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32. RECORD OF TERRESTRIAL ORGANIC MATTER COMPOSITION IN AMAZON FAN SEDIMENTS[1]

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ABSTRACT

Elemental, stable carbon isotope, and lignin analyses were carried out to characterize the organic matter in sediments from Site 932 on the Amazon Fan. The lignin compositions of sedimentary organic matter in Subunits IIA and IIB at this site resembled those of fine- and coarse-suspended particles from the present-day Amazon River. The lignin concentrations and isotopic composition of organic carbon suggest that the organic matter in Subunit IIA sediments is composed of varying amounts of marine (85% to 20%) and terrestrial (15% to 80%) contributions, whereas in Subunit IIB, it is exclusively terrestrial in origin. The compositions of lignin phenols indicate that the vegetation of the Amazon Basin did not change appreciably during the period represented by the sediments in Site 932. The data also illustrate the depositional differences that were responsible for the formation of the various lithologic units at the site.

INTRODUCTION

Submarine fans are thought to form by the accumulation of terrestrial materials transported during periods of low sea level. During glacial periods, rivers discharge at the edges of continental shelves, directly depositing sediments on continental slopes. In the past, these processes have resulted in some of the most massive soft-sediment deposits in the deep sea, including the Amazon Fan. Formed by sediments eroded from the Andes and transported by one of the largest rivers in the world, the Amazon Fan provides a record of past conditions in the Amazon River Basin. As such, the compositions of fan sediments can provide information regarding the tropical paleoclimate of the Western Hemisphere that is complementary to pollen records from land (e.g., Absy et al., 1991; Van der Hammen and Absy, 1994; Van der Hammen et al., 1992).

One important facet of this investigation is the study of sedimentary organic matter as an indicator of continental paleovegetation and past depositional conditions. This approach is especially relevant given the extensive organic geochemical studies conducted on the modern Amazon River (Ertel et al., 1986; Hedges et al., 1986a, 1986b; 1992; 1994; Quay et al., 1992; Richey et al., 1990) and Amazon shelf (Showers and Angle, 1986; Aller et al., 1991; Blair and Aller, 1995; Goñi et al., 1995). In addition, organic analyses provide data that are independent and complementary information to palynological and inorganic geochemical studies of the Amazon Fan (Flood, Piper, Klaus, et al., 1995).

Lignin-derived phenols obtained from CuO oxidation are an important tool in the geochemical characterization of sedimentary organic matter (Hedges, 1975; Goñi, 1992). Lignin is a polyphenolic macromolecule that is uniquely synthesized by terrestrial vascular plants (Sarkanen and Ludwig, 1971). Upon CuO oxidation, lignin yields a variety of characteristic vanillyl (monomethoxylated), syringyl (dimethoxylated), and cinnamyl phenols (Fig. 1) that can be used as biomarkers. Due to high resistivity against microbial attack (Kirk, 1984), lignin and lignin-derived phenols can be used to characterize and trace terrestrially derived organic matter in a wide variety of environments. For example, CuO oxidation analyses of vascular plants have shown lignin compositions to vary predictably among plant types (Hedges and Mann, 1979a; Hedges et al., 1986a; Goñi and Hedges, 1992). These distinctive compositions have been used to discern the sources of vascular plant detritus in a variety of environments (e.g., Hedges and Mann, 1979b; Ugolini et al., 1981; Wilson et al., 1985; Requejo et al., 1986; Hedges et al., 1988b; Goñi and Hedges, 1992; Prahl et al., 1994). In particular, changes in lignin phenol compositions have been used to reconstruct past inputs of vascular land plant materials to lacustrine (Hedges et al., 1982; Ishiwatari and Uzaki, 1987) and marine sediments (Prahl et al., 1994). One of the aims of the present study is to characterize lignin compositions in various deposits of the Amazon Fan and relate them to paleovegetation changes in the Amazon River Basin associated with climatic cycles (e.g., Brown, 1987; Van der Hammen and Absy, 1994; Van der Hammen et al., 1992).

Because fan deposits include marine as well as terrigenous materials, the second important aim of this study is to quantify the sources of organic carbon preserved in sediments from different lithostratigraphic units. Lignin phenols, in combination with the stable isotopic composition of organic carbon, have been previously used to estimate the fraction of terrestrial materials in various modern (Hedges and Parker, 1976; Hedges and Mann, 1979b; Gough et al., 1993; Prahl et al., 1994) and ancient marine sediments (Prahl et al., 1994). In this study, I apply a similar approach to estimate the fraction of terrestrial organic carbon in Amazon Fan sediments. Such data provide information on past depositional conditions along the fan and also can be used to constrain diagenetic reactions within sediments.

METHODOLOGY

Site Description

Sediments from Holes 932A and 932B were sampled at ~10-m intervals (i.e., once every core). Correlation between Holes 932A and 932B was achieved by magnetic and biostratigraphic data as explained by the Shipboard Scientific Party (1995). All reported sample depths are in meters below seafloor (mbsf). Site 932 (5°12.682′N, 47°1.770′W) is located on the eastern part of the Amazon Fan (Fig. 2). At this site, we sampled Channel-levee System 6B, the oldest part of the Upper Levee Complex.

Two lithologic units were recognized at this site: Unit I (0–0.7 mbsf), a Holocene nannofossil-foraminifer clay; and Unit II (0.7–168.3 mbsf), mud with interbedded laminae and beds of silt and very fine sand. Unit II was divided into Subunit IIA (0.7–47 mbsf), char-

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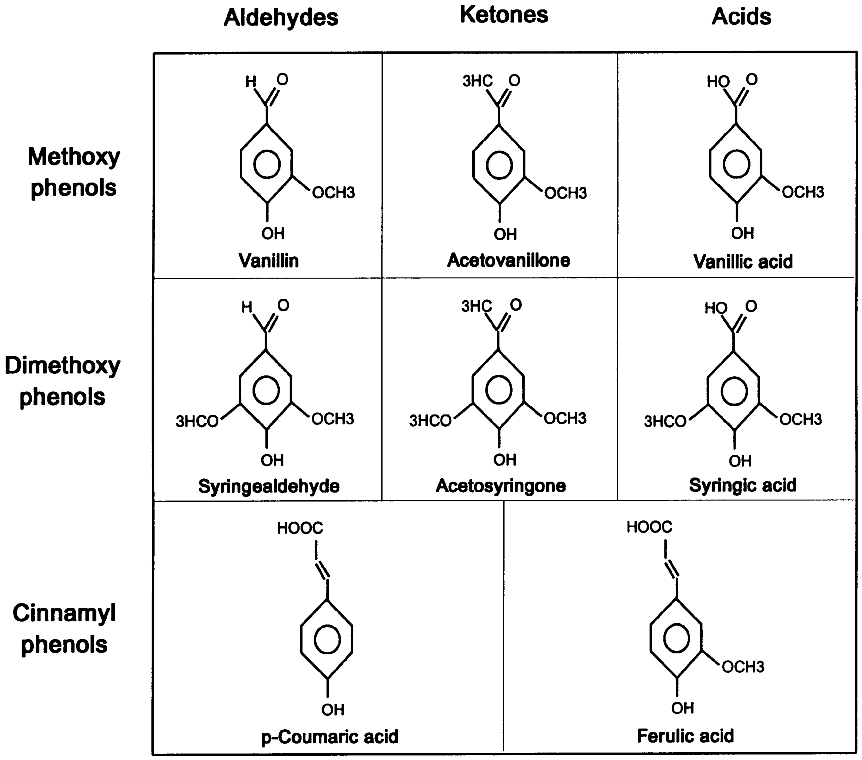

Figure 1. Structures of major lignin-derived CuO reaction products.

acterized by bioturbated dark olive gray clay; and Subunit IIB (47–168 mbsf), predominantly composed of dark olive gray silty clay with silt and very fine laminae (see Shipboard Scientific Party, 1995, for a complete description of the site).

