, although there appears to be a clear relationship between OC:SA and organic matter preservation, the mechanistic Q26 Q27 Q28

basis for this relationship still remains to be determined. Mayer (1999)[bib100] notes that while most surface area appears to be within mesopores of <10 nm diameter (Mayer, 1994a [bib99]), these pores may be too small to allow attack by extracellular enzymes, hence offering protection from degradation (Mayer, 1994a [bib99], b[bib99]).

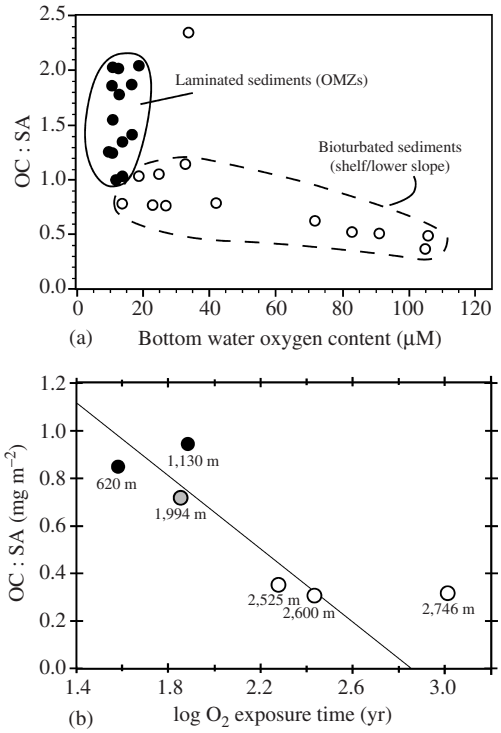
P0350 In addition to physical protection via association with detrital mineral phases, preservation of labile organic matter through association with other matrices is also possible. In particular, "encapsulation" of labile organic matter within refractory organic polymers (Knicker *et al*., 1996 [bib84]; Zang *et al*., 2001[bib184]) or within biogenic mineral lattices are possible means of stymieing organic matter degradation during burial.

S0115 ***6.07.5.3.2 Role of anoxia***

P0355 While a protective role of minerals is inferred from the consistency of OC:SA values in open continental margin sediments, there are depositional environments that yield OC:SA values well above those predicted from sorptive controls, and where other modes of preservation must be invoked. In particular, sediments underlying anoxic or low oxygen bottom waters, or where molecular oxygen does not penetrate to a significant extent into the sediment, are characteristically rich in organic matter and tend to exhibit elevated levels of OC with OC:SA values in excess of those characteristic of margin sediments overlain by oxygenated waters (Bergamaschi *et al*., 1997[bib11]; Keil and Cowie, 1999[bib80]; Figure 17). While such depositional settings account for only $\sim$5% of Q29 total OC burial (Table 1), they are of importance in relation to understanding the formation of organic-rich sedimentary rocks that are responsible for reserves of petroleum. These organic-rich sediments also represent potentially valuable, high fidelity archives of past ocean conditions, since they tend to be free from sediment mixing due to bioturbation and often accumulate relatively rapidly. They are hence conducive for preservation of labile organic compounds that carry the highest information contents. While the extent of exposure to molecular oxygen prior to entering the anoxic realm is thus frequently considered as a master variable influencing OM preservation (e.g., Demaison, 1991[bib28]), much debate persists concerning the specific factors leading to enhanced organic matter burial under oxygen deficient or anoxic conditions. Indeed, is there a causal or even correlative relationship between the presence of a minimum in bottom water oxygen (BWO) concentration and the preservation of organic matter in the underlying marine sediments (Pederson and Calvert, 1990[bib125]; Cowie and Hedges, 1992[bib24])? Q30

P0360 Various approaches have been taken towards assessing the role of oxygen in OM degradation. Laboratory incubations under controlled conditions have provided detailed information on the influence of aerobic versus anaerobic microbial degradation of phytoplankton biomass (e.g., Harvey and Macko, 1997[bib55]). Investigation of natural systems includes comparison of surface sediments from depocenter and periphery of anoxic or dysoxic basins (e.g., Gong and Hollander, 1997[bib45]), examination of depth transects traversing OMZs that impinge on continental margins (e.g., Keil and Cowie, 1999 [bib80]), and comparison of turbidites overlying pelagic sediments that were subjected to oxygen "burn-down" (Cowie *et al*., 1995[bib25]; Prahl *et al*., 1997[bib129]; Hoefs *et al*., 1998[bib69], 2002[bib70]; Middelburg *et al*., 1999[bib111]). Keil and Cowie (1999)[bib80] examined OC:SA relationships in relation to BWO concentrations in sediments from the NE Arabian Sea. Sediments deposited under the oxygen minimum had OC:SA ratios in excess of 1.1 mg OC m^{-2}, while samples shallower or deeper than the oxygen-depleted water mass (BWO >35 uM) exhibited OC:SA Q31 ratios that fall within the typically observed range F18 (0.5–1.1 mg OC m^{-2}) (Figure 18(a)). These data indicate that organic matter preservation is enhanced within the general locale of the BWO minimum in NE Arabian Sea sediments. While OM loadings are 2–5 times the monolayer equivalent in anoxic sediments, there often remains a direct relationship between OM content and mineral surface area. Hedges and Keil (1995) [bib60] speculate that organic materials sorbed in excess of a monolayer may be partially protected as result of equilibration with DOM-rich porewaters, and brief OETs.

