

A molecular evaluation of bulk organic carbon-isotope chemostratigraphy for terrestrial correlations: An example from two Paleocene–Eocene tropical sequences

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ABSTRACT

The dynamics associated with the carbon cycle and the linkage between the oceans, the atmosphere, and land plants provide an opportunity to correlate marine and terrestrial sedimentary sequences using stable isotopes of carbon ($\delta^{13}\text{C}$), but few studies have tested this approach. For instance, it has been proposed that changes in plant community (e.g., gymnosperm-dominated vs. angiosperm-dominated) could have significantly altered/amplified the carbon-isotope ratios of bulk sedimentary organic matter derived from land plants ($\delta^{13}\text{C}_{\text{TOM}}$), compared to that of the marine carbonates ($\delta^{13}\text{C}_{\text{carbonate}}$). Here, $\delta^{13}\text{C}_{\text{TOM}}$ values in a terrestrial sequence of the Colombian tropics are compared to the composite Paleocene–Eocene $\delta^{13}\text{C}_{\text{carbonate}}$ curve from Zachos et al. (2001) to evaluate the use of $\delta^{13}\text{C}_{\text{TOM}}$ values as a reliable chronostratigraphic tool. Sediments of the studied terrestrial sequences were deposited in a transitional setting dominated by mudstones, coals, and small lenses of sandstones (Late Cretaceous–Middle Paleocene sediments) and in a mixture of deltaic and fluvial conditions (Late Paleocene–Early Eocene sediments). The biostratigraphic control was based on palynological zones for the region. The $\delta^{13}\text{C}_{\text{TOM}}$ values for the studied terrestrial sequence show three carbon-isotope excursions, which correlate closely with those present in the marine record. The $\delta^{13}\text{C}_{\text{TOM}}$ values decreased from -24.2% to -26.5% in sediments accumulated during Early to Middle Paleocene, increased from -26.5% to -23.8% during the Late Paleocene, and decreased from -23.8% to -26.5% near the Paleocene–Eocene boundary (52–50 Ma). Selected biomarkers indicate that most of the organic matter derived from both gymnosperms and angiosperms. Moreover, the analyses of selected biomarker ratios (CPI, Pr/Ph, P_{aq} , and $\beta\beta/\beta\beta + \alpha\beta$ hopanes) show some diagenetic transformation in the preserved organic matter. However, no correlation between diagenesis and $\delta^{13}\text{C}_{\text{TOM}}$ values was detected, thus suggesting that $\delta^{13}\text{C}_{\text{TOM}}$ could be correlated with $\delta^{13}\text{C}_{\text{carbonate}}$ values. The close correspondence that was found between $\delta^{13}\text{C}_{\text{TOM}}$ and $\delta^{13}\text{C}_{\text{carbonate}}$ values ($\Delta^{13}\text{C}_{\text{TOM-carbonate}} \sim -27\%$) provides support to the hypothesis that a tight land-plant–oceans linkage exists through geologic timescales via atmospheric carbon dioxide.

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1. Introduction

Significant chemical, physical, and biological changes in both marine and terrestrial environments have affected the carbon cycle during the Phanerozoic (e.g., Arens and Jahren, 2000; Beerling et al., 2001; Freeman and Colarusso, 2001; Hesselbo et al., 2002; Thomas et al., 2002; Hesselbo et al., 2003; Jahren et al., 2005; Jaramillo et al., 2006; Kaiser et al., 2006; Smith et al., 2007) by affecting the magnitude of carbon fluxes between different carbon reservoirs over geologic time scales and by altering the partitioning of carbon isotopes. If these perturbations of the carbon cycle are global in scale, they could offer an opportunity to correlate marine and

terrestrial sedimentary sequences, which at the moment is limited to a few proxies. Some studies have in fact proposed the use of stable isotopes of carbon as a chronostratigraphic tool for marine and terrestrial sequences (e.g., Scholle and Arthur, 1980; Hasegawa, 1997; Arens and Jahren, 2000; Strauss and Peters-Kottig, 2003; Hesselbo et al., 2007). These studies rely on two key assumptions: (1) both $\delta^{13}\text{C}_{\text{carbonate}}$ values and $\delta^{13}\text{C}$ values of organic matter derived from higher plants reflect parallel changes in the carbon isotopic composition of the marine and terrestrial realms, and (2) measured $\delta^{13}\text{C}$ values are identical to those of the pristine materials.

The first assumption is based on the notion that isotopic equilibrium is reached within the different reservoirs over geologic timescales (i.e., differences in isotopic values remain constant after equilibration) (e.g., Gröcke, 2002; Strauss and Peters-Kottig, 2003). Despite the importance of the secular changes over long-term time scales ($>10^6$ yrs), significant partitioning of carbon isotopes occurs over short-term timescales, which ultimately drives the isotopic

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composition of both marine carbonates ($\delta^{13}\text{C}_{\text{carbonate}}$) and terrestrial plants ($\delta^{13}\text{C}_{\text{plant}}$).

The second assumption has been challenged by several studies showing that carbon isotopic composition of bulk terrestrial organic matter ($\delta^{13}\text{C}_{\text{TOM}}$) may not faithfully reflect pristine $\delta^{13}\text{C}_{\text{plant}}$ values (e.g., Gröcke, 1998, 2002; Bergen and Poole, 2002) due to the preferential preservation of different plant components during diagenesis (e.g., Beerling and Royer, 2002). These plant components have a different isotopic composition relative to that of whole plant tissues (Bergen and Poole, 2002), and their carbon isotopic composition varies as a result of the different isotope fractionation effects occurring during biosynthesis (Galimov, 1985; Farquhar et al., 1989; Hayes, 2001; Gröcke, 2002). In addition, aerobic bacteria preferentially metabolize ^{12}C -enriched organic matter during diagenesis, potentially enriching the remaining organic compounds in ^{13}C and possibly making $\delta^{13}\text{C}_{\text{TOM}}$ values more positive relative to $\delta^{13}\text{C}_{\text{plant}}$ values (Hartgers et al., 1994; Bergen and Poole, 2002). To date, only a few studies (e.g., Bergen and Poole, 2002; Poole et al., 2004) have tested the effects of diagenesis on $\delta^{13}\text{C}$ values from fossilized plant parts (e.g., wood) using reliable tools (e.g., molecular biomarkers). For that reason, the goal of this study is to test whether $\delta^{13}\text{C}_{\text{TOM}}$ values mirror the isotopic shifts that are recorded in marine carbonates during coeval time intervals. Moreover, the effect of diagenetic processes and differences in the source of organic matter are evaluated to infer their effect on $\delta^{13}\text{C}_{\text{TOM}}$ values. To achieve these goals, the Lower Paleogene marine carbon-isotope record (Zachos

