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A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico

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Abstract—Organic matter in surface sediments from two onshore-offshore transects in the northwestern Gulf of Mexico was characterized by a variety of techniques, including elemental, stable carbon, radiocarbon, and molecular-level analyses. In spite of the importance of the Mississippi River as a sediment source, there is little evidence for a significant terrigenous input based on the low carbon:nitrogen ratios (8–5) and the enriched δ^{13}C values of bulk sedimentary organic carbon (−19.7‰ to −21.7‰). Radiocarbon analyses, on the other hand, yield depleted Δ^{14}C values (−277‰ to −572‰) which indicate that a significant fraction of the sedimentary organic carbon (OC) in all these surface sediments must be relatively old and most likely of allochthonous origin. CuO oxidations yield relatively low quantities of lignin products (0.4–1.4 mg/100 mg OC) along with compounds derived from proteins, polysaccharides, and lipids. Syringyl:vanillyl and cinnamyl:vanillyl ratios (averaging 1.6 and 0.5, respectively) and acid:aldehyde ratios for both vanillyl and syringyl phenols (averaging 0.8 and 1.2, respectively) indicate that the lignin present in sediments originates from nonwoody angiosperm sources and is highly degraded. The δ^{13}C values of lignin phenols in shelf sediments are relatively depleted in ^{13}C (averaging −26.3‰) but are increasingly enriched in ^{13}C at the slope sites (averaging −17.5‰ for the two deepest stations). We interpret these molecular and isotopic compositions to indicate that a significant fraction (≥50%) of the lignin and, by inference, the land-derived organic carbon in northwestern Gulf of Mexico sediments ultimately originated from C_4 plants. The source of this material is likely to be soil organic matter eroded from the extensive grasslands of the Mississippi River drainage basin. Notably, the mixed C_4 and C_3 source and the highly degraded state of this material hampers its recognition and quantification in shelf and slope sediments. Our data are consistent with higher than previously estimated inputs of land-derived organic carbon to regions of the ocean, such as the Gulf of Mexico, with significant sources of terrigenous C_4-derived organic matter. *Copyright © 1998 Elsevier Science Ltd*

1. INTRODUCTION

While it is generally agreed that organic carbon (OC) preservation in marine sediments is an important process in the global cycle of carbon and other bioactive elements such as oxygen and sulfur (e.g., Berner, 1989; Kump and Garrels, 1986; Walker, 1986); the role and importance of terrigenous OC (OC_{TERR}) preservation has been the subject of some debate (e.g., Hedges, 1992; Emerson and Hedges, 1988; Smith and MacKenzie, 1987). Some studies, for example, suggest that OC_{TERR} is currently deposited primarily on the inner continental shelves and that little is exported to the outer shelves and continental slopes (e.g., Hedges and Parker, 1976; Gearing et al., 1977; Hedges and Mann, 1979a). However, other investigations (e.g., Gagosian et al., 1987; Prahl and Muehlhausen, 1989; Druffel et al., 1986) indicate that a significant amount of the organic matter (OM) delivered to pelagic sediments is of terrestrial origin.

Higher estimates of OC_{TERR} burial in areas of the ocean beyond the immediate regions near river mouths have important implications for the interpretation of the marine sedimentary record and the understanding of the oceanic carbon cycle. For example, higher OC_{TERR} contents would lower estimates of past primary productivity and autochthonous carbon fluxes based on the %OC of marine sediments (e.g., Müller and Suess, 1979; Pedersen, 1983; Sarnthein et al., 1987). Elevated OC_{TERR} estimates would also force a reassessment of remineralization efficiencies of autochthonous OM (e.g., Martin et al., 1987; Westrich and Berner, 1984). Because terrigenous OM generally contains lower levels of nitrogen and phosphorous than its marine counterpart (e.g., Redfield et al., 1963; Hedges et al., 1986; Ruttenberg and Goñi, unpubl. data), the revised OC_{TERR} estimates should also affect our understanding of nutrient cycling in marine sediments. Finally, better constraints on the sources of OM may shed additional light on the processes responsible for its preservation in ocean sediments (e.g., Keil et al., 1997a; Hedges and Keil, 1995; Mayer, 1994; Lee, 1992; Calvert and Pedersen, 1992; Emerson, 1985).

Broad biochemical compositional differences between the OM present in shelf and slope sediments have been documented for the Washington Margin (Goñi and Hedges, 1992; Keil et al., 1994, 1998; Prahl et al., 1994; Prahl, 1985; Hedges and Mann, 1979a). In this location, shelf sediments, composed mainly of coarser silts and sands, display high yields of lignin-derived products but are relatively depleted in higher plant *n*-alkanes and cutin-derived markers. In contrast, sediments from the slope region, which are mostly fine silts and clays, contain OM that is lignin-poor and relatively enriched in cutin markers and *n*-alkanes. Furthermore, based on the distribution

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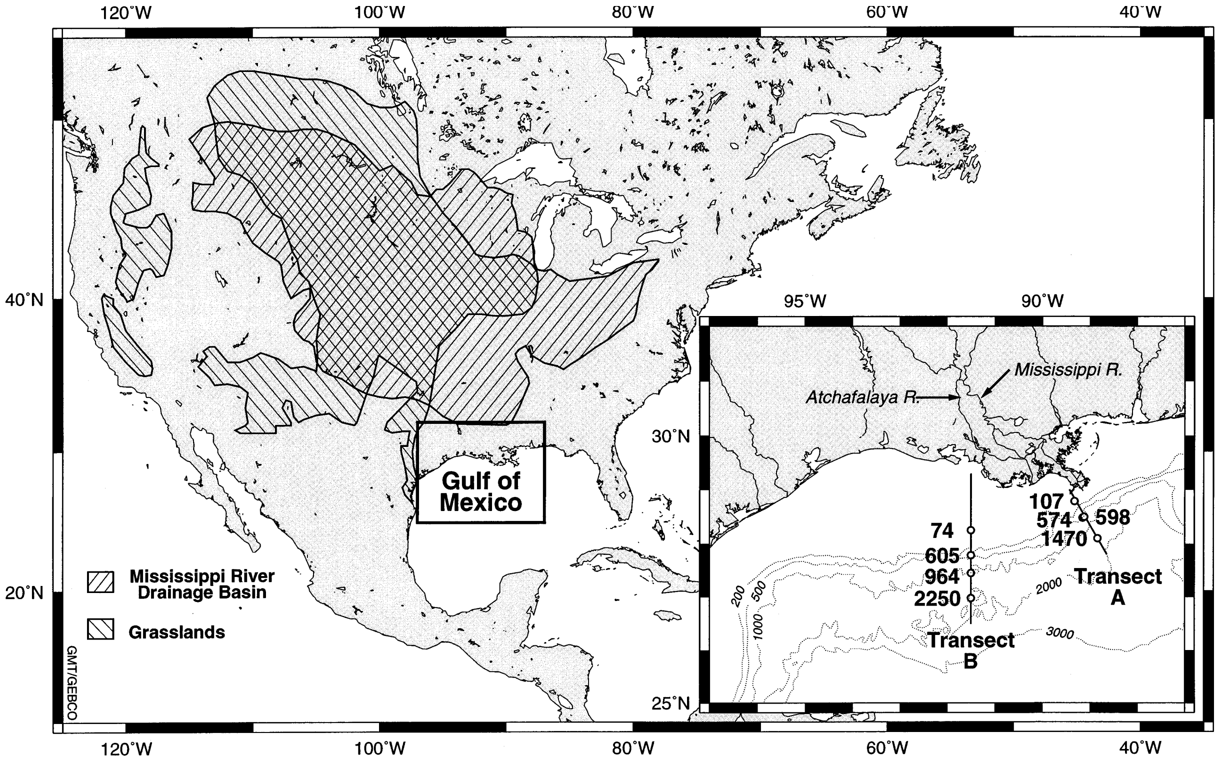

Fig. 1. Map of the drainage basin of the Mississippi River (U.S. Geological Survey Circular 1001), the extent of grasslands in North America (Sims and Coupland, 1979) and the marine sediment sampling locations in the Gulf of Mexico.

of CuO reaction products, the lignin in the shelf appears fresher (better preserved) than that in the slope region of the Washington Margin. Similar patterns are also observed in sediments of the North West Mediterranean Sea and North East Atlantic Ocean (Gough et al., 1993). Such distributions can be explained by a process in which lignin-poor terrestrial OM associated with the finer terrigenous mineral fraction is preferentially transported offshore, while lignin-rich coarser material remains in shelf deposits (Keil et al., 1998; Prahl, 1985). Notably, these compositional differences among the various fractions of terrigenous OM may have led to the disparity in estimates of OC_{TERR} in ocean sediments. For example, while estimates of terrestrial contributions based on lignin phenol concentrations indicate OC_{TERR} is a minor component ($\leq$10%) of the sedimentary OM in slope sediments (Hedges and Mann, 1979a; Prahl et al., 1994), calculations based on *n*-alkanes suggest significantly higher (30%) terrestrial inputs (Prahl et al., 1994).

In this study, we attempt to reevaluate the importance of land-derived OM in surface sediments of the northwestern Gulf of Mexico, a topic previously studied by Hedges and Parker (1976), Gearing et al. (1977), and Eadie et al. (1994). In spite of the importance of the Mississippi River system as a sediment source, these authors have concluded that even within 10 km from the river mouth, marine OM is the dominant source ($\geq$50%) of sedimentary OC. Furthermore, previous studies (Ruttenberg and Goñi, 1997) of this area showed that sedimentary organic carbon:total nitrogen and organic carbon:organic phosphorous ratios could not be explained by simple mixing of single terrestrial and marine endmembers. Here, we seek to investigate the apparent dilution of such a strong terrestrial input and the observed trends in bulk parameters by further characterizing the sources and composition of land-derived OM at both the molecular and isotopic level. Two significant developments aid us in this task: (1) the characterization of CuO oxidation products derived from non-lignin biochemical sources, such as proteins, lipids, polysaccharides, cutins, and phenolic compounds (Goñi and Hedges, 1990a, 1995) and (2) the ability to measure the $\delta^{13}C$ values of individual lignin-derived CuO oxidation products by isotope ratio monitoring-Gas Chromatography-Mass Spectrometry (irm-GC-MS; Goñi and Eglinton, 1996; Goñi et al., 1997).

The irm-GC-MS technique has been applied to determine the isotopic composition of lignin CuO reaction products from a variety of sample matrices, including vascular plant tissues, isolated sedimentary OM, and bulk sediments (Goñi and Eglinton, 1996). The results from this prior study highlight the large differences between the $\delta^{13}C$ signatures of lignin phenols from C_3 ($\delta^{13}C = -30.4‰ \pm 3.9‰$) and C_4 ($\delta^{13}C = -16.9 \pm 2.7‰$) plants. These and similar data for other compound types (e.g., *n*-alkanes; Collister et al., 1994) are consistent with the lesser discrimination against ^{13}C displayed by the phosphoenolpyruvate (C_4) pathway for photosynthetic carbon fixation relative to the ribulose bisphosphate (C_3) pathway (e.g., O'Leary, 1981; Fogel and Cifuentes, 1993). Goñi and Eglinton (1996) also showed that the characteristic $\delta^{13}C$ values of lignin phenols can be used to

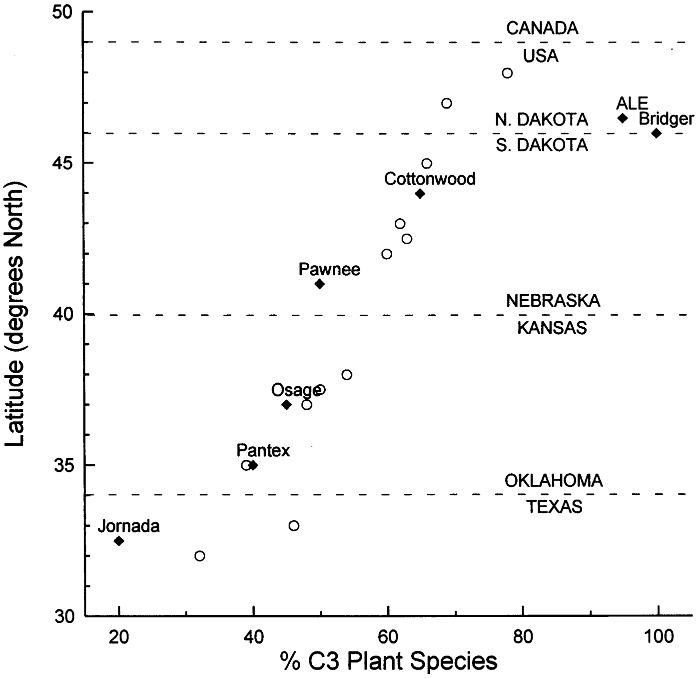

Fig. 2. Distribution of C_3 species as a percentage of all total plant species in comparison to latitude. Data includes field sites (◆, labeled names) from the Grassland Biome program (French, 1979) and additional sites (○) within the Mississippi River drainage (data from Teeri and Stowe, 1976; Fig. 1). State and U.S./Canada boundaries are indicated for reference.

elucidate C_3 and C_4 lignin sources in moderately degraded geochemical mixtures.