P0365 Thus, Hedges and Keil (1995)[bib60] argue that organic matter preservation throughout much of the ocean may be controlled largely by competition between sorption on mineral surfaces at different protective thresholds and oxic degradation. The presence of reducing conditions slows OC degredation, leading to elevated OC contents. As an extension of this line of thinking, Hedges *et al*. (1999) hypothesize that organic matter Q32 preservation in continental margin sediments is controlled by the average residential period experienced by the accumulating organic particles in the water column and in the oxygenated pore waters immediately beneath the sediment–water interface. Trends in oxygen penetration depth, organic element composition, and mineral surface area for surface sediments collected along an offshore transect across the Washington continental shelf, slope, and adjacent Cascadia basin



F0090 **Figure 18** Oxygen controls on the degradation of OC. (a) Organic carbon to mineral surface area ratio (OC : SA) for core top sediments from the northeastern Arabian Sea plotted as a function of BWO content. Open symbols denote bioturbated sediments lying under relatively oxygenated waters on the shelf and lower slope. Solid symbols denote laminated sediments lie beneath water with the lowest BWO values (i.e., OMZ) (after Keil and Cowie, 1999[bib80]). (b) Organic carbon to surface area (OC : SA) ratios for surface sediments from the Washington margin (northeastern Pacific Ocean) as a function of OET. Samples with short OETs derive from the shelf and upper slope (solid and shaded symbols). Samples with longer OETs are from the lower slope and Cascadia basin (open symbols). Water depths, in meters, are indicated (after Hedges *et al.*, 1999).

support this notion. Sediment accumulation rates decrease and dissolved molecular oxygen penetration depths increase offshore, resulting in a seaward increase in OETs from decades (mid-shelf and upper slope) to millennia (outer Cascadia basin). Organic contents and compositions were essentially constant at each site, but varied between sites. In particular, OC:SA ratios decreased and indicators for the level of degradation increased with increasing OET (Figure 18(b)), indicating that sedimentary organic matter experiences a clear "oxic effect" (Hedges *et al.*, 1999). The OET concept helps to integrate contributing factors such as sediment accumulation rate and BWOlevels that have been invoked in the past to explain OM preservation in accumulating continental margin sediments. However, we are still lacking a detailed mechanistic basis for this observed control on degradation exerted by BWO conditions.

6.07.5.3.3 Chemical protection S0120

Intrinsically refractory biomolecules. While P0370 evidence exists for the physical protection of organic compounds from degradation (e.g., via association with mineral surfaces), and for enhanced preservation due to limited exposure to oxygenated conditions, organic matter persists in many oceanic sediments where conditions are not conducive for OM preservation based on either of the above criteria. For example, deltaic sediments often exhibit OC:SA coatings that are significantly lower than the "monolayer equivalent" (Keil *et al.*, 1997[bib83]). Submonolayer equivalent OM coatings are also observed in deep-sea turbidite sediments where organic-rich margin sediments, originally sequestered under anoxic conditions on the margins, have been redeposited in abyssal locations and are exposed to oxygenated bottom waters. Submonolayer organic coatings are also observed in continental rise and abyssal plain sediments where slower sediment accumulation rates and deeper O_2 penetration depths result in increased OETs, and little OM preservation.