et al., 2001) is compared to that of a terrestrial sequence from the South American tropics. This chronostratigraphic interval was selected for the study because several isotopic anomalies have been reported in several marine sequences accumulated during the Early Paleogene (e.g., Koch et al., 1992; Veizer et al., 1999; Zachos et al., 2001; Hollis et al., 2005), thus providing an excellent reference for comparing $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{13}\text{C}_{\text{TOM}}$ values. The effect of diagenesis on $\delta^{13}\text{C}_{\text{TOM}}$ values is evaluated through the use of geochemical biomarkers. Biomarker parameters are also used qualitatively to evaluate microbial- vs. plant-derived contributions to organic matter, thereby allowing an evaluation of the potential effect of microbial degradation on $\delta^{13}\text{C}_{\text{TOM}}$ values. These results will then permit us to determine whether $\delta^{13}\text{C}_{\text{TOM}}$ values are a reliable proxy for chronostratigraphic and paleoclimatic studies.

2. Geological setting and sampling site

The samples for this study were collected from well sites located in two contiguous basins in northern South America. Site-A ($8^{\circ}12'\text{N}$, $72^{\circ}11'\text{W}$) is located within the Catatumbo basin, whereas Core-B ($9^{\circ}34'16''\text{N}$, $73^{\circ}16'45''\text{W}$) is located within the Cesar–Rancheria basin (Fig. 1). Sampling was performed at about 10 m intervals on each site to cover the desired time span (Latest Cretaceous–Early Eocene), yielding a set of 134 samples (69 from the Site-A and 65 from the Core-B wells). The time span encompassed by the samples was chronostratigraphically constrained with the aid of pollen biozones, previously calibrated with the marine

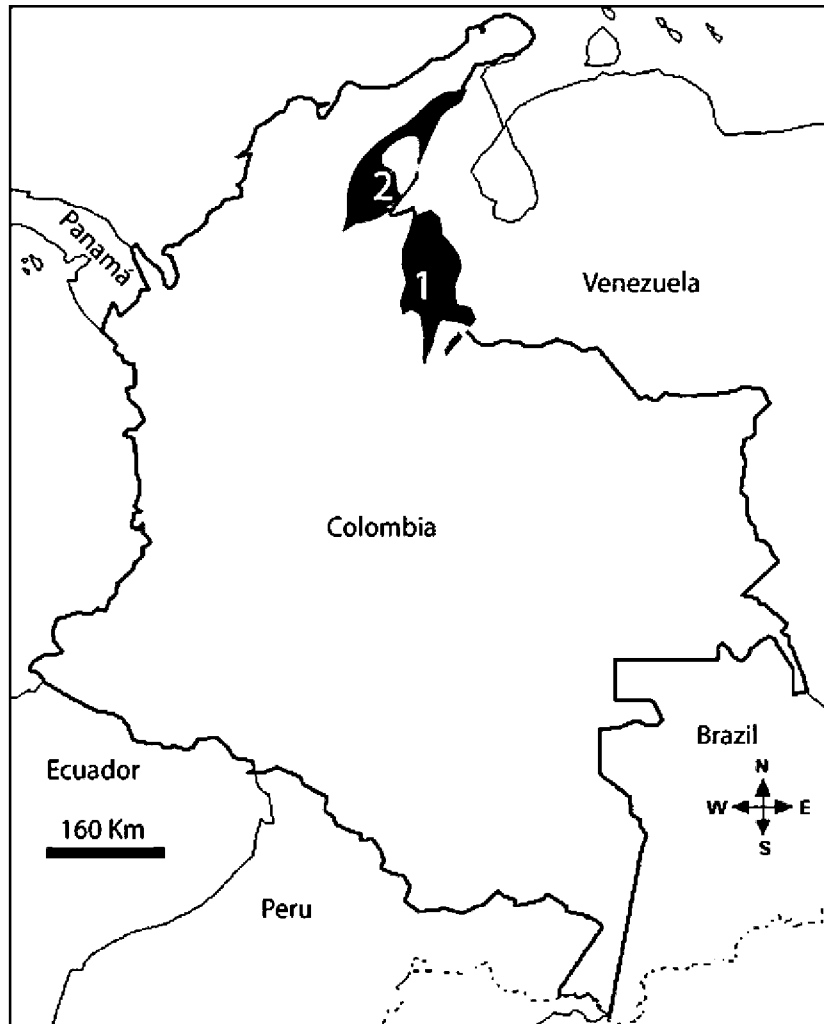


Fig. 1. Map of Colombia, South America, showing the sedimentary basins for the two sections studied (modified from www.ingeminas.gov.co). Numbers 1 and 2 correspond to the well cuttings of the Site-A and Core-B sections (Catatumbo and Cesar–Rancheria basins, respectively).

chronostratigraphic record (Jaramillo and Rueda, 2004; Jaramillo et al., 2005) (Fig. 2). The average sedimentation rates were estimated on the basis of the ages provided by the pollen biozones for each sedimentary basin and the thickness of each biozone in the wells. For the sampled interval, the average sedimentation rates were similar for both sequences (41.36 m/M.y. for Site-A and 41.44 m/M.y. for Core-B). These sampled sediments consisted of mudstones, coals, and small lenses of sandstones probably accumulated in a transitional setting from the Late Cretaceous to the Middle Paleocene (Catatumbo and Barco Formations) and in a mixture of deltaic and fluvial settings, possibly including oxbow lake environments, that existed from Late Paleocene to Early Eocene (Cuervos Formation).

3. Analytical methods

3.1. Bulk sediment isotopic analysis

Stable carbon-isotope values of bulk sediment ($\delta^{13}C_{TOM}$) were measured via flash-pyrolysis at 1100 °C in a Costech elemental analyzer fitted to a Thermo Finnigan Delta plusXL isotope ratio mass spectrometer (Department of Geological and Atmospheric Sciences at Iowa State University). Carbonate was removed from the samples by HCl digestion. Analytical precision and accuracy were determined on the basis of repeated analysis of two internal lab standards calibrated against the internationally accepted V-PDB standard. Overall uncertainty was better than 0.08‰. Organic carbon content was determined on the basis of the liberated CO₂ in the elemental analyzer. To minimize noise in the obtained data, a five-point moving average was applied to the $\delta^{13}C_{TOM}$ values for a better comparison between $\delta^{13}C_{carbonate}$ and $\delta^{13}C_{TOM}$.

Comparisons between $\delta^{13}C_{TOM}$ and other geochemical parameters were performed using original, non-smoothed isotopic values.

