

4. ELEMENTAL, STABLE ISOTOPIC ($\delta^{13}\text{C}$), AND MOLECULAR SIGNATURES OF ORGANIC MATTER IN LATE PLEISTOCENE–HOLOCENE SEDIMENTS FROM THE PERUVIAN MARGIN (ODP SITE 1229)¹

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ABSTRACT

A high-resolution elemental, isotopic, and molecular record of organic matter was established for the uppermost sediments of Hole 1229E (0–700 cm below seafloor), drilled during Ocean Drilling Program (ODP) Leg 201 on the Peruvian margin. Diagnostic parameters of organic matter (OM) such as the atomic C_{org} over total nitrogen ratio (C/N), the organic carbon isotopic signatures ($\delta^{13}C_{\text{org}}$), and lignin-derived biomarker concentrations ($\Sigma 8$) all suggest that terrigenous OM influx was more important during glacial than interglacial periods on the Peruvian shelf. In contrast to other shelf environments, however, fluctuations in lignin ratios ([Ad/Al]_v, S/V, and C/V) across the Pleistocene–Holocene transition point to shifting composition in terrigenous OM sources from coarse and undegraded woody materials during the Last Glacial Maximum (LGM) to much more altered and finer soft tissue materials during the Holocene. In addition, the total OM content preserved in the Peruvian shelf sediments was lower during the LGM. This observation is in agreement with prior work in the region and may be explained by a migration of the upwelling cells toward deeper sections of the shelf during glacial lower sea level stances. The potential decrease in upwelling strength at ODP Site 1229 and other similar shallow sites of the region may thus have been responsible for lower water

¹Louchouart, P., Naehr, T.H., Silliman, J., and Houel, S., 2006. Elemental, stable isotopic ($\delta^{13}\text{C}$), and molecular signatures of organic matter in late Pleistocene–Holocene sediments from the Peruvian margin (ODP Site 1229). In Jørgensen, B.B., D'Hondt, S.L., and Miller, D.J. (Eds.), *Proc. ODP, Sci. Results*, 201, 1–21 [Online]. Available from World Wide Web: <http://www-odp.tamu.edu/publications/201_SR/VOLUME/CHAPTERS/113.PDF>. [Cited YYYY-MM-DD]

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column productivity and decreased preservation potential (decrease in oxygen minimum conditions) of settling organic matter. Finally, during the Holocene, the shifts in C_{org} concentrations, (C/N) ratios, and $\delta^{13}C_{org}$ signatures are not entirely controlled by terrigenous OM inputs in this system. Apparent terrigenous signatures during that period seem to be derived from diagenetic processes in addition to potential source changes.

INTRODUCTION

It has been shown that, during glacial stages, continental margins tend to preserve a higher proportion of terrigenous organic matter (OM) than during interglacial conditions (Jasper and Gagosian, 1990, 1993; Lyle et al., 1992; Goñi, 1997; Visser et al., 2004). However, no work has provided a high-resolution study of OM over a specific glacial-interglacial transition, which is critical to sustain the work performed to understand microbial degradation dynamics in relation to changing oxidative conditions and source of reduced carbon during these periods. Thus, the central aspect of this study was the generation of a detailed and high-resolution geochemical analysis of OM components preserved in a core from the Peruvian shelf (Ocean Drilling Program [ODP] Leg 201, Hole 1229E) during the last glacial-interglacial climatic transition. In addition, we have also studied the signature of specific biomarkers (lignins) that can provide further information on dominant terrigenous vegetation and land-based conditions during this transition.

Several authors (Brown, 1987; van der Hammen and Asby, 1994; Piperno, 1997; van der Kaars et al., 2000; Hope, 2001) have suggested that during the Last Glacial Maximum (LGM), savanna vegetation expanded at the expense of forest ecosystems in the Amazon and Indonesian Basins as the result of enhanced aridity of tropical to equatorial areas. Piperno (1997) even proposed that full-grown forest refuges might have existed along rivers and streams contributing disproportionate amounts of nongrass materials to the rivers and the Amazonian Fan during the LGM despite an overall reduction in the nonriverine forest ecosystems. Indeed, the importance of glacial aridification of tropical ecosystems is still being debated, since very few indicators of grasslike vegetation (i.e., molecular markers of grassy tissues) have been recorded in submarine fans draining the Amazon Basin during the LGM (Goñi, 1997; Haberle, 1997; Kastner and Goñi, 2003). Using similar vascular biomarker signatures, Visser et al. (2004) demonstrated that in the Southeast Asian tropics, an increase in winter monsoons during the LGM generated moist conditions that allowed tropical rainforests to vegetate exposed shelves during glacial maxima, contributing a continuous source of tree-derived materials to the shelf sediments as opposed to grass materials, which would be expected from savanna-dominated systems under drier conditions.

Continental margins thus have the potential to record glacial-interglacial fluctuations in the marine vs. terrigenous sources of OM, as well as variations in the composition of the terrigenous OM pool. We present here elemental, isotopic, and biomarker data in a core from the Peruvian margin spanning the late Pleistocene through the Holocene.

Since the Peruvian margin is a site of major upwelling and receives very little riverine discharges, the composition of its sediments should be disproportionately controlled by marine sources. Terrigenous com-

ponents should thus contribute only a minor proportion of the total OM pool and a much lower one than in similar high-productivity systems such as that of the western African margin (Farrimond et al., 1990b). Hence, this may be an ideal setting for the study of glacial–interglacial shifts in OM signatures of predominant marine origin and to test if this shelf system still receives similar trends in terrigenous OM influx, across the LGM to the present, as was reported for other major shelf environments.

