Flood, R.D., Piper, D.J.W., Klaus, A., and Peterson, L.C. (Eds.), 1997
Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 155

33. RELATIONSHIPS BETWEEN ORGANIC CARBON PRESERVATION AND MINERAL SURFACE AREA IN AMAZON FAN SEDIMENTS (HOLES 932A AND 942A)[1]

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ABSTRACT

Mineral surface area (SA), neutral sugar (aldose) concentrations, and organic carbon content (OC) were measured in two holes from Ocean Drilling Program (ODP) Leg 155 (Holes 932A and 942A) and compared to analogues from the modern Amazon River and Delta. Nearly all (>90%) of the OC in the ODP holes was tightly associated with the mineral phase; the two phases could not be quantitatively separated after sonication and density fractionation. Organic matter in Holes 932A and 942A can thus be functionally defined as adsorbed. There is a relationship between OC and a sediment transport pathway prior to deposition. When OC is normalized to a mineral surface area (OC:SA), sediments that were rapidly deposited and strongly influenced by the river had average OC:SA ratios of 0.46 and 0.39 mgCm^{-2} for Holes 932A and 942A. Sediment deposited indirectly through nepheloid transport had lower OC:SA ratios (average 0.32 and 0.24 mgCm^{-2}). For comparison, OC:SA ratios of suspended sediments from the Amazon River average 0.67 mgCm^{-2}, and modern Amazon Delta sediments have a loading of ~0.30 mgCm^{-2}. Although aldose concentrations in Hole 932A decreased downcore, corresponding molecular compositional patterns do not suggest extensive in situ diagenesis. Rather, the aldose composition throughout Hole 932 lithologic Subunits IIA and IIB is similar to that of fine suspended particulate materials carried by the modern Amazon River, which are largely composed of degraded material derived from plants and riverine microorganisms. The aldose data support isotopic and lignin compositional evidence for a terrestrial-riverine source of organic matter in Unit II of Hole 932A, as suggested by Goñi (this volume).

INTRODUCTION

In modern marine sediments, organic coatings on mineral surfaces vary predictably as a function of sediment oxidative history (Hedges and Keil, 1995). Because a large portion—typically approaching 90%—of the organic carbon (OC) preserved in recent marine sediments is present as organic films on mineral surfaces (Mayer, 1994; Keil et al., 1994), normalization of organic content to mineral surface area (SA) provides a means of delineating geographic regions of different carbon burial. Five zones in modern marine-fluvial systems have thus far been defined (Hedges and Keil, 1995; Mayer, 1995). Upper continental slope and shelf sediments contain OC at loadings of 0.5–1.1 mgOCm^{-2}, and account for roughly 45% of Holocene OC burial. Sediments accumulating within river deltas are loaded at only ~0.30 mgOCm^{-2}, but account for 44% of OC burial because of their high sediment accumulation rates. Pelagic sediments accumulate slowly with very low organic loadings (~0.15 mgOCm^{-2}) and account for less than 5% of current OC burial. Sediments accumulating below highly productive regions, or regions with suboxic bottom waters, have ratios greater than 2 mgOCm^{-2}, and account for ~6% of current OC burial (Hedges and Keil, 1995). Finally, suspended sediments in rivers contain organic carbon at loadings that vary considerably but average 0.70 mgOCm^{-2} (Keil et al., in press).

The two goals of the research presented here were to examine OC:SA ratios in terrestrially derived river fan sediments, a marine sediment type that has been previously overlooked, and to ascertain whether OC:SA patterns observed in Holocene systems are also discernible during the Pleistocene. Previous work on piston cores taken from sediments accumulating under a suboxic water column off the western edge of Mexico (R.G. Keil, J.W. Murray, and A.H. Devol, unpubl. data) has suggested that under low-oxygen depositional conditions, OC:SA ratios are a robust measure of organic matter preservation that can be applied back in the sedimentary record for at least 100 k.y. The present study is a first attempt to investigate the usefulness of OC:SA ratios in Pleistocene marine sediments deposited under oxic bottom-water conditions.

Current Work in the Amazon System

One poorly understood aspect of carbon burial in modern marine sediments is the mechanism that leads to reduced burial (estimated as either weight- or SA-normalized loads) of organic matter in modern deltaic sediments. Rivers deliver presumably recalcitrant organic matter to deltas at sufficient concentrations and surface loadings to bury carbon at "typical" shelf values of 0.5–1.1 mgOCm^{-2}. However, remineralization of organic matter typically exceeds burial within the deltaic regime, and OC:SA ratios average only 0.30 mgOCm^{-2} (Mayer, 1994; Hedges and Keil, 1995). Data from the Amazon River and Delta indicate that only one-fourth to one-third of the organic matter delivered to the Amazon Delta is buried (Showers and Angle, 1986; Aller et al., 1996; Keil et al., in press). The currently favored hypotheses for this low burial efficiency are that heterotrophic bacteria rapidly utilize organic matter by taking advantage of the recurrent redox oscillations in deltaic sediments, or that enhanced degradation of terrestrial organic matter occurs via co-metabolism of planktonic material introduced in the delta (Aller, 1994; Aller et al., 1996).

Paleo-hypothesis

Given the reduced burial of organic matter within deltas and higher burial in other shelf and slope sediments, it has been suggested that OC burial could be enhanced when organic matter delivered by a river is swept immediately to the slope and deep sea (Hedges and Keil, 1995). Such bypassing of a deltaic remineralization "hot-spot" might occur during low sea-level stands, when large submarine fans such as the Amazon Fan accumulated without storage of sediments in a shallow delta. Changes in OC burial might then be discernible in the sed-

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[1] Flood, R.D., Piper, D.J.W., Klaus, A., and Peterson, L.C. (Eds.), 1997. *Proc. ODP, Sci. Results,* 155: College Station, TX (Ocean Drilling Program).

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imentary record as variations in OC:SA ratios with a sediment transport pathway. In other words, the direct deposition of terrestrial mineral material in the Amazon Fan with minimal intermediate mixing or degradation should be reflected by higher OC:SA ratios and greater abundances of terrestrial organic matter relative to marine material. We attempt here to test this hypothesis by estimating the SA-normalized OC content of terrestrially derived sediment and the molecular aldose composition of sedimentary organic matter from two holes (932A and 942A) that received sediment from the Amazon River through two general pathways. The pathways are rapid accumulation via slumping and turbidite flow during times when active channels were near the sample sites, and slow accumulation via nepheloid transport during times when the sites were distal from the active channel. We then compare the data to modern Amazon River and Delta samples.