2. STUDY SITE

2.1. Site Description

The focus of this study is the northwestern Gulf of Mexico (see Ruttenberg and Goñi, 1997 for a detailed description of the area), extending from the continental shelf to the abyssal plain (Fig. 1). Marine primary productivity for shelf waters in this area exceeds 100 g C/m^2/yr (Walsh, 1989). The predominant source of sediment for this region is the Mississippi River system (Van Andel, 1960; Davies and Moore, 1970; Newman et al., 1973), which drains an area of 3.3×10^6 Km^2 (40% of the continental U.S.), carries an average of 210×10^6 tonnes of sediment per year (Milliman and Meade, 1983; Milliman and Syvitski, 1993) and contributes 70–90% of the freshwater to the Gulf of Mexico (Deegan et al., 1986; Dinnel and Wiseman, 1986). Sediments entering the Gulf are deposited in the well-developed delta and further dispersed along the shelf and to deeper regions via resuspension and near-bottom turbidity currents (Davies and Moore, 1970; Prior and Coleman, 1978; Lyndsay et al., 1984). Currently, the main channel of the Mississippi River is highly impacted by human activities, including dredging and the construction of levees and flood-control dams. Approximately 30% of the Mississippi river flow is diverted to the Atchafalaya River at Tarbert Landing, LA (located several hundred miles north of the river mouth). The Red River joins the Atchafalaya River south of Tarbert Landing and contributes an additional ca. 33% to the Atchafalaya River discharge (Bratkovich et al., 1994).

The Mississippi River drainage basin includes most of North America's grasslands (Fig. 1; Sims and Coupland, 1979), which cover an area of 3.7×10^6 Km^2 (Lauenroth, 1979). The native vegetation of the North America's grasslands is composed primarily of C_4 and C_3 grasses. The photosynthetic rates of C_4 plants at temperatures above 10°C are considerably higher than those of C_3 plants (Black, 1971). This difference is believed to control the latitudinal distribution of vegetation (Fig. 2) observed in North American prairies (Teeri and Stowe, 1976; French, 1979), in which warm-season C_4 species are most abundant in the southern regions whereas cool-season C_3 species dominate the northern ranges. The prairie lands of the Great Plains have been extensively exploited by humans over the last century. In general, the semi-arid grasslands located in southern portion of the Mississippi River drainage basin are mostly rangelands (Coupland, 1979; Sprague, 1959). In contrast, northern latitude grasslands are subject to more intensive cultivation, including corn (C_4 plant) and wheat (C_3 plant), and are used predominantly as croplands.

2.2. Sample Description

Sediments were collected from various sites along two transects perpendicular to the shore of the Gulf of Mexico (Fig. 1) during January 1987 on the R/V Gyre (Table 1; Ruttenberg and Goñi, 1997). Transect A extends NW-SE from Southwest Pass, one of the main distributaries of the Mississippi River Delta. Transect B runs N-S along the 91°30′ longitude line that roughly corresponds to the Atchafalaya River outflow. Sedimentation rates were determined using ^{210}Pb inventories for the sites on transect A (Ruttenberg, 1990; Lin, 1990) and varied inversely with water depth, from 0.8 cm/y at the 107 m station to 0.005 cm/y at the 1470 m station (Table 1). The composi-

Table 1. Bulk compositions of sediments from northwestern Gulf of Mexico transects

Site Location		Site Depth (m)	Sed. Rate (cm/yr)	%TOC	%TN	$\%CaCO_3$	[C/N]a	$\delta^{13}C_{OC}$ (‰)	$\Delta^{14}C_{OC}$ (‰)	Age_{OC} (ybp)	fM
Latitude	Longitude										
Transect A											
28°47.77′N	89°19.14′W	107	0.8[a]	1.37	0.19	2.0	8.4	−21.1	−275.8	2580	0.727
28°29.90′N	89°80.90′W	574	0.2[b]	1.42	0.20	3.8	8.3	−20.4	−291.1	2720	0.713
28°30.30′N	89°06.80′W	598	0.2[b]	1.30	0.18	3.8	8.4	−20.6			
28°06.20′N	88°50.40′W	1470	0.005[b]	0.91	0.17	16.6	6.2	−19.7	−393.0	3960	0.610
Transect B											
28°14.90′N	91°30.00′W	74	c	0.92	0.14	7.7	7.6	−20.9	−367.0	3630	0.637
27°47.00′N	91°29.80′W	605	c	1.24	0.18	11.5	8.0	−21.6	−383.5	3840	0.620
27°27.30′N	91°30.10′W	964	c	0.57	0.13	28.7	5.1	−20.0	−386.4	3880	0.617
26°58.86′N	91°30.06′W	2250	c	0.34	0.08	25.4	5.0	−21.7	−572.1	6770	0.430

Abbreviations: %TOC, weight percent total organic carbon; %TN, weight percent total nitrogen; $\%CaCO_3$, weight percent calcium carbonate; [C/N]a, atomic organic carbon/total nitrogen ratio; $\delta^{13}C_{OC}$ (‰), stable carbon isotope composition of organic carbon in the per mil notation (VPDB); $\Delta^{14}C_{OC}$, radiocarbon isotope composition of organic carbon; Age_{OC} (ybp), radiocarbon age of organic carbon in years before present; fM, fraction of modern organic carbon; Sed. Rate, sedimentation rates: [a]Ruttenberg (1990); [b]Lin (1990); [c]data not available; but sedimentation rates in this region of the Gulf generally lower than for comparable depths along transect A. Weight percent and stable carbon isotope data are from Ruttenberg and Goñi (1997), radiocarbon data are from Goñi et al., (1997). The NOSAMS Accession numbers for the individual $^{14}C_{OC}$ analyses are as follows (listed in the order tabulated): Transect A—OS-10633, OS-10867, OS-10634; Transect B—OS-10635, OS-10866, OS-10868, OS-10636.

tions of these sediments are predominantly clay (50–75%), silt (25–45%), and fine sand (1–10%; Lin, 1990). According to Griffin (1962), montmorillonite is the most abundant (45–70%) clay mineral in sediments from this area of the Gulf, followed by illite (10–38%) and kaolinite (5–20%). Based on these compositions and those from soils and sediments from river tributaries, Griffin (1962) concluded that most of the clay exported to the Gulf by the Mississippi River originates from its western drainage basin (e.g., Mississippi, Missouri, Platte, Arkansas, and Red Rivers) with a minor contribution from the kaolinite-rich clays typical of the eastern tributaries (e.g., Ohio River).

3. ANALYTICAL METHODS

Box and gravity cores were utilized to collect sediments along the two transects. Both coring techniques recovered intact sediment/water interfaces at all locations. After core retrieval, sediments were sampled at 2 cm depth intervals. Surface sediments from the top 0–2 cm horizon were sampled and analyzed in this study. Samples were stored frozen (−20°C) after collection, freeze dried upon return to the laboratory, and ground to pass through a 125 μm sieve prior to analysis.

3.1. Bulk Analyses

Weight percentages of total carbon (TC) and total nitrogen (TN) were determined in duplicate (without acidification) by combustion (1000°C) on a Perkin Elmer 2400 CHN Elemental Analyzer. The average standard deviations of these measurements was ±2%. Total inorganic carbon (TIC) was determined with an automated carbonate system by measuring the increase in pressure (BARATRON absolute pressure transducer) due to CO_2 liberated upon acidification (100% phosphoric acid at 80°C) of sediments (Ostermann et al., 1990). The precision of the analysis is better than 1% of the measured value. Organic carbon was determined by difference; OC = TC -TIC (Goñi, 1997). Based on the errors of the TC and TIC measurements (2% and 1%, respectively), the error associated with OC determination is ca. 3% (Taylor, 1982).

3.2. Stable Carbon Isotopes

Stable carbon isotopic compositions of sedimentary organic carbon ($\delta^{13}C_{OC}$) were determined on acidified (at least two 1N HCl treatments at room temperature) samples by automated on-line combustion coupled with conventional isotope ratio-mass spectrometry (Finnigan MAT Delta-S mass spectrometer). Details are given by Fry et al. (1992). By convention, the $^{13}C/^{12}C$ ratio of the organic carbon is reported relative to the PDB standard (VPDB) in $\delta^{13}C$ (‰) units. The standard deviation for this procedure is better than 0.05‰.

3.3. Accelerator Mass Spectrometry (AMS) ^{14}C Analysis

Radiocarbon measurements were made at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (WHOI). CO_2 gas samples derived from the combustion of bulk OC from preacidified sediments were purified, quantified, and converted to graphite AMS targets following established procedures (Vogel et al., 1987; McNichol et al., 1992). ^{14}C measurements are reported as $\Delta^{14}C$ (‰), fraction modern (fM), and ^{14}C age according to established conventions (Stuiver and Polach, 1977; Stuiver, 1980).

3.4. CuO Oxidation

CuO oxidations were carried out according to the procedure developed by Hedges and Ertel (1982) and modified by Goñi and Hedges (1992) and Goñi and Eglinton (1996). Briefly about 400 mg of sediment was oxidized under alkaline conditions (8% NaOH) with CuO at 155°C for 3 h in stainless steel pressurized vessels. Once the reaction vessels were opened, known amounts of trans-cinnamic acid and ethylvanillin were added to the solution as recovery standards. The aqueous solutions were acidified to pH 1 with concentrated HCl and extracted with diethyl ether. Water was removed from the extracts with Na_2SO_4 and the ether evaporated under a stream of N_2. Once dried, samples were stored frozen until gas chromatographic (GC) analysis. GC analyses were performed according to the conditions specified by Goñi and Eglinton (1996). The CuO reaction products were redissolved in pyridine and derivatized with bis(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TCMS) immediately prior to injection. Aldehyde lignin phenols were quantified based on the recoveries of ethylvanillin whereas trans-cinnamic acid was used to estimate the yields of all other lignin and nonlignin products. The yields of the major lignin phenols were calculated using the individual response factors derived from periodically injected mixtures of commercial standards. Nonlignin products (for which commercial standards were not available) were quantified using the response factor of *t*-cinnamic acid. The average precision for compounds with yields ≥ 0.04 mg/100 mg OC was 5%, and 15% for compounds with yields < 0.04 mg/100 mg OC.

3.5. Gas Chromatography-Mass Spectrometry

Compound identification was achieved by Gas Chromatography-Mass Spectrometry (GC-MS) using a Hewlett-Packard 5890 GC interfaced to a VG Autospec-Q hybrid MS (EI, 50 eV). Identical chromatographic conditions (i.e., column type and temperature program) were used in GC and GC-MS. GC-MS was critical to elucidate the identities of CuO reaction products from several samples that exhibited complex chromatograms.

3.6. Compound Specific Isotope Analyses

Isotope ratio monitoring-Gas Chromatography-Mass Spectrometry (irm-GC-MS) was used to measure the $\delta^{13}C$ values (‰) of individual lignin-derived CuO reaction products according to the procedure outlined by Goñi and Eglinton (1996). Details concerning the instrumental design and methodology for irm-GC-MS have been described previously (Hayes et al., 1990; Freeman, 1991; Ricci et al., 1994). The analyses presented in this study were performed at the Isotope Laboratory in the Ecosystems Center located in the Marine Biological Laboratory (Woods Hole, Massachusetts, USA) using a Varian 3000 GC linked to a Finnigan MAT Delta-S mass spectrometer. Perdeuterated aliphatic hydrocarbon standards (C_{20}, C_{24}, and C_{36} *n*-alkanes) of known isotopic composition were coinjected into the irm-GC-MS instrument with each sample to calibrate the mass-spectrometer. We used *t*-cinnamic acid of known isotopic composition to calculate $\delta^{13}C$ signature of the added derivative carbon. This value was then used to correct for derivative carbons and determine the $\delta^{13}C$ signature of each lignin phenol (e.g., Goñi and Eglinton, 1994, 1996). The precision of this approach was determined through multiple analyses of the same sample and ranged from ±1 to ±2‰ depending on the chromatographic resolution of each individual compound. The lower precision of these measurements relative to bulk $\delta^{13}C_{OC}$ analyses is due to a combination of errors associated with the derivative correction, chromatographic behavior, and complexity of the samples.

3.7. Propagation of Error and Statistical Significance

We evaluated the variance of compositional parameters by estimating the propagation of error associated with all measurements according to statistical theory (Taylor, 1982; Goñi and Eglinton, 1996). We used the two-sample z-test for means with a level of significance $\alpha = 0.05$ in order to test hypotheses about the difference between variables of known variance.