3.2. Biomarker analysis

A set of 27 samples from the initial 134 were selected for biomarker analysis on the basis of their organic carbon content and on their relative stratigraphic location to represent the entire sequence. Soluble organic matter (SOM) extractions followed the methodology proposed by Otto et al. (2005). The saturated and aromatic fractions were separated from the extracted SOM through micro-column chromatography, using activated silica gel. The aliphatic and aromatic fractions were then derivatized with 100 µL of N, O,-bis (trimethylsilyl) trifluoroacetamide and trimethylchlorosilane (BSTFA/TMS 99:1) at 65 °C for 30 min. Gas chromatography–mass spectrometry (GC–MS) analyses of the derivatized samples were performed on an Agilent model 6890 GC coupled to a Micromass GC-TOF MS (Chemistry Department at Iowa State University) and on an Agilent A 6890 N gas chromatograph/5973 network mass spectrometer (Department of Geological and Atmospheric Sciences at Iowa State University). Separation was achieved with a fused DB5 silica capillary column and with helium as the carrier gas. The GC operating temperature ramp was as follows: temperature was held at 65 °C for 2 min, and then increased from 65 to 300 °C at a rate of 6 °C/min, with final isothermal hold at 300 °C for 15 min. The sample was injected splitless with the injector temperature at 300 °C. The mass spectrometer was operated in the electron impact mode (EI) at 70 eV ionization energy and scanned from 40 to 650 Da. Individual compounds were identified by comparison of their mass spectra and retention times with those of published compounds and by interpreting mass fragmentation patterns. Relative abundances of the different compounds were calculated using

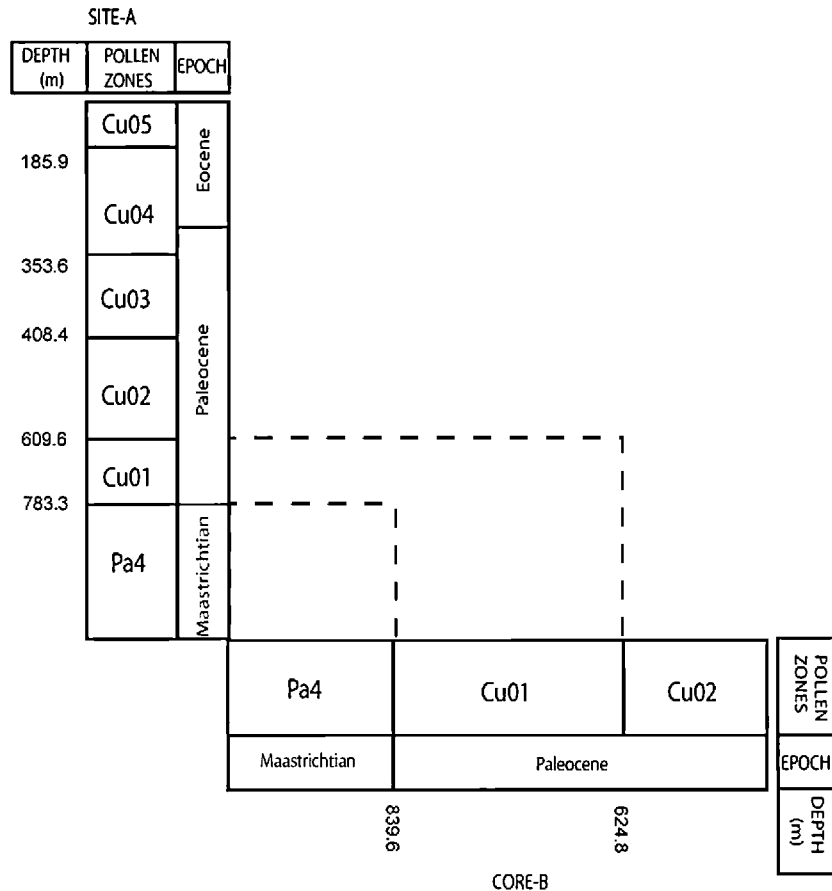


Fig. 2. Chronostratigraphy for the Catatumbo and Cesar–Rancheria basins. The geologic ages are based on the palynological zones of Jaramillo and Rueda (2004) and Jaramillo et al. (2005). Sedimentation rates for both sites were similar (Cu01 top coincides in both Site-A and Core-B sections). Top of Pa4 at 65.2 Ma; Top of Cu01 at 60.9 Ma; Top of Cu02 at 57 Ma; Top of Cu03 at 55.8 Ma; Top of Cu04 at 51.9 Ma.

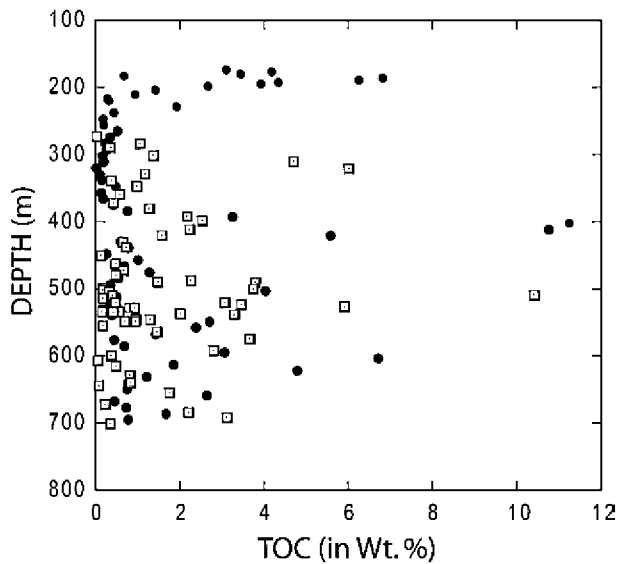


Fig. 3. Total organic carbon content (TOC) in weight percentage for the Site-A (filled circles) and Core-B (unfilled squares) samples.

peak areas in the total ion current (TIC) of the derivatized total extracts. Some individual compounds were identified using the GC trace and the mass spectrum of a selected ion mass (SIM).

4. Results

4.1. Bulk geochemical parameters

4.1.1. Total organic carbon

Most of the samples analyzed are mudstones that vary in color from black or dark gray to slightly dark brown, typical for samples with relative high content of organic matter. Visible wood fragments were observed in some of the samples. Organic carbon contents (C_{org}) vary between 0.01 and 11.24 wt.% (Fig. 3). The lowest carbon contents were found in the Barco Formation (average C_{org} = 0.96 wt.%), corresponding to depths

between 460 and 350 m below surface in the Site-A well. The highest contents were found in samples from the Cuervos Formation (average C_{org} = 2.00 wt.%), corresponding to depths between 350 and 150 m in the Site-A well.