Site Descriptions

In this report, the holes will be discussed from the bottom (oldest) to the top. Two holes were sampled: Hole 932A (5°12.682′N, 47°1.770′W) and Hole 942A (5°44.546′N, 49°5.464′W). Although ~175 m of sediment was retrieved from both hole locations with good recoveries (Shipboard Scientific Party, 1995a, 1995b), the time interval represented by Hole 932A is shorter than that represented by Hole 942A. Approximately 130 k.y. of sediment was recovered at Site 932 (Maslin et al., this volume), whereas a ~200 k.y. record was recovered from Site 942 (Showers et al., this volume). The following descriptions of sediment depositional pathways are derived by using guidelines established by Flood, Piper, Klaus, et al. (1995) and by relying on the age models developed for the sites (Maslin et al., Showers et al., both this volume).

Site 932

Site 932 is located on the eastern edge of the Amazon Fan, within Channel-levee System 6B, the oldest part of the Upper Levee Complex. Two lithographic units were recognized at the site (Shipboard Scientific Party, 1995a). Unit II (0.7−168.3 mbsf) is mud interbedded with beds of silt and clay. This unit has been divided into Subunits IIA and IIB. Subunit IIB (47−168 mbsf) is a dark olive-green silty clay containing very fine laminae of turbidity-current origin, and Subunit IIA (0.7−47 mbsf) is a bioturbated dark olive-gray clay. Unit I (0−0.7 mbsf), a Holocene nannofossil-foraminifer clay, was not sampled for this study.

Subunit IIB sediments were deposited between 71 and 75 ka (oxygen isotope late Stage 4, early Stage 5; Maslin et al., this volume). During this time, the sea level was ~50 m lower than at present, and a large river delta was probably absent. Channel-levee System 6B was a site of active transport of riverine sediment, most likely in the form of turbidity currents that originated in the Amazon Canyon. Subunit IIA spans from isotope Stages 2 through the beginning of isotope Stage 4. Isotope Stage 3 (24−59 ka) is located between 14 and 43 mbsf. According to the model of Maslin et al. (this volume), the last glacial maximum (LGM; 18−28 ka) corresponds to ~10−22 mbsf. During the time that Subunit IIA was deposited, Site 932 received sediment from the Amazon River indirectly. The site was not located near an active channel, so that sediment likely came through a nepheloid layer transport of fine components. As the active channel moved farther away, the sediment accumulating at Site 932 became finer. The cessation of Amazon material reaching Site 932 is marked by the occurrence of Unit I.

Site 942

Site 942 is a hemipelagic site located on the crest of an abandoned levee to the west of the main portion of the Amazon Fan. Six lithologic units were recognized at the site. An age model for Hole 942A has been presented by Showers et al. and Schneider et al. (both in this volume). Site 942 contains several carbonate-rich layers that help define changes in lithology (Shipboard Scientific Party, 1995b). These layers were not sampled for this study.

The oldest section, Unit VI (60–170 mbsf), was deposited during isotope Stage 6 (>130 ka). This homogeneous dark gray silt is characterized by relatively direct sediment input, as indicated by the high accumulation rates and the presence of thin turbidite layers similar to Subunit IIB at Site 932. Also similar to Subunit IIB from Site 932, this unit received sediment largely via slumping of rapidly deposited material in the Amazon Canyon and turbidity current transport to the site during a period when the active channel was very near the site. During deposition of the uppermost part of Unit VI, the sea level gradually decreased. The sharp transition from Unit VI to Unit V (~65.2–66.07 mbsf) is characterized by a rapid sea-level rise that resulted in permanently reduced riverine sediment input to the location of Hole 942A. Unit V corresponds to isotope Stage 5e.

Unit IV (40.18–65.2 mbsf) corresponds to isotope Stages 5a to 5d (~75–130 ka), a time of generally high sea level. The canyon and channel apparently remained during this high sea level, but the sediments deposited during this time are probably derived, in part, from reworked shelf sediments. Units II (0.66–28.1 mbsf) and III (28.1–40.18 mbsf) correspond to isotope Stages 2 and 3. During these times, sediment at Site 942 was deposited indirectly via nepheloid transport during generally low sea level. It is unclear whether the sediment that accumulated at this site is totally derived from the Amazon River or whether smaller Brazilian rivers north of the Amazon River contributed (Shipboard Scientific Party, 1995b). Unit I, a Holocene nannofossil-rich clay, was not sampled for this study.

METHODOLOGY

Samples were taken from Holes 932A and 942A at ~10 m intervals (i.e., once per core). We wished to exclusively sample terrestrially derived sediment, thus carbonate-rich materials were omitted. Noncalcareous samples were taken without regard to shifts in sediment lithology, frozen aboard ship, and transported to the laboratory prior to thawing, subsampling, and analysis. A more detailed description of shipboard sampling protocol is provided by Goñi (this volume).

Total carbon and nitrogen were measured directly using a Carlo Erba CHN analyzer (Model 1106). Samples were combusted at 1050°C. Gases were separated using a Microanalysis E-3000 widebore column, and detected by thermal conductivity detection (TCD). Precision for total carbon and nitrogen averaged ±2%. Organic carbon was determined after pretreatment with acid to remove inorganic carbonate. Samples were then weighed into silver sample boats and exposed to concentrated HCl vapors at 25°C for 24 hr, dried for 2 hr at 50°C, and analyzed for total carbon (Hedges and Stern, 1984). Precision for organic carbon was typically better than ±5% of the measured value. Inorganic carbon was estimated as the difference between total carbon and organic carbon.

The mineral surface area was determined using the one-point BET (Brunauer-Emmett-Teller adsorption isotherm) method on a Quantachrome Monosorb Surface area analyzer. Prior to analysis, sediment surfaces were cleaned of organic matter via heating to 350°C for 12 hr followed by a 4 hr cool-down period. Although this differs from the peroxide treatment used by Mayer (1994), unpublished studies in our laboratory using low-organic sediments (<5%) indicate that no systematic differences in mineral surface area occur between techniques. For mineral surface area measurement, flowing nitrogen gas, at a mole percentage of 0.28 (the balance being helium), was adsorbed to mineral surfaces at −78°C. After adsorption, N_2 was liberated from the mineral surface by gentle warming and measured using

TCD. Accuracy for BET analyses of known minerals is generally considered to be ±5% (AUPAC, 1989). Precision for the samples reported here was better than 1%.

Carbohydrates were hydrolyzed to their neutral sugar (aldose) monomers, and then the aldoses were measured using the method of Cowie and Hedges (1984b). Sediment samples were pretreated with 72 wt% H_2SO_4 for 2 hr at room temperature, diluted to 1.2 M H_2SO_4 and hydrolyzed at 100°C for 3 hr. The hydrolyzate mixtures were neutralized with $Ba(OH)_2$ and desalted by ion exchange after the $BaSO_4$ precipitate was removed by centrifugation. After evaporation to dryness, the aldose mixture was equilibrated for 36–48 hr in a 0.2 wt% $LiClO_4$ pyridine solution and then derivatized with Regisil for 10 min at 50°C. The resulting trimethylsilyl derivatives were eluted with He carrier gas on an HP 5890 gas chromatograph fitted with a split injector (1:10) and a 25 m × 0.20 mm ID fused silica capillary column coated with DB-1 (methylsilicone) liquid phase. Oven temperature was increased at 4°C per min from 140°C (4-min hold) to 270°C (4-min hold). Glycerol was routinely added after hydrolysis as a carrier and individual aldoses were quantified vs. authentic standard mixtures using adonitol as an internal recovery standard.