4. RESULTS

4.1. Bulk Sediment Compositions

4.1.1. Elemental compositions

The elemental compositions of sediments from both transects are presented in Table 1. In transect A, weight percent OC (%OC) ranges from 1.4 to 1.3% in three stations shallower than 600 m, decreasing to 0.9% at the 1470 m site. In contrast, three of the four stations in transect B have %OC values significantly lower than 1%. The only exception is the station at 605 m water depth (%OC = 1.2). The weight percent of $CaCO_3$ is very low (≤4%) in the shallower portion of transect A, increasing to 17% at the deepest site. In transect B sites, $CaCO_3$ contents range from 8% at 74 m to 29% at 964 m and are higher than values at comparable depths from transect A. Total nitrogen content on both transects ranges from 0.1 to 0.2%, with the station at 2250 m of transect B displaying the lowest values (0.08%). Atomic carbon nitrogen ratios ([C/N]a) are ca. 8 for all sites shallower than 605 m in both transects. In contrast, deeper sediments have [C/N]a ratios that are significantly lower than those from shallower sites, ranging from 6 to 5.

4.1.2. Stable carbon isotopic compositions

The $\delta^{13}C_{OC}$ values for all sediments vary within a relative narrow range from −21.7 to −19.7‰ (Table 1). In transect A, there is a slight but significant trend towards more enriched $\delta^{13}C_{OC}$ values with increasing water depth. A similar depth-related trend is not evident in transect B. Notably, transect B displays the two most depleted $\delta^{13}C_{OC}$ values of the whole data set, including −21.7‰ as the isotopic signature of sedimentary OM from the deepest station (2250 m).

4.1.2. Radiocarbon compositions

AMS analyses reveal $\Delta^{14}C$ values for sedimentary OC that range between −276.8‰ at the 107 m site to −572.1‰ at the 2250 m location. These values translate to ^{14}C ages that range between 2580 ybp and 6770 ybp and increase significantly with water depth along both transects (Table 1). In transect A, the age of OC varies from 2580 (107 m) to 3960 ypb (1470 m) whereas, in transect B, the ages range from 3630 (74 m) to 6770 ybp (2250 m).

4.2. CuO Oxidation Products from Sedimentary OM

Gulf of Mexico sediments yield a complex suite of CuO reaction products (Fig. 3) that include lignin-derived phenols, lipid-derived carboxylic acids (*n*-fatty acids, branched fatty acids and dicarboxylic acids), cutin-derived hydroxyfatty acids as well as products from proteins, polysaccharides, and tannin-like substances (Table 2). The origins and chemical precursors of these products have been discussed previously (Hedges and Mann, 1979b; Goñi and Hedges, 1990a, 1992, 1995) and are listed in Table 2. In the case of protein products, the individual amino acid precursors of each product are also listed.

In transect A (Fig. 4a), the carbon-normalized yields of lignin phenols decrease steadily and significantly with water depth from 1.4 (107 m) to 0.5 mg/100 mg OC (1470 m). None of the other major types of CuO products displays a similar trend with depth. For example, all stations in transect A display similar yields of protein and polysaccharide products (1.4 ± 0.1 mg/100 mg OC) and lipid products (0.46 ± 0.03 mg/100 mg OC). Additionally, both hydroxybenzoic acid and cutin acid yields are comparably low (<0.25 mg/100 mg OC) in all four sites of transect A. The lignin phenol yields for sediments from the four sites of transect B (0.53 ± 0.04 mg/100 mg OC) are statistically indistinguishable (Fig. 4a). In contrast, the yields of both protein and polysaccharide products (1.3 mg/100 mg OC) and lipid products (0.44 mg/100 mg OC) increase significantly from the two shallower stations to the two deeper ones (2.0 and 0.65 mg/100 mg OC, respectively). Overall, lignin phenols account for 40–15% of total GC-amenable CuO reaction products from transect A and 20–16% in transect B (Fig. 4b). Protein and polysaccharide products are the dominant compounds of both transects, accounting for 60–40% of the total CuO yields. Lipid product yields are also important along both transects, representing 20–13% of the total CuO yields. Hydroxybenzoic acids and cutin acids combined account for 5–7% of the total CuO product yields in all sites.

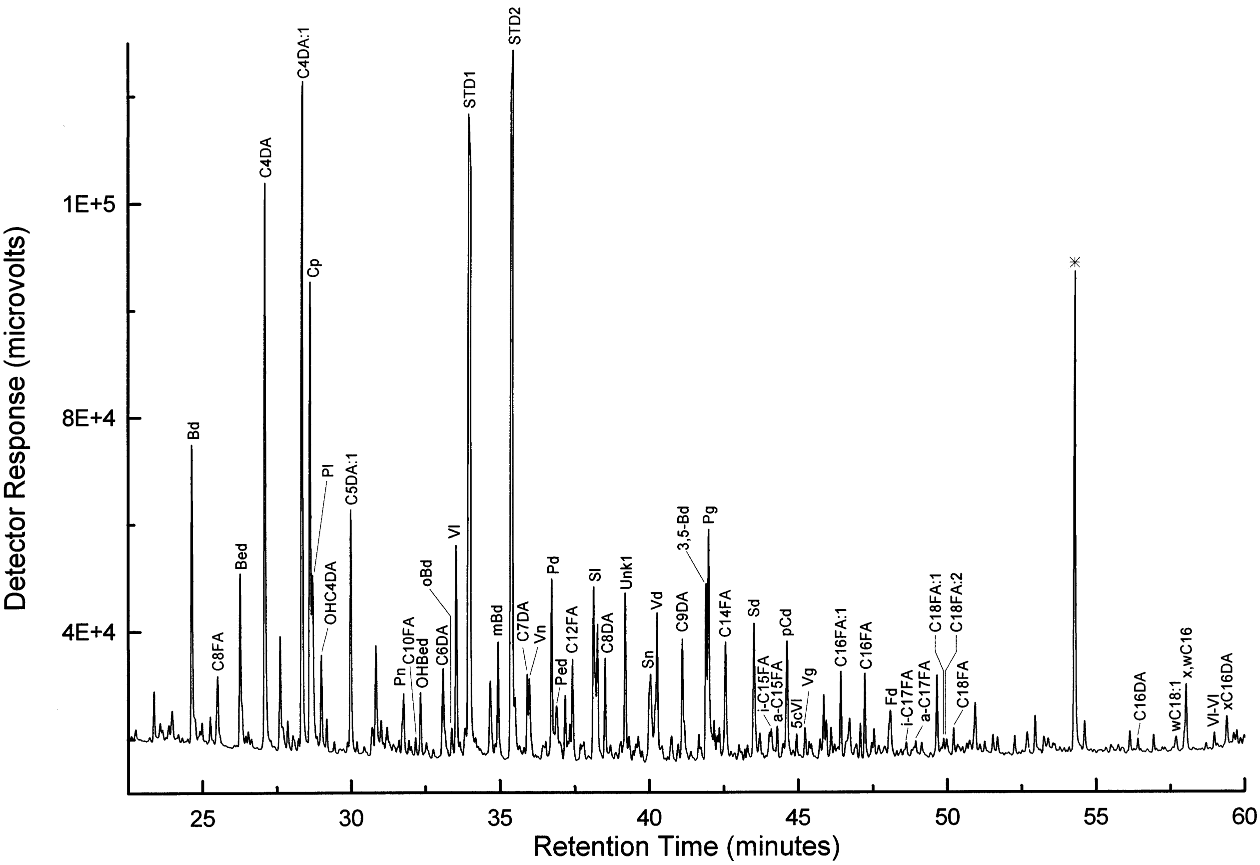

Fig. 3. Gas Chromatographic trace of CuO products from Gulf of Mexico sediments (transect A; 598 m). Peak codes correspond to the compound names in Table 2. STD1, *t*-cinnamic acid; STD2, ethylvanillin; Unk1, nitrogen-containing compound of unknown structure; *, contaminant.

4.3. Isotopic Composition of Individual Lignin-Derived Phenols

The application of irm-GC-MS to Gulf of Mexico sediments is constrained by the low concentrations of lignin phenols and complex chromatographic traces obtained from most samples (e.g., Fig. 3). This latter constraint hinders the integration of chromatographic peaks from several relatively abundant compounds such as syringealdehyde, acetosyringone, and vanillic acid. In most samples, only syringic acid was sufficiently resolved and in high enough yield ($>$0.1 mg/100 mg OC; Table 2) to garner statistically robust estimates of δ^{13}C (Table 3). Nevertheless, we were able to estimate δ^{13}C values of other products in a few selected samples, particularly those in transect A with relatively high yields ($\geq$0.06 mg/100 mg OC). Three samples from transect A (107, 598, and 1470 m) and all four samples from transect B were analyzed by irm-GC-MS.

In transect A, the δ^{13}C value of syringic acid increases significantly from -29‰ at 107 m to -15‰ at both 598 and 1470 m (Table 3). Albeit not represented in all samples, *p*-coumaric acid displays a similar trend with depth. In contrast to these two lignin phenols, vanillin displays more depleted values (<-26.5‰) at both 107 and 598 m. In transect B, the isotopic composition of syringic acid ranges between -24‰ (964 m) and -20‰ (2250 m) and fails to display a trend with water depth. The δ^{13}C value of syringealdehyde is also relatively enriched (≈ -22‰) at the 74 m station. As in transect A, vanillin is the exception because it has a much more depleted δ^{13}C signature of -30‰.

5. DISCUSSION

5.1. Molecular-Level Characterization Sedimentary OM

5.1.1. *Marine OM*

Many of the nonlignin reaction products derived from the oxidation of proteins, polysaccharides, lipids, and phenolic polymers have both terrestrial and marine sources (Goñi and Hedges, 1992, 1995). However, marine organisms such as plankton and bacteria generally contain a higher fraction of proteins and lipids in their OM relative to vascular plants (e.g., Cowie and Hedges, 1992; Lee et al., 1971; Goosens et al., 1986). Furthermore, the depth-related distributions of protein and polysaccharide, and lipid products (Fig. 4) suggest these compounds may provide general information as to the sources of nonterrigenous OM (e.g., phytoplankton, zooplankton, macrophytes, bacteria) present in Gulf of Mexico sediments.

The most abundant protein and polysaccharide products in all sediments (Table 2) are those derived from aspartic acid (2-butene-1,4-dioic) and glutamic acid (butane-1,4-dioic acid). Other important products include those derived from proline