Based on the occurrence of paleomagnetic events (Cisowski, 1995), including the Lake Mungo Excursion (32 ka) at 25 mbsf and the Laschamp Excursion (43 ka) at 27.5 mbsf, it appears that most of Subunit IIA sediments were deposited during isotopic Stages 2 and 3. Maslin et al. (this volume) have developed an age model for this site that places isotopic Stage 2 (12 to 24 ka; Imbrie et al., 1984), between ~7 and 14 mbsf. The depth interval corresponding to isotopic Stage 3 (24 to 59 ka) is between 14 and 43 mbsf. According to this model, the last glacial maximum (LGM, between 18 and 28 ka) is represented by samples between ~10 and 22 mbsf. The assigned age of sediments at 45 mbsf (just above Subunit IIB) is ~65 ka. It therefore appears that part of isotopic Stage 4 (59 to 71 ka) is also contained within Unit IIA. The above chronology for Subunit IIA sediments is consistent with ^{14}C dates obtained from samples at this site (Maslin et al., this volume).

The age of Subunit IIB sediments, on the other hand, is not as well constrained. Based on sedimentological data, the deepest sediments (168 mbsf) recovered from Site 932 have a maximum age of 75 ka (Maslin et al., this volume). Such tentative dating requires sedimentation rates for Subunit IIB of over 10 m/k.y., well within the ranges obtained from channel-levee deposits in other parts of the fan (Shipboard Scientific Party, 1995). Hence, it is likely that most of Subunit IIB sediments were deposited during the late part of Stage 4 and perhaps the very early part of isotopic Stage 5 (71–128 ka).

Sample Collection

All sediments were taken from Unit II core sections that did not receive acetone treatment to seal endcaps, thus avoiding possible organic contamination. After sampling, sediments were placed in K-Pack bags, sealed, and kept frozen until analysis. Prior to analysis in the laboratory, all sediments were freeze-dried and ground to pass through a Tyler equivalent 42 mesh (355 µm-opening) screen.

Analytical Methods

Elemental Analysis

Weight percentages of total carbon (TC) and total nitrogen (TN) were determined in duplicate (without acidification) by conventional combustion at elevated temperature (1000°C) on a Perkin Elmer 2400 CHN Elemental Analyzer. The average mean deviation of these measurements was ±2%. Total inorganic carbon (TIC) was determined by a computer-controlled system as described by Ostermann et al. (1990). The procedure involves the acidification of sediments at 80°C with 100% phosphoric acid. Upon acidification, sedimentary carbonate is evolved into H_2O and CO_2, and the resulting pressure change is monitored within the closed system. After calibration with calcium carbonate standards, the increase in pressure is used to calculate the carbonate content of sediment samples assuming all TIC is in the form of $CaCO_3$. The precision of the system is better than 1% of the measured value. Total organic carbon (TOC) was determined by difference; TOC = TC – TIC.

CuO Oxidation

CuO oxidations were carried out according to the procedure developed by Hedges and Ertel (1982) and modified by Goñi and Hedges (1992). Briefly ~400 mg of sediment was oxidized under alkaline conditions (8% NaOH) with CuO at 155°C for 3 hr in stainless steel pressurized vessels. Once the reaction vessels were opened, known amounts of *trans*-cinnamic acid and ethylvanillin were added to the solution The aqueous solutions were acidified to pH 1 with concentrated HCl and extracted with ethyl 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.

To quantify lignin CuO reaction products, dried extracts were redissolved in a known volume of pyridine (~400 µL). A fraction of this volume was reacted at 60°C for 15 min with excess amounts of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 1% trichloromethylsilane (Regis Chemical Company) in order to silylate all exchangeable hydrogens. A small volume of this solution (typically 0.5 µL) was injected on-column into a Hewlett-Packard 5890 GC fitted with a 60-m-fused silica column (0.32 mm I.D.) coated with methylsilicone stationary phase (DB-1; J and W Scientific) and a flame ionization detector. Helium was used as the carrier gas. The oven temperature program started at 70°C (5 min initial hold time) and increased to 320°C at a rate of 4°C per minute (with a final hold time of 20 min). All lignin phenols were quantified based on the yields ethylvanillin and *trans*-cinnamic acid recovery standards and their individual response factors relative to periodically injected mixtures of commercial standards.

Compound identification was achieved by conventional gas chromatography-mass spectrometry (GC-MS), using a Hewlett-Packard 5890 GC linked to 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.

Bulk Isotopic Analyses

Stable isotopic compositions of TOC ($\delta^{13}C_{TOC}$) were determined from pre-acidified (2N HCl) sediments by automated on-line combustion followed by conventional isotope ratio-mass spectrometry (Finnigan MAT Delta-S mass spectrometer). Analyses were performed at the Stable Isotope facility of the Ecosystem Center in the Marine Biological Laboratory (Woods Hole, Massachusetts). Details of the procedure are given by Fry et al. (1992). By convention, the $^{13}C/^{12}C$ ratio of the organic carbon in any sample (SMP) is reported relative to the PDB carbonate standard (STD) in the $\delta^{13}C$ parts per thousand or per mil (‰) notation according to Equation 1:

$$\delta^{13}C = \left[\frac{\left(^{13}C/^{12}C\right)_{SMP}}{\left(^{13}C/^{12}C\right)_{STD}} - 1\right] \times 1000 \ . \qquad (1)$$

RESULTS

Elemental Compositions

Weight percentages of TIC, TOC, and TN for sediments from Site 932 are tabulated in Table 1. Elevated TIC concentrations of 0.5% and 0.7% are obtained at 0.8 and 21 mbsf, respectively. Assuming all inorganic carbon is in the form of $CaCO_3$, these values represent weight percent $CaCO_3$ contents of 3.7% and 5.6%, respectively. All other samples display TIC concentrations of equal or less than (≤) 0.25% that correspond to a $CaCO_3$ content ≤2%. The lowest %TIC values (<0.05%) are obtained from two samples at 3.6 and 11.5 mbsf.

Sediments above 41 mbsf have TOC concentrations ≤0.8%. Below this depth, TOC concentrations are higher (1.1% at 50 and 59 mbsf) and steadily decrease downhole to 0.8% at 164 mbsf. TN concentrations range from 0.10% to 0.13% throughout the core, except for a lower value of 0.08% at 0.8 mbsf. The above TOC and TN compositions result in atomic organic carbon:total nitrogen ratios ([C/N]a) that range from 7.3 (11.5 mbsf) to 10.3 (49.5 mbsf) and do not display a clear downhole pattern. These results agree well with data from shipboard elemental analyses (Shipboard Scientific Party, 1995).

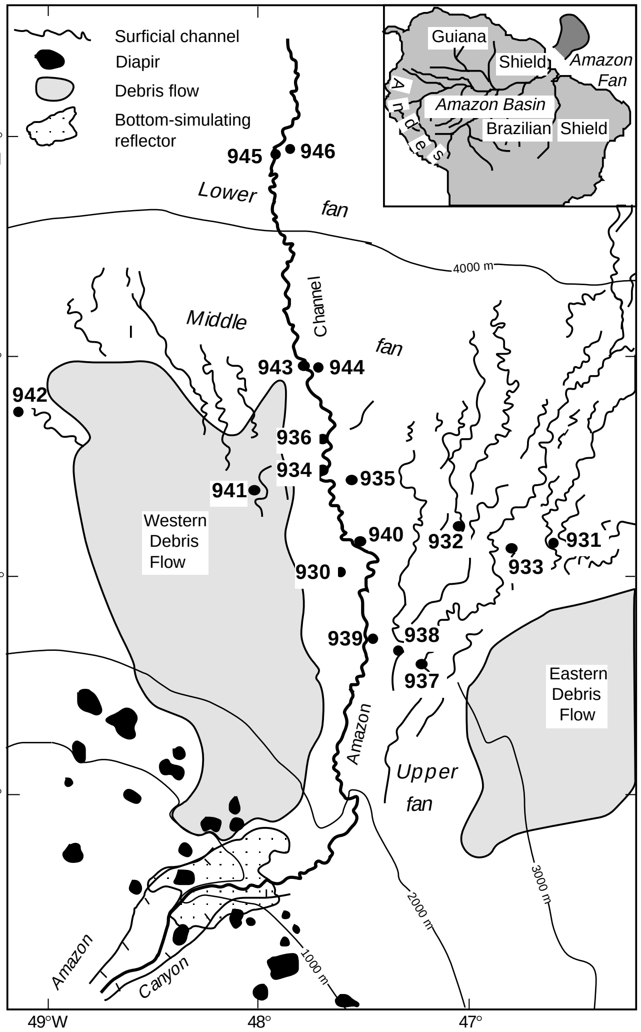

Figure 2. Location of Site 932. From Flood et al. (1995); modified from Damuth et al. (1988), and Manley and Flood (1988).