The residual organic matter in such sediments is P0375 often inferred to be highly refractory, and it is assumed that the structural attributes of the organic matter may be pivotal in dictating its survival. The concept of "selective preservation" of one type of natural product over another was introduced by Tegelaar *et al.* (1989)[bib162] and others. Evidence in support of selective preservation stems from analyses of insoluble macromolecules in sediments and in precursor organisms (Gelin *et al.*, 1999[bib42]). Solid-state NMR spectra and pyrolytic degradation of OM in many recent and ancient sediments indicate the presence of a highly aliphatic component(s) (Van de Meent *et al.*, 1980[bib168]; Eglinton, 1994). Q33 The nature and origin of this type of aliphatic component had been the subject of considerable debate until it was found that several types of organisms synthesize highly aliphatic biopolymers (Largeau *et al.*, 1984[bib90]; Nip *et al.*, 1986 [bib116]; Goth *et al.*, 1988[bib48]; Zelibor *et al.*, 1988[bib185], Gelin, 1996[bib40], Gelin *et al.*, Q34 1997[bib41], 1999[bib42]). These natural products were then proposed as the source of this sedimentary component. The recalcitrance of these aliphatic macromolecules is indicated by their relative enrichment in oxidized layers of pelagic turbidite sequences (Hoefs *et al.*, 1998 [bib69]).

The concept of chemical recalcitrance is not P0380 restricted to aliphatic biopolymers and one

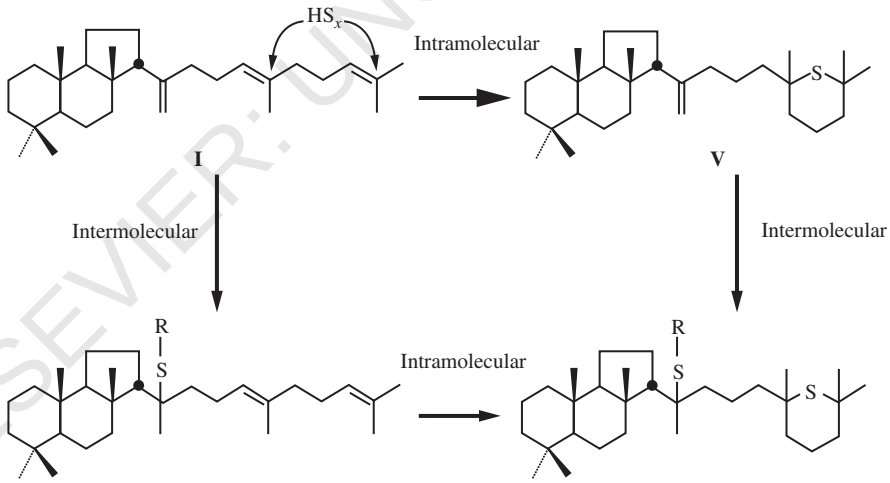
guideline for assessing reactivity and conformational relationships pertinent to the preservation of other types of biomacromolecules are structural comparisons between proteins of the same generic type occurring in hyperthermophiles and their low-temperature counterparts. X-ray-based structural studies have revealed that very F19 minor differences evident in molecular structure and conformation brought about by a few α-amino acid substitutions can have dramatic effects on the reactivities and thermal stabilities of such molecules (Danson and Hough, 1998[bib26]). The corollary for stability of marine organic matter is that similar minor changes in molecular content and architecture induced by mineralization and diagenetic processes may lead to sharp contrasts in biochemical reactivity and hence preservation Q35 (Eglinton, 1998; Hedges *et al.*, 2000[bib64]).

P0385 *Formation of organosulfur compounds.* One factor that distinguishes organic matter accumulation under anoxic or suboxic conditions from their oxic counterparts is the presence of sulfide from microbial sulfate reduction in bottom waters and sediment pore waters. It has been established that certain organic compounds can readily react with reduced sulfur species (H_2S polysulfides) under ambient conditions (Vairavamurthy and Mopper, 1987[bib167]), providing a potential means of sequestering labile, extremely oxygen-sensitive organic molecules, such as functionalized or polyunsaturated lipids. Evidence for the reaction of organic matter with sulfides stems from laboratory studies (e.g., Krein and Aizenshtat, 1994[bib86]; Schouten *et al.*, 1994 [bib145]), together with down-core profiles of the content and isotopic composition of organically bound sulfur (Francois, 1987[bib36]; Mossmann *et al.*, 1991[bib114]; Eglinton *et al.*, 1994; Putschew *et al.*, 1996[bib131]; Hartgers *et al.*, 1997[bib54]).

P0390 Numerous studies have investigated potential mechanisms of OM sulfurization during early diagenesis. Sulfur is considered to react in both an intramolecular and intermolecular fashion (Figure 19). Intramolecular incorporation leads to the formation of cyclic OSC (e.g., thianes, thiolanes, and thiophenes). In intermolecular reactions, the formation of sulfide or polysulfide bridges between molecules generated a wide variety of sulfur-cross-linked macromolecules (Sinninghe Damste *et al.*, 1989[bib151]; Kohnen *et al.*, 1991[bib85]).