Table 2. CuO oxidation yields (mg/100 mg OC) from Gulf of Mexico sediments

			TRANSECT A (water depth in m)				TRANSECT B (water depth in m)			
Compound	Code	Chemical precursor	107	574	598	1470	74	605	964	2250
Ligin Products										
Vanillin	Vl	G-LIG	0.244	0.106	0.132	0.031	0.071	0.034	0.033	0.050
Acetovanillone	Vn	G-LIG	0.079	0.036	0.050	0.007	0.039	0.021	0.007	trace
Vanillic Acid	Vd	G-LIG	0.137	0.081	0.089	0.014	0.053	0.039	0.040	0.039
5-Carboxyvanillin	5cVl	G-LIG	0.032	0.033	0.016	0.024	0.019	0.034	0.044	0.033
Vinillylglyoxylic acid	Vg	G-LIG	0.021	0.010	0.013	0.005	0.010	0.006	0.007	0.021
Syringealdehyde	Sl	S-LIG	0.349	0.092	0.169	0.041	0.043	0.133	0.137	0.027
Acetosyringone	Sn	S-LIG	0.169	0.115	0.107	0.088	0.086	0.084	0.109	0.094
Syringic acid	Sd	S-LIG	0.142	0.092	0.090	0.062	0.066	0.061	0.083	0.094
p-Coumaric acid	pCd	nw-LIG	0.085	0.045	0.059	0.037	0.042	0.042	0.047	0.052
Ferulic acid	Fd	nw-LIG	0.071	0.040	0.048	0.033	0.039	0.030	0.045	0.050
p-Hydroxyacetophenone	Pn	P-LIG	0.040	0.030	0.037	0.032	0.035	0.030	0.039	0.058
		Total Lignin	**1.37**	**0.679**	**0.810**	**0.373**	**0.504**	**0.515**	**0.592**	**0.517**
Protein & Polysacc. Products										
p-Hydroxybenzaldehyde	Pl	P-LIG, PR (Tyr)	0.129	0.097	0.115	0.164	0.119	0.090	0.105	0.122
p-Hydroxybenzoic acid	Pd	P-LIG, PR (Tyr)	0.094	0.055	0.055	0.036	0.053	0.050	0.048	0.038
Benzoic acid	Bd	PR,(Phe, Trp)	0.110	0.110	0.112	0.124	0.109	0.142	0.156	0.178
Phenylacetic acid	Bed	PR (Phe)	0.095	trace	0.075	0.075	0.096	0.074	0.094	0.073
α-Hydroxyphenylacetic acid	OHBed	PR (Phe)	0.026	0.024	0.026	0.020	0.031	0.025	0.031	0.024
p-Hydroxyphenylacetic acid	Ped	PR (Tyr)	0.037	0.038	0.032	0.081	0.032	0.036	0.053	0.145
p-Hydroxyphenylglyoxylic acid	Pg	PR (Tyr)	0.141	0.066	0.107	0.036	0.097	0.074	0.070	0.061
Butane- 1,4-dioic acid	C4DA	PR(Glu), PS	0.240	0.333	0.210	0.353	0.194	0.286	0.66	0.382
2-Butene-1,4-dioic acid	C4DA:1	PR (Asp), PS	0.345	0.40	0.294	0.460	0.256	0.37	0.64	0.392
Pentene-1,5-dioic acid	C5DA:1	PS (PEC, ALG)	0.077	0.115	0.090	0.107	0.073	0.117	0.172	0.124
2-Carboxypyrrole	Cp	PR (Pro)	0.019	0.007	0.169	0.034	0.231	0.016	0.046	0.202
Hydroxybutane-1,4-dioic acid	OHC4DA	PR (Thr), PS	0.049	0.053	0.041	0.057	0.043	0.073	0.129	0.009
		Total Prot. Polys.	**1.36**	**1.30**	**1.33**	**1.55**	**1.33**	**1.36**	**2.21**	**1.75**
Lipid Products										
Octanoic acid	C8FA	E-LIP	0.029	0.030	0.035	0.036	0.034	0.041	0.047	0.038
Decanoic acid	C10FA	E-LIP	0.009	0.010	0.008	0.007	0.029	0.011	0.010	0.008
Dodecanoic acid	C12FA	E-LIP	0.041	0.039	0.039	0.046	0.040	0.050	0.077	0.080
Tetradecanoic acid	C14FA	E-LIP	0.065	0.064	0.059	0.061	0.059	0.061	0.079	0.079
Hexadecenoic acid	C16FA:1	E-LIP	0.036	0.038	0.031	0.042	0.024	0.031	0.043	0.044
Hexadecanoic acid	C16FA	E-LIP (Palmitic acid)	0.034	0.027	0.031	0.037	0.032	0.029	0.049	0.072
Octadecenoic acid	C18FA:1	E-LIP (Oleic acid)	0.009	trace	0.008	0.005	0.027	0.008	0.006	0.014
Octadecadienoic acid	C18FA:2	E-LIP (Linoleic acid)	0.011	0.010	0.011	0.009	0.007	0.009	0.014	0.014
Octadecanoic acid	C18FA	E-LIP (Stearic acid)	0.009	0.009	0.012	0.014	0.012	0.013	0.017	trace
iso-Pentadecanoic acid	i-C15FA	E-LIP	0.019	0.016	0.014	0.018	0.034	0.013	0.024	0.013
anteiso-Pentadecanoic acid	a-C15FA	E-LIP	0.019	0.015	0.013	0.017	0.015	0.013	0.020	trace
iso-Heptadecanoic acid	i-C17FA	E-LIP	0.010	0.008	0.008	0.007	0.008	0.006	0.009	trace
anteiso-Heptadecanoic acid	a-C17FA	E-LIP	trace	0.008	0.005	0.006	trace	0.006	0.008	0.006
Hexane-1,6-dioic acid	C6DA	O-LIP	0.037	0.044	0.051	0.057	0.034	0.046	0.084	0.070
Heptane-1,7-dioic acid	C7DA	O-LIP	0.027	0.037	0.029	0.044	0.028	0.034	0.098	0.039
Octane-1,8-dioic acid	C8DA	O-LIP	0.037	0.038	0.040	0.042	0.031	0.029	0.049	0.061
Nonane-1,9-dioic acid	C9DA	O-LIP	0.057	0.052	0.046	0.060	0.030	0.031	0.050	0.066
		Total Lipids	**0.452**	**0.448**	**0.440**	**0.506**	**0.447**	**0.432**	**0.683**	**0.612**
Hydroxy Benzoic acid										
o-Hydroxybenzoic acid	*o*Bd	TAN	0.017	0.012	0.013	0.013	0.014	0.019	0.019	0.020
m-Hydroxybenzoic acid	mBd	TAN	0.053	0.055	0.048	0.054	0.049	0.065	0.098	0.081
3,5-Dihydroxybenzoic acid	3,5-Bd	TAN	0.066	0.044	0.050	0.024	0.032	0.036	0.029	0.048
		Total Hydroxy Benzoic Acids	**0.136**	**0.111**	**0.111**	**0.091**	**0.095**	**0.120**	**0.146**	**0.148**
Cutin Products										
16-Hydroxyhexadecanoic acid	ωC16	CUT	0.010	0.009	0.005	0.009	0.008	0.008	0.013	0.009
Hexadecane-1,16-dioic acid	C16DA	CUT	0.016	0.015	0.006	0.010	trace	0.009	0.018	0.011
18-Hydroxyoctadec-9-enoic acid	ωC18:1	CUT	0.008	trace	0.009	trace	0.006	trace	trace	0.010
Dihydroxyhexadecanoic acid[†]	x,ωC16	CUT	0.020	0.009	0.033	0.006	0.025	0.007	0.008	0.012
Hydroxyhexadecane-1,16-dioic acid[‡]	xC16DA	CUT	0.026	0.010	0.018	0.005	0.013	0.011	0.006	trace
		Total Cutin acids	**0.080**	**0.048**	**0.072**	**0.034**	**0.056**	**0.035**	**0.049**	**0.045**

Chemical precursor abbreviaitons: G-LIG, guaiacyl ligin; S-lignin, syringyl liginin; nw-LIG, nonwoody tissue lignin; P-LIG, *p*-hydroxy lignin; PR, protein; PS, polysaccharide (including cellulose, chitin, pectin and alginic acid0; E-LIP, ester-bound lipid; O-LIP, ether-bound lipid; TAN, tannin; CUT, cutin; Tyr, tyrosine; Trp, tryptophan; Phe, Phenylalanine; Glu, glutamic acid; Asp, aspartic acid; Pro, Proline; Thr, threonine.

Other abbreviations: trace, < 0.005 mg/100 mg OC; [†], composed mainly of 9,16- and 10,16-dihydroxyhexadecanoic acid isomers; [‡]. Composed mainly of 7- and 8-hydroxyhexadecane-1,16-dioic acid isomers

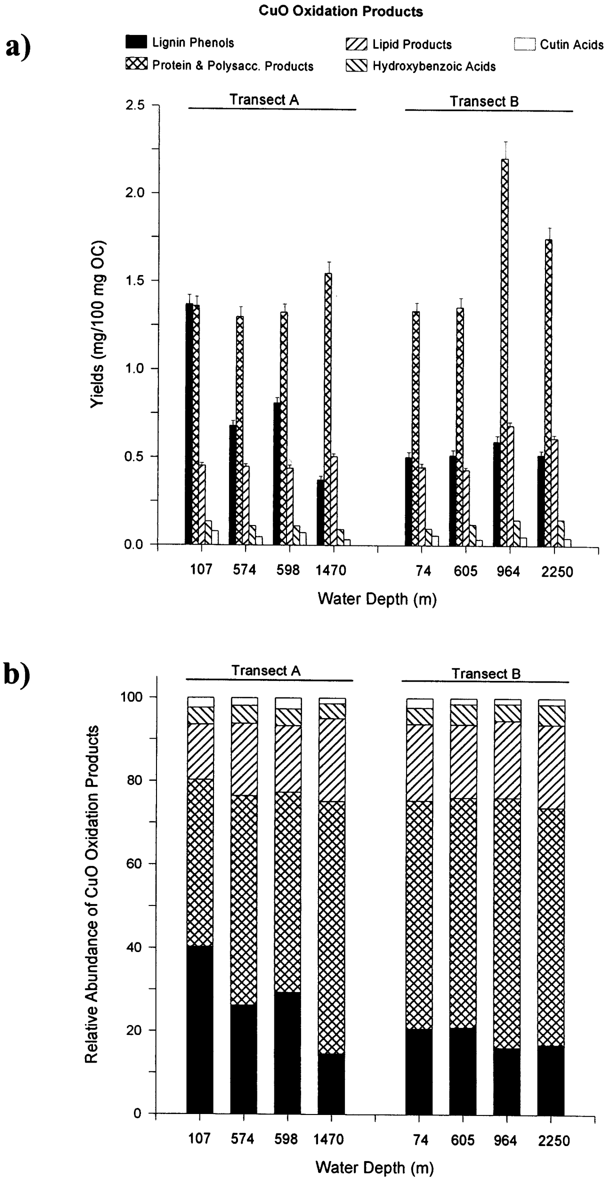

Fig. 4. (a) Carbon-normalized yields and (b) relative abundances of major CuO oxidation products from Gulf of Mexico sediments.

(2-carboxypyrrole), tyrosine (*p*-hydroxyphenylglyoxylic acid), and phenylalanine (benzoic acid). Notably the CuO reaction product (of still undetermined structure; Goñi and Hedges, 1995) derived from acidic polysaccharides (e.g., pectin, alginic acid) and characteristic of marine macrophytes (e.g., kelps) is absent from all sediments analyzed. Overall, the distribution of protein and polysaccharide products is consistent with the compositions obtained from a variety of marine organic matter sources (including phytoplankton and bacteria; Goñi and Hedges, 1995). However, the predominance of 2-butene- and butane-1,4-dioic acids is a distinctive feature of these sediments, which may be related to diagenetic processes and/or specific organic inputs.

Alkaline CuO oxidation efficiently hydrolyzes ester bonds releasing intact fatty acids without significant alteration (Goñi and Hedges, 1995). Hence, lipid-derived CuO oxidation products have the potential to provide perhaps the best opportunity to discriminate marine OM sources because of the distinct signatures obtained from different biological endmembers (Goñi and Hedges, 1995). In this study, whole sediments were used for CuO oxidation so that the lipid compositions presented below include both free and bound fatty acids. One way to graphically illustrate the source indicator potential of these products is through compositional fingerprints derived from their relative yields (Fig. 5). These graphs reveal that tetradecanoic acid is the most abundant fatty acid in all samples. Dodecanoic, hexadecanoic, and hexadecenoic acids increase in importance at the deeper sites. Hexane-1,6-dioic and nonane-1,9-dioic acid are the dominant diacids. Overall, diacids appear to increase in relative importance with depth in both transects. Branched fatty acids represent a minor fraction of the total lipid yield in most sediments, the major exception being the 74 m sample.

Comparison of the sedimentary (Fig. 5a) and biological lipid product fingerprints (Fig. 5b), along with the absence of the acidic polysaccharide product (Table 2), suggest that neither macrophytes nor gram-positive bacteria represent a major fraction of the marine OM released by CuO oxidation from these samples. Instead, the distribution of lipids and protein products is consistent with planktonic sources with perhaps an appreciable contribution by gram-negative bacteria and, in the case of the 74m sample, by gram-positive bacteria. Because of diagenetic effects and the incomplete analytical coverage of potential sources, a more detailed quantitative characterization of marine OM inputs falls beyond the scope of this study.

