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Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico

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The sources and burial processes of organic matter in marine sediments are not well understood, yet they are important if we are to have a better understanding of the global carbon cycle[1]. In particular, the nature and fraction of the terrestrial organic carbon preserved in marine sediments is poorly constrained. Here we use the chemical and stable carbon isotope signatures of oxidation products from a macromolecular component (lignin)[2] of the terrigenous organic matter preserved in offshore surface sediments in the Gulf of Mexico to complement similar data from an existing onshore transect[3] in this region. The complete onshore–offshore data set, along with radiocarbon dates of the bulk organic material at the same sites, allows the differentiation of material originating from plants that photosynthesize using the C_4 mechanism from those that undergo C_3 photosynthesis. We conclude that the offshore lignins derive from erosion of the extensive grassland (C_4) soils of the Mississippi River drainage basin, and that the nearshore lignins originate largely from C_3 plant detritus from coastal forests and swamps. This distribution is probably due to the hydrodynamic sorting of the different source materials[4] during their seaward transport. These results suggest that previous studies[3,5] have significantly underestimated the terrigenous fraction of organic matter in offshore sediments by not recognizing the contribution of C_4 vegetation to the carbon-isotope composition. Such an underestimate may force revisions in the assessment of past marine primary productivity and associated organic carbon fluxes[6], and of organic matter preservation/remineralization[7] and nutrient cycling[8] in marine sediments.

The Gulf of Mexico is an extensively studied marine environment in which the fraction of organic carbon preserved in marine sediments that is of terrigenous origin (OC$_{\mathrm{terr}}$) may be particularly high, owing to the proximity of continental land masses. Draining an area[9] of 3.3×10^6 km^2, which includes most of North America's grasslands[10] (Fig. 1), the Mississippi River system is the predominant source of sediment[9] and fresh water[11] to the Gulf. We collected surface (0–2 cm) sediments from two transects perpendicular to the shore extending across the shelf and slope (Fig. 1). The elemental and isotopic compositions of organic matter from these sediments are shown in Table 1.

Conventional ^{14}C ages of bulk sedimentary OC range between 2,580 and 6,770 yr BP, and generally increase with water depth. On the basis of published sedimentation rates[12], the average ages of marine phytodetritus in surface (0–2 cm) sediments should range between 3 (nearshore) and 400 (offshore) calendar yr. The large difference between ^{14}C and estimated calendar ages suggests that, even after accounting for sediment mixing and the reservoir effect on marine OC (ref. 13), a significant fraction of the sedimentary OC must be relatively 'old', and most likely allochthonous in origin. Moreover, because OC$_{\mathrm{terr}}$ ^{14}C ages are not subject to oceanic reservoir corrections, this material must be composed to a large extent of reworked OC (ref. 14). Non-zero apparent ^{14}C ages for surface sediments are commonly observed on continental shelf or