RESULTS AND DISCUSSION

The method we used to estimate organic carbon in these sediments differs from that used aboard ship during routine sample processing. Shipboard processing involved estimating organic carbon by difference between total carbon (measured using a Carlo Erba Model NA1500 CHNS analyzer) and inorganic carbon (after liberation of CO_2 by acidification and measuring the gas with a coulometer; Emeis and Kvenvolden, 1986). We estimated organic carbon directly by CHN analysis after acidification to volatilize inorganic carbon (Hedges and Stern, 1984). A comparison of results obtained with both methods yielded no significant difference in organic carbon estimates (slope = 1.01 ± 0.02, $r^2 = 0.991$, $n = 38$).

Within both holes, fluctuations in OC content range over a factor of 100%, whereas mineral SA measurements change by less than 50%. This is also typical of modern marine sediments (Mayer, 1994; 1995) and indicates that changes in OC are more likely to affect the OC:SA ratio than changes in mineral SA. Given that OC content tends to drive changes in OC:SA ratios for sediments where the SA value is relatively stable, we have interpreted changes in OC:SA to be due to fluctuations in the input or diagenetic stability of the organic matter that reaches a given site (Hedges and Keil, 1995).

Description of Hole 932A

Organic carbon contents for Hole 932A range from 0.69% to 1.07% with a shift to lower values above the Subunit IIA/IIB boundary (~40 mbsf; Table 1; Fig. 1). Accompanying the shift in OC is a transition to more nitrogen-rich material as reflected in higher atomic N:C ratios (Fig. 1). With decreasing age in Subunit IIB, both %OC and N:C ratios gradually exceed the values observed in Subunit IIA. Nitrogen-specific mineral surface area measurements show a gradual increase in mineral surface area uphole (Fig. 1). Subunit IIB sediments thus have a lower mean SA value (19.9 m^2g^{-1}) than Subunit IIA (23.0 m^2g^{-1}), consistent with a larger mean grain size for the predominantly silty sediment matrix of Subunit IIB (Shipboard Scientific Party, 1995a). When the organic carbon content is normalized to the mineral surface area (OC:SA ratio), the shift in carbon abundance at the Subunit IIA/IIB boundary becomes more apparent (Fig. 1). Additionally, whereas both OC and SA increase up through Subunit IIB, their ratio is almost constant (Fig. 1). There was therefore a shift in relative organic carbon preservation (OC:SA) at Site 932A during isotope Stage 3, when sediment deposition changed from “rapid and direct” (Subunit IIB) to “slow and indirect” (Subunit IIA; see later discussion).

Description of Hole 942A

The range of OC contents observed in Hole 942A (0.48% to 0.99% OC) is wider than that of Hole 932A (Table 1; Fig. 2). Unit VI has an OC content of ~0.93%, as does Unit II. Hole 942A exhibits a minimum in OC within Unit III–Subunit IVB. In general, the N:C ratio of sediment from Hole 942A is ~0.08. Subunits IVA and IVB are characterized by distinctly higher and lower ratios, respectively (Fig. 2). This is in agreement with data collected aboard ship and may indicate that Subunits IVA and IVB represent extremes in the types of organic matter preserved (Goñi, this volume).

The mineral surface area within Hole 942A averages 24.5 m^2g^{-1}, significantly higher overall than values measured for Hole 932A. High SA values are consistent with smaller mineral components (clays) as observed in the mineralogical data (Flood, Piper, Klaus, et al., 1995) and is expected in a pelagic location such as Site 942. Surface area values are relatively steady at ~24 m^2g^{-1} throughout Units IV−VI. The upper units show greater variability in SA, which is characterized as a minimum coarse sediment in Unit III, grading up to finer sediment in Unit II (Fig. 2). Surface area normalization (OC:SA ratio) attenuates the fluctuations observed in both OC and mineral SA and highlights the sharp decrease in carbon content (lower OC:SA ratio) at the Subunit IVB/Units V/VI boundary (Fig. 2). Due to the concurrent shift toward finer grain sizes (higher SA) from Unit IV to Units III and II, the increase in OC in Fig. 2A is not as evident when plotted as OC:SA (Fig. 2B). Changes in OC:SA ratios correlate inversely with shifts in N:C ratios (Fig. 2C). The data are consistent with greater organic carbon preservation at the location of Hole 942A during the deposition of Unit VI, when the site received riverine input more quickly and more directly.

Aldose Yields and Compositions of Hole 932A

Molecular-level characterizations of sedimentary organic matter allow the refinement of trends observed in bulk organic measurements. For instance, lignin phenols, found only in vascular plants, provide a way of tracing terrestrial inputs into marine systems (Goñi, this volume). Although not specific to terrestrial sources, measurements of the aldose monomers hydrolyzed from carbohydrates provide useful information regarding diagenesis, source, and reactivity of sedimentary organic matter (Cowie and Hedges, 1984a, 1984b). Because aldoses have been extensively studied in the modern Amazon River (Hedges et al., 1994), the subaqueous Amazon Delta (R.G. Keil, E. Tsamakis, and J.I. Hedges, unpubl. data), and in many marine settings (Hernes et al., 1996), they act as biomarkers, thus allowing the comparison of samples from Hole 942A to modern counterparts.

Aldoses liberated by acid hydrolysis were quantified for 11 sediment samples from Hole 932A (Table 2), and one sediment from Hole 942A (107.5 mbsf). In Hole 932A, absolute yields (milligrams per gram of sediment) of total aldoses increased steadily uphole (Table 2; Fig. 3) from a value of 0.53 for the deepest sediment (163.6 mbsf) to 2.57 for the top (3.6 mbsf) sample. The corresponding trend for carbon-normalized total aldose yield (TCH_2O) was similar in shape, ranging from a low of 6.8 mg per 100 mg OC at depth to a high of 34.7 mg total aldose per 100 mg OC for the uppermost sediment (Fig. 3). The most pronounced difference in the two profiles is that normalization to OC accentuates the difference between low values (<20 mg TCH_2O) for the seven lower Subunit IIB samples and the high values (>20 mg TCH_2O) for Subunit IIA.