Table 3. δ^{13}C values (‰) of CuO oxidation products

	TRANSECT A (water depth in m)			TRANSECT B (water depth in m)			
	107 Avg. ± s.d.	598 Avg. ± s.d.	1470 Avg. ± s.d.	74 Avg. ± s.d.	605 Avg. ± s.d.	964 Avg. ± s.d.	2250 Avg. ± s.d.
TOC	−21.1 ± 0.1	−20.4 ± 0.1	−19.7 ± 0.1	−20.9 ± 0.1	−21.6 ± 0.1	−20.0 ± 0.1	−21.7 ± 0.1
Vanillin	−26.7 n.a.	−28.0 ± 0.7	— —	−29.9 n.a.	— —	— —	— —
Syringealdehyde	— —	— —	— —	−22.0 n.a.	— —	— —	— —
Syringic acid	−29.0 n.a.	−15.3 ± 1.2	−15.2 ± 0.6	−22.0 n. a.	−21.8 ± 1.7	−23. n.a.	−19.9 ± 1.0
p-Coumaric acid	−28.5 n.a.	−15.1 n.a.	— —	— —	— —	— —	— —

Abbreviations: Avg., average; s.d. standard deviation; n.a., not available; −, indicates insufficient chromatographic separation for statistically robust irm-GC-MS determination (see text for details)

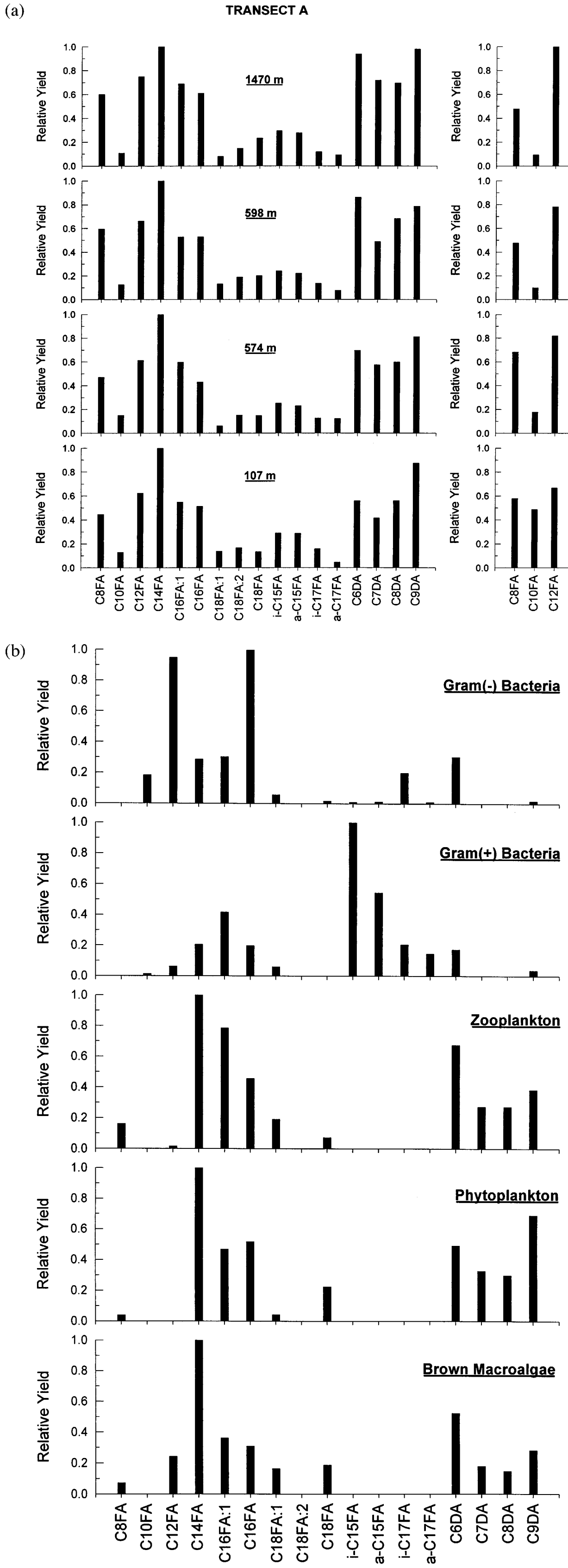

Fig. 5. Compositional fingerprints of lipid-derived CuO reaction products for (a) Gulf of Mexico sediments and (b) biological OM sources (data from Goñi and Hedges, 1995). All compound codes correspond to reaction products listed in Table 2.

Table 4. Compositional parameters of Gulf of Mexico sedimentary organic matter

		TRANSECT A (water depth in m)				TRANSECT B (water depth in m)			
Parameter	Code	107	574	598	1470	74	605	964	2250
Total Lignin Phenol Yield (mg/100 mg OC)	Tlig	1.37	0.68	0.81	0.37	0.50	0.51	0.59	0.52
Vanillyl + Syringyl Phenol Yield (mg/100 mg OC)[*]	Λ*	1.12	0.52	0.64	0.24	0.36	0.37	0.41	0.30
Syringyl: Vanillyl Ratio	S/V	1.29	1.13	1.22	2.39	1.01	2.06	2.53	1.50
Cinnamyl: Vanilly Ratio	C/V	0.30	0.32	0.36	0.87	0.42	0.53	0.70	0.71
Vanillyl Acid:Aldehyde Ratio	[Ad/Al]v	0.56	0.76	0.67	0.46	0.75	1.16	1.18	0.78
Syringyl Acid: Aldehyde Ratio	[Ad/Al]s	0.41	1.00	0.53	1.51	1.53	0.46	0.61	3.47
3,5-Ddihydroxybenzoic Acid:Vanillyl Phenol Ratio	3,5-Bd/V	0.13	0.17	0.17	0.30	0.16	0.27	0.22	0.33
Atomic Organic Carbon:Organic Nitrogen Ratio[†]	Org[C/N]a	11	11	12	9	12	11	8	13

[*] Sum of vanillyl + syringyl phenol yields (Λ) was calculated in order to compae directly to data from Hedges and Parker (1976); [†]organic nitrogen corrected for the inorganic nitrogen content estimated from Fig. 7 (see text for details)

5.1.2. Terrigenous OM

Several parameters based on lignin oxidation products have been widely used to characterize the sources of lignin and $\mathrm{OC_{TERR}}$ in marine samples (e.g., Hedges and Mann, 1979a; Ertel and Hedges, 1984; Prahl et al., 1994). For example, the ratio of syringyl:vanillyl phenols (S/V) can provide information regarding the angiosperm vs. gymnosperm origin of lignin. Further information about lignin sources (woody vs. nonwoody tissues) can be gained from the ratio of cinnamyl:vanillyl phenols (C/V). All Gulf of Mexico sediments yield S/V ratios $\geq$1 and C/V ratios $\geq$0.3 (Table 4). In transect A, S/V ratios increase significantly from values of ca. 1.3 at stations shallower than 600 m to a value of 2.4 at 1470 m. S/V ratios also increase significantly over the first three stations (74, 605 and 964 m) of transect B, decreasing to 1.5 at 2250 m. C/V ratios display a very similar overall trend with depth in both transects. In transect A, C/V ratios are significantly higher at 1470 m than in the other three shallower sites (0.8 vs. 0.3, respectively). In transect B, C/V ratios at the two deepest stations ($\sim$0.7) are significantly higher than those obtained at 74 and 605 m.

A plot of S/V vs. C/V ratios indicates that nonwoody angiosperm tissues (leaves and grasses) are the major sources of lignin in all the Gulf of Mexico sediments (Fig. 6). Grasses are generally characterized by higher C/V ratios than leaves (e.g., Hedges et al., 1986; Goñi and Hedges, 1992). Hence, the general trend towards higher C/V ratios in samples from the 600–1600 m range could indicate an enhanced grass lignin source in distal sediments. However, microbial degradation of vascular plant tissues is known to drastically alter both S/V and C/V ratios (e.g., Hedges et al., 1988; Hedges and Weliky, 1989; Benner et al., 1991; Haddad et al., 1992; Opsahl and Benner, 1995). Therefore, it is imprudent to differentiate vascular plant sources much further beyond the general nonwoody angiosperm origin already deduced.

The diagenetic state of lignin in natural samples often can be estimated from the ratio of acid to aldehyde vanillyl ([Ad/Al]v) and syringyl ([Ad/Al]s) CuO oxidation products (e.g., Hedges et al., 1988; Goñi et al., 1993; Opsahl and Benner, 1995). Acid:aldehyde ratios for both vanillyl and syringyl phenols are $\geq$ 0.4 in all Gulf of Mexico sediments analyzed in this study (Table 4). In transect A, [Ad/Al]v ratios range from 0.5 to 0.7, whereas [Ad/Al]v values in transect B range from 0.7 to 1.2. However, due to the large propagation of error associated with ratioing small numbers, there is no significant difference among the [Ad/Al]v ratios obtained from different depths within each transect. Furthermore, the average [Ad/Al]v values obtained from both transects (0.6 and 1.0, respectively) are not statistically different. In contrast, on transect A [Ad/Al]s ratios at 107 and 598 m (0.4 and 0.5, respectively) are significantly lower than those obtained at 574 m (1.0) and 1470 m (1.5). On transect B significantly lower [Ad/Al]s ratios are also obtained at 605 and 964 m relative to those obtained from 74 m (1.5) and 2250 m (3.5).

The consistently large [Ad/Al] ratios indicate a highly degraded state for the lignins in all Gulf of Mexico sediments. Oxidative degradation of lignin sidechains by certain microorganisms, such as white-rot fungi, often produce characteristically elevated [Ad/Al] ratios (i.e., $>$0.4; Hedges et al., 1988; Goñi et al., 1993). Ratios greater than 0.4 have been measured in fine suspended river sediments (e.g., Hedges et al., 1986) and the fine fractions of surface soils (e.g., Prahl et al., 1994). Samples that yield even higher [Ad/Al] ratios (0.6–4) include the humic horizons (A and B) of mineral soils (e.g., Ziegler et al., 1986) and humic substances (both humic and fulvic acids) derived from sediments and soils (e.g., Ertel and Hedges, 1984). Hence, the elevated [Ad/Al] ratios characteristic of most offshore samples are evidence of the extensively degraded nature of the particle-bound terrigenous OM in Gulf of Mexico sediments. Because white-rot fungi and other efficient lignin-degrading organisms (e.g., soft-rot fungi; Nelson et al., 1995), predominate in terrestrial environments such as soils (Eriksson et al., 1990), it is likely that this decay occurred prior to marine deposition.

Hydroxylated fatty acids derived from cutin, a polyester macromolecule that constitutes an integral part of the cuticles covering soft parts (e.g., leaves, needles) of vascular plants (Holloway, 1982), have been used to further differentiate $\mathrm{OC_{TERR}}$ sources (e.g., Goñi and Hedges, 1990a). All of the Gulf sediments analyzed display generally low yields of cutin acids. Unlike nonwoody vascular plant tissues, which mainly yield dihydroxyhexanedecanoic acid (Goñi and Hedges, 1990a), the cutin acid signature of all sediments (Table 2) contains relatively high amounts of hexadecane-1,16-dioic acid and monohydroxylated fatty acids (such as 16-hydroxyhexadecanoic and 18-octadecenoic acids). This distribution is consistent with a high degree of cutin alteration caused by the

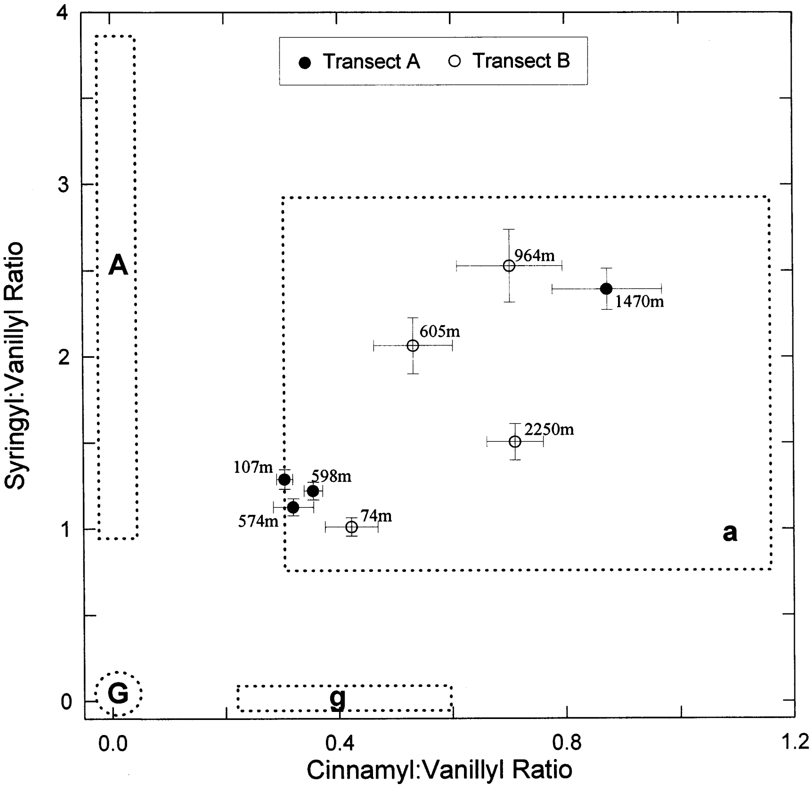

Fig. 6. Plot of cinnamyl:vanillyl (C/V) vs. syringyl:vanillyl (S/V) phenol ratios for Gulf of Mexico sediments. Included are the compositional ranges (delineated by dotted lines) of major vascular plant tissues (Hedges and Mann, 1979; Hedges et al., 1986; Goñi and Hedges, 1992) Tissue abbreviations: G, gymnosperm woods; g, gymnosperm needles; A, angiosperm woods; a, angiosperm leaves and grasses.

preferential decay of polyhydroxylated cutin acids over their monohydroxylated counterparts (Goñi and Hedges, 1990c; Opsahl and Benner, 1995). The relative abundances of the 8,16-, 9,16-, and 10,16- dihydroxyhexadecanoic acid isomers are ca. 10%, 30%, and 60% in those samples where the measurement was possible. These isomeric compositions are consistent with an angiosperm origin (Goñi and Hedges, 1990a); however, additional analyses of vegetation from the Mississippi drainage basin are needed in order to further constrain cutin sources.