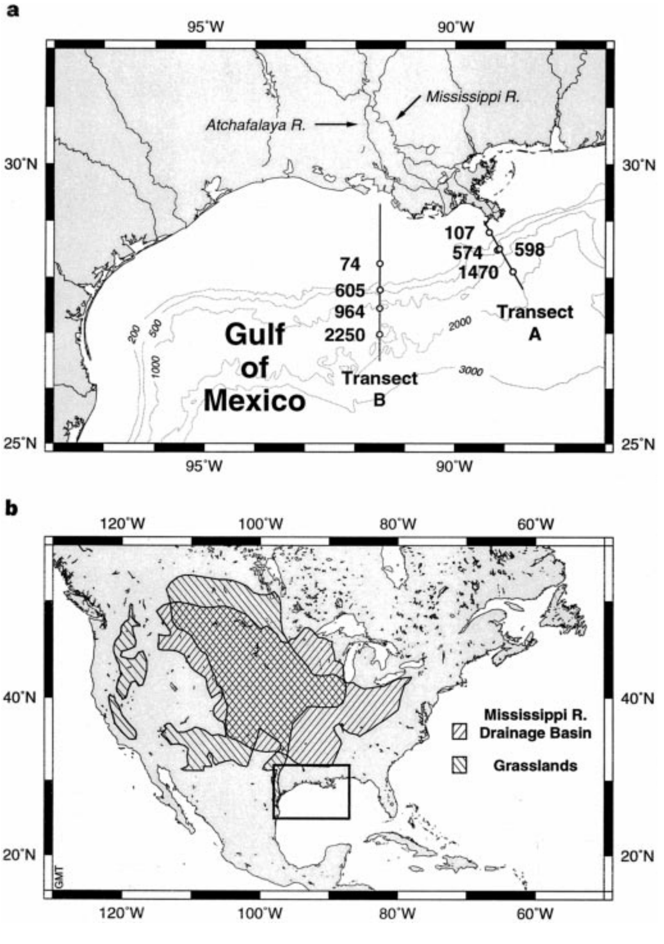

Figure 1 a, Map of the sampling locations and water depths (m) in the Gulf of Mexico. **b**, Map of the extent of the drainage basin of the Mississippi River and the grasslands in North America[10]. The area shown in **a** is an enlargement of the box in **b**.

slope environments, and are typically interpreted as resulting from relic OC_{terr} inputs[15].

Sedimentary total organic carbon $\delta^{13}C$ values from both transects vary from −21.7 to −19.7‰ and display little trend with water depth[12]. These generally enriched values agree well with previously published data (Fig. 2), and have been used as evidence for the dominance of autochthonous marine over terrestrially derived organic matter in offshore regions[3]. Such interpretations have assumed that the OC_{terr} reaching the Gulf of Mexico is derived primarily from C_3 vascular plants ($\delta^{13}C_{OC} \approx -26$‰). However, it is difficult to reconcile the proposed predominance of marine OC with the ^{14}C ages discussed above. Here we present data that contradict the assumption of an exclusively C_3 origin for OC_{terr} and thus may help resolve this apparent discrepancy.

Carbon-normalized yields of phenols derived from vascular (land) plant lignin are generally low (≤1.5 mg per 100 mg OC) for both transects (Table 1), and are consistent with previous observations (Fig. 2). Source parameters based on the phenol data from both transects show ratios of cinnamyl : vanillyl (C/V) ≥ 0.2 and syringyl : vanillyl (S/V) ≥ 1 (Table 1). These elevated C/V and S/V values indicate that lignin in these Gulf of Mexico sediments has a predominantly non-woody, angiosperm origin[16] (for example, leaves and grasses). Because microbial degradation of vascular plant tissues alters both of these ratios[17], it is imprudent to differentiate vascular plant sources much beyond this level of interpretation.

All sediments yield ratios of acid : aldehyde (ad/al) for both vanillyl and syringyl phenols that are ≥0.4 and generally increase offshore, reaching values as high as 3.5 (Table 1). Oxidative