MATERIALS AND METHODS

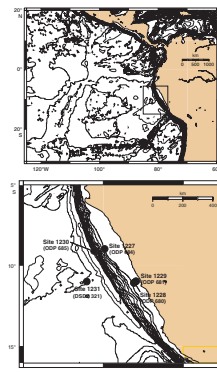
Site Description

ODP Site 1229 is located on the Peru shelf at ~150 m water depth (Fig. F1) and in the immediate vicinity of ODP Leg 112 Site 681 (Suess and von Huene, 1988). During Leg 201, sediments from Hole 1229E were sampled at 10-cm intervals from 0 to ~700 cm below seafloor (cmbsf). Lithologic Subunit IA (0–40.7 meters below seafloor [mbsf]) is characterized by alternations of olive-green well-laminated diatom ooze and clay-rich silt and clay- and silt-rich diatom ooze (Shipboard Scientific Party, 2003). Shipboard chemical measurements of pore water showed a pronounced anomaly between 100 and 300 cmbsf (Shipboard Scientific Party, 2003) consisting of brief maxima in alkalinity, dissolved inorganic carbon (DIC), ammonium, and sulfide coinciding with a brief negative excursion in dissolved sulfate. The same anomaly is also apparent in the ammonium and alkalinity profiles of ODP Site 681 (Suess, von Huene, et al., 1988). Based on radiocarbon analyses, Fink et al. (2006) reconstructed the sedimentation chronology for the uppermost section of Hole 1229E (~400 cm). Their results suggest a ~2-m section at the top of the hole that represents rapid and continuous accumulation at this site during the late Holocene (~100 cm/k.y.). Deposition during the middle part of the Holocene (2–8 ka), however, seems to have been very slow (~10–20 cm/k.y.) and results in a reduction of the thickness between the uppermost Holocene sediments (0–200 cmbsf) and the Pleistocene/Holocene boundary (~380 cmbsf). To assist our interpretations in characterizing the processes responsible for the observed fluctuations in geochemical parameters, the ^{14}C dates from these authors (Fink et al., 2006) have been incorporated on all vertical profiles used in the present study.

Elemental Analyses

Immediately after shipboard sampling, sediments were frozen and shipped under ice to Corpus Christi, Texas (USA), where they were freeze-dried and subsequently homogenized. Weight percentage of organic carbon (C_{org}) and total nitrogen (TN) were determined using an automated ANCA-SL elemental analyzer coupled with a PDZ-Europa 20-20 continuous-flow isotope mass spectrometer (EA-CFMS). Carbonate was removed prior to analysis by vapor-phase acidification with HCl for 24 hr followed by drying at 40°C for 24 hr (Hedges and Stern, 1984; Harris et al., 2001). During all sample runs, two to three quantitative standards (glucosamine) were included after every four to five samples. The average precision of elemental analyses determined from replicate analyses of selected samples is $\pm 2\%$ –5% for both C_{org} and TN.

F1. Locations of Leg 201 sites, p. 16.



Isotopic Analyses

Stable isotopic signatures of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) were determined on preacidified samples using the same automated EA-CFMS mentioned above. Details of the procedure are provided in Fry et al. (1992). The continuous-flow mode minimizes the sample size needed for analysis, and samples as small as 2 mM C can be analyzed with a precision of 0.1‰, thus greatly reducing analytical effort. Isotopic compositions are reported in $\delta^{13}\text{C}$ notation and are referenced to Peedee belemnite (PDB) standard. The $\delta^{13}\text{C}$ notation is defined as follows:

$$\delta^{13}\text{C} = \left\{ \left[\frac{(^{13}\text{C} - ^{12}\text{C})_{\text{sample}}}{(^{13}\text{C} - ^{12}\text{C})_{\text{standard}}} \right] - 1 \right\} \times 1000. \quad (1)$$

CuO Oxidation and Molecular Analyses

Alkaline CuO oxidation (Hedges and Ertel, 1982) was performed on intervals of Hole 1229E to obtain a suite of biomarkers, which include phenolic compounds derived from the lignin biopolymer (an unambiguous biomarker for vascular plants). Because of time and cost constraints, CuO oxidation analyses were only performed on samples from the surface to ~450 cmbsf. The deepest section of this record covers the Pleistocene–Holocene transgression and offers information on potential changes in OM source fluctuations across this boundary. The CuO oxidation method has undergone revisions and adaptations since its initial conception in the early 1980s (Hedges and Ertel, 1982), which have led to “cleaner” chemistry, change and decrease in solvent utilization, and increased sample throughput (Goñi and Hedges, 1992; Louchouarn et al., 2000; Dalzell et al., 2005). Briefly, a sediment amount providing 2–4 mg C_{org} (Louchouarn et al., 2000) is oxidized under alkaline conditions with CuO at 155°C for 3 hr in pressurized stainless steel mini-reaction vessels (3 mL; Prime Focus Inc.). The aqueous solution is then acidified with 6-N HCl and extracted three times with ethyl acetate. Extracts are dried with Na_2SO_4 and then evaporated to dryness using a LabConco solvent concentrator. The CuO reaction products are redissolved in a small volume of pyridine (200–500 μL) and a subsample is derivatized with *bis*-trimethylsilyl trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS).

Separation and quantification of trimethylsilyl derivatives of CuO oxidation byproducts were performed by gas chromatography–mass spectrometry (GC-MS) on a Varian quadrupole GC-MS system (3800/1200 L) fitted with a fused capillary column (CP-Sil 8 CB/MS, 60 m \times 0.25 mm inner diameter; Varian Inc.). Each sample was injected, under splitless injection mode, into a straight glass liner inserted into the GC injection port, and He was used as the carrier gas (~1.3 mL/min). The GC oven was temperature-programmed from 100°C, with no initial delay, to 300°C at 4°C/min and held constant at the upper temperature for 10 min. The GC injector and GC/MS interface were both maintained at 300°C. The mass spectrometer was operated in the electron impact mode (EI, 70 eV), in scan mode. Compound identification was performed using column retention times and by comparing the full spectra of each sample to those produced by commercially available standards. Quantification was performed using relative response factors adjusted to *trans*-cinnamic acid (CnAd) as the internal standard. Replicate analyses of standard estuarine sediments (i.e., National Institute of Standards [NIST] standard reference material [SRM] 1944; $N = 6$) showed that the analytical precision of the major CuO oxidation prod-

ucts and related parameters averaged ~5%. The yields and composition parameters produced in this study match those obtained with both microwave digestion (Goñi and Montgomery, 2000; Houel et al., 2006) and with larger reaction vessels with conventional oven procedure (Louchouarn et al., 2000). The average standard deviation obtained from replicate analyses of ODP samples was somewhat higher (15% ± 10%; range = 3%–30%). This is likely caused by very low levels of terrigenous organic matter (see below), which generate higher variability during quantification (cf. Visser et al., 2004).