Stable Carbon Isotopic Compositions

The stable carbon isotopic compositions of TOC ($\delta^{13}C_{TOC}$) from Site 932 sediments are presented in Table 1 in the conventional per mil (‰) notation. $\delta^{13}C_{TOC}$ values range from −23.2‰ to −26.1‰ in the top 40 mbsf. Below this depth, $\delta^{13}C_{TOC}$ values remain constant at −27.4‰ ± 0.1‰. Notably, the two sediments with the most enriched $\delta^{13}C_{TOC}$ compositions (at 0.8 and 21 mbsf) also display the highest TIC concentrations.

Lignin Phenol Yields

All sediments from both Subunits IIA and IIB yield chromatographic traces that include lignin-derived CuO oxidation products (Fig. 3). All phenols are detected with organic carbon (OC) normalized yields >0.01 mg/100 mg OC (Table 2). In general, vanillyl and syringyl phenols predominate throughout Site 932. In all samples, the most abundant lignin products are the two aldehydes, vanillin, and syringealdehyde.

Total lignin phenol yields range from 0.4 to 1.5 mg/100 mg OC in the top 21 mbsf. An intermediate value, 2.1 mg/100 mg OC, is measured at 40 mbsf. Higher lignin yields (>2.5 mg/100 mg OC) are observed below this depth, with two samples at 64 and 164 mbsf dis-

Table 1. Elemental and isotopic composition of bulk sediments.

Core, section, interval (cm)	Depth (mbsf)	Total C (wt%)	TIC (wt%)	TOC* (wt%)	TN (wt%)	$CaCO_3$ (wt%)	[C/N] atomic	Del ^{13}C TOC
155-932B-								
1H-1, 82–88	0.82	1.03	0.45	0.58	0.08	3.74	8.5	–23.2
155-932A-								
1H-3, 57–67	3.57	0.73	0.03	0.70	0.10	0.28	8.1	–26.0
2H-4, 104–114	11.54	0.70	0.01	0.69	0.11	0.06	7.3	–25.5
3H-4, 105–109	21.05	1.42	0.67	0.75	0.11	5.61	7.9	–24.2
5H-4, 106–116	40.06	0.89	0.10	0.79	0.12	0.84	7.7	–26.1
6H-4, 100–110	49.50	1.27	0.21	1.06	0.12	1.75	10.3	–27.6
7H-4, 89–99	58.89	1.25	0.19	1.06	0.14	1.58	8.8	–27.5
8H-4, 30–40	64.35	1.24	0.23	1.01	0.13	1.95	9.0	–27.5
9H-4, 110–120	77.53	1.22	0.20	1.02	0.13	1.68	9.1	–27.4
10H-5, 43–54	86.90	1.19	0.25	0.94	0.12	2.12	9.1	–27.4
11X-4, 87–97	96.76	1.16	0.22	0.94	0.13	1.84	8.4	–27.4
12X-4, 31–41	105.81	1.12	0.13	0.99	0.12	1.07	9.6	–27.4
13X-3, 97–107	114.57	1.20	0.23	0.97	0.12	1.95	9.4	–27.4
14X-4, 57–67	125.37	1.10	0.19	0.91	0.13	1.59	8.2	–27.3
15X-4, 63–73	135.13	1.01	0.17	0.84	0.13	1.39	7.6	–27.4
16X-3, 75–85	143.45	0.99	0.18	0.81	0.10	1.52	9.4	–27.4
17X-3, 107–117	153.27	1.00	0.20	0.80	0.11	1.69	8.5	–27.3
18X-4, 43–54	163.63	0.96	0.17	0.79	0.11	1.45	8.3	–27.3

Notes: C= carbon; TIC = total inorganic carbon; TOC* = total organic carbon calculated by difference; TN = total nitrogen; CaCO3 = calculated assuming all TIC is calcite; C/N = atomic carbon/total nitrogen; Del ^{13}C = carbon isotopic composition (‰).

playing yields ≥4.0 mg/100 mg OC. Samples with the lowest lignin yield (≤0.8 mg/100 mg OC) at 0.8 and 21 mbsf correspond to sediments that have the highest weight percent $CaCO_3$ and the heaviest $\delta^{13}C_{TOC}$ compositions.

DISCUSSION

Sources of Terrigenous Organic Matter in Amazon Fan Sediments

The yields of lignin phenols obtained from Site 932 sediments (Table 2) can be summarized by various compositional parameters (Table 3), such as the ratios of total syringyl and cinnamyl phenol yields over total vanillyl yields (S/V and C/V, respectively). These parameters vary systematically among vascular plants (Hedges and Mann, 1979a; Hedges et al., 1986a; Goñi and Hedges, 1992) due to characteristic differences in lignin composition. For example, gymnosperm lignins are predominantly composed of monomethoxylated (vanillyl) phenols and, thus, are characterized by low S/V ratios (S/V ~ 0). In contrast, angiosperm plants, which can synthesize dimethoxylated (syringyl) phenols, contain lignin with high S/V ratios (4 ≥ S/V ≥ 0.6). Furthermore, non-woody tissues of vascular plants, such as leaves, needles, and grasses, are thought to incorporate cinnamyl phenols into their lignins. Hence, gymnosperm and angiosperm nonwoody vascular plant tissues generally yield elevated C/V ratios (0.8 ≥ C/V ≥ 0.1) relative to their wood counterparts (C/V < 0.05). Based on these characteristic distributions, S/V and C/V ratios have been used extensively to differentiate terrigenous sources of sedimentary organic matter (e.g., Hedges et al., 1986a, 1988b; Gough et al., 1993).

S/V ratios of Site 932 sediments are fairly constant with depth (Fig. 4), ranging from 0.7 to 0.9, except for two elevated values (> 1.2) at 64 and 164 mbsf. In contrast, C/V ratios are relatively high (> 0.1) in the top 12 mbsf, drop to 0.07 at 21 mbsf, and remain constant (0.08 to 0.09) throughout the rest of the site. A plot of C/V vs. S/V (Fig. 5) shows that lignin compositions of most sediments from Subunits IIA and IIB are consistent with mixed angiosperm wood and leaf origins. In fact, these S/V and C/V ratios are very similar to the compositions obtained from coarse and fine suspended particulate materials from the modern Amazon River mainstem (Hedges et al., 1986a). The lignin compositions of the two samples in Subunit IIB with elevated S/V ratios (64 and 164 mbsf) may be due to the presence of angiosperm wood fragments that, based on modern-day compositions (Hedges et al., 1986a), have high S/V ratios (Fig. 5). The high total lignin phenol yields (Table 2) of these two samples are consistent with the presence of woody debris that have been observed in levee sediments from several sites (Flood, Piper, Klaus, et al., 1995).