4.1.2. Carbon isotopic composition of organic matter

The $\delta^{13}C_{TOM}$ values for the Site-A samples range from -21.2% to -29.9% , and they show three carbon-isotope excursions: a positive shift centered at 350 m and two negative shifts centered at 500 and 200 m (Fig. 4). The $\delta^{13}C_{TOM}$ values for Core-B samples range from -24.3% to -27.0% . The three carbon-isotope excursions found in the Site-A samples chronostratigraphically correlate with those found in marine carbonates (Zachos et al., 2001; Fig. 4). The $\delta^{13}C_{TOM}$ values decrease from -24.2% to -26.5% from 65 to 58 Ma. This shift correlates with that in the $\delta^{13}C_{carbonate}$ record from 1.75‰ to 0.5‰ for the same interval. A positive shift in $\delta^{13}C_{TOM}$ values occurs in the Late Paleocene (58–56 Ma), with values becoming less negative from -26.5% to -23.8% . In the $\delta^{13}C_{carbonate}$ record, this excursion is represented by a shift from 0.5‰ to 2.5‰. The third excursion occurs near the Paleocene–Eocene boundary (~52 Ma), with values changing from -23.8% to -26.5% in $\delta^{13}C_{TOM}$ and from 2.50 to -0.25% in $\delta^{13}C_{carbonate}$. One aspect that is absent in the $\delta^{13}C_{TOM}$ record is the sharp spike in marine carbonate $\delta^{13}C$ values at the Paleocene–Eocene boundary (55 Ma), which corresponds to the PETM event (Koch et al., 1992; Zachos et al., 2001). Its absence in the $\delta^{13}C_{TOM}$ data set is probably due to the large sampling intervals (~0.2 M.y./sample) employed for this study and the short duration (~0.02 to 0.07 M.y.) of this event (Smith et al., 2007).

4.2. Molecular composition of organic matter

Analyses of the aromatic fraction revealed undetectable concentrations of these compounds, possibly due to the high detection limit of the instrument utilized for the analysis of this fraction (Agilent A 6890 N gas chromatograph/5973 network mass spectrometer). Thus, this study reports the compounds identified in the aliphatic fraction of SOM. Four major families of organic compounds were identified in the aliphatic fraction: n-alkanes, regular acyclic isoprenoids, sesqui- and triterpenoids. Mid- and short-chain n-alkanes, and triterpenoids were the most abundant types of compounds present in the studied samples (Fig. 5).

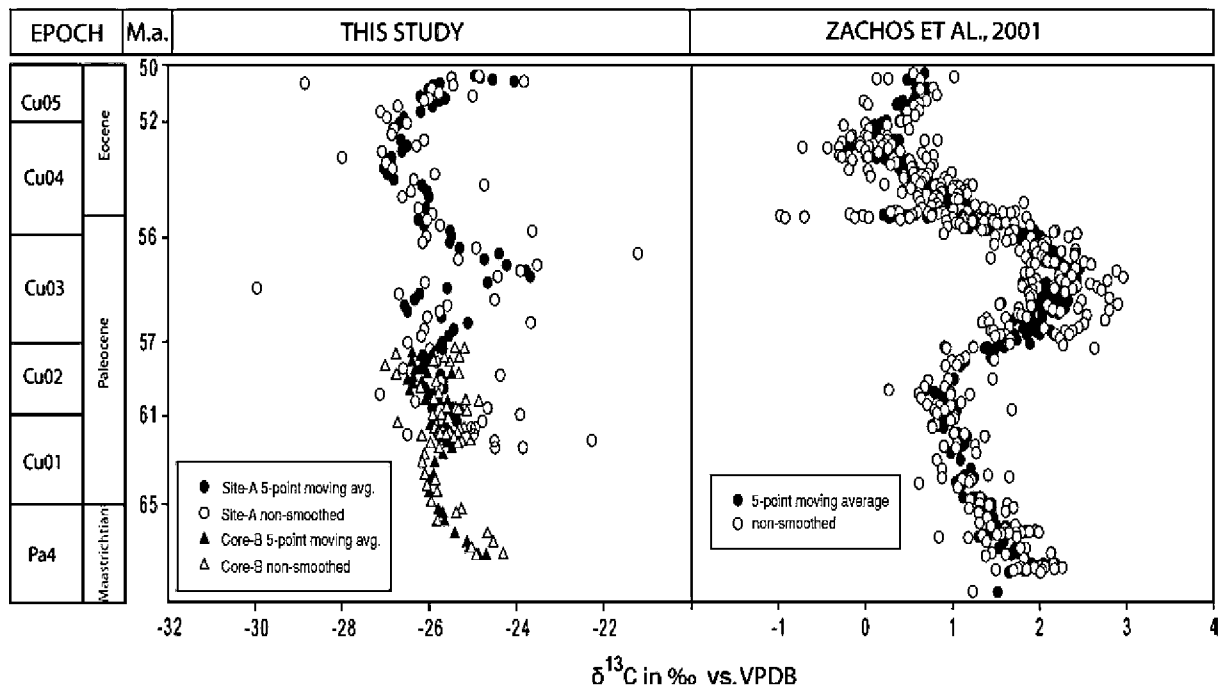


Fig. 4. Comparison between the carbon isotopic composition of bulk terrestrial organic matter ($\delta^{13}C_{TOM}$, left panel) and that of marine carbonates ($\delta^{13}C_{carbonates}$, from Zachos et al., 2001, right panel) during the Late Cretaceous–Early Eocene.

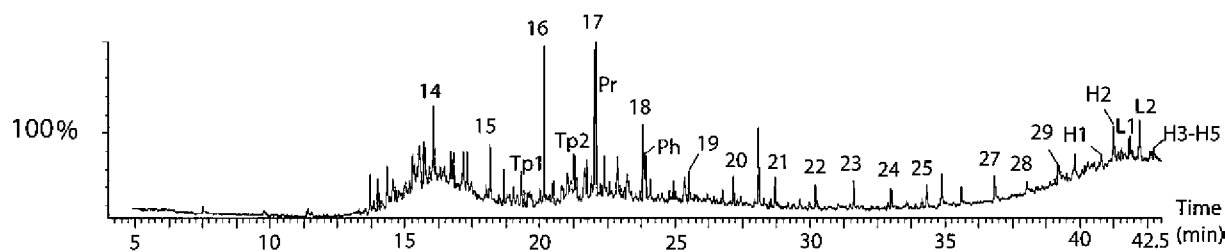


Fig. 5. GC-trace from the Core-B section (359.5 m), displaying the common pattern found through all the samples selected for biomarker analyses (i.e., same distribution of compounds in all samples). Retention times in the x-axis are in minutes, whereas relative abundances are in the y-axis. Peaks with numbers correspond to n-alkanes. Pr and Ph are isoprenoids, Tp1 and Tp2 are sesquiterpenoids, L1 and L2 are non-hopanoid triterpenoids, and H1–H5 are hopanoids.