Table 1 Compositional and isotopic parameters from Gulf of Mexico sediments

		Depth of transect A (m)				Depth of transect B (m)			
Parameter	Code	107	574	598	1,470	74	605	964	2,250
Organic carbon by weight (%)	% OC	1.4	1.4	1.3	0.9	0.9	1.2	0.6	0.3
Calcium carbonate by weight (%)	$\%CaCO_3$	2.0	3.8	3.8	16.6	7.7	11.5	28.7	25.4
Radiocarbon composition of organic carbon (‰)*	$\Delta^{14}C_{OC}$	−276.8	−291.1		−393.0	−367.0	−383.5	−386.4	−572.1
Radiocarbon age of organic carbon (yr BP)†	Age_{OC}	2,580	2,720		3,960	3,630	3,840	3,880	6,770
Lignin phenol yields (mg per 100 mg OC)									
Vanillyl phenols	V	0.563	0.309	0.309	0.085	0.202	0.159	0.136	0.143
Syringyl phenols	S	0.766	0.437	0.386	0.252	0.215	0.374	0.422	0.236
Cinnamyl phenols	C	0.156	0.085	0.107	0.070	0.081	0.072	0.092	0.102
Total	T_{lig}	1.49	0.83	0.80	0.41	0.50	0.60	0.65	0.48
Vanillyl + syringyl phenols‡	Λ	1.28	0.70	0.67	0.31	0.39	0.49	0.51	0.33
Lignin compositional parameters									
Syringyl : vanillyl ratio	S/V	1.36	1.41	1.25	2.98	1.07	2.35	3.09	1.65
Cinnamyl : vanillyl ratio	C/V	0.28	0.28	0.34	0.83	0.40	0.45	0.67	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
Stable isotopic compositions (‰)§									
Bulk OC‖	$\delta^{13}C_{OC}$	−21.1		−20.4	−19.7	−20.9	−21.6	−20.2	−21.7
Syringealdehyde	$\delta^{13}C_{Sl}$					−22.0			
Syringic acid	$\delta^{13}C_{Sd}$	−29.0		−15.3	−15.2	−22.0	−21.8	−23.8	−19.9
p-Coumaric acid	$\delta^{13}C_{Cd}$	−28.5		−15.4					
Vanillin	$\delta^{13}C_{Vl}$	−26.7		−28.0		−29.9			

Where no data are given, $\delta^{13}C$ was not determined owing to unsatisfactory resolution by irm-GC-MS. Irm-GC-MS data for other lignin phenols not included in this table are not available because of their low overall and insufficient chromatographic resolution which precluded accurate $\delta^{13}C$ determination. In all samples, syringic acid was the most suitable of all lignin compounds for irm-GC-MS.

* Measured by AMS.

† The error in $Age_{OC} \leq 60$ years for all samples.

‡ Sum of vanillyl + syringyl phenol yields (Λ) was calculated by excluding cinnamyl phenols to compare directly to previous data[3].

§ All isotopic compositions, except for $\delta^{13}C_{OC}$ which was measured by direct combustion (precision of 0.1‰) were measured by isotope ratio monitoring-gas chromatography-mass spectrometry (irm-GC-MS).

‖ Data from ref. 12. The precision of the irm-GC-MS measurements has been determined previously[2], and for these samples is better than 1‰ for most compounds, but ranges up to 1.7‰ for syringic acid from the 605-m station.

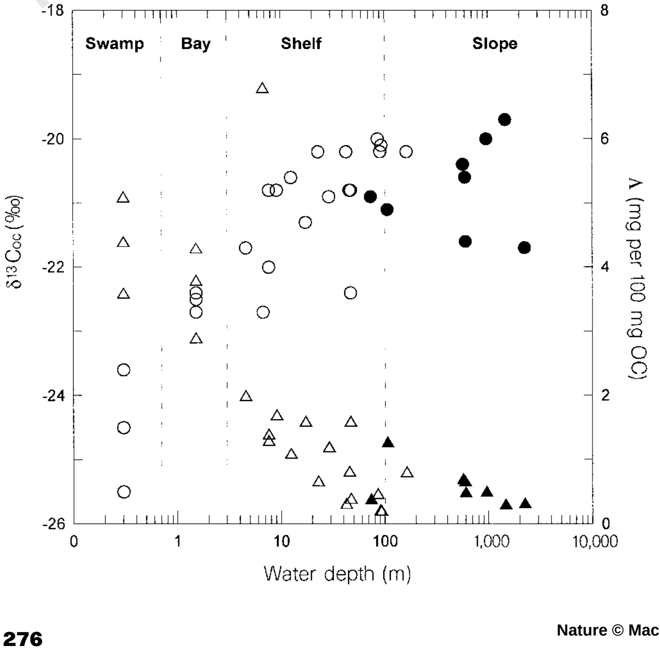

Figure 2 Distribution of $\delta^{13}C_{OC}$ (circles) and Λ (triangles) in surface sediments from various water depths of the Gulf of Mexico. Open symbols indicate data from several transects, including the Mississippi River south pass, southwest pass, Atchafalaya River and Terrebone Bay[3]. Filled symbols show data for samples from both transects (A and B) analysed in this study (Table 1).