A general pattern of increasing aldose yields with decreased age is observed within both Subunits IIA and IIB. The aldose yields of 5–40 mg per 100 mg OC are lower than typically observed in fresh vascular plant tissues (~50–125), but within the general range for plankton and bacteria (~5–20). Total aldose yields and aldose compositions from the one deep sediment in Hole 942A are similar to those obtained from the deeper section of Hole 932A.

Table 1. Elemental and mineral surface area data for selected intervals from Holes 932A and 942A.

Core, section, interval (cm)	Depth (mbsf)	%TC	%TN	%OC	(C:N)a	(N:C)a	%IC	Mineral SA (m^{2}g^{-1})	OC:SA (mgOCm^{-2})	Deposition
155-932A-										
1H-3, 57–67	3.57	0.782	0.067	0.735	12.7	0.079	0.046	25.4	0.29	I
2H-4, 104–114	11.54	0.784	0.076	0.709	10.9	0.092	0.075	21.2	0.33	I
3H-4, 105–109	21.05	1.596	0.079	0.699	10.4	0.096	0.897	21.1	0.33	I
5H-4, 106–116	40.06	1.000	0.080	0.785	11.5	0.087	0.214	22.3	0.35	I
6H-4, 100–110	49.50	1.345	0.089	1.057	13.8	0.072	0.289	25.0	0.42	D
7H-4, 89–99	58.89	1.576	0.092	1.054	13.3	0.075	0.523	22.6	0.47	D
8H-4, 30–40	64.35	1.542	0.092	0.984	12.5	0.080	0.558	19.6	0.50	D
9H-4, 110–120	77.53	1.260	0.090	1.040	13.5	0.074	0.220	22.7	0.46	D
10H-5, 43–54	86.90	1.498	0.085	0.980	13.5	0.074	0.518	21.6	0.45	D
11X-4, 87–97	96.76	1.306	0.085	0.950	13.0	0.077	0.356	18.4	0.52	D
12X-4, 31–41	105.81	1.214	0.088	0.940	12.5	0.080	0.274	20.5	0.46	D
13X-3, 97–107	114.57	1.245	0.085	0.920	12.6	0.079	0.324	20.8	0.44	D
14X-4, 57–67	125.37	1.225	0.093	0.917	11.5	0.087	0.309	19.1	0.48	D
15X-4, 63–73	135.13	1.117	0.082	0.821	11.6	0.086	0.296	19.8	0.41	D
16X-3, 75–85	143.45	1.169	0.080	0.800	11.7	0.087	0.226	17.9	0.45	D
17X-3, 107–117	153.27	1.159	0.085	0.830	11.3	0.088	0.328	17.8	0.47	D
18X-4, 43–54	163.63	1.035	0.078	0.771	11.5	0.087	0.264	18.9	0.41	D
155-942A-										
1H-2, 7–17	1.57	0.975	0.086	0.897	12.2	0.082	0.078	32.5	0.28	I
2H-4, 38–48	8.68	1.154	0.080	0.790	11.5	0.087	0.364	29.0	0.27	I
3H-4, 38–48	18.18	1.073	0.075	0.720	11.2	0.089	0.353	27.7	0.26	I
4H-4, 50–60	27.80	0.627	0.051	0.480	10.9	0.092	0.147	19.4	0.25	I
5H-4, 77–87	37.31	1.020	0.064	0.570	10.3	0.097	0.450	22.4	0.25	I
6H-1, 35–42	42.15	0.848	0.074	0.515	8.1	0.123	0.333	23.6	0.22	I
7H-6, 14–24	58.94	0.730	0.053	0.562	12.4	0.080	0.169	23.0	0.24	I
9H-4, 36–46	73.03	1.137	0.061	0.902	17.1	0.058	0.235	27.3	0.33	D
10H-5, 75–85	86.55	1.242	0.067	0.876	15.3	0.066	0.366	23.5	0.37	D
11H-5, 12–22	94.05	1.382	0.078	0.957	14.4	0.070	0.425	24.3	0.39	D
12H-5, 40–50	101.99	1.410	0.077	0.902	13.6	0.073	0.507	22.9	0.39	D
13X-3, 46–56	107.46	1.466	0.088	0.872	11.6	0.086	0.593	23.7	0.37	D
16X-4, 77–87	134.57	1.455	0.086	0.994	13.4	0.074	0.461	23.4	0.42	D
17X-4, 80–90	144.30	1.351	0.082	0.935	13.4	0.075	0.416	24.0	0.39	D
18X-4, 54–64	153.64	1.366	0.090	0.995	13.0	0.077	0.371	21.9	0.45	D
19X-4, 38–48	163.18	1.398	0.087	0.992	13.3	0.075	0.406	23.2	0.43	D
20X-2, 31–41	169.71	1.407	0.093	0.990	12.4	0.081	0.416	24.8	0.40	D

Notes: mbsf = meters below seafloor; %TC = percent total carbon; %TN = percent total nitrogen; %OC = percent organic carbon; (C:N)a = atomic carbon to nitrogen ratio; (N:C)a = atomic nitrogen to carbon ratio; %IC = percent inorganic carbon; SA (m^{2}g^{-1}) = N_2-specific mineral surface area; and OC:SA (mgOCm^{-2}) = organic carbon to mineral surface area ratios. The final column denotes whether a sample has been grouped as "directly" deposited (D) or indirectly deposited (I).

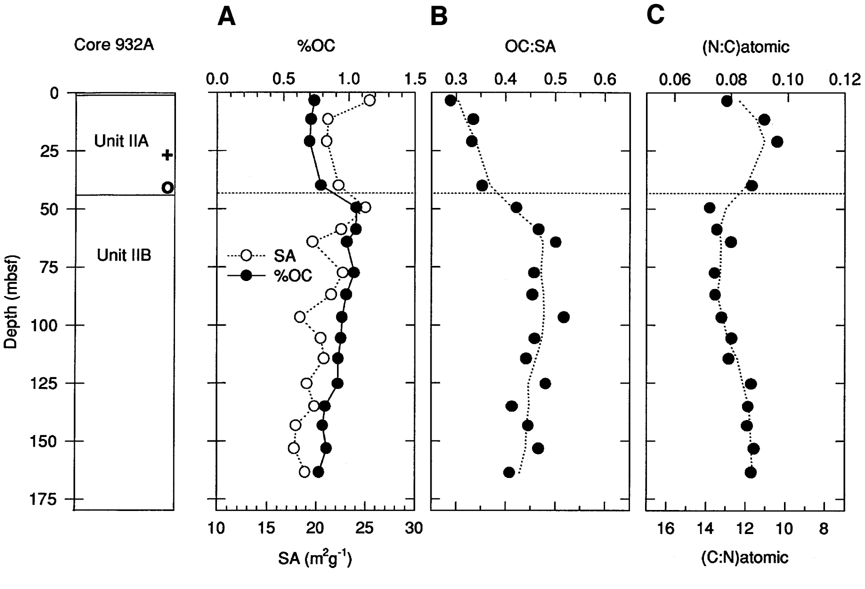

Figure 1. Elemental compositions of Hole 932A. **A.** %OC = percent organic carbon, and SA = mineral surface area. **B.** OC:SA = organic carbon to mineral surface area ratios. **C.** Atomic N:C ratios. Lithographic notes on the left reproduced from shipboard measurements (see Flood, Piper, Klaus, et al., 1995). Age markers represent well-constrained ages for certain sections of each hole, as determined from biostratigraphic analysis: + = Lake Mungo Excursion (30 ka); open circle = *Pulleniatina obliquiloculata* datum (40 ka); and dashed lines in the last two panels represent running three-point averages .