4.2.1. n-Alkanes and isoprenoids

The n-alkane distribution in the studied samples shows an odd-over-even-predominance, with high abundances of short-chain (<nC₂₀) n-alkanes (Fig. 6). The identified isoprenoids pristane (Pr) and phytane (Ph) are present in most of the samples, with Pr typically being more abundant than Ph. (e.g., Fig. 5). Because of their interdependent response to changes in the depositional environment, Didyk et al. (1978) proposed the use of the pristane/phytane ratio (Pr/Ph) as a proxy for the level of oxicity in the sediments, with low Pr/Ph values (between 1.5 and 2.5) reflecting deposition under dysoxic conditions and high Pr/Ph values indicating deposition under oxic conditions. Core-B Pr/Ph values vary between 0.81 and 2.79 (Fig. 8), with a decreasing trend with depth (Fig. 8). Site-A Pr/Ph values range from 0.94 to 4.59 with no visible trend with depth (Fig. 9). These values suggest a changing level of oxygen in the sediments during the accumulation of the studied sequences.

4.2.2. Sesquiterpenoids and non-hopanoid triterpenoids

Two types of sesquiterpenoids were present in the saturated fraction of SOM: a C-16 sesquiterpenoid and a cadalene-type sesquiterpenoid. The identification of the two sesquiterpenoids was achieved by the presence of the characteristic fragments 183 and 123 in the mass spectra and by comparisons to published spectra of these compounds (Philp, 1985; Otto et al., 1997; Otto and Simoneit, 2001; Bechtel et al., 2003; Hauteville et al., 2006). The non-hopanoid triterpenoids identified in the saturated fraction correspond to lupane-type triterpenoids.

4.2.3. Hopanoids

Hopanoids are compounds occurring in bacteria (Peters et al., 2005; Otto et al., 2005). These compounds, after n-alkanes, were the main constituents present in the saturated fraction of both Core-B and Site-A samples (Fig. 5). The identified hopanoids compounds were 17 α -

22,24,30-trisnorhopane, 17 α (H),21 β (H)-hopane, 17 α ,21 β (H)-norhopane, 17 β (H),21 β (H)-hopane, 17 α (H),21 β (H)-homohopane, 17 β (H),21 β (H)-homohopane, unknown C₃₂ hopanoid, and 17 α (H),21 β (H)-trishomohopane (H1,H2,H3,H4,H5,H6,H7,H8, respectively) (Fig. 5). Both set of samples display similar hopanoid distributions (Fig. 7), although the heavier hopanoids (H5 through H8) were commonly absent in the Core-B samples.

5. Discussion

5.1. The $\delta^{13}\text{C}_{\text{TOM}}$ values as a proxy for changes in the carbon cycle

The carbon isotopic composition of plant-derived organic matter (i.e., bulk organic matter, fossil wood, cuticles, etc.) has been used in geologic studies to evaluate the evolution of the carbon cycle through geologic times (e.g., Hasegawa, 1997; Gröcke et al., 1999; Hesselbo et al., 2003; Strauss and Peters-Kottig, 2003; Smith et al., 2007). The bulk organic matter in the Core-B and Site-A samples displays $\delta^{13}\text{C}$ values around -27‰ (Fig. 4), which are typical for C₃ plants (Farquhar et al., 1989). The good correspondence between the marine and the terrestrial isotope data (Fig. 4) provides support to the notion that a tight linkage exists between the oceans, the atmosphere, and land plants, confirming that perturbations occurring between 50 and 65 Ma were global in extent. However, the implication of the parallelism that exists between the marine and terrestrial $\delta^{13}\text{C}$ values still relies on the assumption that $\delta^{13}\text{C}_{\text{TOM}}$ values truly reflect $\delta^{13}\text{C}_{\text{plant}}$ values. Although $\delta^{13}\text{C}_{\text{TOM}}$ values tend to reflect those of plant-derived organic matter (Lane et al., 2004; Rodelli and Gearing, 1984), other effects, including the extent of microbial alteration, could potentially alter $\delta^{13}\text{C}_{\text{TOM}}$ values by up to 2‰ (Gröcke, 1998, 2002; Bergen and Poole, 2002; Beerling and Royer, 2002). For instance, variations of $\sim 1\text{‰}$ between $\delta^{13}\text{C}_{\text{TOM}}$ and the isotopic composition of charcoal and lignite from the same stratigraphic horizons have been found (Heimhofer et al., 2003; Gröcke et al., 2006). Moreover,

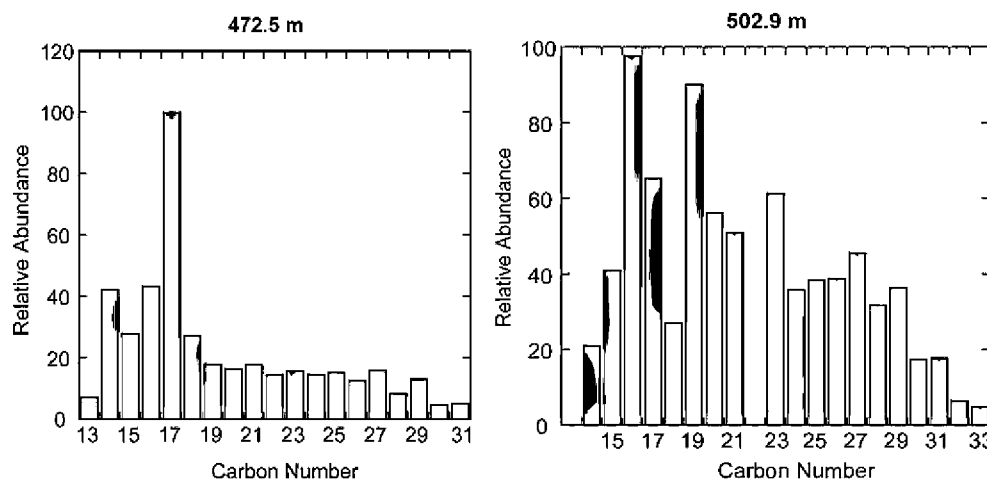


Fig. 6. Histogram of the relative abundance of n-alkanes for representative samples of Core-B (upper panel) and Site-A (lower panel). Sample depth is labeled at the top of each panel.