RESULTS

Elemental Composition

The concentration profiles (in milligram per gram dry weight) of C_{org} and TN are presented in Figure F2. On average, elevated OM concentrations (C_{org} and TN) are apparent in the uppermost 2 m of the core (60.9 ± 14.8 and 5.4 ± 1.4 mg/gdw, respectively). From 200 to 270 cmbsf, C_{org} and TN concentrations show a marked minimum (41.5 ± 5.9 and 3.0 ± 0.6 mg/gdw, respectively). Further fluctuations between 40 and 70 mg/gdw for C_{org} and 2–5 mg/gdw for TN occur downcore during the early part of the Holocene. Organic matter concentrations stabilize at lower levels during the Pleistocene with averages for C_{org} and TN being 34.1 ± 6.9 and 2.4 ± 0.4 mg/gdw, respectively. These values are consistent with prior work in cores from the region that show C_{org} fluctuations, over the late Pleistocene to early Holocene, in the same range as those presented here (30–120 mg/gdw for ODP Hole 680B), with maximum concentrations in the most recent part of the Holocene (Wefer et al., 1990). The atomic C_{org} to TN ratio (C/N) increases continuously down through the Holocene from an initial value of 11–12 in recent sediments at the sediment/water interface to values that reach 14–15 at the base of the Holocene. The C/N ratio shows a further rapid increase across the Holocene/Pleistocene boundary (~380 cmbsf) and stabilizes around 17 ± 1 for the remainder of the core (Fig. F3).

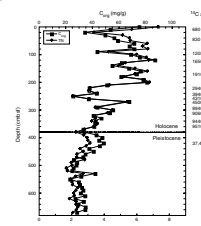
Stable Isotopes

The stable isotopic signatures of organic carbon ($\delta^{13}C_{org}$) from Hole 1229E cover a range of values from less ^{13}C -depleted signatures (-18.5‰) to more strongly ^{13}C -depleted samples (-22.5‰) (Fig. F3). The latest Holocene section of the core (uppermost 2 m) is characterized by overall intermediate carbon isotope values ($-20.4\text{‰} \pm 1.1\text{‰}$) with one interval characterized by a more ^{13}C -depleted signature of -22.5‰ . The section between 150 and 250 cmbsf is characterized by OM more depleted in ^{13}C ($-21.9\text{‰} \pm 0.4\text{‰}$). Below follows an interval (270 and 370 cmbsf) with heavier ^{13}C signatures ($-20.4\text{‰} \pm 0.8\text{‰}$) during the early Holocene. The carbon isotopic signatures remain relatively constant at $-21.5\text{‰} \pm 0.4\text{‰}$ during the Pleistocene.

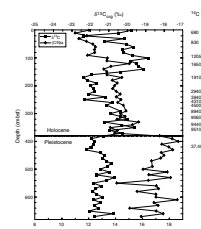
Biomarkers

All sediment samples from Hole 1229E yielded lignin-derived oxidation byproducts, albeit in trace amounts (total range = 2–30 $\mu\text{g/gdw}$). Total lignin phenol concentrations (sum of eight lignin-derived phe-

F2. C_{org} and TN, Hole 1229E, p. 17.



F3. C/N and $\delta^{13}C_{org}$, Hole 1229E, p. 18.



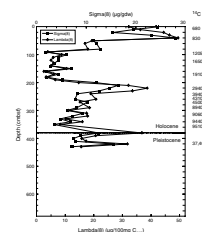
nols [$\Sigma 8$] in micrograms per gram dry weight) (Hedges and Ertel, 1982) show variable levels throughout the core depth. Concentrations reach maxima in the uppermost meter of the core (15–30 $\mu\text{g/gdw}$), between 200 and 250 cmbsf (15 $\mu\text{g/gdw}$), and below 350 cmbsf (15 $\mu\text{g/gdw}$) (Fig. F4). Intervals of minimal lignin concentrations are observed between 100–200 and 250–350 cmbsf (range = 2–5 $\mu\text{g/gdw}$). Carbon-normalized lignin yields (sum of eight lignin-derived phenols normalized to carbon content [$\lambda 8$] in micrograms per 100 mg C_{org}) (Hedges and Ertel, 1982) show a similar pattern. Surface (0–100 cmbsf) and midcore values (200–250 cmbsf) peak at 30–50 $\mu\text{g}/100 \text{ mg } C_{\text{org}}$, whereas sediment intervals in the middle part of the Holocene (100–200 cmbsf) are characterized by low lignin yields (5–15 $\mu\text{g}/100 \text{ mg } C_{\text{org}}$). There is no apparent relationship between the fluctuations in lignin and C_{org} concentrations, but there seems to be a weak correlation between carbon-normalized lignin yields and isotopic signatures (see “Discussion,” below).

DISCUSSION

It has been shown in several shelf environments that sediments in these systems tend to preserve a higher proportion of total organic carbon during glacial stages than during interglacial conditions (Gulf of Mexico, Jasper and Gagosian, 1990, 1993; Californian shelf, Lyle et al., 1992; Indonesian shelf, Visser et al., 2004). These elevated C_{org} concentrations in sediments deposited during glacial intervals may be the result of a combination of increased fluxes of terrigenous OM from continents, higher water column productivity, and increased preservation potential (i.e., reduced oxygen availability at the sediment/water interface). In addition, the higher proportion of terrigenous OM reported during glacial intervals (i.e., Jasper and Gagosian, 1990; Schubert and Stein, 1996; Visser et al., 2004) may be influenced both by higher erosional inputs from continents (Jasper and Gagosian, 1990; Visser et al., 2004) and an increased preservation potential due to the intrinsic recalcitrant nature of this material.