P0395 Formation of organically bound sulfur is promoted by the availability of reactive organic matter (i.e., bearing the appropriate type, position, and number of functional groups), an excess of reduced sulfur species (e.g. HS^-, polysulfides), and a limited supply of reactive iron, which would otherwise outcompete OM for sulfides (Canfield, 1989[bib17]; Hartgers *et al.*, 1997[bib54]). These conditions are characteristic of anoxic basins and OMZs underlying productive upwelling systems on the continental margins. The high flux of labile OM to the sediment provides an abundant source of reactive OM that both possesses the requisite functional groups, and fuels bacterial sulfate reduction, providing reduced sulfides and polysulfides. Shelf and slope sediments distal from sources of terrigenous sediment receive only limited amounts of reactive iron, except in regions of major eolian dust input. In this context, organic matter preservation through formation of organically bound sulfur is unlikely to be important on a global basis.

P0400 Most attention has been focused on the sulfurization of functionalized lipids and its



F0095 **Figure 19** Model for the intramolecular and intermolecular reaction of reduced sulfur species with functionalized lipids. Proposed reaction scheme for sulfur incorporation into (17*E*)-13β(*H*)-malabarica-14(27),17,21-triene (I) (after Werne *et al.*, 2000[bib179]).

influence on lipid preservation and resulting biomarker fingerprints (e.g., Kohnen *et al*., 1991 [bib85]). However, lipids comprise a relatively minor fraction of the input organic matter, and hence the significance of this process as an organic matter preservation mechanism has been uncertain. Recently, it has been shown that carbohydrates can be preserved in a similar manner (Sinninghe Damste *et al*., 1998[bib152]). Carbohydrates comprise a large fraction of the carbon fixed by photoautotrophs, especially certain diatoms which are often the dominant primary producers in upwelling systems. These biopolymers are generally considered to be highly labile and therefore poorly preserved in sediments. However, based on the premise that carbohydrates tend to be isotopically enriched relative to lipids, Sinninghe Damste *et al*. (1998)[bib152] interpret strong relationships between OC content, organic sulfur content, and $\delta^{13}C$ of bulk OC in Jurassic age sediments as a consequence of variable preservation of ^{13}C enriched carbohydrates through sulfurization reactions.

P0405 It remains unclear whether sulfurization of organic matter results in a net increase in OC preservation, e.g., whether sulfurization acts to transform organic matter, but not preserve it. A key issue with respect to this question is the timing of these reactions in relation to competing diagenetic reactions that remove the organic substrates. Circumstantial evidence suggests that these reactions take place quite rapidly (Eglinton *et al*., 1994); however, the identification of both precursor and product (Figure 19) in age-dated sediments from the anoxic Cariaco Basin provides a direct estimate of reaction rates (Werne *et al*., 2000[bib179]; Figure 20). While these results apply only for the precursor in question, they imply that sulfur incorporation is far from instantaneous.

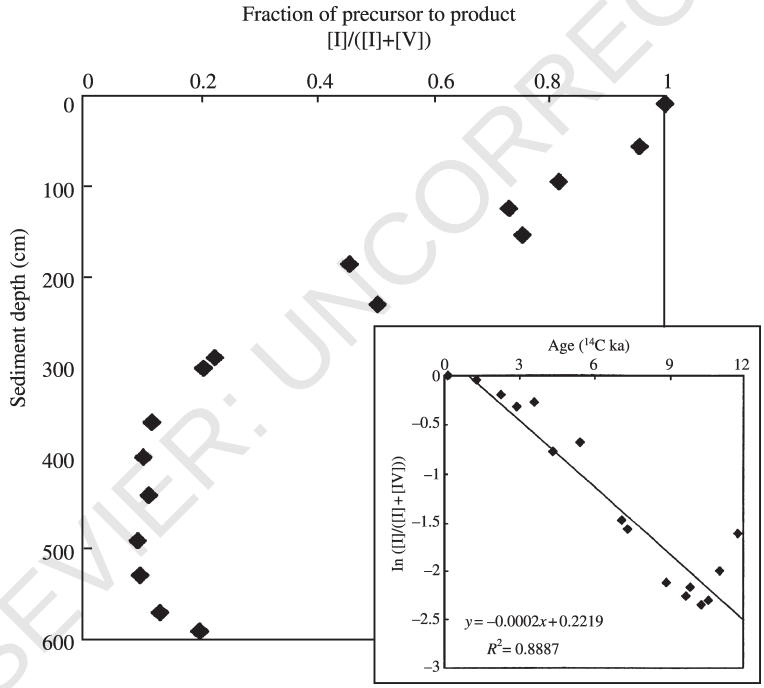
6.07.6 MICROBIAL ORGANIC MATTER PRODUCTION AND PROCESSING: NEW INSIGHTS

S0125

6.07.6.1 Background

S0130

P0410 Compared to OM inputs from sedimentation of biogenic particles resulting from primary production in the overlying water column and transported terrigenous materials, the role of prokaryotic organisms in the production and processing of organic matter is a poorly understood component of the oceanic carbon cycle. Prokaryotes, which include the bacteria and archaea, can be divided into several classes: cyanobacteria, anoxygenic photosynthetic bacteria, heterotrophic