Finally, 3,5-dihydroxybenzoic acid (3,5-Bd) has been proposed as a potential indicator of soil OM based on its distribution across the Washington Margin (Prahl et al., 1994). However, there are marine sources of 3,5-Bd acid such as plankton and notably macrophytes, which liberate large amounts of this compound upon CuO oxidation (Goñi and Hedges, 1995), that may compromise its use as a soil marker. Based on the apparent absence of macrophyte-derived carbon in Gulf of Mexico sediments (see previous discussion on acidic polysaccharide-derived CuO product), the increases in the ratio of 3,5-Bd:vanillyl phenols (3,5-Bd/V) with water depth (Table 4) may reflect the increased importance of soil OM. Prahl and et al. (1994) measured high 3,5-Bd/V ratios (≥ 0.15) in both soils from the Pacific Northwest and slope sediments off the Washington Margin. We observe similarly high ratios in the deeper sections of transect A and in all sediments from transect B. Further work in characterizing soils from the Mississippi drainage basin is needed before this trend, which is largely driven by the decrease of vanillyl phenols yields with increasing water depth, can be unequivocally assigned to soil OM.

5.2. Reassessment of the Importance and Sources of OC_{TERR}

Data from several studies (e.g., Newman et al., 1983; Gearing et al., 1977) are consistent with a minor contribution of OC_{TERR} (of C_3 origin) to the deeper parts of the northwestern region of the Gulf of Mexico (including the outer continental shelf, slope, and abyssal plain). At face value, the higher $CaCO_3$ content, enhanced relative importance of protein, polysaccharide and lipid CuO oxidation products with increasing water depth, and the overall enriched $\delta^{13}C_{OC}$ values are consistent with the significant dilution of land-derived material by marine inputs. Although marine OC clearly appears to become more important with distance from shore, closer examination of the bulk and molecular level sedimentary compositions in this and previous studies raises the possibility that the input of OC_{TERR} to surface sediments of the Gulf of Mexico may have been significantly underestimated (Ruttenberg and Goñi, 1997; Goñi et al., 1997).

5.2.1. *Elemental constraints*

The [C/N]a ratios of all sediments analyzed in this study range from 8 to 5 and are close to the Redfield ratio of marine phytoplankton ([C/N]a ~7; Redfield et al., 1963), suggesting a marine source of sedimentary OC. However, a plot of %TN vs.

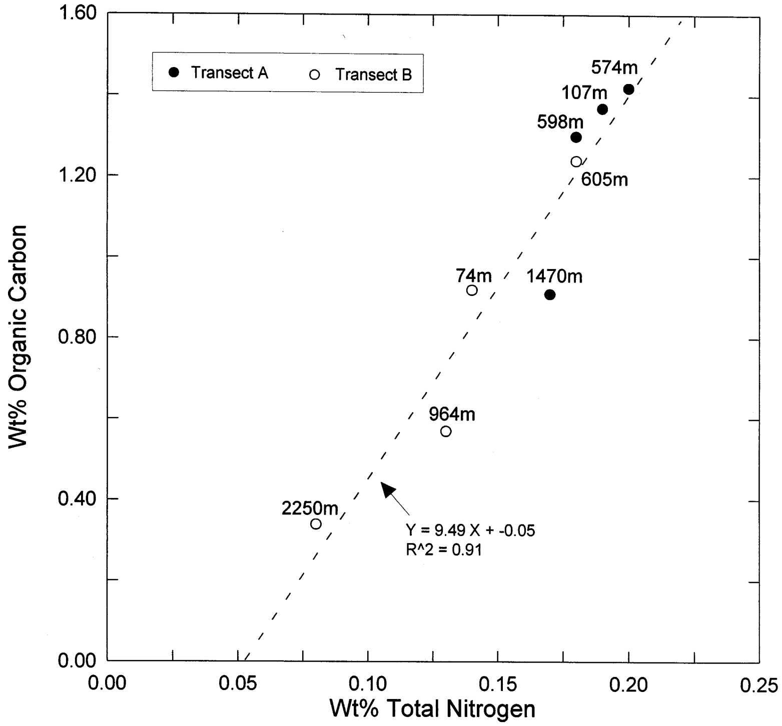

Fig. 7. Plot of %TN vs. %OC for Gulf of Mexico sediments. The %TN intercept at %OC = 0 reflects the percent of inorganic nitrogen (%IN) associated with these sediments. This value was used to calculate the nitrogen content of the sedimentary organic matter (%ON = %TN - %IN).

%OC (Fig. 7) shows a strong linear correlation ($r^2 = 0.9$) between these two variables and a positive %TN intercept at zero %OC. These results are inconsistent with the progressive seaward dilution of terrigenous OM with typical [C/N]a ratios ≥20 by marine OM with Redfield [C/N]a ratios (Ruttenberg and Goñi, 1997). Furthermore, the positive %TN intercept indicates that an important fraction of the nitrogen present in these sediments is inorganic and most likely bound in clays (e.g., Müller, 1977). It is possible to mathematically estimate the organic N content of these samples simply by subtracting the quantity of inorganic N inferred from the %TN intercept in Fig. 7 (≈0.05%) from the measured %TN values. Corrected organic carbon/organic nitrogen ratios range from 8 to 13 and become more equivocal as indicators of marine OM sources (Table 4). Indeed, substantial OM inputs from soils of the Mississippi River drainage, which display [C/N]a ratios of 10–13 (e.g., Tiessen et al., 1984; Parton et al., 1987), cannot be ruled out based on elemental compositions alone (Ruttenberg and Goñi 1997).

5.2.2. *Stable carbon isotopic constraints*

$\delta^{13}C_{OC}$ analyses have also been used as evidence that land-derived OM contributes minimally to the OC in surface sediments of the Gulf of Mexico (e.g., Gearing et al., 1977). These authors interpreted their data in terms of two-endmember mixing of terrigenous OM ($\delta^{13}C_{OC} \sim -26‰$) with typical marine sources ($\delta^{13}C_{OC}$ of −19 to 21‰). The value −26‰ assumes that Mississippi River sediments contain OM predominantly derived from C_3 vascular plants and ignores the possibility of a significant contribution from C_4 sources (Ruttenberg and Goñi, 1997). This assumption may be a major oversight given that the Mississippi River derives a large fraction of its sediment load (Griffin, 1962) from the central North American continent which contains extensive grasslands (Fig. 1; Goñi et al., 1997). Many of these grasslands are dominated by C_4 plant species (Fig. 2; Teeri and Stowe, 1976; French, 1979). Indeed, soil OM from different areas of native prairie (including, Texas, Arizona, Missouri, Minnesota, and Montana) display $\delta^{13}C_{OC}$ values that range from −14‰ to −22‰ depending on the relative importance of C_4 and C_3 species (McPherson et al., 1993; Tieszen and Archer, 1990; Balesdent et al., 1988; Wedin et al., 1995, respectively).

Even in areas later colonized by C_3 arboreal vegetation, soil OM still displays elevated $\delta^{13}C_{OC}$ values (−18 to −23‰) that reflect the importance of C_4-derived OC (Tieszen and Archer, 1990; McPherson et al., 1993). C_4 sources are also apparent in former grasslands planted with C_3 crops (e.g., wheat) for extended periods of time (Balesdent et al. 1988). In these areas, even after over 70 years of continuous cultivation, the $\delta^{13}C_{OC}$ of soil OM ranges from −22 to −23‰. If the extensive grasslands that occupy much of the Mid-west section of the U.S.A. are an important source of fine sediment to the Mississippi River (Griffin, 1962), we would expect the mineral-associated OM exported to the Gulf of Mexico to have a $\delta^{13}C_{OC} > -26‰$. Such an assertion is supported by the relatively enriched $\delta^{13}C_{OC}$ compositions (−19‰ to −24‰) of suspended particles measured by our group in the lower Mississippi and Atchafalaya Rivers (Ruttenberg and Goñi, unpubl.

data) and by John Hedges' group (Onstad et al., in prep.) from various major tributaries in the Mississippi River drainage basin (Canfield, 1997).

5.2.3. Radiocarbon constraints

Based on published sedimentation rates (Lin, 1990; Ruttenberg and Goñi, 1997), the average ages of marine phytodetritus in surface (0–2 cm) sediments should range between 3 (nearshore) and 400 (offshore) calendar ybp. In contrast, conventional ^{14}C ages of bulk sedimentary OC range from 2580 ybp and 6770 ybp (Table 1; Goñi et al., 1997). Even after accounting for sediment mixing and the reservoir effect on marine OC contributing to the sediments (Stuiver et al., 1986), it is difficult to reconcile the previously proposed predominance of marine OC (e.g., Hedges and Parker, 1976; Eadie et al., 1994) with these ^{14}C ages. In fact, the large difference between ^{14}C and estimated calendar ages suggests that a significant fraction of the sedimentary OC must be relatively old and most likely of allochthonous origin. Moreover, because OC_{TERR} ^{14}C ages are not subject to oceanic reservoir corrections, this material must be comprised to a large extent of reworked OC (Eglinton et al., 1997). Nonzero apparent ^{14}C ages for surface sediments are commonly observed on continental shelf/slope environments and are typically interpreted as stemming from relic OC_{TERR} inputs (Druffel et al., 1986; Emerson et al., 1987). These relic inputs likely include the most recalcitrant pools of soil organic matter which typically are associated with mineral material, are most depleted in ^{14}C, and display turnover times exceeding 1,000's of years (e.g., Torn et al., 1997; Trumbore, 1993). Further evidence for past deposition of old-carbon into the Gulf of Mexico are the significantly older radiocarbon of ages of sedimentary organic carbon relatively to $CaCO_3$ measured by Jasper and Gagosian (1990) in deeper sedimentary horizons (30 m) from the Pigmy Basin.

5.2.4. Molecular-level compositional constraints

One of the strongest arguments for a minor contribution of OC_{TERR} to Gulf of Mexico sediments has been the enriched $\delta^{13}C_{OC}$ values and low yields of lignin oxidation products measured in offshore sediments along several transects (Hedges and Parker; 1976). Hedges and Parker (1976) measured high lignin yields (>3 mg/100 mg OC) and depleted $\delta^{13}C_{OC}$ values (<−23‰) in sediments from the most landward sites (fresh water swamps and bays) of these transects (Fig. 8a,b). Inner shelf sediments (7–20 m water depth) are characterized by intermediate lignin yields of 2 to 1 mg/100 mg OC. In contrast, samples from deeper areas of the shelf and slope give lignin yields ranging from 1 to 0.5 mg/100 mg OC. $\delta^{13}C_{OC}$ values range from −22 and −20‰ in virtually all shelf and slope sediments and fail to show a significant trend with depth. Our data from outer shelf and slope sediments is generally consistent with these trends (Fig. 8a,b).

Marked compositional differences exist between lignins from sediments of different depths (Fig. 8). Sediments from depths greater than 100 m display significantly higher S/V ratios indicating an enhanced angiosperm provenance for offshore lignins relative to nearshore counterparts (Fig. 8c). At the same time, deeper (>70 m) samples generally yield higher [Ad/Al]v and [Ad/Al]s ratios (>0.5) than swamp, bay and inner shelf sediments (Fig. 8d). We interpret the striking onshore-offshore trends illustrated in Fig. 8 as the result of the differential deposition of two distinct pools of OC_{TERR}. One pool is comprised of highly altered OM, closely associated with clay particles, and derived from angiosperm grassland soils and deposited in the deeper offshore regions of the Gulf. Consistent with the origin of this OM pool are the low yields and highly degraded nature of lignin reaction products from suspended particles collected in major rivers of the Mississippi River drainage basin (Onstad et al., in prep.; J. Hedges pers. commun.). The second OC_{TERR} pool is composed of fresher vascular plant detritus with a strong gymnosperm source. This material is primarily deposited in bays, estuaries, and the inner shelf along with the coarser and denser mineral particles (silts and sands).

An alternative explanation for the onshore-offshore trends in lignin compositions is the post-depositional degradation of lignin by marine microorganisms which act like white-rot fungi. In this scenario, as the material deposited near the mouth of the river is transported offshore by bottom currents, lignin (and associated terrigenous OM) is degraded under the oxic conditions of surface sediments, resulting in lower yields and elevated [Ad/Al] ratios. Lignin oxidation in marine settings has been observed during the decay of vascular plant tissues (e.g., Opsahl and Benner, 1995; Hedges and Weliky, 1989). Similarly, the loss of terrestrial OM has been postulated to occur in river deltas (Keil et al., 1997a). However, it is not clear that lignin degradation would occur in shelf and slope sediments containing other, presumably more labile forms of (marine) OM (Fig. 4). In general, lignin is the least reactive of the major biochemical pools (including amino acids and carbohydrates) quantified in surface marine sediments (e.g., Cowie and Hedges, 1992) and has been shown to be stable in sediments for thousands of years (e.g., Ishiwatari and Uzaki, 1987; Goñi, 1997). Furthermore, most types of lignin decay are typically characterized by the preferential loss of syringyl and cinnamyl phenols relative to the more recalcitrant vanillyl phenols (Hedges and Weliky, 1989; Benner et al., 1991; Opsahl and Benner, 1995). The higher S/V and C/V ratios in outer shelf and slope sediments relative to sediments from swamps, bays, and the inner shelf (Hedges and Parker, 1976) are, thus, more consistent with a distinct source rather than with in situ decay.