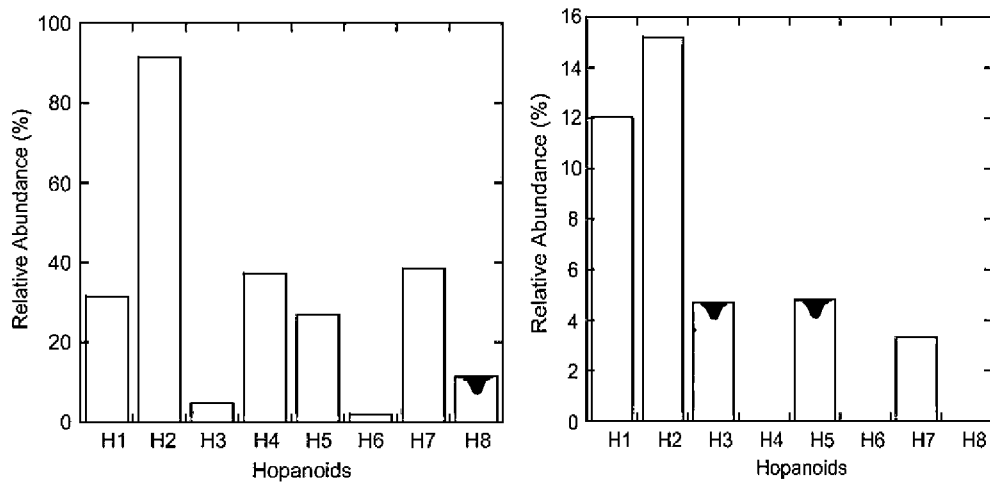


Fig. 7. Histograms of the distribution patterns of hopanoids in representative samples of Core-B (lower panel, depth = 509.9 m) and Site-A (upper panel, depth = 548.6 m). The identified hopanoids compounds correspond to 17 α -22,24,30-trisnorhopane, 17 α (H),21 β (H)-hopane, 17 α ,21 β (H)-norhopane, 17 β (H),21 β (H)-hopane, 17 α (H),21 β (H)-homohopane, 17 β (H),21 β (H)-homohopane, unknown C₃₂ hopanoid, and 17 α (H),21 β (H)-trishomohopane (H1,H2,H3,H4,H5,H6,H7,H8, respectively).

the sedimentological analysis of the studied deposits suggests that some sediments accumulated in environments where the contribution of aquatic plants to the sedimentary organic pool could be significant (e.g., oxbow lakes).

The effect of diagenesis on carbon-isotopic values has been evaluated through different approaches, including those relying on comparisons between $\delta^{13}\text{C}_{\text{TOM}}$ and $\delta^{13}\text{C}$ values of plant cuticles (e.g., Arens and Jahren, 2000), $\delta^{13}\text{C}_{\text{TOM}}$ and $\delta^{13}\text{C}$ values of woody fragments (e.g., Gröcke, 2002) or on evaluations of the level of microbial degradation of fossil wood inferred

from molecular components (biomarkers) (Bergen and Poole, 2002; Poole et al., 2004). For instance, Bergen and Poole (2002) identified high amounts of organic matter derived from bacteria as a result of the alteration of organic matter in fossilized woody fragments, which could potentially alter pristine $\delta^{13}\text{C}_{\text{plant}}$ values, thus constraining the use of $\delta^{13}\text{C}_{\text{TOM}}$ as a reliable proxy in estimating the evolution of the carbon cycle. To evaluate the role of diagenesis and the sources of organic matter on $\delta^{13}\text{C}_{\text{TOM}}$ values, several biomarker ratios were employed in this study because of their demonstrated response to diagenesis and/or their