The use of C/N ratio and stable isotopic signatures of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) are two of many possible approaches to qualitatively assess the proportional inputs of terrigenous vs. marine OM to shelf sediments (Jasper and Gagosian, 1990, 1993; Schubert and Stein, 1996; Visser et al., 2004). Terrigenous OM is relatively depleted in nitrogen, and large inputs of this material to marine sediments often result in C/N ratios >15–20 (Meyers, 1997). In addition, carbon isotope data seem to be appropriate to discriminate between input sources in environments receiving material from terrestrial plants using the C_3 pathway (–27‰ to –30‰) vs. phytoplankton (–18‰ to –20‰) or terrestrial plants using the C_4 pathway (–12‰ to –16‰) (Meyers, 1997). Hence, a combination of elemental (atomic C/N ratios) and stable isotopic signatures of sedimentary OM has been used to infer inputs of marine vs. terrigenous sources of organic matter during glacial–interglacial intermissions (Jasper and Gagosian, 1990, 1993; Goñi, 1997; Visser et al., 2004). Indeed, average C/N values in glacial shelf sediments range from 11 to close to 20, whereas interglacial sediments tend to be characterized by lower C/N values (8–11) (Jasper and Gagosian, 1990; Visser et al., 2004). In previous studies, these shifts in C/N ratios were found to be accompanied by parallel variations in carbon isotope signatures with depleted values during glacial stances (–25‰ to –27‰) vs. heavier signatures during

F4. $\Sigma 8$ and $\lambda 8$, Hole 1229E, p. 19.



interglacial periods (-22‰ to -24‰) (Jasper and Gagosian, 1990, 1993; Goñi, 1997). Both proxies were thus used to characterize oscillations in the terrigenous vs. marine sources of organic matter to shelf sediments with increasing C_{org} concentrations observed in glacial sediments probably resulting from enhanced erosion of exposed continental shelves and direct transport of recalcitrant terrigenous organic matter to bottom sediments (cf. Jasper and Gagosian, 1990, 1993; Goñi, 1997; Visser et al., 2004).

In comparison, the Peruvian margin seems to show specific differences with respect to these studies in terms of sources and inputs of OM. First, the lower OM concentrations in glacial sediments contradict the trend reported above which states that OM concentrations tend to be higher in shelf sediments during glacial periods. In the present study, the 2- to 3-fold increase in C_{org} and TN concentrations from the late Pleistocene to early Holocene (Fig. F2) confirms the reported decrease in OM concentrations during glacial intervals in other shallow Peruvian margin areas (Wefer et al., 1990). Wefer et al. (1990) relate this decrease in OM to a shift of upwelling cells and the oxygen minimum zone (OMZ) to deeper sites along the margin. The resulting lower water column productivity and increased oxygen availability in bottom waters of the shallow sites would have caused higher bioturbation activity and decreased the preservation potential of settling OM. In the uppermost 35 m of ODP Site 686, for example, a relationship between periods of deepening of the water column, resulting in cold, nutrient-rich water intrusions, and high OM preservation has been reported (Farrimond et al., 1990a). Hence, the observed decrease in OM in late Pleistocene section of Hole 1229E is consistent with prior work performed in the area and suggests that changes in sedimentary OM content over the recent glacial–interglacial cycles may be related to migrations of the upwelling cells and the OMZ (Wefer et al., 1990; Farrimond et al., 1990a).

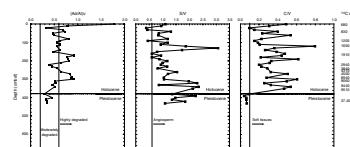
In addition, the quantity of terrigenous OM in recent sediments from the Peruvian margin is exceptionally low for a continental shelf environment (Bergamaschi et al., 1997; Farrimond et al., 1990a, 1990b; Whelan et al., 1990) and suggests that very little terrigenous C_{org} reaches these sediments. Molecular analyses of ODP cores from the Peruvian margin have shown that OM in these sediments is predominately derived from marine primary producers (Farrimond et al., 1990a; Whelan et al., 1990). Whelan et al. (1990) suggest that the low terrigenous influx to this margin system is consistent with the arid nature of the Peru coast, which is only sparsely vegetated. In light of this information, one would thus expect to observe elemental and isotopic signatures of preserved OM to reflect an overwhelming predominance of marine sources. Paradoxically, the high C/N ratios (>12) in most sediment intervals of Hole 1229E, and some relatively light $\delta^{13}\text{C}$ signatures during the middle part of the Holocene (Fig. F3), suggest instead that a substantial fraction of sedimentary OM might be derived from terrigenous sources.

High C/N ratios and light carbon isotopic signatures in sedimentary OM can still be consistent, however, with a large marine source contribution. Both signatures are sensitive to diagenetic and changing environmental conditions, which may complicate source reconstructions to ancient sediments (cf. Macko and Engel, 1993). For example, in systems that are heavily dominated by marine productivity, environmental parameters such as temperature, growth rate, species, and pCO_2 variability may alter carbon isotopic signatures during synthesis (Rau et al., 1989;

Fogel and Cifuentes, 1993; Macko and Engel, 1993; Johnston and Kennedy, 1998). Additionally, postdepositional alteration of stable carbon isotopic signatures has been reported in environments where selective losses of specific biomolecules (i.e., carbohydrates, lipids, and amino acids) lead to a diagenetic ^{13}C enrichment or depletion in the residual organic matter (Benner et al., 1987; Macko and Engel, 1993). Both directions of fractionation have been reported in the literature, and this effect tends to be more important in sediments receiving large quantities of fresh organic matter, which undergoes substantial degradation (cf. Macko and Engel, 1993). The molar ratio of organic carbon to nitrogen has also been shown to increase due to selective diagenetic losses of nitrogen (cf. Macko and Engel, 1993). Hence, these processes (i.e., photosynthesis and diagenesis) may have an impact on the signature of organic matter ultimately preserved in Peruvian margin sediments, particularly in a system that is known to induce large remineralization rates and a strong oxygen-minimum zone within the water column (Reimers, 1982; Suess and von Huene, 1988). Therefore, one must be careful during the assessment of different inputs in relation to specific elemental and isotopic fractionation processes in this system.