F0100 **Figure 20** Progress of intramolecular sulfurization of malabaricatriene (I) with depth in anoxic Cariaco basin sediments. Plot of the ratio of the concentrations of I to the sum of the concentrations of I + V (see Figure 19 for structures) as a function of sediment depth. The progress of transformation of I–V with increasing sediment depth is Q68 indicated by the steady decrease in the relative abundance of the precursor lipid (I). Inset: plot of ln ([I]/([I] + [V])) versus sediment age (= time), used to empirically determine the first-order rate constant for sulfur incorporation (after Werne *et al*., 2000[bib179]).

bacteria, methane oxidizing bacteria, and methanogenic archaea (Balows *et al*., 1992[bib6]). All of these types of prokaryotes have a major impact on either the production or the mineralization of OC in the water column and in sediments. Indeed, viable microbial communities have now been shown to extend hundreds of meters into the sediment column (e.g., Parkes *et al*., 1994[bib121], 2000[bib122]), indicating that fresh microbial biomass may also constitute some fraction of the OM hitherto considered as "preserved" OM remnants from the overlying water column. Thus, the extent to which OM buried in sediments represents organic remnants directly inherited from the overlying surface ocean versus bacterial debris is a subject of some debate. The fact that benthic microorganisms are the last "filter" that OM passes through during burial suggests F21 that their biomass and products might become sequestered irrespective of their reactivity (i.e., there is no one else to "eat" them). It is difficult to distinguish between these inputs, both because of the modified nature of sedimentary OM, and the fact that heterotrophic organisms utilizing multicarbon substrates will inherit the isotopic characteristics of the OM they act upon (Hayes, 1993 [bib57]).

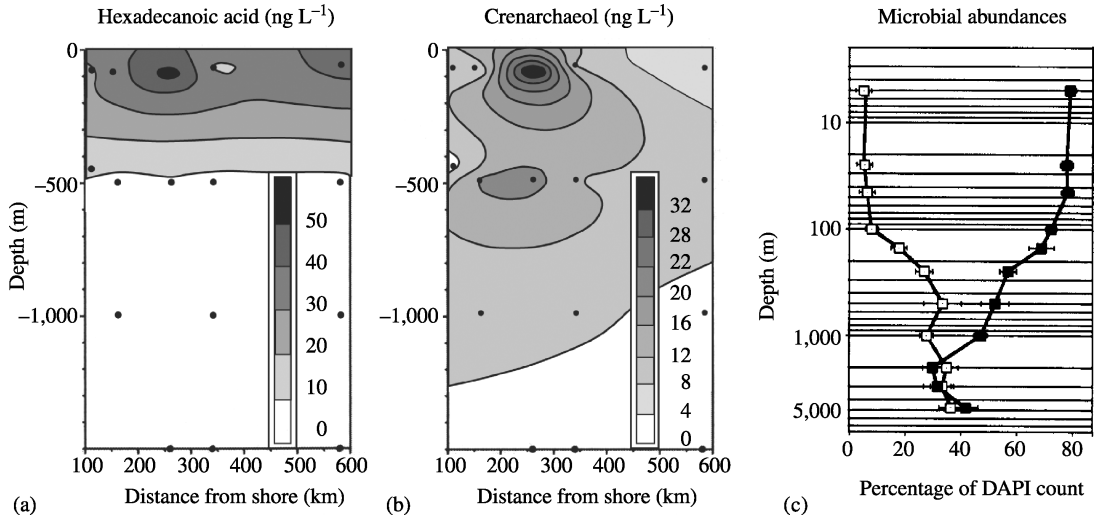
P0415 *De novo* biosynthesis and associated reworking of organic matter by prokaryotes does not imply that all of this microbially processed organic material is transferred to the sedimentary record. Evidence of contributions from prokaryotic organisms is abundant in the form of molecular fossils (e.g., hopanoids) that are virtually ubiquitous in the sedimentary record. However, while the presence of specific biomarkers may be diagnostic of specific prokaryotic inputs, their abundance is not necessarily in proportion to these inputs (the same is, of course, true for all F22 biomarkers and incidentally POMin general). Sinninghe Damste and Schouten (1997)[bib150] reviewed evidence for prokaryotic biomass inputs to sedimentary organic matter. They argue that several lines of evidence point to limited contributions or poor preservation of bacterial biomass in the sedimentary record. Their conclusions are based on, among other things: (i) isotopic mass balance in various sedimentary settings; (ii) the effects of bacterial oxidation in organic matter-rich turbidites; and (iii) the absence of apparently recalcitrant biomacromolecules, such as aliphatic biopolymers, in prokaryotes.