Additional parameters that have been used to characterize lignins in sedimentary mixtures are the ratios of acid to aldehyde among the vanillyl and syringyl phenols. In general, aerobic degradation increases the ratios of vanillic acid/vanillin ([Ad/Al]v) and syringic acid/syringealdehyde ([Ad/Al]s) in the remaining lignin due to the partial oxidation of carbon sidechains from phenolic structural units (e.g., Hedges et al., 1988a; Goñi et al., 1993). For example, whereas most undegraded woods have [Ad/Al]v and [Ad/Al]s ratios that are ≤0.2, degradation by white-rot fungi causes these ratios to increase to as much 0.5. Prolonged lignin degradation can increase both [Ad/Al] ratios to values over 1 (Nelson et al., 1995). Acid/aldehyde ratios have been used to characterize the diagenetic state of lignins in geochemical mixtures and differentiate their sources (e.g., Ertel et al., 1986; Hedges et al., 1986a).

CuO oxidation of Subunit IIA sediments yields [Ad/Al]v and [Ad/Al]s ratios (Table 3) that are greater than 0.4 in the top 21 mbsf and display an intermediate value of 0.4 at 40 mbsf (Fig. 6). All of Subunit IIB sediments below this depth have [Ad/Al]v and [Ad/Al]s ratios that consistently range from 0.30 to 0.35.

The acid/aldehyde ratios displayed by most of Subunit IIA sediments suggest that the lignin in these samples is highly biodegraded. The lower values obtained from the oxidation of Subunit IIB sediments indicate a lesser degree of degradation. These lignin compositional trends are also consistent with the organic matter compositions of modern-day coarse and fine suspended Amazon River sediments (Hedges et al., 1986a). For example, a plot of [Ad/Al]v vs. S/V (Fig. 7) shows that most Subunit IIB sediments plot between the coarse and fine modern end-members, except for two samples with high S/V ratios likely associated with woody debris. Subunit IIA sediments, on the other hand, have elevated [Ad/Al]v ratios consistent with a predominant fine suspended sediment origin. One exception is the sample at 11.5 mbsf with [Ad/Al]v ratio of 0.55, which may represent post-depositional lignin degradation or, alternatively, elevated input of black-water tributaries, which currently display [Ad/Al]v > 0.6 (Hedges et al., 1986a).

Organic Matter Composition in Amazon Fan Sediments

The stable carbon isotopic composition of sedimentary organic matter has been extensively used to differentiate terrestrial and marine sources of organic matter in both modern and ancient sediments

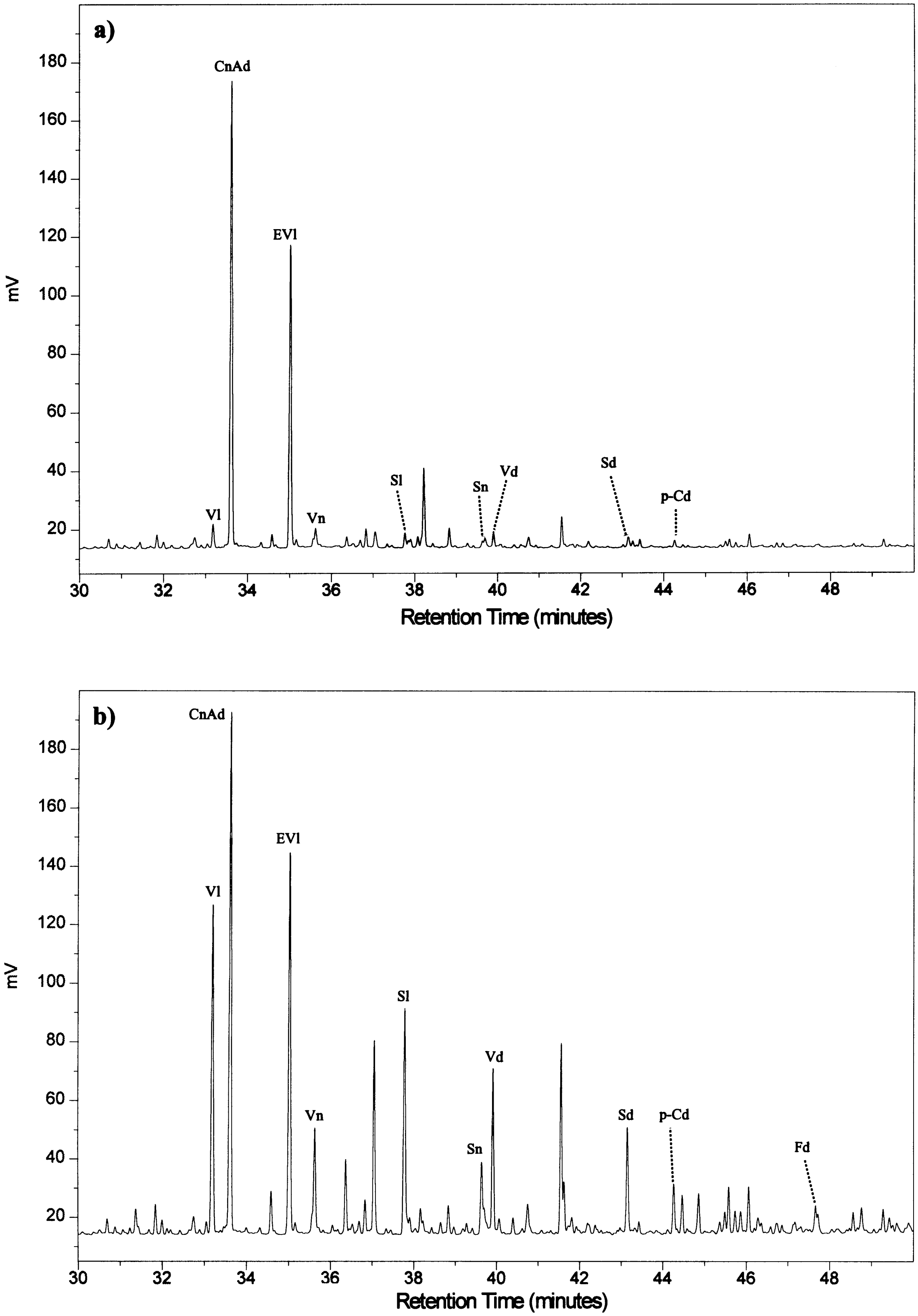

Figure 3. Gas chromatographic traces of the CuO reaction products from (**A**) Subunit IIA sediments (155-932A-3H-4, 105–109 cm) and (**B**) Subunit IIB sediments (155-932A-10H-5, 43–54 cm). Compound codes are according to Table 2. Recovery standards include *trans*-cinnamic acid (CnAd) and ethylvanillin (EVl).

Table 2. Carbon-normalized yields (mg/100 mg OC) of lignin phenols.