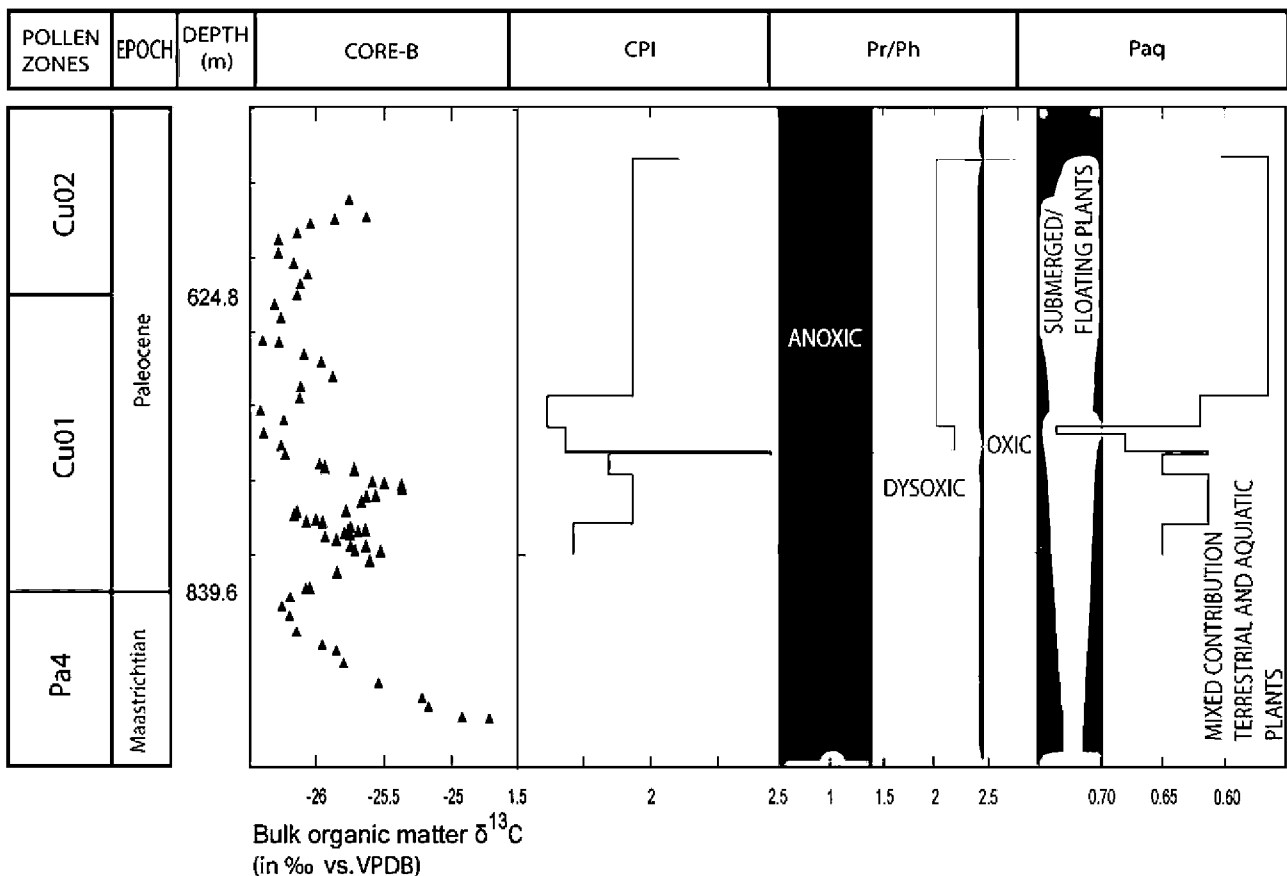


Fig. 8. Stratigraphic variability of the Carbon Preference Index (CPI), pristane/phytane (Pr/Ph) ratio, aquatic/terrestrial plants (Pa_q) ratio, and smoothed carbon isotopic composition ($\delta^{13}\text{C}$) in the Core-B.

specificity to different sources of organic matter (e.g., vascular plants, algae, bacteria). These ratios were calculated from the relative abundances of the different compounds identified in the saturated fraction of the SOM.

The saturated fraction shows that n-alkanes display an overall odd-over-even predominance (Figs. 8 and 9), which is usually associated with significant input of organic matter from terrestrial vascular plants (Bechtel et al., 2003; Otto et al., 2005). Odd number long-chain n-alkanes are major components of plant cuticular waxes formed as a result of elongation and further decarboxylation from a fatty acid precursor (e.g., palmitate) (Harwood and Russel, 1984). Although this odd-over-even predominance of n-alkanes is a good indicator of terrestrial contributions, Peters et al. (2005) suggested that a better evaluation of the potential contribution of land plants to the bulk organic matter can be achieved with the Carbon Preference Index (CPI) ratio, which is determined through the following equation:

$$\text{CPI} = 1/2 * (25 + 27 + 29 + 31 + 33) / (24 + 26 + 28 + 30 + 32) + 1/2 * (25 + 27 + 29 + 31 + 33) / (26 + 28 + 30 + 32 + 34)$$

The numbers in the equation represent the number of carbons in an n-alkane molecule. CPI values for the Site-A and the Core-B samples range from 1.24 to 1.92 and from 1.6 to 2.47, respectively (Figs. 8 and 9). While CPI values of the Site-A samples increase with depth (Fig. 9), those of the Core-B samples show no trend and they fall within a narrow range (1.7–2.1), with the exception of the values at 470 m (Fig. 8). These obtained CPI values are lower than those commonly observed for extant vascular plants (Van Dongen et al., 2006), which are commonly >3, but they do suggest significant contributions of organic matter derived from these higher plants, since CPI values greater than 1 correspond to a predominantly land-plant input (e.g., Ficken et al., 2000; Schefuß et al., 2003; Muri et al., 2004; Peters et al., 2005; Van Dongen, 2006). Although both n-alkane distribution and CPI values suggest the predominance of vascular plant-derived organic matter, the presence of short chain lipids in the saturated fraction in significant abundances (~80% in average, Figs. 6 and 7) suggests other type of contributions different than those of

terrestrial land plants. Short-chain lipids are commonly associated with the input of organic matter derived from freshwater photosynthetic algae and/or macrophytes (submerged/floating plants) (Cranwell et al., 1987; Mello and Maxwell, 1990; Bechtel et al., 2003; Muri et al., 2004; Van Dongen et al., 2006). Because some aerobic bacteria decompose organic matter when anoxic conditions are not rapidly reached, short-chain lipids could also come from such organisms (e.g., Cranwell et al., 1987; Bechtel et al., 2003), and their contribution to the studied sediments cannot be ruled out.

Despite the potential influence of lacustrine algae and/or bacterial organic matter, the odd-over-even predominance showed by the CPI index shows that, within the high molecular weight n-alkanes, land-plant-derived organic matter contributed significantly to the bulk of the straight-chain compounds. The compounds nC₂₅, nC₂₇, nC₂₉, and nC₃₁ are the dominant compounds, rather than even number long-chain n-alkanes, which are synthesized by bacteria and marine organisms (Tissot and Welte, 1984; Peters et al., 2005).

Because of the abundance of short-chain lipids and their possible origin (freshwater photosynthetic organisms), the terrestrial/freshwater plants (P_{aq}) ratio developed by Ficken et al. (2000) can be used to assess the source of most of the long-chain lipids preserved in the studied sediments. The P_{aq} ratio is defined as the ratio between the abundance of mid-chain n-alkanes (nC₂₃, nC₂₅) produced by submerged/floating freshwater plants (macrophytes) over the amount of long-chain n-alkanes (nC₂₇, nC₂₉, nC₃₁) produced by terrestrial plants:

$$P_{aq} = (23 + 25) / (27 + 29 + 31)$$

P_{aq} values <0.4 suggest a predominant terrestrial input, values >0.75 reflect a primary submerged/floating plants contribution, and values between 0.4 and 0.75 reflect a mixture. The overall decreasing trend in P_{aq} values towards shallower (younger) depths indicates a transition towards more terrestrial conditions in younger samples (Figs. 8 and 9). Core-B samples display lower values relative to those from the Site-A 1 samples, suggesting a higher input of terrestrial