P0420 In addition to the prokaryotes whose identity, physiology, and ecological role has been established, relatively recent studies using culture-independent r-RNA analyses of environmental samples have revealed genetic diversity within natural microbial communities that greatly exceeds estimates based on classical microbiological techniques. These findings underline our presently limited view of microbial activity and its biogeochemical consequences. Below, two examples are provided that highlight the potential influences of microbial processes on sedimentary organic matter composition.

6.07.6.2 Planktonic Archaea S0135

P0425 Recent culture-independent, r-RNA gene surveys have indicated the ubiquity and importance of planktonic archaea in the ocean, particularly in subsurface waters (DeLong, Fuhrman papers). For example, Karner *et al*. (2001)[bib79] found pelagic crenarcheota (group 1) comprised a large fraction of total marine picoplankton, equivalent in cell numbers to bacteria at depths greater than 1,000 m (Figure 21). The fraction of crenarchaeota increased with depth, reaching 39% of the total DNA-containing picoplankton detected. Moreover, the high proportion of cells containing significant amounts of r-RNA suggests that most pelagic deep-sea microorganisms are metabolically active. The oceans are estimated to harbor $\sim 1.3 \times 10^{28}$ archaeal cells and 3.1×10^{28} bacterial cells, suggesting that pelagic crenarchaeota represent one of the ocean's single most abundant cell types.

P0430 The physiologies, ecological niches, and biogeochemical roles of these organisms are yet to be fully determined. Their imprint on the sedimentary record is only now being appreciated. Sinninghe Damste *et al*. (2002)[bib153] quantified intact tetraether lipids of marine planktonic crenarchaeota in SPOM from the NE Arabian Sea. In contrast to eukaryotic and bacterial lipids (sterols and fatty acids, respectively), which were highest in surface waters, maximum concentrations of crenarchaeol (Figure 22), generally occurred at 500 m near the top of the OMZ (Figure 21). This indicates that these crenarcheota are not restricted to the photic zone of the ocean (consistent with molecular biological studies). Sinninghe Damste *et al*. (2002)[bib153] suggest that the coincidence of maximum abundances of crenarcheotal membrane lipids with the core of the OMZ indicates these organisms are probably facultative anaerobes. Moreover, calculations of cell numbers (based on membrane lipid concentrations) support other recent estimates for their significance in the World's oceans. Schouten *et al*. (1998)[bib146] investigated acyclic and cyclic biphytane carbon skeletons derived from planktonic archaea in a number of lacustine and marine sediments. They found these compounds to be amongst the most abundant lipids in sediments, and sometimes were present in greater proportion to those synthesized by eukaryotes and bacteria, indicating that these organisms may be an important source of sedimentary organic matter.

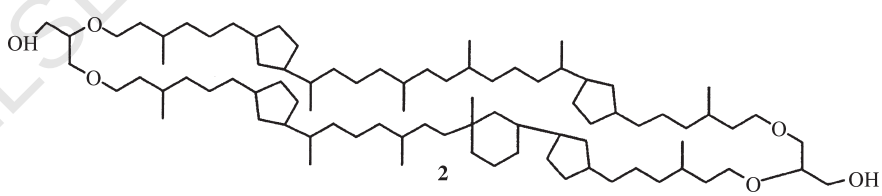


F0105 **Figure 21** Comparison of vertical distribution of biomarker and microbial abundances in oceanic water columns. (a) Contour plots of concentration (in nanograms per liter) of hexadecanoic acid. (b) Crenarchaeol at various depths in the water column and distances from shore on a northwest-to-southeast transect off Oman in the Arabian Sea (after Sinninghe Damste *et al*., 2002[bib153]). Hexadecanoic acid serves as a biomarker proxy for eukaryotic and bacterial biomass and clearly shows the expected surface maximum, with concentrations dropping off steeply with increasing water depth. In contrast, crenarchaeol, a molecular biomarker for planktonic crenarchaeota, shows two maxima with one near 50 m and the other ~500 m. (c) Vertical distributions of microbial concentrations in the North Pacific subtropical gyre: bacteria (solid squares) and planktonic crenarchaeota (open squares). Effectively, there are two microbial domains which were determined using a DAPI nucleic acid stain (after Karner *et al*., 2001[bib79]). These data show the increasing proportion of planktonic archaea in deep waters, with the result that at depths greater than 2,000 m, the crenarchaeota are as abundant as the bacteria.