Aldose compositions, expressed as weight percentages (wt%), do not vary widely among sediment units. Average compositions for samples from Subunit IIA are, however, slightly depleted in glucose and enriched in galactose vs. Subunit IIB samples. The weight percent of glucose relative to total aldoses from these samples increases in proportion to decreasing δ^{13}C, with all but one of the Subunit IIB samples yielding 30 wt% or more glucose. This relationship suggests that the slightly higher glucose percentages of Subunit IIB samples may be related to a stronger terrestrial source and is consistent with large glucose yields typical of vascular plant tissues (Cowie and Hedges, 1994a). Elevated glucose is unlikely to result from greater in situ diagenesis within the older Subunit IIB samples, because glucose is preferentially lost during biodegradation (Hedges et al., 1994; Hernes et al., 1996), opposite to the observed trend.

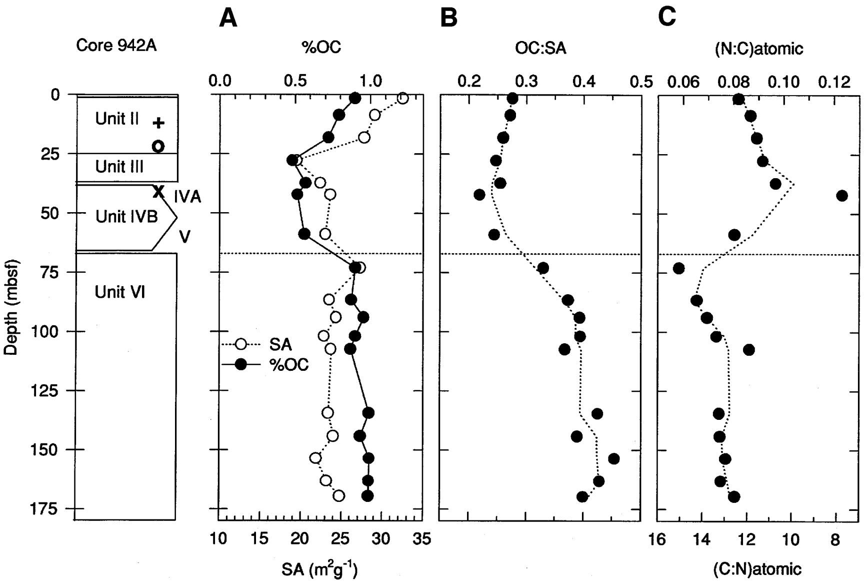

Figure 2. Elemental compositions of Hole 942A. **A.** %OC = percent organic carbon, and SA = mineral surface area. **B.** OC:SA = organic carbon to mineral surface area ratios. **C.** Atomic N:C ratios. Lithographic notes on the left reproduced from shipboard measurements (see Flood, Piper, Klaus, et al., 1995). Age markers represent well-constrained ages for certain sections of each hole, as determined from biostratigraphic analysis: + = Lake Mungo Excursion (30 ka); open circle = *Pulleniatina obliquiloculata* datum (40 ka); X = Blake Event (105 ka); and dashed lines in the last two panels represent running three-point averages.

Table 2. Aldose yields for Hole 932A and one sample from Hole 942A, expressed as mg aldose per 100 mg organic carbon.

Core, section, interval (cm)	Aldose yield (mg/100mgOC)									Total yield	
	LYX	ARA	RIB	XYL	RHA	FUC	MAN	GAL	GLC	TCH$_2$0	Deposition
155-932A-											
1H-3, 57–67	1.08	4.32	0.54	3.11	3.65	2.03	5.68	5.14	9.19	34.73	I
2H-4, 104–114	0.85	2.82	0.42	2.11	2.25	1.55	3.52	3.52	5.49	22.54	I
3H-4, 105–109	1.00	3.43	0.71	3.29	3.00	2.14	5.14	4.71	6.71	30.14	I
5H-4, 106–116	1.01	2.53	0.38	2.41	2.28	1.14	5.32	3.42	6.46	24.94	I
6H-4, 100–110	0.85	1.13	0.38	0.66	1.51	0.47	2.64	1.22	3.01	11.87	D
7H-4, 89–99	0.48	2.19	0.29	1.52	1.62	0.76	2.76	2.29	5.24	17.14	D
8H-4, 30–40	0.61	1.84	0.20	1.22	1.63	0.71	2.75	2.04	4.69	15.71	D
9H-4, 110–120	0.58	1.73	0.19	1.15	1.64	0.67	2.69	1.92	4.52	15.10	D
12X-4, 31–41	0.64	1.60	0.32	1.17	1.49	0.64	2.66	1.81	4.47	14.79	D
15X-4, 63–73	0.49	1.46	0.24	1.10	1.34	0.49	2.44	1.46	3.90	12.93	D
18X-4, 43–54	1.30	0.65	0.26	0.13	0.26	0.39	0.91	0.78	2.21	6.88	D
155-942A-											
13X-3, 46–56	0.57	1.26	0.23	1.15	1.38	0.57	2.41	1.49	3.56	12.64	D

Notes: LYX = lyxose; ARA = arabinose; RIB = ribose; XYL = xylose; RHA = rhamnose; FUC = fucose; MAN = mannose; GAL = galactose; GLC = glucose; TCH$_2$O = total saccharide (aldose) per 100 mg OC. I = indirect deposition (Cores 155-932A-1H through 5H) and D = direct (Cores 155-932A-6H through 18X). Core 155-942A-13X was also deposited under direct conditions.

Comparison with Modern Counterparts

Before comparing data from Holes 932A and 942A to modern sediments in the Amazon River and Delta, the ODP data were split into two groups: direct and indirect sedimentation (Table 1). Criteria for assigning data to these two groups comes largely from the lithology described by Flood, Piper, Klaus, et al. (1995), the age models for each core (Maslin et al., Showers et al., Schneider et al., all this volume), and by noting whether each individual sample was recovered from a lithographic unit that received a large volume of river sediment per unit time. Samples from a lithographic interval representing a very large amount of sediment transport per unit time were grouped as "direct" (directly influenced by river sediment discharge via slumping and turbidite flow). Samples falling in the "indirect" category are representative of intervals when less sediment accumulated over a given time span, and when particle transit also included slow movement through a nepheloid layer. These categories should not be taken too literally, for it is thought, at least for Subunit IIB of Hole 932, that "direct" sediment accumulation at the site resulted only after component particles were rapidly deposited in the canyon and then transported to the site via turbidity current flow initiated by slumping. Other demarcation terms also could be "rapid" and "slow" accumulation. It should also be noted that we specifically sampled carbonate-poor sediments in order to maximize investigation of terrestrially derived sediments and minimize complexities due to large inputs of authigenic minerals.