degradation of lignin side-chains by microorganisms such as white-rot fungi often produces ad/al > 0.4 (ref. 18). Furthermore, materials containing highly altered lignin (such as fine suspended river sediments[19] and humic horizons of mineral soils[20]) display values ranging from 0.4 to 4. Hence the ad/al ratios reported here, which are consistent with previous data[3], indicate that all sedimentary lignins have been subjected to a high degree of oxidative degradation.

In transect A, individual lignin phenols, most notably syringic acid, display significantly more depleted isotopic compositions at the 107-m site (−29‰) than those at deeper sites (−15‰). In contrast, the δ^{13}C values of most lignin phenols at all sites from transect B are relatively enriched (~−22‰). These compound-specific δ^{13}C values indicate that the sources of lignin to the Gulf of Mexico vary according to water depth and geographical location. Previously determined isotopic compositional ranges for individual lignin phenols[2] suggest that the OC_{terr} in the deeper sections of both transects has a dominant C_4 source. In contrast, OC_{terr} from the shallowest sections contains a high fraction of C_3-derived lignin. Vanillin is different from other phenols because it is fairly depleted (−27 to −30‰) in sediments from both transects. One possible explanation for these vanillin compositions could be the occurrence of a small amount of C_3 lignin from gymnosperm wood, which would yield vanillyl phenols exclusively, in sedimentary mixtures otherwise containing lignin from non-woody angiosperm C_4 sources.

From the chemical (S/V, C/V and ad/al) and isotopic (δ^{13}C and Δ^{14}C) data, we infer that the source of the OC_{terr} present in the slope and abyssal plain of this region of the Gulf is highly reworked, recalcitrant soil organic matter (probably sorbed to fine mineral gains) exported from the extensive grasslands of the Mississippi River drainage basin[10]. The vegetation in North American grasslands is composed of C_3 and C_4 plants, with cool-season C_3 species dominating in the northern ranges and warm-season C_4 species in the southern regions[21]. The δ^{13}C compositions of soil OC from the Great Plains correspond to the latitudinal distribution of vegetation and range from −14 to −23‰ (ref. 22). The ^{14}C-depleted values of OC and the highly degraded nature of lignins from offshore sediments are consistent with the bulk of OC_{terr} at these locations being composed of recalcitrant fractions of soil organic matter with turnover times exceeding 1,000 years (ref. 23). The low lignin yields (typical of recalcitrant soil organic-matter pools[20]) obtained from the interior regions of the Gulf of Mexico do not therefore negate the possibility of a significant OC_{terr} contribution. In contrast, a large fraction of the OC_{terr} in the shelf regions of the Gulf of Mexico (Fig. 2) seems to be less-degraded organic matter from C_3 sources, probably in the form of plant detritus from forests and swamps present in the lower reaches of the Mississippi River[24].

We do not yet know what causes these striking onshore–offshore trends in OC_{terr} composition. 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}. The result of this process is the preferential transport of grassland soil organic matter 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 organic matter, containing waterlogged vascular plant detritus, is retained in bays, estuaries and the inner shelf, along with silt and sand-sized mineral particles. Such hydrodynamic sorting processes have previously been inferred to explain the chemical compositions of sedimentary organic matter off the Washington margin[4,25] and the Amazon and Bengal deep sea fans[26,27]. In this case, however, hydrodynamic sorting also seems to control the isotopic composition of OC_{terr}. Aeolian transport provides an additional means of contributing compositionally distinct OC_{terr} to the deeper regions of the Gulf of Mexico through entrainment of fine clay particles and their associated organic matter. However, the east–northeast trajectories of present-day prevailing winds suggest that this process is relatively unimportant.