Several studies have shown that source-specific biomarkers can add useful information to further constrain reconstructions of terrestrial vs. marine inputs from isotopic and elemental data (Jasper and Gagosian, 1993; Prahl et al., 1994; Goñi, 1997; Louchouarn et al., 1999; Benner et al., 2005). In Amazon Fan sediments, for example, vascular plant biomarkers (lignin- and cutin-derived molecules) have helped confirm the importance and origin of terrigenous inputs to these sediments (Goñi, 1997; Kastner and Goñi, 2003). We have thus used a similar approach to test for potential fluctuations in terrigenous organic matter inputs to sediments of Hole 1229E over the Pleistocene–Holocene transition. The lignin-derived concentrations and carbon-normalized yields in this core (Fig. F4) are extremely low in comparison to other coastal sediments (Louchouarn et al., 1999) but are consistent with prior work performed by Bergamaschi et al. (1997) on a surface sediment sample from the Peruvian margin (420 $\mu\text{g/gdw}$ and 500 $\mu\text{g}/100 \text{ mg } C_{\text{org}}$, respectively). These authors conclude that such low lignin values in this system are due to a substantial dilution of terrestrial organic matter by autochthonous material and coincide with low terrigenous inputs from an arid coastal zone (Whelan et al., 1990). The range of values observed in Hole 1229E (2–30 $\mu\text{g/gdw}$ and 5–50 $\mu\text{g}/100 \text{ mg } C_{\text{org}}$, respectively) confirms prior observations in the region (Farrimond et al., 1990a; Whelan et al., 1990) and suggests that the combination of very low riverine discharge to the Peruvian shelf, sparse vegetation on the Peru coast, and large fluxes of autochthonous materials are responsible for a minimal contribution of terrigenous organic matter to the Peruvian shelf. In addition, intrinsic ratios of lignin-derived materials demonstrate that chemically intact vascular plant material is only a minor constituent of terrigenous organic matter preserved in Peruvian margin sediments during most of the Holocene. A high acid/aldehyde ratio of lignin-derived vanillyl phenols ([Ad/Al]_v) in bulk sediments (0.6) is indicative of strong oxidative degradation of parent plant materials (Goñi et al., 1993, 1998). Except for a few low values (0.3–0.4) particularly in late Pleistocene–early Holocene sediments, the (Ad/Al)_v ratios in Hole 1229E range from 0.4 to 1.7 with an average of 0.6 ± 0.3 (Fig. F5), suggesting that organic matter in this core is moderately to highly degraded, particularly in the Holocene section of the core. These values do not vary in a consistent

F5. [Ad/Al]_v, S/V, and C/V, Hole 1229E, p. 20.

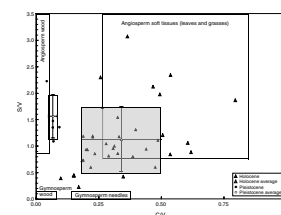


manner with respect to lignin concentrations and suggest that the oxidative degradation of lignin polymers is likely to have occurred on land rather than during postdepositional anaerobic diagenesis in this system. Similar values and conclusions were reported for a 150,000-yr profile from a core collected between Sulawesi and Borneo (Visser et al., 2004).

In addition, our core profile shows lignin compositional parameters such as the ratios of syringyl and cinnamyl phenols to vanillyl phenols (S/V and C/V ratios, respectively) that vary with no particular trend during the Holocene but may suggest a shift, particularly in C/V ratios, from the late Pleistocene to early Holocene (Fig. F5). On a first approach, these ratios are used to discriminate between taxonomic plant groups (gymnosperms vs. angiosperms) and tissues types (soft tissue vs. woody tissues) in environmental mixtures (Goñi and Hedges, 1992; Opsahl and Benner, 1995; Klap et al., 1999). A ratio of syringyl to vanillyl phenols appreciably greater than zero in such mixtures is usually indicative of the presence of at least some angiosperm tissue, whereas a ratio of cinnamyl to vanillyl phenols greater than zero suggests that nonwoody materials are present in the sample. Such signatures, however, also vary appreciably with respect to size fractions with fine particles in soils and sediments characterized by increased S/V and C/V signatures, as well as acid/aldehyde ratios due to sorption of highly degraded nonwoody constituents on clay particles (Hedges and Oades, 1997; Louchouarn et al., 1999; Hedges et al., 2000; Farella et al., 2001; Houel et al., 2006). The S/V and C/V ratios observed during the Holocene in Hole 1229E (Fig. F6) are relatively high and are consistent with mixed inputs of degraded angiosperm plant tissue appearing as either fine debris or colloidal material sorbed on mineral surfaces (cf. Houel et al., 2006). These ratios give no indication that substantial compositional changes in the terrestrial material reaching the Peruvian margin sediments have occurred during the Holocene. However, the shift in C/V and (Ad/Al)v ratios across the Pleistocene–Holocene transition (Figs. F5, F6) suggest that during the LGM, the sources of terrigenous OM were composed of less degraded woody materials, an observation that is in contrast to previous reports of no compositional changes in terrigenous OM inputs to shelf environments over glacial–interglacial transitions (Southeast Asia, Amazon Fan) (Kastner and Goñi, 2003; Visser et al., 2004). This latter finding is further significant in that it also contradicts the proposed hypothesis that grassland cover increased during the LGM in tropical systems (van der Hammen and Asby, 1994; Piperno, 1997; van der Kaars et al., 2000; Hope, 2001). It is true that the Peruvian margin does not drain a large tropical forest ecosystem as is the case for the Amazon Fan. However, the present molecular results point to increased erosional inputs of woody materials from the continents during the LGM rather than soft tissues, as would be expected under large-scale aridification of forest ecosystems. Finally, the high C/N values, low $\delta^{13}\text{C}_{\text{org}}$ signatures, and increased lignin concentrations during the late Pleistocene all point to a higher proportion of preserved OM of terrigenous origin in sediments of the LGM. This finding is in accord with prior work in other continental shelf systems. In contrast to the Indonesian shelf, however, the decreasing total C_{org} concentrations suggest that marine productivity may have decreased at this site during the LGM.

The increased proportion in lignin concentrations of some sediment intervals of the Holocene (0–50 cmbsf and 200–270 cmbsf) (Fig. F4) seem to suggest as well that an increased proportion of terrigenous organic matter is responsible for the lighter isotopic signatures observed

F6. S/V vs. C/V, Hole 1229E, p. 21.



during these periods. In particular, the peak in lignin concentrations occurs during a minimum in C_{org} and TN concentrations and $\delta^{13}\text{C}_{\text{org}}$ signatures suggesting that higher inputs of terrigenous OM during that time coincided with lower inputs of total OM and/or a decrease in the preservation of marine OM. In addition, the strong increase in C_{org} and TN concentrations and sudden drop in lignin concentrations at ~200 cmbsf (Figs. F2, F4) might suggest that the influx and/or preservation of marine OM increased substantially at this site. Despite this large shift in OM quantity and quality, however, $\delta^{13}\text{C}$ and C/N signatures change slowly to reflect, only at 100 cmbsf, signatures more typical of marine material (Fig. F3). Hence, because the fluctuations in terrigenous OM content cannot explain the low $\delta^{13}\text{C}_{\text{org}}$ values in the 150- to 200-cmbsf interval nor the downcore increase in C/N ratios during the Holocene (Fig. F3), we believe that other processes, in addition to source variations, need to be invoked to explain the apparent terrigenous elemental and isotopic signatures observed in the Holocene.