OC:SA Ratios

When OC:SA ratios are plotted as a function of sample type, data from the sites tend to fall between those for the modern Amazon Delta and River (Fig. 4A). Although samples from times of more direct sedimentation of terrigenous material have a lower average OC:SA ratio than the modern river (representing an average loss of about a factor of 2), they still fall within the broad range observed for modern riverborne particles. In contrast, samples from indirect (or low) sedimentation periods lie outside the boundary observed in modern rivers (relative decrease of a factor of 3), and fall within the boundary observed for the modern delta (Fig. 4A). This pattern suggests that the extent to which terrestrial organic matter is preserved in these two holes is a function of the delivery pathway of terrigenous mineral material to the sites. When the sedimentation pathway from the river to the site is rapid and more direct, both organic matter content and OC:SA ratios are higher. There appears to be less loss of organic matter during direct deposition. This conclusion is supported by a comparison of OC:SA ratios with stable carbon isotope compositions of

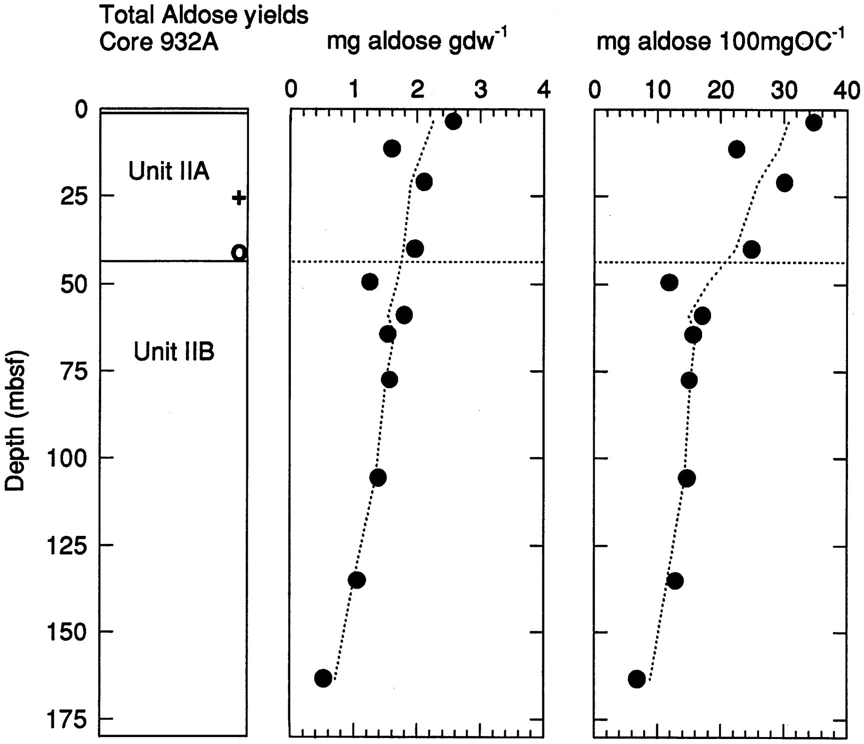

Figure 3. Total aldose yields for Hole 932A as a function of sediment depth (mbsf).

the samples (Fig. 4B; also see Goñi, this volume). Samples that have been directly deposited have $\delta^{13}C$ compositions identical to that of particles suspended in the river. If marine-derived OC were added to the samples prior to burial, the $\delta^{13}C$ compositions would be expected to shift toward more positive values (typical marine OC has a $\delta^{13}C$ composition of ~–20‰). Assuming carbon isotopes are a robust indicator of terrigenous material, there is therefore little evidence of the addition of marine organic material to the samples; the preserved material is nearly exclusively terrestrial in origin. This is also suggested by the low inorganic carbon content and the aldose compositions of the samples.

Indirectly deposited sediment particles appear to have lost more of their original organic matter and to have had appreciable marine material added to the matrix. Loss of riverine organic material is indicated by OC:SA ratios that are a factor of 3 lower than for the modern river. The more positive $\delta^{13}C$ ratios indicate additional marine organic matter (Fig. 4B; also see Goñi, this volume). These two trends could co-evolve by one of three possible mechanisms: independent (uncoupled) transport of organic and mineral to the site, addition of organic-poor marine mineral matter to the sediment, or diagenetic loss (or replacement) of terrestrial organic matter prior to deposition. The first possibility, that organic matter and mineral inputs are finite and independent, and that elevated SA values in the indirectly deposited sediments simply lead to lower OC:SA ratios, is not likely because modern river and delta samples show no such trend in hydrodynamically sorted samples (Keil et al., 1994; Keil et al., in press. In addition, the organic and mineral fractions of both the ODP samples and modern counterparts cannot be physically separated via density fractionation. Evidence against the second hypothesis comes from the lack of a negative correlation between weight percentages of inorganic carbon (IC) and OC ($r^2 = 0.05$, $m = 0.24 \pm 0.18$, $n = 38$), or between IC and OC:SA ($r^2 = 0.14$, $m = 0.27 \pm 0.31$, $n = 38$). The third hypothesis is thus favored.

It is interesting to note that the directly influenced sediments from Hole 942A are ~50–80 ka older than those from Hole 932A. The older sediments (Hole 942A, Unit VI) have slightly lower OC:SA ratios (0.39) relative to the younger directly influenced sediments (Hole 932A, Subunit IIB, OC:SA = 0.46). This difference could be due either to more advanced in situ diagenesis during the additional 50 ka when the sediments were in place, or to an enhanced loss during the transport to Site 942. Core 155-942A-3H was deposited at the same approximate time (~75 ka) as Cores 155-932-74 through 18X. The difference in OC:SA between these samples may be due to the direct deposition at Site 932 (average OC:SA of 0.46) vs. the indirect deposition at the more distal site (OC:SA of 0.26).