Applying isotopic mass balance[2] to the δ^{13}C values of syringic acid, it is possible to evaluate the importance of C_4 lignin in sediments from both transects (Fig. 3). The relative abundances of lignin sources can then be used to estimate the average isotopic signature of OC_{terr} (Fig. 3). These calculations, bearing in mind the assumptions involved[2], show that C_4-derived OC modifies the isotopic signature of OC_{terr} ($\delta^{13}C_{terr} = -20$‰ to −22‰) in offshore Gulf sediments such that it is indistinguishable from marine OC ($\delta^{13}C_{mar} = -19$‰ to −21‰). In such instances, quantitative assessments of terrigenous organic matter inputs using bulk $\delta^{13}C_{OC}$ are difficult to accomplish, and may have led to an underestimation of allochthonous contributions[3,5].

Grasslands (both tropical and temperate) presently occupy nearly one-fifth of the Earth's surface[28]. Given their wide distribution, our findings underscore the potential importance of grassland soils as sources of OC_{terr} to present-day oceans. The distribution and composition of grasslands are intimately connected with climate[22,28], so, climatic variability may have affected the export of OC_{terr} not only to contemporary but also to past oceans. For example, increased input of terrigenous C_3 carbon to the Gulf of Mexico during periods of low sea level has been inferred from the

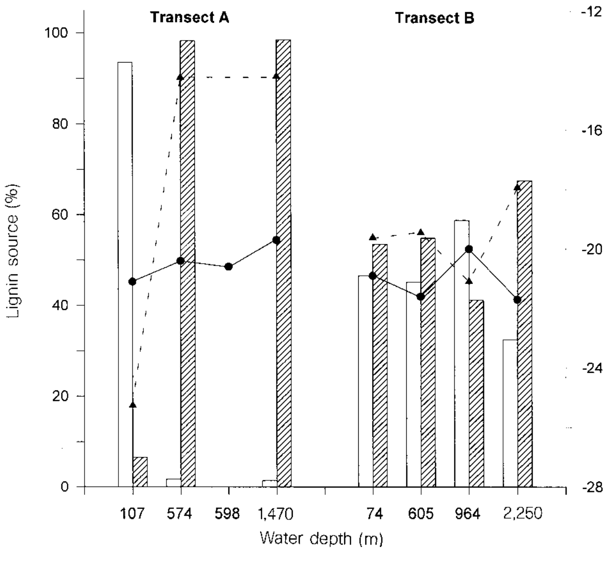

Figure 3 Relative contribution of C_3 (white bars) and C_4 (shaded bars) vascular plants as sources of sedimentary lignin in the Gulf of Mexico, based on the isotopic composition of syringic acid (measured by irm-GC–MS) from sediments (Table 1) and from C_3 and C_4 end-members[2] (−30‰ and −15‰, respectively). The estimated isotopic composition of terrigenous organic carbon ($\delta^{13}C_{terr}$, triangles) and the measured δ^{13}C values bulk organic carbon ($\delta^{13}C_{OC}$, circles) are also shown. Details of the approach used to estimate $\delta^{13}C_{terr}$ have been discussed previously[2]. Briefly, using isotopic mass balance, it is possible to estimate the relative abundance of C_3 and C_4 terrestrial organic matter sources in marine sediments from the δ^{13}C values of individual lignin phenols. However, the same lignin phenol may be derived from two different sources in vastly different quantities, depending on the nature and composition of the precursor (such as plant tissues versus soil OC). Hence, when interpreting these data, the role of oxidation yield in determining the isotopic signature of a given CuO product must be considered[2]. Given these constraints, we used the δ^{13}C values of the best-resolved lignin phenol, syringic acid (Table 1), to semi-quantitatively estimate the fraction of C_3 and C_4 angiosperm lignin in Gulf of mexico sediments. This choice appears justified because the lignin in most of the sediments analysed in this study seems to be derived from highly degraded angiosperm sources, and syringic acid is the best marker available for such material.