The slow “recovery” of isotopic values toward marine signatures could be due to a strong diagenetic fractionation in the sediments through regeneration of isotopically enriched components (peptides) leaving depleted residual organic matter in the sediments (i.e., lipids). The potential for selective regeneration of protein-rich material in an upwelling system such as this is important and is consistent with high C/N ratios in residual matter. Another potential source of light carbon to sediments is the active uptake, by photosynthetic organisms, of depleted CO_2 derived from organic matter regeneration at or close to the sediment/water interface (Fogel and Cifuentes, 1993). Such a process has been observed in coastal zones heavily influenced by remineralization of organic matter in the water column (Fogel et al., 1988) and may be a source of isotopically light CO_2 used by primary producers leading to depleted autochthonous organic matter (Fogel and Cifuentes, 1993). Although these two processes are not mutually exclusive, they suggest that the shifts in particular organic matter conditions may be the product of high remineralization activity within the water column and/or at the sediment/water interface. This hypothesis is consistent with the interstitial water anomalies in alkalinity, DIC, ammonium, and sulfide observed between 100 and 300 cmbsf at Sites 1228 and 1229 (Shipboard Scientific Party, 2003). Three possible explanations were provided in the report for this anomaly: (1) it may result from ongoing activity in a microbial hotspot at this shallow sediment depth, (2) it may be a chemical relic of past microbial activity and is now relaxing back to a diffusional steady state, or (3) it may be due to the recent establishment of an oxygen minimum at this water depth, causing the extinction of a bioirrigating benthos and a stimulation of sulfate reduction. The available data do not allow us to provide anything other than speculations with regard to which process may be responsible for the link between the observed particulate OM signatures and the observed anomaly in interstitial water chemicals. It seems, however, that these shifts in sedimentary parameters may be the product of both a change in OM sources and increased microbial activity in these systems.

SUMMARY AND FUTURE WORK

The organic matter deposited in surface sediments of Hole 1229E (0–700 cmbsf) shows strong elemental and isotopic signature changes that

are not exclusively due to fluctuations in OM sources. Strong shifts in C_{org} are not entirely controlled by terrigenous OM inputs in this system and thus apparent terrigenous isotopic and elemental signatures seem to be derived from diagenetic processes and productivity fluctuations in addition to potential source changes. It is yet difficult to estimate the true extent of glacial–interglacial changes in OM inputs and signatures in these sediments. However, our elemental, isotopic, and molecular data suggest that there was a decrease in input of terrigenous OM during the LGM–Holocene transgression. These results are consistent with prior paleoceanographic work in continental margins, which show that terrigenous OM influx was more important to these environments during glacial than interglacial periods (Jasper and Gagosian, 1990, 1993; Visser et al., 2004). The analysis of deeper sections of Hole 1229E and of Hole 1228B, which covers a longer time period with better chronological constraint (Fink et al., 2006), should provide an ideal time series to further evaluate the glacial–interglacial changes in organic matter input to this system.

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Figure F1. Location of sites from ODP Leg 201. Site 1229 lies in the close vicinity to ODP Site 681 from Leg 112.