Aldose Measurements

Aldose measurements provide information that can be used to evaluate the diagenesis of organic matter and to potentially assign sources of that material (Cowie and Hedges, 1984a). Glucose is the predominant aldose in all samples from Hole 932A, followed by mannose and galactose. Comparison of aldose weight percentages from the ODP holes to those from coarse and fine suspended particulate materials recovered from the lower Amazon River (Fig. 5) show that aldose compositions (fingerprints) of ODP samples closely resemble those of fine particulate material transported by the modern river. For example, the presence of measurable amounts of fucose and ribose, and the low overall weight percentages of glucose vs. values >50% typical of vascular plant tissues (Table 2), indicate that the bulk of the aldoses may have an aquatic (algal or bacterial) origin (Cowie and Hedges, 1984a). This fingerprint is routinely observed in fine suspended sediment (1–63 µm) of the modern Amazon River, which is thought to be derived in part by highly degraded higher plant material and in part by riverine microorganisms (Hedges et al., 1994). In contrast, coarse particulate matter (>63 µm) in the river has an aldose fingerprint similar to that of terrestrial plants (Hedges et al., 1994), and marine-derived algal material is typically depleted in rhamnose and lyxose. Although contrasts are subtle, Subunit IIB sediments from Hole 932 (directly deposited) have major aldose compositions and total yields (TCH_2O) that are closer to those of Amazon fine suspended matter than are corresponding parameters for samples from the overlying Subunit IIA (indirect sedimentation). Subunit IIA aldose compositions are between that of Amazon River suspended

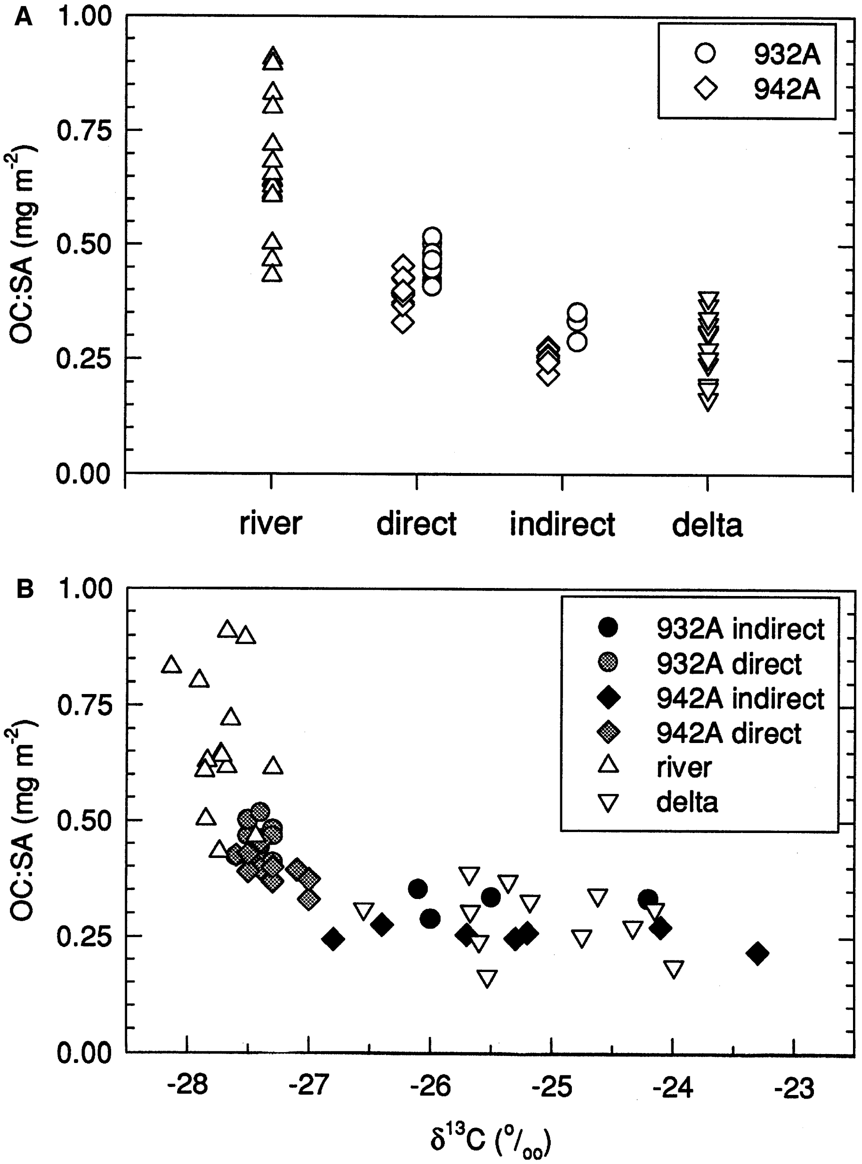

Figure 4. Comparison of OC:SA ratios from Holes 932A and 942A to data collected from the current Amazon River and Delta. **A**. Range in OC:SA for modern river suspended sediments. The sediment is presumed to have been deposited at either Hole 932A or 942A directly from the river mouth, indirectly at the two locations, and/or isolated from the modern Amazon Delta. **B**. Data plotted against the organic δ^{13}C isotope ratio. Modern Amazon River data from Keil et al. (in press) were used with permission as well as carbon isotope compositions from Goñi (this volume).

sediments and marine-derived materials. Parallel similarities have also been observed for stable carbon isotope compositions and lignin-derived phenols (Goñi, this volume). Goñi finds little evidence for the diagenetic loss of lignin, also in agreement with the conclusions presented here based on surface loadings and aldose data. We caution that interpretations of source based solely on aldose measurements are considerably weak compared to those made with more robust indicators such as stable carbon isotopes, lignin phenols, lipids, and amino acids.

Although downward decreases in total aldose yields suggest advancing in situ diagenesis, saccharide compositional patterns do not. The composition of aldose mixtures in Hole 932A Subunit II sediments is similar to that of fine suspended particulate materials carried by the modern Amazon River and show little sign of diagenetic alteration. Selective losses of specific aldoses would be expected if extensive diagenesis were occurring (Cowie and Hedges, 1984a; Hernes et al., 1996). If carbohydrate diagenesis is occurring in situ, it appears to be nonselective, which is distinctly different from patterns observed in modern settings (Hedges et al., 1994; Hernes et al., 1996). Ongoing analyses of amino acid compositions for these same sediments should help test for progressive degradation within Amazon cone sediments and provide additional comparisons to suspended particulate material presently being delivered by the Amazon River to the adjacent continental shelf. At present, saccharides in Hole 932A appear to have suffered little diagenetic loss since deposition.