Core, section, interval (cm)	Depth (mbsf)	TOC (wt%)	Vanilly phenols			Syringyl phenols			Cinnamyl phenols		Total* phenols
			Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd	
155-932B-											
1H-1, 82–88	0.82	0.58	0.11	0.08	0.05	0.08	0.04	0.04	0.02	0.01	0.44
155-932A-											
1H-3, 57–67	3.57	0.70	0.42	0.16	0.18	0.39	0.12	0.17	0.08	0.03	1.54
2H-4, 104–114	11.54	0.69	0.34	0.16	0.19	0.27	0.10	0.14	0.06	0.02	1.27
3H-4, 105–109	21.05	0.75	0.21	0.12	0.10	0.16	0.09	0.07	0.02	0.01	0.77
5H-4, 106–116	40.06	0.79	0.62	0.25	0.26	0.48	0.17	0.19	0.07	0.04	2.08
6H-4, 100–110	49.50	1.06	0.87	0.31	0.30	0.76	0.23	0.23	0.09	0.05	2.84
7H-4, 89–99	58.89	1.06	0.85	0.31	0.28	0.73	0.22	0.24	0.08	0.04	2.74
8H-4, 30–40	64.35	1.01	1.02	0.31	0.35	1.33	0.44	0.38	0.08	0.07	3.98
9H-4, 110–120	77.53	1.02	0.83	0.28	0.31	0.73	0.24	0.24	0.09	0.03	2.73
10H-5, 43–54	86.90	0.94	0.94	0.29	0.32	0.89	0.27	0.27	0.09	0.06	3.14
11X-4, 87–97	96.76	0.94	0.86	0.28	0.33	0.77	0.24	0.25	0.09	0.04	2.87
12X-4, 31–41	105.81	0.99	0.85	0.28	0.31	0.73	0.22	0.24	0.08	0.04	2.74
13X-3, 97–107	114.57	0.97	1.02	0.32	0.35	0.90	0.27	0.28	0.09	0.06	3.28
14X-4, 57–67	125.37	0.91	0.91	0.28	0.28	0.79	0.23	0.23	0.08	0.05	2.85
15X-4, 63–73	135.13	0.84	1.03	0.37	0.37	0.86	0.29	0.28	0.08	0.05	3.35
16X-3, 75–85	143.45	0.81	1.04	0.32	0.39	0.95	0.26	0.33	0.09	0.05	3.43
17X-3, 107–117	153.27	0.80	0.99	0.33	0.35	0.85	0.26	0.27	0.09	0.04	3.17
18X-4, 43–54	163.63	0.79	1.04	0.32	0.35	1.81	0.27	0.28	0.08	0.06	4.21

Notes: TOC = total organic carbon; Vl = vanillin; Vn = acetovanillone; Vd = vanillic acid; Sl = syringealdehyde; Sn = acetosyringone; Sd = syringic acid; Cd = p-coumaric acid; Fd = ferulic acid. * = sum of all lignin phenols.

Table 3. Lignin compositional parameters.

Core, section, interval (cm)	Depth (mbsf)	S/V	C/V	[Ad/Al]v	[Ad/Al]s
155-932B-					
1H-1, 82–88	0.82	0.70	0.14	0.49	0.52
155-932A-					
1H-3, 57–67	3.57	0.88	0.14	0.43	0.43
2H-4, 104–114	11.54	0.74	0.12	0.54	0.53
3H–4, 105–109	21.05	0.74	0.06	0.48	0.42
5H-4, 106–116	40.06	0.75	0.09	0.41	0.39
6H-4, 100–110	49.50	0.83	0.09	0.35	0.31
7H-4, 89–99	58.89	0.83	0.08	0.32	0.33
8H-4, 30–40	64.35	1.29	0.09	0.34	0.29
9H-4, 110–120	77.53	0.85	0.09	0.37	0.33
10H-5, 43–54	86.90	0.93	0.10	0.34	0.31
11X-4, 87–97	96.76	0.86	0.09	0.39	0.33
12X-4, 31–41	105.81	0.82	0.08	0.37	0.32
13X-3, 97–107	114.57	0.87	0.09	0.34	0.31
14X-4, 57–67	125.37	0.85	0.09	0.31	0.29
15X-4, 63–73	135.13	0.81	0.08	0.36	0.33
16X-3, 75–85	143.45	0.89	0.08	0.37	0.35
17X-3, 107–117	153.27	0.83	0.08	0.35	0.32
18X-4, 43–54	163.63	1.38	0.08	0.33	0.15

Notes: S/V = ratio of sum of syringyl phenols over sum of vanillyl phenols; C/V = ratio of sum of cinnamyl phenols over sum of vanillyl phenols; [Ad/Al]v = ratio of vanillic acid over vanillin; [Ad/Al]s = ratio of syringic acid over syringealdehyde.

(e.g., Newman et al., 1973; Gearing et al., 1977; Fry and Sherr, 1984; Showers and Angle, 1986; Gearing, 1988; Arthur et al., 1994). Such application is based on the distinct isotopic signatures of C_3 terrestrial plants, $\delta^{13}C_{TOC}$ = –27‰ to –28‰, and marine plankton, $\delta^{13}C_{TOC}$ = –18‰ to –23‰ (e.g., Degens, 1969; Smith and Epstein, 1971; Deines, 1980). The downhole distribution of $\delta^{13}C_{TOC}$ values (Table 1) indeed suggests that organic matter in Subunit IIA sediments is a mixture of "typical" terrestrial and marine sources, whereas sediments in Subunit IIB contain exclusively terrestrial carbon.

The quantitative application of these estimates, however, is often limited by the uncertainties in end-member compositions. For example, terrestrial organic matter sources also include vascular plants (predominantly grasses) that utilize the C_4 pathway to fix carbon (e.g., O'Leary, 1981). These organisms typically have $\delta^{13}C_{TOC}$ values that range from –10‰ to –16‰ (e.g., Fry and Sherr, 1984). Therefore, significant inputs of C_4 plants can lower sedimentary $\delta^{13}C_{TOC}$ and invalidate two end-member calculations. Similarly, the $\delta^{13}C_{TOC}$ from marine plankton has been shown to vary significantly depending on environmental and physiological conditions (e.g., Laws et al., 1995; Goericke et al., 1994; Rau et al., 1989). Hence, modern estimates of the isotopic signature of phytoplankton may not reflect past counterparts (e.g., Jasper and Hayes, 1993; Jasper et al., 1994).

Several studies have shown the useful application of organic biomarkers, such as lignin phenols, to constrain the isotopic signatures of end-members (Hedges and Parker, 1976; Hedges and Mann, 1979b; Jasper and Gagosian, 1993; Prahl et al., 1994). For example, the carbon normalized yields of lignin phenols can be plotted vs. $\delta^{13}C_{TOC}$ (Fig. 8) to estimate the isotopic signature of the marine end-member in sedimentary mixtures. This approach assumes that as terrigenous and marine organic material intermix in sediments, the carbon normalized concentrations of lignin are diluted by non-lignin containing organic matter derived from planktonic sources.

As is shown in Figure 8, this dilution leads to progressively lower total lignin yields from Subunit IIA samples (solid squares) as $\delta^{13}C_{TOC}$ values steadily increase. This relationship, however, does not hold for Subunit IIB samples (open squares), which have lignin yields that range from 2.5 to 4.5 mg/100 mg OC but invariant $\delta^{13}C_{TOC}$ values near –27.5‰. Plotting the average compositions of coarse and fine suspended sediments from the modern Amazon River (Hedges et al., 1986a) reveals a possible explanation for the observed trends. The lignin yields and isotopic composition of sediments from Subunit IIB can be explained as a mixture of organic matter from mainstem coarse and fine suspended river sediments with negligible marine inputs.

In contrast, the compositions of Subunit IIA sediments are consistent with varying mixtures of organic materials from suspended fine river particles and marine organic matter. As expected from a simple two end-member mixture, the relationship between lignin phenol yields and $\delta^{13}C_{TOC}$ is linear ($r^2 = 0.9$). Extrapolating a short distance to zero lignin yield (i.e., pure marine organic matter) reveals a composition of –22.5‰ for the marine end-member ($\delta^{13}C_{MAR}$) at that time. This value is considerably lighter than the isotopic composition of modern suspended particulate organic carbon (–19.5‰) from surface waters of the outer Amazon shelf (Showers and Angle, 1986). The $\delta^{13}C_{TOC}$ differences between these two marine end-members may reflect differences in water column conditions (e.g., CO_2 concentrations, temperature) and phytoplankton composition and physiology (e.g., growth rates; Laws et al, 1995). Alternatively, the lighter values calculated for the sedimentary marine carbon could be due to the preferential loss of isotopically heavier proteins and polysaccharides during post-depositional degradation of planktonic remains (Degens, 1969; Benner et al., 1987). Evidence supporting the first explanation are the somewhat lighter $\delta^{13}C$ values of foram tests from glacial times relative to their interglacial counterparts obtained at this site (Maslin et al., this volume).