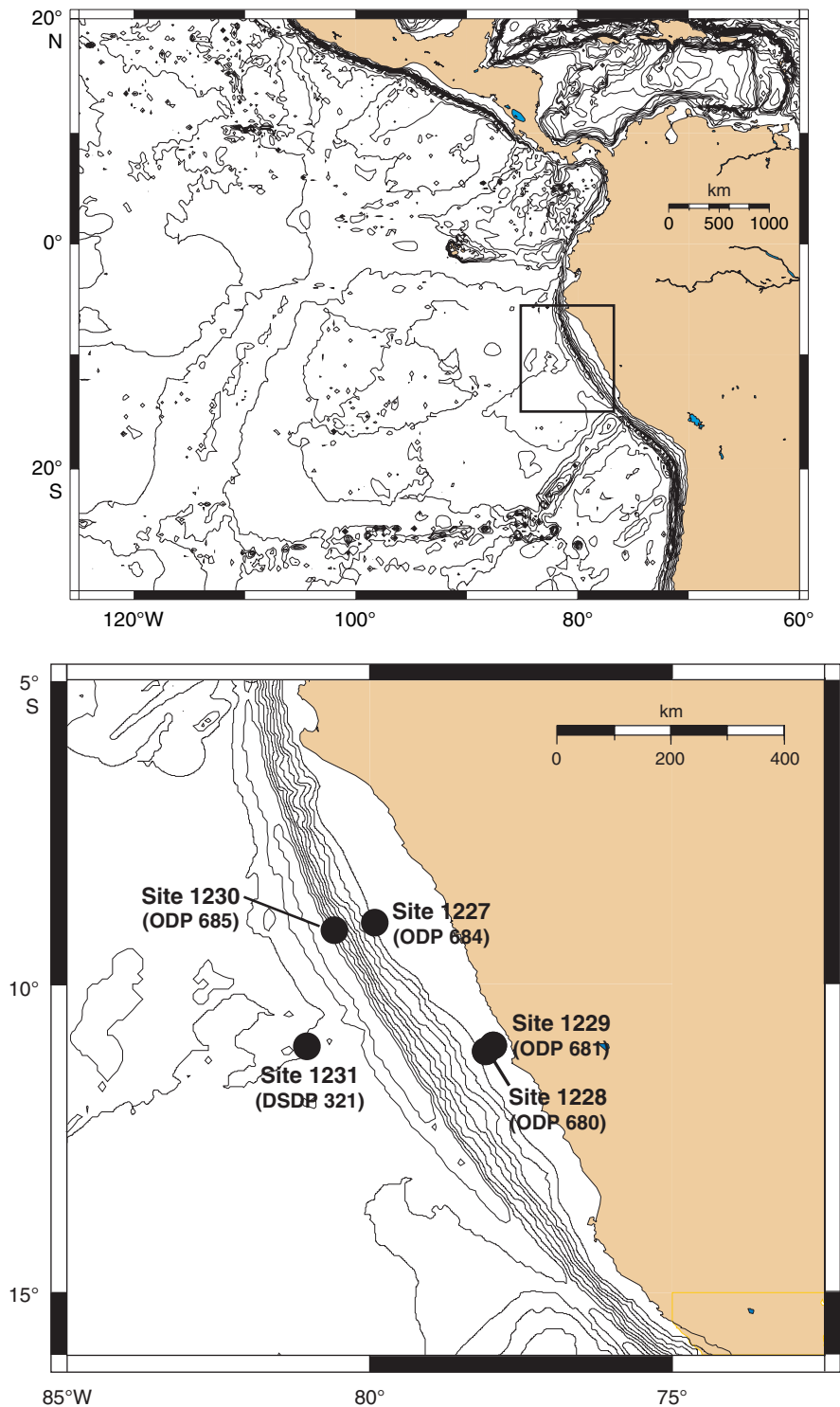


Figure F2. Downcore variations in organic carbon (C_{org}) and total nitrogen (TN) in Hole 1229E. ^{14}C ages are from Fink et al. (2006)

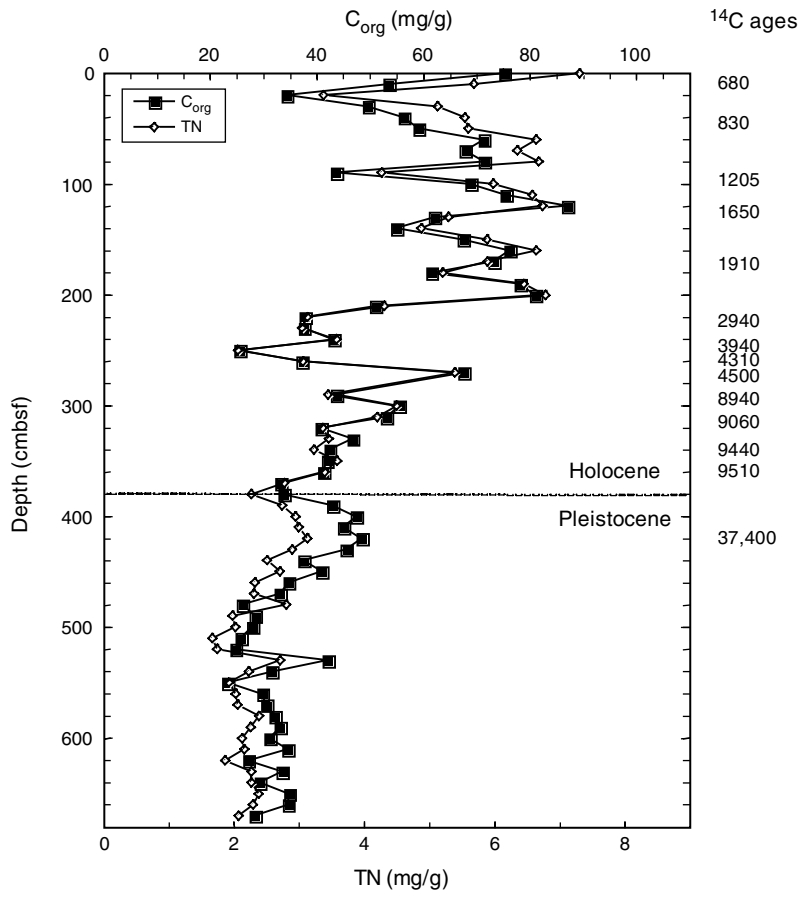


Figure F3. Downcore variations in atomic C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ in Hole 1229E. ^{14}C ages are from Fink et al. (2006).

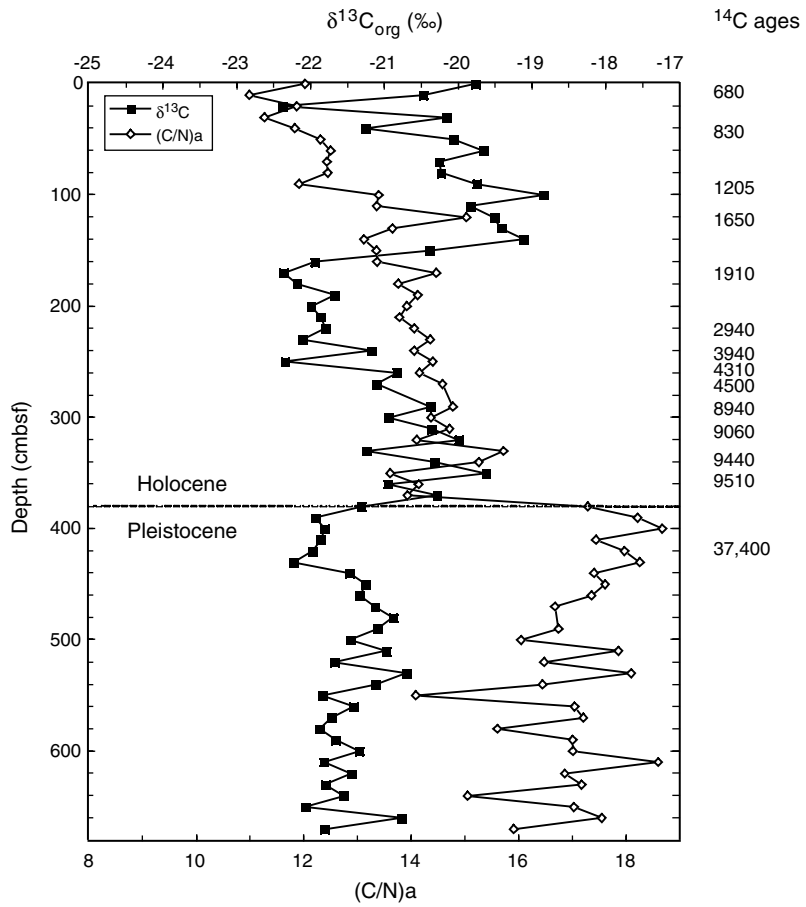


Figure F4. Downcore variations in lignin concentrations ($\Sigma 8$: $\mu\text{g/gdw}$) and carbon-normalized yields ($\lambda 8$: $\mu\text{g}/100\text{ mg C}_{\text{org}}$) in Hole 1229E. ^{14}C ages are from Fink et al. (2006).