SUMMARY

Mineral surface area-normalized organic matter loadings for Holes 932A and 942A are higher than observed in the modern Amazon Delta, but lower than that of the modern river suspended particle load. Lower OC:SA ratios for Hole 942A relative to Hole 932A are consistent with its more distal location from the Amazon River. Indirectly deposited sediment for both holes have low OC:SA ratios, consistent with that observed in other slowly accumulating sediments at similar depths in the modern ocean (Hedges and Keil, 1995). Sediments thought to be directly influenced by riverine input via either direct sedimentation or input via slumping and resulting turbidity current flow are enriched in total organic matter by up to a factor of 2 over sediments reaching these locations indirectly. They are composed predominately of terrestrial organic matter as illustrated by their aldose, lignin (Goñi, this volume) and carbon isotope compositions. These compositional differences between sediments that have

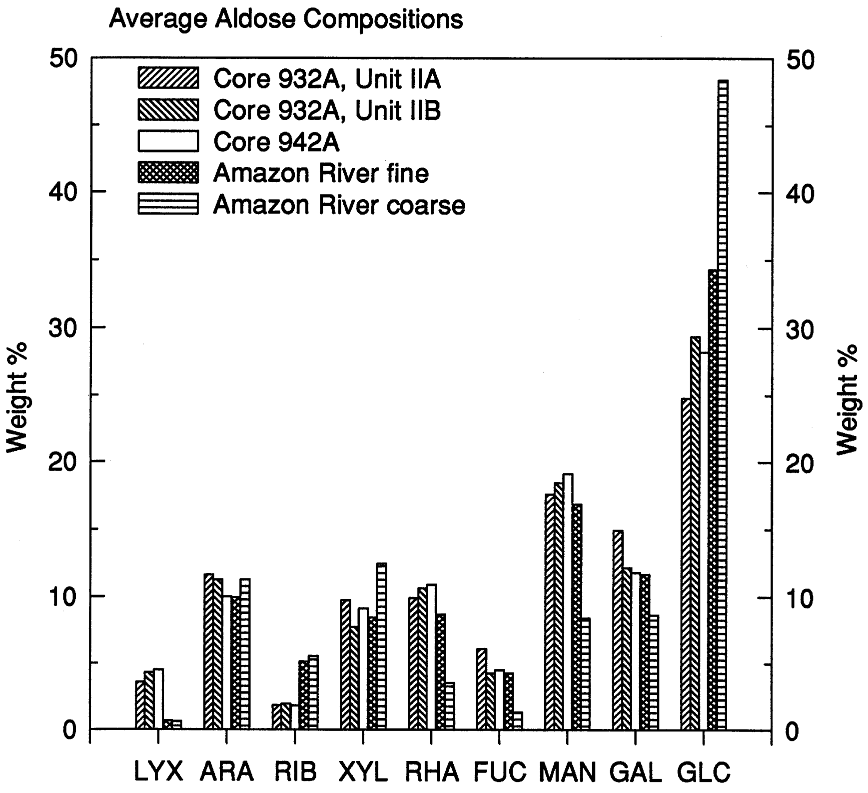

Figure 5. Average aldose compositions for all samples from Hole 932A and for one sample from Hole 942A. For comparison, the aldose compositions of modern Amazon River fine and coarse particulate material are also shown. Abbreviations are the same as in Table 2.

been directly and indirectly deposited are hypothesized to be the result of increased diagenesis and the reworking of organic matter (terrestrial and marine) during indirect deposition at low sedimentation rates. If this interpretation is correct, it implies that preservation efficiencies of terrestrial organic matter can be altered measurably depending on the pathway prior to deposition. The efficiency of organic matter preservation within Amazon Delta and Fan deposits therefore probably changes significantly as a complex function of sediment transport history, sea level, and glacial stage. Large variation in organic carbon burial efficiency for the Amazon River and other major rivers could have a great impact on regional and global carbon budgets.

ACKNOWLEDGMENTS

We thank Crystal Thimsen, Elli Tsamakis, and Mark Borsuk for their technical assistance. The first author acknowledges the movies of Audrey Hepburn as a sanity-stabilizing diversion during manuscript preparation. Roger Flood provided excellent detailed comments and advice on this manuscript. Larry Mayer and one anonymous referee provided very helpful insight into the work.

REFERENCES

Aller, R.C., 1994. Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. *Chem. Geol.,* 114:331–345.

Aller, R.C., Blair, N.E., Zia, Q., and Rude, P.D., 1996. Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments. *Cont. Shelf Res*., 16:753–786.

AUPAC (International Union of Pure and Applied Chemistry). 1989. Reporting physiosorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Appl. Chem.,* 57: 603–619.

Cowie, G.L., and Hedges, J.I., 1984a. Carbohydrate sources in a coastal marine environment. *Geochim. Cosmochim. Acta,* 48: 2075–2088.

————, 1984b. Determination of neutral sugars in plankton, sediments, and wood by capillary gas chromatography of equilibrated isomeric mixtures. *Anal. Chem.,* 56:497–504.

Emeis, K.-C., and Kvenvolden, K.A., 1986. Shipboard organic geochemistry on *JOIDES Resolution*. *ODP Tech. Note,* 7.

Flood, R.D., Piper, D.J.W., Klaus, A., et al., 1995. *Proc. ODP, Init. Repts*., 155: College Station, TX (Ocean Drilling Program).

Hedges, J.I., Cowie, G.L., Richey, J.E., Quay, P.D., Benner, R., Strom, M., and Forsberg, B.R., 1994. Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids. *Limnol. Oceanogr*., 39: 743–761.

Hedges, J.I., and Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem*., 49: 81–115.

Hedges, J.I., and Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnol. Oceanogr*., 29: 657–663.

Hernes, P.J., Hedges, J.I., Peterson, M.L., Wakeham S.G., and Lee, C., 1996. Neutral carbohydrate geochemistry in the Central Equatorial Pacific. *Deep-Sea Res*., 43:1181–1204.

Keil, R.G., Mayer, L., Quay, P., Richey, J., and Hedges, J.I., in press. Loss of organic matter from riverine particles in deltas. *Geochim. Cosmochim. Acta*.

Keil, R.G., Tsamakis, E., Fuh, C.B., Giddings, C.A., and Hedges, J.I., 1994. Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. *Geochim. Cosmochim. Acta,* 58: 879–893.

Mayer, L.M., 1994. Surface area control of organic carbon accumulation in continental shelf sediments—a hypothesis. *Geochim. Cosmochim. Acta,* 58:1271–1284.

————, 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis—a comment. *Mar. Chem*., 49:123–126.

Shipboard Scientific Party, 1995a. Site 932. *In* Flood, R.D., Piper, D.J.W., Klaus, A., et al., *Proc. ODP, Init. Repts.,* 155: College Station, TX (Ocean Drilling Program), 175–199.

Shipboard Scientific Party, 1995b. Site 942. *In* Flood, R.D., Piper, D.J.W., Klaus, A., et al., *Proc. ODP, Init. Repts.,* 155: College Station, TX (Ocean Drilling Program), 537–567.

Showers, W.J., and Angle, D.G., 1986. Stable isotope characterization of organic carbon accumulation on the Amazon continental shelf. *Cont. Shelf Res*., 6: 227–244.

Date of initial receipt: 1 December 1995
Date of acceptance: 12 July 1996
Ms 155SR-237

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