Given the constrained $\delta^{13}C_{MAR}$ value (Fig. 8), and assuming the $\delta^{13}C_{TOC}$ of the terrestrial end-member is similar to the isotopic composition of the organic carbon associated with the fine sediments from the modern Amazon River mainstem ($\delta^{13}C_{TERR}$ = –27.0 ‰), it is possible to calculate the percent of terrestrial organic carbon (%TERR) present in Site 932 sediments from their isotopic composition ($\delta^{13}C_{SED}$) according to isotopic mass balance (Equation 2):

$$\%TERR = \frac{\left(\delta^{13}C_{SED} - \delta^{13}C_{MAR}\right)}{\left(\delta^{13}C_{TERR} - \delta^{13}C_{MAR}\right)} \times 100\,. \qquad (2)$$

In the case of Subunit IIB sediments, the average between fine and coarse modern Amazon River sediments (–27.4‰) was used for the isotopic composition of the terrestrial end-member.

Figure 9 illustrates the downhole variations in %TERR composition of organic carbon. As expected, Subunit IIA sediments have variable amounts (15%–80%) of terrestrial organic carbon that, based on its lignin composition, can be entirely assigned to a source similar to fine suspended sediments from the modern Amazon River. In contrast, Subunit IIB sediments appear to be entirely composed of terrestrial organic matter. The compositions of these terrigenous materials can be modeled as mixtures of modern organic matter from coarse and fine suspended end-members, except for the previously mentioned samples containing vascular plant debris. In fact, using the carbon-normalized yields of total lignin phenols (Fig. 8), it is possible to estimate the fraction of terrestrial organic matter associated with fine and coarse river sediments. Such calculation reveals that the lignin compositions and concentrations of most Subunit IIB samples can be explained as 80 to 20 mixtures of fine and coarse particles compositionally similar to modern counterparts suspended in the Amazon River.

Paleovegetation and Paleoclimatic Implications

The lignin compositions discussed above indicate that terrigenous organic matter in Subunits IIA and IIB sediments at Site 932 has similar compositions to materials currently being transported in suspension by the lower mainstem Amazon. Most of the differences in lignin signatures among units can be accounted for by the differential transport of fine and coarse suspended sediments (e.g., Figs. 5, 7). These compositions suggest that the predominant flora of the Amazon River Basin, which is responsible for the lignin compositions observed in river sediments (Hedges et al., 1986a), may have not varied significantly in the depositional period represented by Holes 932A and 932B.

Several authors (Brown, 1987; Van der Hammen and Asby, 1994) have postulated the expansion of savanna vegetation in the Amazon Basin as the result of enhanced aridity of the area during the LGM. Grass-dominated vegetation is recognizable by the distinct and characteristic lignin compositions of sediments from rivers draining present-day grassland (Hedges et al., 1982; Goñi and Hedges, 1992). In the modern Amazon Basin, C_4 grasses are characterized by heavier $\delta^{13}C_{TOC}$ compositions (–12‰) and elevated C/V ratios (1.3), relative to the predominant C_3 flora (Hedges et al., 1986a). However, because only two samples were analyzed from depths corresponding to the LGM (11.5 and 21 mbsf), it is difficult to critically assess the paleovegetation changes during this period. Nevertheless, the isotopic and lignin compositions of these two samples are similar to those from other Subunit IIA sediments and consistent with a mixture of marine and terrestrial carbon of a predominant C_3 source. As already mentioned, the only distinct composition of LGM lignins is the slightly higher [Ad/Al] ratios of the sample at 11.5 mbsf (e.g., Fig. 7). It thus appears that the constant lignin composition throughout Site 932 sediments reflects similar overall vegetation in the Holocene and late Pleistocene and argues against the development of extensive grasslands during the LGM.

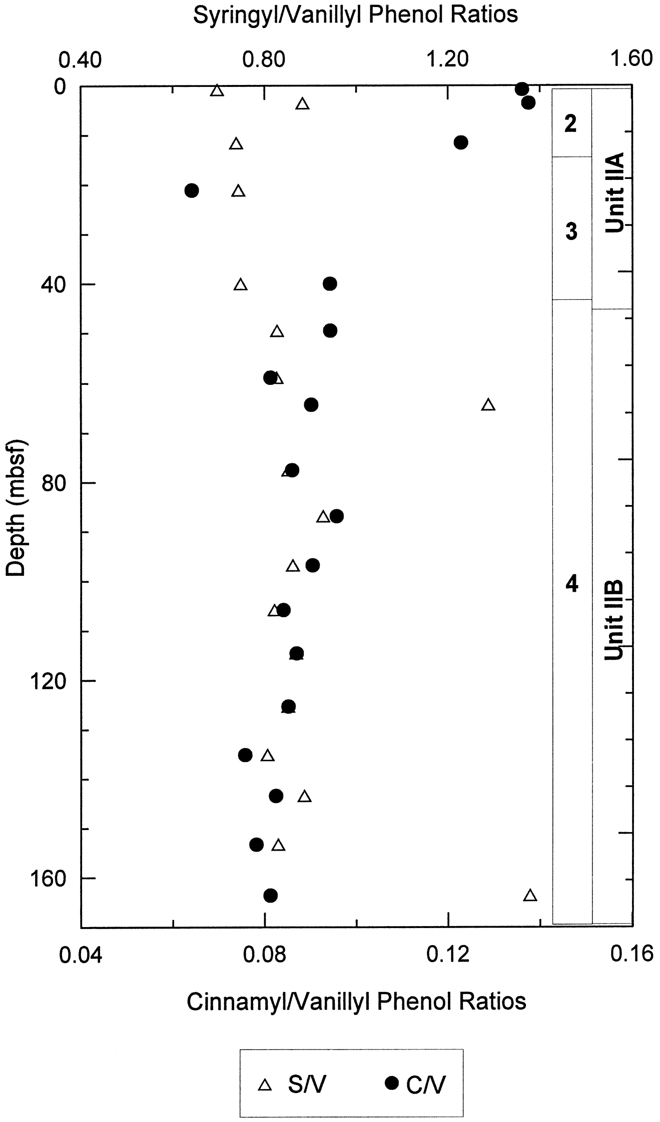

Figure 4. Downhole distribution of syringyl/vanillyl and cinnamyl/vanillyl ratios at Site 932.

Further evidence for the absence of extensive savannas during cold periods of low sea-level stand are the isotopic compositions of organic carbon from Subunit IIB sediments, $\delta^{13}C_{TOC}$ = –27.5‰, typical of C_3 plants. C_4 plants, which are abundant in modern grasslands and savannas, have a distinctly heavier isotopic signature (averaging –13‰). Expansive Amazon savannas during the late Pleistocene therefore should have affected the $\delta^{13}C_{TOC}$ of sediments exported by the river and deposited on the fan. It is important to note, however, that both lignin and isotopic data are the subject of sensitivity arguments regarding the extent of savanna coverage needed to significantly change the organic composition of the bulk riverine suspended sediment load. The relatively constant compositions of terrigenous organic matter observed throughout Site 932 therefore do not preclude small scale changes in vegetation coverage. These results are