5.2.5. Compound-specific isotopic constraints

The most unequivocal evidence for the distinct origins and compositions of land-derived OC are the contrasting isotopic signatures of lignin phenols from shallow and deeper regions of the Gulf of Mexico (Table 3). Unlike previous studies (e.g., Hedges and Parker, 1976; Gearing et al., 1977), these compound-specific δ^{13}C values indicate that the sources of to the Gulf of Mexico are not uniform, but vary depending on water depth and geographic location (Goñi et al., 1997). For example, based on previously determined isotopic compositional ranges for vegetation types (Goñi and Eglinton, 1996), the measured isotopic composition of most lignin phenols (including syringic acid, syringealdehyde, and *p*-coumaric acid) indicate that the lignin in the deeper sections of both transects has a dominant C_4 source. Vanillin is an exception to this trend because, unlike

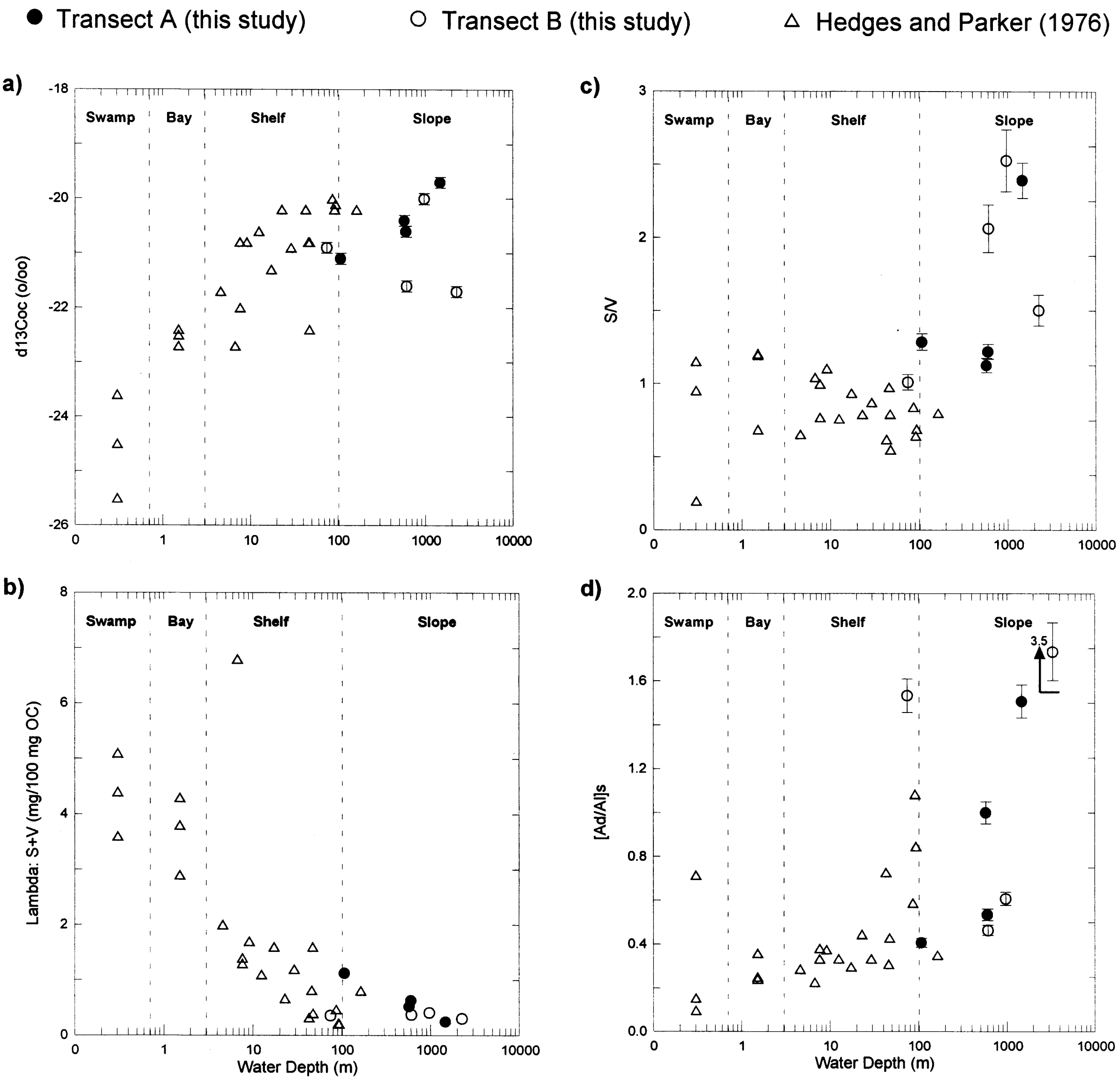

Fig. 8. Distribution of (a) $\delta^{13}C_{OC}$, (b) lambda (sum of syringyl and vanillyl carbon normalized yields) values, (c) syringyl:vanillyl ratios, S/V, and (d) acid:aldehyde ratios of syringyl phenols, [Ad/Al]s, in surface sediments from various water depths of the Gulf of Mexico. Plots include data from this study as well as previously published data (Hedges and Parker, 1976) from several transects across the study area, including the Mississippi River South Pass, Southwest Pass, Atchafalaya River, and Terrebone Bay.

other phenols, it displays fairly depleted $\delta^{13}C$ values (-27 to -30‰) in sediments from both transects.

In order to explain the contrasting $\delta^{13}C$ values of lignin phenols from the same sediment sample (e.g., vanillin vs. syringic acid in the 598 m sample), it is important to consider two factors: first, not all lignin phenols are oxidatively hydrolyzed from their respective macromolecular precursors with the same efficiency (e.g., Goñi and Eglinton, 1996). Second, not all types of terrigenous materials give lignin phenol products at the same yields upon CuO oxidation. To illustrate the influence of these factors we compare the results of theoretically mixing two different materials with variable quantities and compositions of lignin phenols (Table 5). For example, organic matter from a C_3 gymnosperm wood tissue (e.g., Goñi and Hedges, 1992) would give elevated yields of vanillin and vanillic acid per 100 mg OC, but no syringealdehyde or syringic acid (Table 5). In contrast, highly degraded organic matter (e.g., Ziegler et al., 1986) from a mineral C_4 grassland (angiosperm) soil would give much lower yields of all four of these compounds upon CuO oxidation (Table 5).

A sediment sample that contains 95% of the OC derived from soil OM and 5% derived from wood would give the lignin phenol yields and compositional parameters tabulated in Table 5. Due to the differences in lignin yields between the two endmembers, 68% of the vanillin yield in the mixture is derived from wood whereas only 17% of the vanillic acid and none of

Table 5. Lignin parameters and δ^{13}C values of organic matter resulting from mixing of two endmembers containing different quantities and compositions of lignin phenols.

	Endmember A Gymnosperm Wood	Endmember B C4 Grassland Soil	A + B Mixture 5% Wood-95% Soil
Lignin Yields (mg/100 mg OC)			
Vanillin	10.00	0.25	0.74
Vanillic acid	2.00	0.50	0.58
Springealdehyde	0.00	0.50	0.48
Syringic acid	0.00	1.00	0.95
Lignin Parameters			
Syringyl : Vanillyl ratio	0.00	2.00	1.09
Vanillyl Acid : Aldehyde Ratio	0.20	2.00	0.78
Syringyl Acid:Aldehyde ratio	—	2.00	2.00
δ^{13}C**C Values** (‰)			
Total OC	−27.0	−13.0	−13.7
Vanillin	−30.0	−15.0	−25.2
Vanillic acid	−30.0	−15.0	−17.6
Syringealdehyde	−30.0	−15.0	−15.0
Syringic acid	−30.0	-15.0	−15.0

Lignin yields for Endmembers A and B are based on values obtained by Goñi and Hedges (1992) and Ziegler et al. (1986), respectively. δ^{13}C values for both endmembers are based on isotopic compositions obtained by Goñi and Eglinton (1996). Details of the calculation are explained in the text.

the syringealdehyde and syringic acid yields from this mixture originate from wood. The distinct contributions from the two endmembers to the yields of lignin phenols cause the isotopic compositions of the individual compounds to vary among individual compounds and to be quite different from that of the bulk OC. For example if the wood is −27‰ and the soil OM is −13‰, then the 5–95 mixture would be −13.7‰ (Table 5). In contrast, if we assume that the δ^{13}C compositions of individual compounds are −30‰ for all lignin phenols from C_3 origin and −15‰ for all lignin phenols from C_4 sources (Goñi and Eglinton, 1996), the isotopic compositions expected for the various phenols in the sediments would range from −25.2‰ for vanillin to −15‰ for both syringealdehyde and syringic acid. Although the results from these calculations do not match perfectly those measured in Gulf of Mexico sediments (e.g., 598 m sample), they demonstrate the potential variability among related lignin phenols due to the differences in yield efficiencies from various terrigenous endmembers. Better coverage of endmember compositions for the Mississippi River drainage basin/Delta system is needed to further constrain the sources of OC_{TERR} in Gulf of Mexico sediments.

5.3. Sources and Distribution of OC_{TERR} in Gulf of Mexico Sediments

The high C/V and S/V ratios and the enriched isotopic signature of lignin phenols discussed above are consistent with a significant C_4 origin for the land-derived OC deposited in offshore sediments from Gulf of Mexico. Such assertion is partially based on the fact that lignin is a major biochemical component of vascular plant biomass and, as such, a robust tracer of terrigenous OM (e.g., Goñi and Hedges, 1992). Further evidence for the accuracy of the lignin phenols as tracers of OC_{TERR} in Gulf of Mexico sediments are the enriched $\delta^{13}C_{OC}$ compositions measured in Mississippi River particulates (Onstad et al., in prep.; Ruttenberg and Goñi, unpubl. data), which are consistent with a significant C_4 plant origin. Thus, based on these data and the high [Ad/Al] ratios, we conclude that most of the OC_{TERR} in offshore sediments from the Gulf has an important component derived from C_4 plants and is highly degraded. The mixed C_3 and C_4 vegetation (Teeri and Stowe, 1976) and long turnover times (≥1,000 years) of the most recalcitrant pools of OM in soils from temperate grasslands (Parton et al., 1987, 1993) is consistent with most of this OC_{TERR} being derived from North American grasslands in the Mississippi River drainage basin.

5.3.1. *Consideration of alternative sources*

Marsh-derived OM represents a potential alternate source of C_4-derived OC_{TERR} to the Gulf of Mexico. The Mississippi River delta plain contains extensive marshes along the salinity gradient (Gooselink, 1984; Feijtel et al., 1985) with C_4 plants dominating brackish and salt-water marshes (DeLaune, 1986). A significant seaward export of C_4-derived marsh OC could potentially explain the relatively enriched $\delta^{13}C_{OC}$ values observed in these transects. This explanation, however, is unlikely for two reasons. First, Louisiana's Mississippi River delta and surrounding environments are rapidly subsiding and act as particle sinks (e.g., Hatton et al., 1983). Second, an important contribution of modern marsh-derived OM to offshore sediments would result in young, ^{14}C-rich OC_{TERR} rather than the old, ^{14}C-depleted source needed to explain sedimentary compositions.

An alternate explanation for the older ages of OC in the Gulf of Mexico sediments analyzed in this study is the potential contribution of relict Δ^{14}C-dead) carbon to sedimentary OM. One likely source of ^{14}C-dead carbon is the erosion of sedimentary rocks containing fossil organic matter from the drainage basin of the Mississippi River and the transport of this material to the Gulf of Mexico. This process could supply ancient OC to the shelf and slope, thus, suppressing the $^{14}C_{OC}$ ages of terrigenous OM without the need to invoke old soil carbon. At this point this possibility remains untested. However, one approach that may be used to address this question is to carry out radiocarbon analyses on specific biomarkers (e.g., Eglinton et al., 1996; 1997) of soil OM and sedimentary rocks to verify their individual ages.

Another potential source of ^{14}C-dead carbon is the input of fossil hydrocarbons to Gulf of Mexico sediments. Indeed, petroleum reserves in the shelf and natural oil seeps in the slope of the northern Gulf of Mexico are well documented and could potentially lower the Δ^{14}C signature of affected samples. As part of the R/V Gyre cruise in January 1987, sediments were collected near an identified oil seep located along transect B at 688 m of water depth. These sediments contain measurable amounts of lignin phenols (0.4 mg/100 mg OC) but display significantly depleted $\delta^{13}C_{OC}$ values of $-24.1‰$ related to the abundance of isotopically depleted hydrocarbons (Ruttenberg and Goñi, 1997). The contrast in isotopic and elemental compositions between the oil seep sample and all other Gulf of Mexico sediments, expanding 2,000 m of water depth, suggest that fossil carbon inputs are localized and unlikely to account for the Δ^{14}C data (Table 1). However, the issue of fossil carbon inputs to the Gulf of Mexico is clearly an open one that needs to be carefully evaluated (J. Whelan, pers. commun.).