S0140 ### 6.07.6.3 Anaerobic Methane Oxidation

P0435 A second newly recognized group of prokaryotes are the methane oxidizing archaea. Nearly 90% of the methane produced in anoxic marine sediments is recycled through anaerobic microbial oxidation processes (Cicerone and Oremland, 1988[bib23]; Reeburgh *et al*., 1991[bib138]). However, the organisms and biochemical processes responsible for the anaerobic oxidation of methane (AMO) have largely evaded elucidation until recently. Convergent lines of molecular, carbon-isotopic, and phylogenetic evidence have now implicated archaea in consortia with sulfate reducing bacteria as the primary participants in this process (Hoehler *et al*., 1994[bib71]; Boetius *et al*., 2000[bib13]; Pancost *et al*., 2000[bib120]; Hinrichs *et al*., 1999[bib67]).

P0440 Lipids of these organisms are distinguished by their ether-linked nature and highly ^{13}C-depleted values. Hinrichs *et al*. (2000)[bib68] investigated microbial lipids associated with AMO in gas hydrate-bearing sediments from the Eel River Basin, offshore Northern California, as well as sediments from a methane seep in the Santa Barbara Basin. In addition to archaeal markers (*sn*-2-hydroxyarchaeol), these lipids are accompanied by additional ^{13}C-depleted glycerol ethers and fatty acids. Hinrichs *et al*. speculate that these ^{13}C-depleted lipids are produced by (unknown) sulfate reducing bacteria growing syntrophically with the methane utilizing archaea. Interestingly, these authors note that at all of the methane seep sites examined, preservation of aquatic products is enhanced because enhanced consumption of sulfate by the methane oxidizing consortium depletes the sulfate pool that would otherwise have been available for remineralization of materials from the water column.



F0110 **Figure 22** Molecular structure of crenarchaeol (after Sinninghe Damste *et al*., 2002[bib153]).

P0445 The identification of ^{13}C-depleted ($\delta^{13}C$ values as low as -58 per mil) archaeal cyclic biphytanes in particulate matter from the Black Sea, where more than 98% of the methane released from sediments is apparently oxidized anaerobically Q36 (Reeburgh *et al*., 1981), provides evidence for AMO in euxinic waters (Schouten *et al*., 2001 [bib147]). However, the same isotopically depleted compounds were not detected in the underlying sediments, suggesting that the responsible organisms are in low abundance and/or leave no characteristic molecular fingerprint in the sedimentary record.

S0145 6.07.7 SUMMARY AND FUTURE RESEARCH DIRECTIONS

P0450 Our understanding of the composition and cycling of organic matter in the oceans has changed tremendously since the 1990s. Through the use of new analytical tools, we have a greater appreciation of the complexity of dissolved and POMwhile, at the same time, we can view its biomolecular building blocks with greater clarity. Despite these advances, many important unanswered questions provide impetus for continued research.

P0455 Questions of the origin and composition of marine macromolecular organic matter continue to challenge us. A key point that has emerged, especially from NMR studies, is that the formation of randomly cross-linked macromolecules ("humic substances") is no longer considered a primary pathway in the formation of either HMW DOM or sedimentary OM. Rather, these materials seem to be comprised of biochemicals that have been directly inherited from their biological precursors (primarily marine algae and bacteria) with minimal alteration. Three questions immediately arise: (i) Why are traditional wet chemical approaches unable to detect much of these apparently intact biopolymers? (ii) Given this close similarity to natural products, why is it that this material not readily biodegraded in the water column and sediments? (iii) What are the processes that render normally labile macromolecules unavailable to heterotrophic microorganisms and their hydrolytic enzymes? These issues are particularly perplexing in the case of deep-water DOM, where physical mechanisms of preservation such as sorption on mineral grains or physical encapsulation cannot be invoked, where a large fraction of the macromolecular pool is polysaccharide in nature and, paradoxically, exhibits radiocarbon ages of several millennia! It is evident that our knowledge of the fundamental factors that control organic matter degradation and transformation is far from complete. However, subtle modifications of the molecular structure of a biochemical (e.g., changes in protein conformation) are known to influence susceptibility to attack by degrading chemicals and enzymes. New analytical methods that can detect small changes in biopolymer structure are urgently required, together with new experimental approaches that can assess the impact of such molecular rearrangements on organic matter preservation at a mechanistic level.