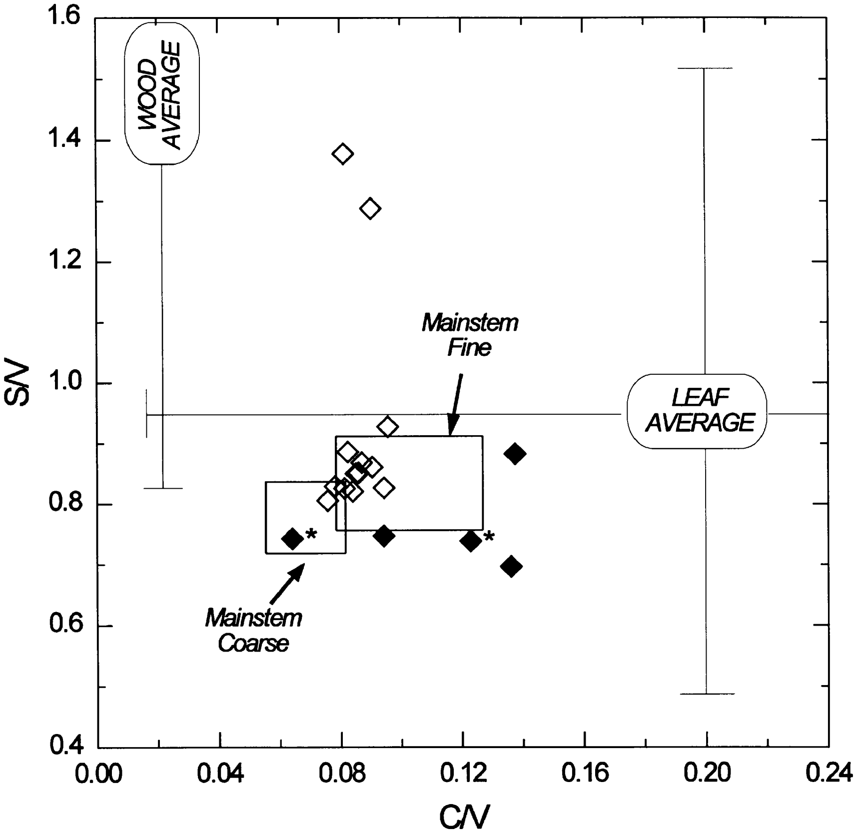

Figure 5. Plot of C/V vs. S/V ratios for Site 932 sediments. Included are the compositional ranges of wood and leaf tissues from several tropical species and average ±1 standard deviation compositions of modern coarse and fine suspended sediments from the mainstem of the Amazon River (Hedges et al., 1986a). Solid diamonds = Subunit IIA sediments; open diamonds = Subunit IIB sediments; * = samples from the LGM.

consistent with pollen data from the same site (Haberle, this volume) that fail to show significant increases in spores from savanna plants.

Implications for Amazon Fan Depositional History

The composition of terrigenous organic matter and the relative abundances of marine vs. terrestrial organic carbon in Subunits IIA and IIB sediments from Holes 932A and 932B clearly indicate two distinct depositional regimes at this site. Subunit IIA sediments have a lignin composition characteristic of fine Amazon suspended sediments and isotopic compositions that suggest terrestrial inputs between 80% and 15% of the TOC. The finer texture suggests riverine materials were hydrodynamically sorted prior to deposition (Keil et al., 1994; Hedges and Keil, 1995), whereas the moderate terrigenous contributions are consistent with a more distal source. These compositions agree with the lower estimated sedimentation rates, predominance of clays, and the presence of burrows in Subunit IIA sediments (Shipboard Scientific Party, 1995). Overall, the characteristics of Subunit IIA sediments are indicative of more "hemipelagic" depositional conditions at times when the active channel(s) of sediment transport was far removed from Site 932. The variations in relative abundance of terrestrial and marine organic carbon are probably the result of variable terrigenous and marine sedimentation rates and differences in the extent of post-depositional oxidation.

In contrast, Subunit IIB has 100% terrestrial TOC that is partially derived from fine (80% to 90%) and coarse (20% to 10%) Amazon River suspended sediments and plant debris. The complete predominance of terrestrial materials in these sediments is remarkable, given the fact that modern-day sediments on the shelf have isotopic compositions that indicate a significant dilution by marine carbon (e.g., Showers and Angle, 1986; Goñi et al., 1995). Similar dominant terrigenous signals during glacial lowstands are also obtained in other river fan sediments, such as the Mississippi Cone in the Gulf of Mexico (Newman et al., 1973). Such "pure" terrestrial compositions suggest the rapid and direct deposition of materials with little chance for a remixing of plankton remains.

The organic composition of Subunit IIB sediments are consistent with their lithologic characteristics (silty clay with interbedded laminae of silt and fine sands) being typical of channel-levee deposits. All of these compositions indicate that Subunit IIB (Channel 6B) was deposited at a time when the active channel occupied this part of the fan and the Amazon River discharged its sediment load in a focused area at the shelf edge. The relative abundances of fine and coarse sedimentary organic matter likely reflect changes in the transport mechanism of the material supplied by the river (e.g., type and magnitude of turbidites).

SUMMARY AND FUTURE WORK

The composition of terrigenous organic matter accumulating in the Amazon Fan during the past glacial period suggests that vegetation in the Amazon drainage basin did not change appreciably during the late Pleistocene. There is no clear evidence for the widespread development of savannas during isotopic Stages 2 through 4. Further characterization of terrestrial organic carbon from other channel-levee systems of different ages can be used to confirm the absence of change in the LGM, which was only briefly sampled at Site 932, and to provide information on the vegetation during earlier glaciations (e.g., isotopic Stage 6).

The organic carbon in channel-levee deposits at Site 932 is 100% terrestrial in origin. In contrast, the organic matter in the more "hemipelagic" section on top of the abandoned levee exhibits decreased terrigenous contributions (80% to 15%). To estimate the total quantity of terrestrial organic carbon exported by the Amazon River during past glacial periods, we need to analyze sediments from levee flanks

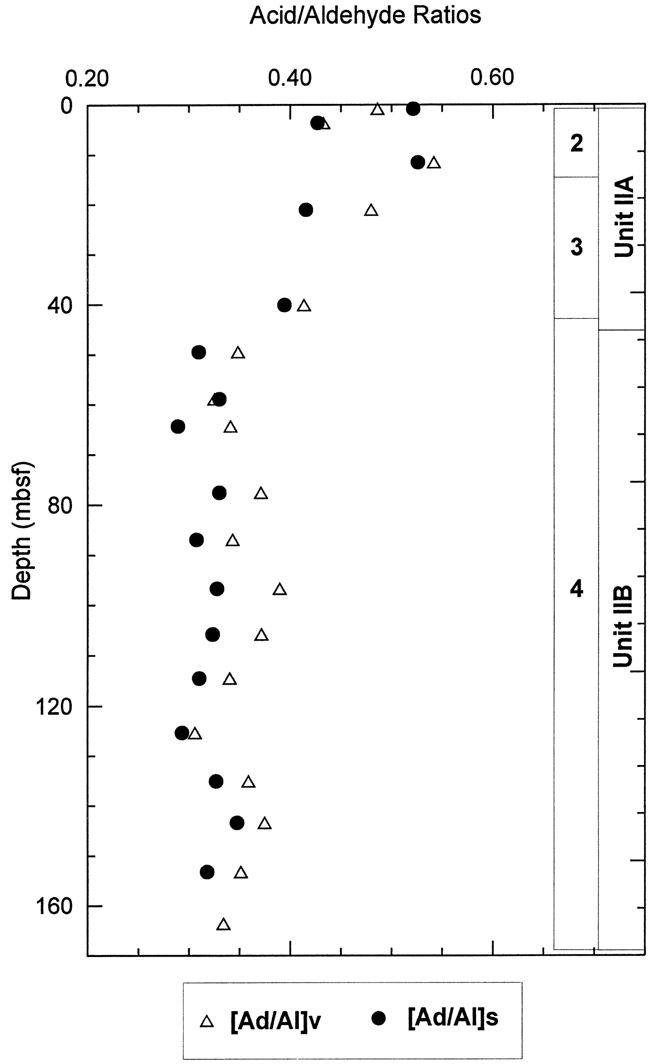

Figure 6. Downhole distribution of syringyl and vanillyl acid/aldehyde at Site 932.

and other non-channelized deposits. In addition, it will be important to estimate the variations in terrestrial organic carbon abundances downfan. Both of these goals are attainable given the sampling coverage during Leg 155.