5.3.2. *Effects of hydrodynamic sorting of sediment particles*

Accepting the premise that mixed C_3 and C_4 OC_{TERR} sources are delivered to the Gulf of Mexico, we now address the underlying process(es) that are responsible for the striking onshore-offshore trends described above. We propose that hydrodynamic sorting caused by the resuspension and cross-shelf transport of particles may serve to physically segregate distinct pools of OC_{TERR} (Keil et al., 1994, 1998). The result of this process is the preferential transport of grassland soil OM closely associated with the finer-grained mineral load (clays) of the Mississippi River to interior regions of the northwestern Gulf of Mexico. In contrast, coarser and denser OM, containing water-logged C_3 vascular plant detritus (likely derived from the abundant upland and lowland forests in the delta; Kniffen and Hilliard, 1988) is retained in bays, estuaries and the inner shelf along with silt and sand-sized mineral particles. Such hydrodynamic sorting processes have been previously inferred to explain compositions of sedimentary organic matter off the Washington margin (Prahl, 1985; Keil et al., 1994; Prahl et al., 1994), the Amazon and Bengal deep sea fans (Goñi, 1997; Keil et al., 1997b; France-Lanord and Derry, 1994), and the Pigmy Basin in the northern Gulf of Mexico (Jasper, 1995). Importantly, the results of our study imply that these processes appear to control not only molecular compositions, but also the carbon isotopic compositions of OC_{TERR}. Further evidence for the distinct, size-specific isotopic signals of soil OC can be found in the recent work by Bird and Pousai (1997) on savanna and forest soils from Northern Australia. This work indicates that C_4-derived carbon is preferentially added to the fine size fractions while C_3-derived carbon is incorporated into the coarser fractions.

Aeolian transport provides an additional means of contributing compositionally distinct OC_{TERR} to the off-shore regions of the oceans through entrainment of fine clay particles and their associated organic matter. However, East-Northeast trajectories of present day prevailing winds would suggest that this process is of minor importance in the Gulf of Mexico.

5.4. Quantitative Importance of Terrigenous OM

5.4.1. *Implications for surface sediments from the Gulf of Mexico*

Previous studies have assumed a uniform composition of the land-derived materials exported to the Gulf of Mexico (e.g., Hedges and Parker, 1976; Gearing et al., 1977). The data discussed above indicate that such an assumption is likely invalid and thus may have contributed to the underestimation of terrestrial contributions to Gulf of Mexico sediments. In this section, we use the δ^{13}C values of individual lignin phenols to explore the origin (e.g., C_3 vs. C_4 plants) and importance of OC_{TERR} in these samples. This approach utilizes a simple two-endmember isotopic mixing equation to estimate the fraction of C_4 and C_3 lignin (f_{C4} and f_{C3}, respectively) from the isotopic composition of the lignin phenol in the sample (δL_S) and the average isotopic values of that compound in C_3 and C_4 endmembers (δL_{C3}, δL_{C4}, respectively).

$$\delta Ls = \delta L_{C3} \times f_{C3} + \delta L_{C4} \times f_{C4} \quad \text{where} \quad 1 = f_{C3} + f_{C4}$$

Adopting this approach, we use the δ^{13}C values of syringic acid (Table 3) to estimate the fraction of C_3 and C_4 lignin in the Gulf of Mexico sediments. We assume values of $\delta L_{C4} = -15‰$ and $\delta L_{C3} = -30‰$ for endmember compositions of syringic acid (Goñi and Eglinton, 1996). In transect A, these calculations suggest that most (>90%) of the lignin in the shallowest station (107 m) is of C_3 origin, whereas the dominant lignin source in the deeper sites is C_4 (Fig. 9). In contrast, C_3 and C_4 sources contribute to roughly equal proportions of the lignin in most sediments from transect B. The exception is the deepest station (2250 m), in which C_4 lignin represents ca. 70% of the total.

A markedly different picture arises if vanillin is used instead of syringic acid in the calculation (Fig. 9). According to these estimates, C_3 plants are the dominant (80–100%) source of vanillin in those samples where its isotopic composition was measured. The challenges of using this compound-specific approach to quantitatively estimate of the sources of sedimentary OM are clear from these results and the above discussion on individual compound yields. Furthermore, in order to translate lignin abundances into the contribution of C_3 and C_4 sources to total OC, both sources need to contain the same fraction of their OC as lignin. This requirement is unlikely to be met when vascular plant detritus, composed mainly of polysaccharides and lignin, are mixed with soil OM which contains a much smaller fraction of these recognizable biopolymers (e.g., Ziegler et al., 1986; Kögel, 1986; Kögel-Knabner et al., 1991; Almendros and Sanz. 1992; Almendros et al., 1996). Therefore, even though the total amount of C_3- and C_4-derived OC may be the same, the low lignin concentration and diminished yields of lignin CuO products from soil OM may result in an underestimation of C_4 contributions. These caveats may explain the high C_3 lignin estimates obtained from the shallower sites in transect A.

Because of the compositional differences among the shallower and deeper samples, it is difficult to extrapolate the relative abundances of lignin sources to represent the entire OM pool. Nevertheless, assuming δ^{13}C values for terrestrial OC endmembers ($C_3 = -26‰$ and $C_4 = -14‰$, respectively), it is possible to use the syringic acid-based estimates of lignin sources (C_3 vs. C_4) to calculate the isotopic signature of the land-derived OC in each sample (Fig. 9). Such an exercise

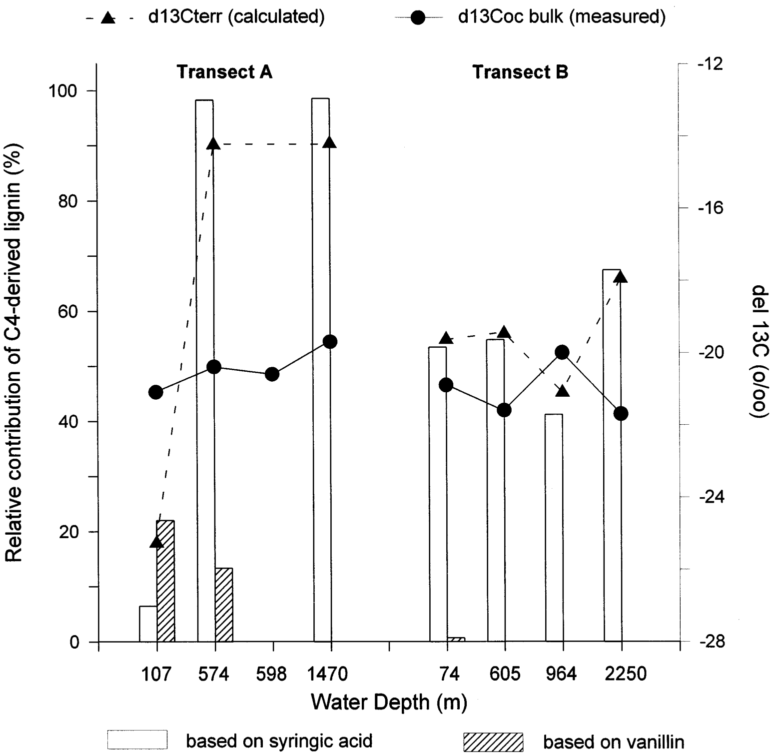

Fig. 9. Relative contribution of C_4 vascular plants as sources of sedimentary lignin in the Gulf of Mexico. Open bars indicate contributions calculated using the $\delta^{13}C$ values of syringic acid whereas the estimates derived from vanillin are expressed by the hatched bars (only three samples yielded sufficiently resolved vanillin peaks to allow for the determination of their isotopic values by irm-GC-MS). Plotted in the same graph are the $\delta^{13}C$ values of the terrestrial organic carbon at each site calculated from the syringic acid data according to the procedure outlined in the text. For comparison the measured $\delta^{13}C_{OC}$ values for each bulk sediment sample are also included.

illustrates the potential variability in isotopic composition of terrestrial OM in Gulf of Mexico sediments. Figure 9 also shows that when both C_3 and C_4 sources are equally important, as is the case in transect B, land-derived OC ($\delta^{13}C_{TERR} = -20$ to -22‰) can be isotopically indistinguishable from marine sources ($\delta^{13}C_{MAR} = -19$ to -21‰). In such instances, quantitative estimates of marine and terrigenous OM using $\delta^{13}C_{OC}$ are difficult to accomplish because they are extremely sensitive to the choice of endmember values. The close agreement between $\delta^{13}C_{TERR}$ and $\delta^{13}C_{OC}$ values in transect B suggest that terrigenous OM might represent a much higher fraction of sedimentary organic carbon than previously deduced.

5.4.2. Broader implications from temporal and spatial perspectives

Previous studies by Newman et al. (1973) and Jasper and coworkers (Jasper and Gagosian, 1993; Jasper and Hayes, 1993) show that the $\delta^{13}C_{OC}$ values of glacial sediments from various sites in the northwestern Gulf of Mexico are considerably more depleted than those from interglacial periods. These authors attribute these isotopically depleted compositions to an enhanced flux of terrigenous C_3 carbon during periods of low sea level stand. However, the latitudinal distribution of C_3 and C_4 grasses in present-day North American grasslands (Fig. 2) suggests that the observed downcore variations may also reflect vegetation changes towards a more C_3 dominated (colder-temperature) grassland in the ice-free regions of the Mississippi River drainage basin during glaciations. Downcore studies of the $\delta^{13}C$ values of lignin phenols (as well as other biomarkers; e.g., Bird et al., 1995) should prove helpful in deciphering whether $\delta^{13}C_{OC}$ variations reflect climate-driven shifts in vegetation pattern (C_3 vs. C_4) or variations in the flux of OC_{TERR}. Such an approach would greatly complement paleovegetation studies conducted on the continents (e.g., Dorn and DeNiro, 1984; DeNiro, 1987; Tieszen and Boutton, 1989; Johnson et al., 1993; van der Hammen and Absy, 1994; Cerling et al., 1993; Parton et al., 1993).

The results presented here raise the question as to the global significance of OM export from grassland soils to marine sediments. Tropical and temperate grasslands currently occupy nearly one fifth of earth's surface (Parton et al., 1995). Furthermore, low latitude rivers dominate global sediment discharge to the oceans (Milliman and Meade, 1983). Given the areal extent of C_4 vegetation and our discovery of terrigenous C_4-derived soil OM in Gulf of Mexico sediments, the possibility of significant inputs of isotopically enriched OC_{TERR} to the world's oceans must be considered. Further studies in areas of the ocean that potentially receive inputs from continents with extensive savannas (e.g., North America, Africa, Asia) are needed to assess whether or not this process has been underestimated in previous investigations utilizing traditional analytical approaches (e.g., bulk $\delta^{13}C_{OC}$ analyses).

6. CONCLUSIONS AND FUTURE WORK

The work presented here reinforces previous studies showing distinct compositional differences in land-derived OM deposited at different depths on continental margins. As in other continental margins, the principal mechanism responsible for the compositions measured in surface sediments from the northern Gulf of Mexico is most likely the hydrodynamic sorting and the preferential offshore transport of less dense materials derived from the North American continent and exported by the Mississippi River to the outer continental shelf and slope regions of the Gulf.

Temporal offsets in the depositional histories of nearshore and offshore sediments may also be responsible for some of the differences observed with water depth. For example, deeper sediments may contain land-derived organic matter of older age and representative of different past climatic or hydrologic conditions in the river drainage basin. The newly developed approach utilizing compound specific radiocarbon analysis (Eglinton et al., 1996, 1997) could serve to assign ages to individual $\mathrm{OC}_{\mathrm{TERR}}$ markers. The comparison of these data to bulk $^{14}\mathrm{C}_{\mathrm{OC}}$ ages can aid in differentiating these processes.

The distribution and isotopic composition of lignin phenols indicate that sedimentary lignin (and by inference $\mathrm{OC}_{\mathrm{TERR}}$) in the outer shelf and slope regions of the northern part of the Gulf of Mexico has a significant C_4 vascular plant component. Although there are several analytical challenges associated with the derivation of quantitative estimates of OM sources based in compound-specific isotope data, this approach may be the only means for deciphering the origins of $\mathrm{OC}_{\mathrm{TERR}}$ to this and other oceanic regions.

$\mathrm{OC}_{\mathrm{TERR}}$ deposited in the offshore regions of the Gulf of Mexico appears highly degraded and likely has undergone passage through previous soil cycles. Further characterization of soils and river sediments in the Mississippi River drainage basin will help to quantitatively characterize this globally important but poorly understood carbon pool (e.g., Hedges, 1992).

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