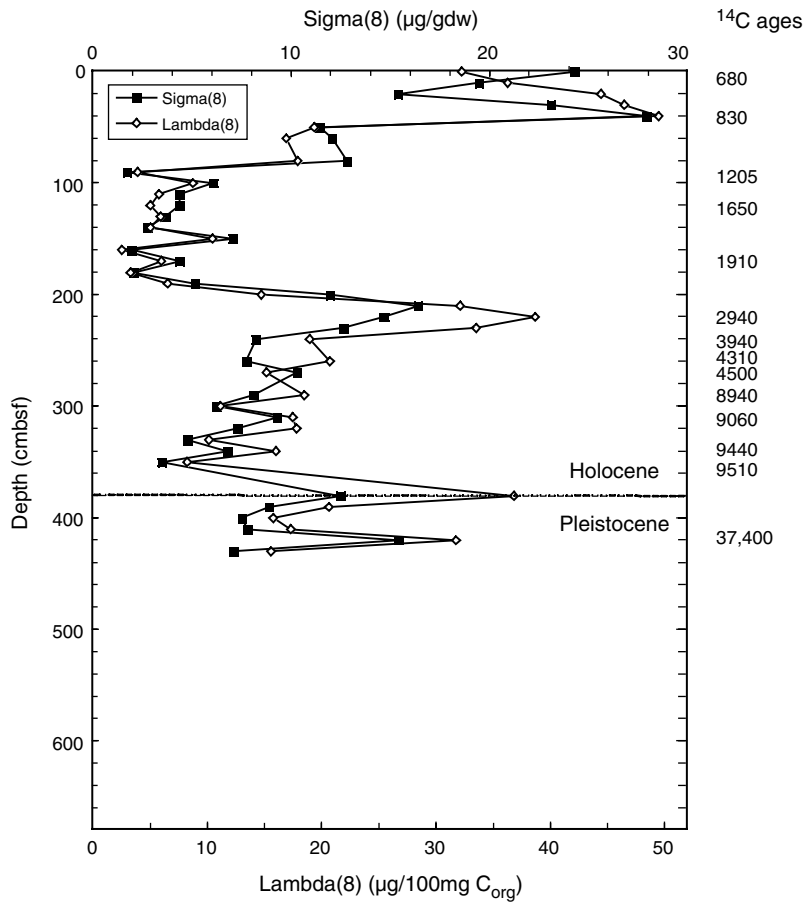


Figure F5. Downcore variations in the acid to aldehyde ratio of vanillyl phenols ([Ad/Al]_v), as well as the ratios of syringyl to vanillyl phenols (S/V), and cinnamyl to vanillyl phenols (C/V), in Hole 1229E. ¹⁴C ages are from Fink et al. (2006).

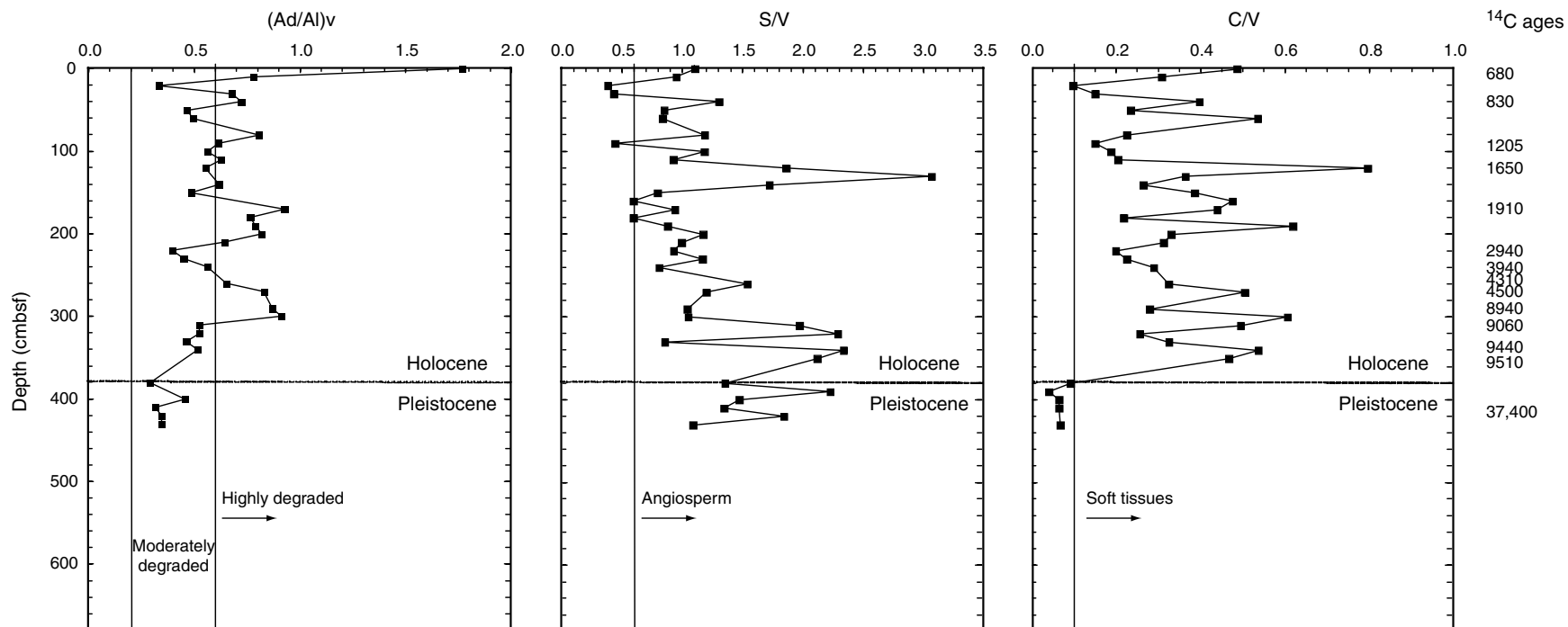


Figure F6. Plot of syringyl to vanillyl phenol ratios (S/V) vs. cinnamyl to vanillyl phenol ratios in Hole 1229E. Compositional ranges from plant matter from Goñi (1997) and Goñi et al. (1998). The gray box with the open triangular symbol represents the average signature ratios ± 1 SD for the Holocene data set. The transparent box with the open circular symbol represents the average signature ratios ± 1 SD for the Pleistocene data set.