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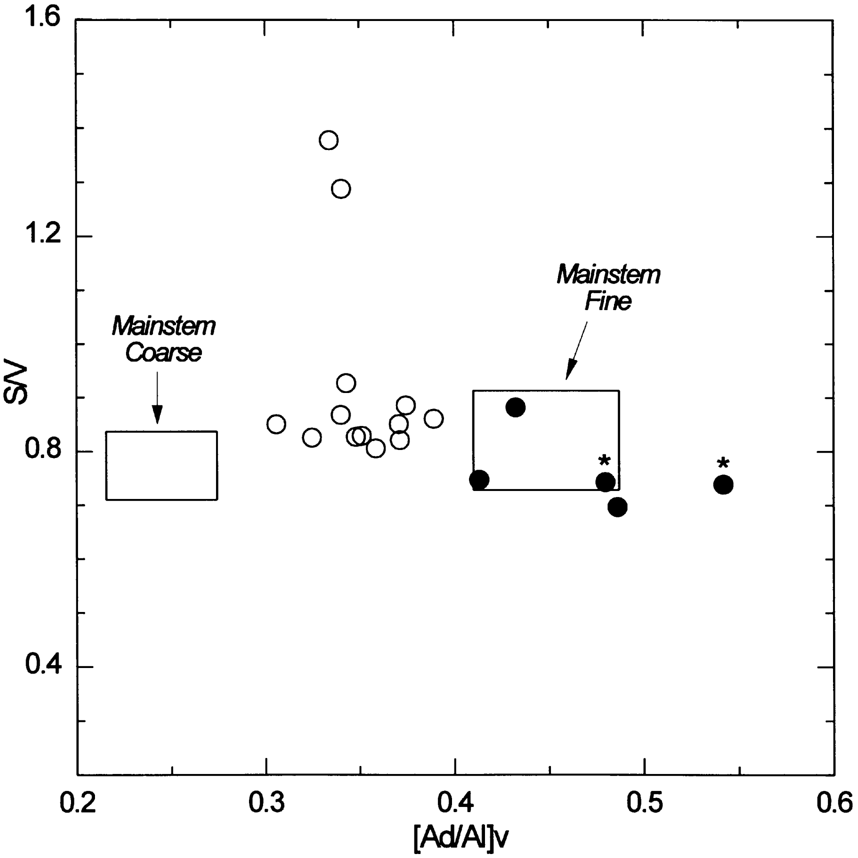

Figure 7. Plot of [Ad/Al]v vs. S/V ratios for Site 932 sediments. Included are the average ±1 standard deviation compositions of modern coarse and fine suspended sediments from the mainstem of the Amazon River (Hedges et al., 1986a). Solid circles = Subunit IIA sediments; open circles = Subunit IIB sediments; * = samples from the LGM.

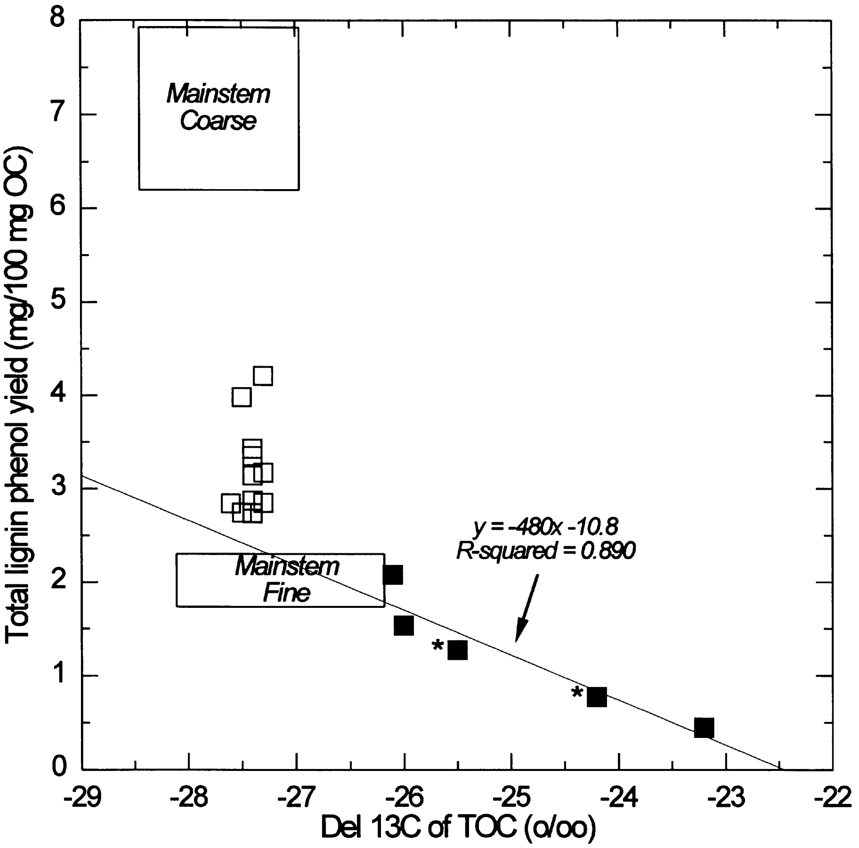

Figure 8. Plot of the stable carbon isotopic composition of TOC ($\delta^{13}C_{TOC}$) and total carbon normalized yields of lignin phenols for Site 932 sediments. Included are the average ±1 standard deviation compositions of modern coarse and fine suspended sediments from the mainstem of the Amazon River (Hedges et al., 1986a). Solid squares = Subunit IIA; open squares = Subunit IIB sediments; * = samples from the LGM.

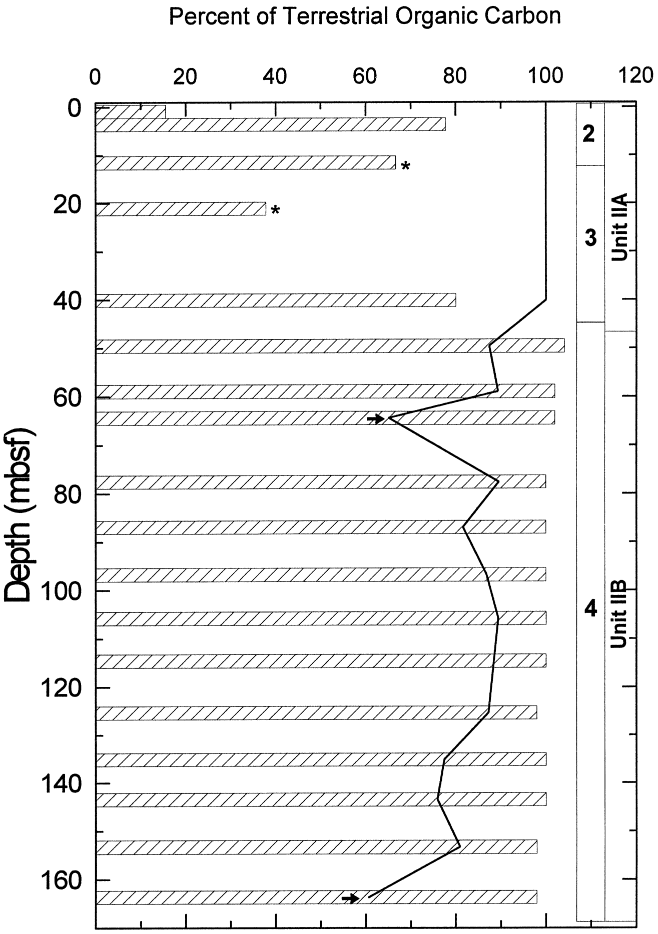

Figure 9. Downhole distribution of percent TOC from terrestrial origin (bars) and the percent of terrestrial organic carbon that is associated with fine suspended Amazon River sediments (line). * = samples from the LGM. The two low percent fine values marked with arrows indicate sediments with apparent contribution of vascular plant debris that affect the percent fine calculation.

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