considerably depleted $\delta^{13}C_{OC}$ signatures obtained from sediments deposited during glacial epochs[5]. However, the observed glacial–interglacial isotopic variations could instead reflect changes from a C_3-dominated (colder temperature) vegetation in the Mississippi River drainage basin during glaciations to a more C_4-dominated vegetation in the Holocene epoch. This latter interpretation is supported by the known temperature-dependent latitudinal distribution of plants in present-day North American grasslands[21]. Application of these and other biological marker $\delta^{13}C$ data[29], in combination with compound-specific radiocarbon analysis[14], to downcore studies of marine sediments may help us to understand the changes in vegetation (C_3 versus C_4) resulting from continental climate change in North America and other areas of the world[22,27–30]. ☐

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Trade-off between parasitoid resistance and larval competitive ability in *Drosophila melanogaster*

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The extent to which an organism is selected to invest in defences against pathogens and parasites depends on the advantages that ensue should infection occur, but also on the costs of maintaining defences in the absence of infection. The presence of heritable variation in resistance suggests that costs exist, but we know very little about the nature or magnitude of these costs in natural populations of animals[1]. A powerful technique for identifying trade-offs between fitness components is the study of correlated responses to artificial selection[2,3]. We have selected *Drosophila melanogaster* for improved resistance against an endoparasitoid, *Asobara tabida*. Endoparasitoids are insects whose larvae develop internally within the body of other insects, eventually killing them, although their hosts can sometimes survive attack by mounting a cellular immune response[4–6]. We found that reduced larval competitive ability in unparasitized *D. melanogaster* is a correlated response to artificial selection for improved resistance against *A. tabida*. The strength of selection for competitive ability and parasitoid resistance is likely to vary temporally and spatially, which may explain the observed heritable variation in resistance.

Parasitoids are very common natural enemies of many insects, developing either externally or internally on their hosts[7]. Endoparasitoids frequently suspend development as eggs or first-instar larvae while their hosts feed and grow in size, although during this period they can be destroyed by encapsulation, a cellular immune response. Parasitoids avoid host defences by hiding in tissue away from circulating haemocytes, by avoidance of recognition through molecular mimicry, or through debilitating the immune response by toxins or symbiotic viruses[6]. Individual hosts often differ in their ability to encapsulate parasitoids, and selection, quantitative genetic and isofemale-line studies have shown this to have a genetic basis[8–11]. The presence of additive genetic variation in encapsulation ability suggests that there are costs to the possession of defences against parasitoids, although these costs have yet to be identified in any host–parasitoid interaction.

Asobara tabida (Hymenoptera, Braconidae) is a common larval parasitoid of *Drosophila* species on fermenting substrates in Europe. In central and northern Europe its main host is *D. subobscura*, in which it is never encapsulated, although it is also found on *D. melanogaster* at low frequencies[12]. In Mediterranean Europe *D. melanogaster* is the main host. Our base stock population of *D. melanogaster* was derived from 250 flies caught in the wild near Leiden in the Netherlands and maintained in the laboratory for three generations before the start of the experiment. The wasps used in the selection experiments were a laboratory strain derived originally from insects caught in Sospel, France, and cultured on *D. subobscura* to prevent adaptation to *D. melanogaster*. The base stock encapsulated only 5% of the eggs of the laboratory strain of *A. tabida*, a figure typical of fly populations from northern Europe[13].

The base stock was split into eight lines, four of which were selected for increased encapsulation ability, the others acting as controls. Each new generation of the selection lines was bred from flies that had survived parasitoid attack (the encapsulated parasitoid egg remains in the body of the fly and can be seen through the wall of