P0460 Our limited understanding of OM composition is not restricted to the macromolecular pool. Our knowledge of the initial biological signatures carried in particles and DOM also remains highly limited. Surveys of marine microbes for their molecular signatures have largely been dictated by what can be grown axenically in culture. However, many important organisms are not available through laboratory culture, including the most abundant photoautotroph in the sea, Prochlorococus, and some of the most abundant heterotrophic microbes, the planktonic crenarchaeota. Clearly, given the recently recognized prevalence of these microbes in the contemporary ocean, it will be important to further study their roles in carbon and other biogeochemical cycles. The molecular signature that these organisms carry is only now being studied and much work is required to accurately interpret their corresponding molecular stratigraphic records.

P0465 A second key question for future research concerns the fate of terrestrial organic matter in the oceans. Two lines of evidence that have long argued against a significant terrestrial input are the stable carbon isotopic ($\delta^{13}C$) and elemental Corg/N composition of oceanic dissolved and particulate organic matter. Recent findings of extensive terrestrial organic matter degradation and exchange in deltaic systems have reinforced this notion. However, interpretation of bulk elemental and isotopic data is not necessarily straightforward. Organic matter–mineral associations, while a key determinant in OM preservation, are highly dynamic, and fluvial and eolian contributions of ^{13}C-enriched, nitrogen-replete soils OM derived from C4 vascular plant debris blurs traditional distinctions based on these parameters, undermining their diagnostic capability. Several other new lines of evidence including the recognition that terrestrial OC inputs to the oceans are largely dominated by numerous small, low latitude rivers draining mountainous regions, the recognition that BC in marine sediments could account for up to 30% of total OC in some continental margin deposits, and finally that relict OC eroding from sedimentary rocks on the continent represents an additional terrigenous component, all suggest that terrestrial OC may be an underestimated component of the oceanic carbon reservoir.

P0470 Multiple lines of further investigation are clearly warranted in order to address this important and complex issue. Small, low-latitude river systems have been undersampled, and our understanding of the composition and mode of terrestrial OM export from the continental shelf and slope is not well developed. At a mechanistic level, the manner in which different forms of organic are associated with particles, and move between dissolved and solid phases both during transit from the land to the oceans, and within sediment pore waters, requires detailed investigation. The timescales over which organic matter exchange and degradation take place in relation to the timescales for terrestrial OC delivery to the oceans is an important consideration in this context. Our ability to recognize and quantify terrigenous OC in the marine environment must also be improved. With respect to the preservation POMin sediments, reactivity depends on both the intrinsic lability of the molecular structures present and on the associated material matrix. While a strong causal relationship has been established between the properties of the matrix (e.g., mineral type and surface area) and efficiency of organic matter preservation, we are lacking a mechanistic basis for it. Future research strategies need to address the nature of the associations of OM with mineral surfaces and their effects on the reactivities toward chemical and biological agents. Similarly, while recent studies have demonstrated the link between bottom and porewater oxygen concentration and the extent of sedimentary OM degradation, we do not yet know whether the key reactant is molecular oxygen itself.

P0475 One striking aspect of marine organic geochemistry is that its material basis extends from the smallest molecules (methane, α-amino acids, short-chain fatty acids, etc.) through the ubiquitous but complex, HMW DOM to a highly diverse range of organic particles (BC, marine snow, necromass, etc.). No single set of tools is adequate to address the composition of all these materials and the ways in which they function. A variety of different analytical approaches is required. Bulk chemical, physical, and isotopic characterization, microscopy (TEM, SEM, etc.), spectroscopic techniques (NMR, etc.), fractionation and chromatographic techniques, and chemical degradation, have all been used to derive useful information. As we look ahead to the future, it is evident that many exciting opportunities lie at the interface between molecular biology and molecular organic geochemistry. For example, a better knowledge of the genetic machinery that directs the synthesis and degradation of biopolymers may help to unravel questions of OC preservation as DOC in the deep ocean and as POC in marine sediments. Such studies may also help to close the gap between organic matter characterization at the bulk and molecular level.

P0480 Finally, it is clear that human activity has and will continue to have an impact on the oceanic carbon cycle and associated biogeochemical processes. By the beginning of the 1990s, atmospheric CO_2 comprised $\sim$750 Gt C, and this has continued to rise at a rate of $\sim$3.4 Gt yr^{-1}. The oceans represent a major sink for anthropogenic CO_2 and it is imperative that we develop a better understanding of how organic matter cycling is impacted in order to assess the long-term consequences and health of the planet.

ACKNOWLEDGMENTS

S0155 The authors wish to dedicate this contribution to the memory of John I. Hedges. John was a source of inspiration; his contributions to marine organic geochemistry are immeasurable, but clearly evident from the extensive citations of his work throughout this chapter. The field of marine organic geochemistry has suffered a tremendous setback with his untimely departure.

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