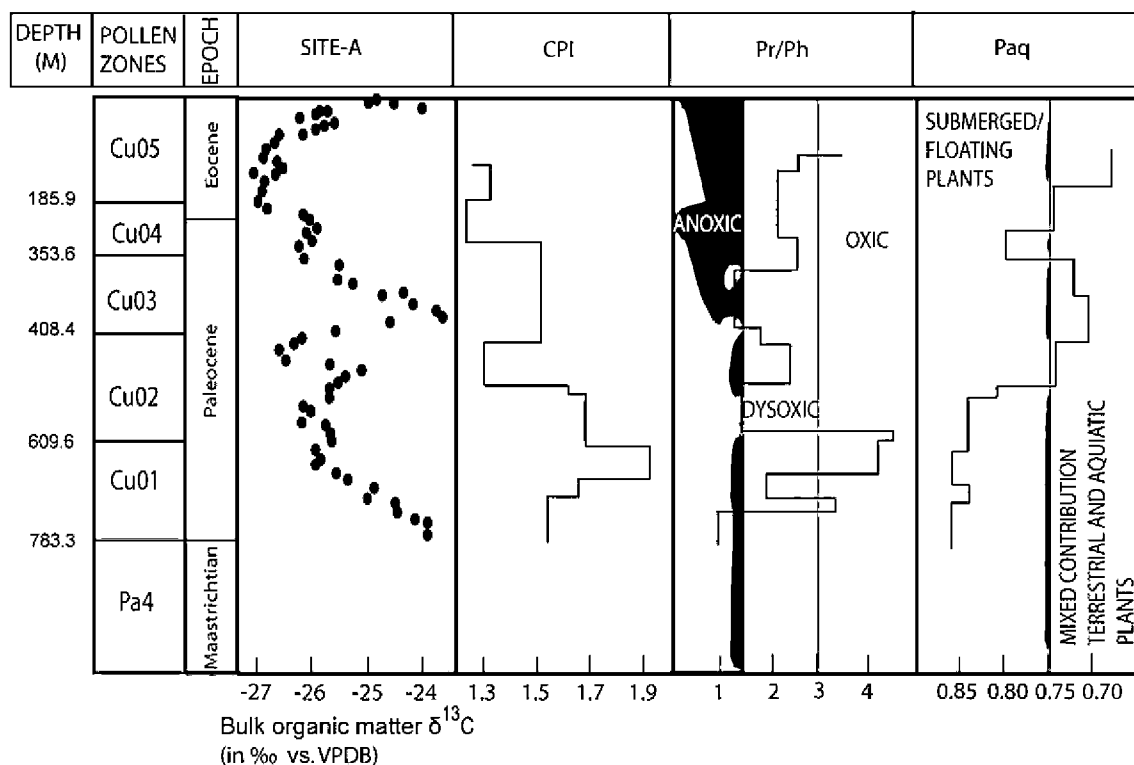


Fig. 9. Stratigraphic variability of the Carbon Preference Index (CPI), pristane/phytane (Pr/Ph) ratio, aquatic/terrestrial plants (P_{aq}) ratio, and smoothed carbon isotopic composition ($\delta^{13}\text{C}$) in the Site-A well.

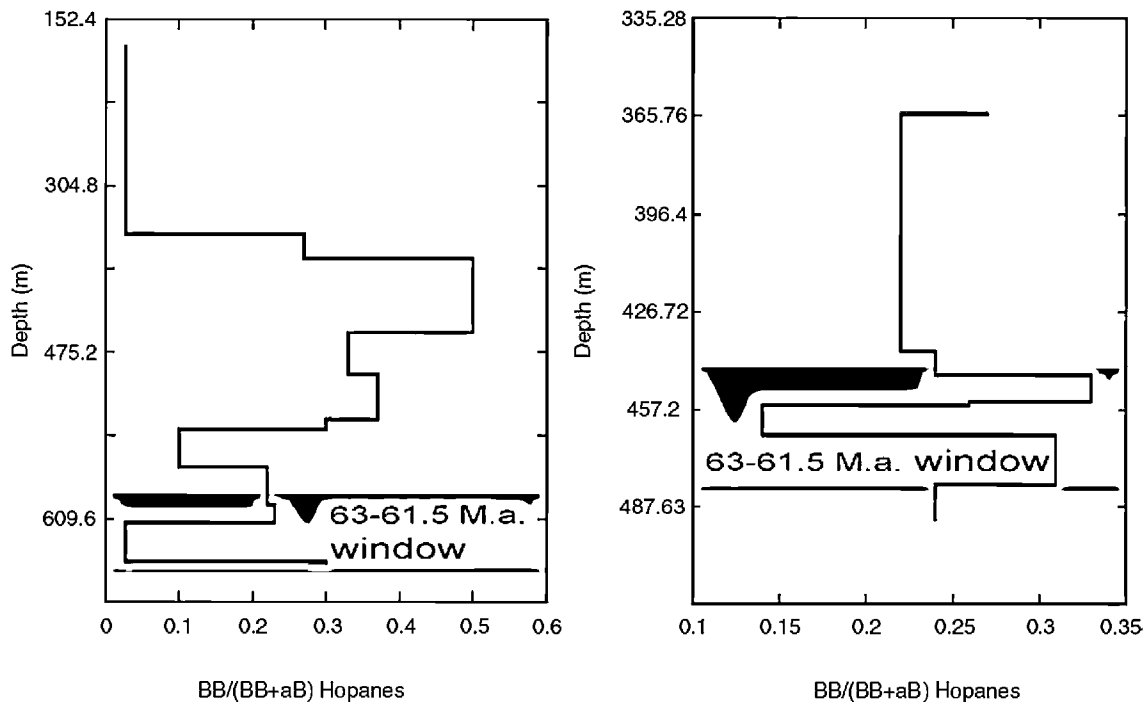


Fig. 10. Distribution of $\beta\beta/(\beta\beta + \alpha\beta)$ hopanes ratios in the Site-A (left graph) and Care-B (right graph) sections. The gray stripe is used here to highlight the behavior of the ratio during the same time span in both sections.

plants to the bulk organic matter into the Cesar–Rancheria basin or the result of a poor preservation conditions (i.e., conditions not allowing plant-derived organic matter to be preserved in sediments) in the Catatumbo basin (Site-A). This index, thus, suggests a mixed contribution of terrestrial and freshwater plants.

Supporting the conclusion that higher plant-derived organic matter is present in the studied sediments, sesquiterpenoids were identified in the saturated fraction (Fig. 5). Bicyclic sesquiterpenoids have been identified in a variety of geological materials, from recent and ancient sediments to coals, oils, peats, ambers, and fossil resins (Otto et al., 1997; Otto and Simoneit, 2001; Bechtel et al., 2002, 2003; Tuo and Philp, 2005; Hauteville et al., 2006). Sesquiterpenoids are widely distributed among vascular plants, including both angiosperms and gymnosperms (Otto and Simoneit, 2001). The exception is cadalene, which is a compound that appears to be related to gymnosperm-derived material (Otto et al., 1997; Bechtel et al., 2003). Although cadalene has been recognized as a major component of resins in several conifer (gymnosperm) species (Philp, 1985; Otto et al., 1997), it has also been reported to result from the degradation of resins produced by some angiosperm species (Otto et al., 1997).

Both cadalene and the C_{16} sesquiterpane were identified in the studied samples (Tp_1 and Tp_2 , Fig. 5), suggesting the contribution of gymnosperm-derived organic matter to the studied sediments. In addition to the possible contribution of gymnosperms, the following angiosperm-associated triterpenoids were found in the saturated fraction: lupane- (L_2) and normoretane-type (L_1) compounds. These two compounds have been found in leaf, wood, root, and bark tissues of these plants (Sukh, 1989; Bechtel et al., 2003). The presence of these compounds in the studied sediments, coupled with the presence of sesquiterpenoids, supports the CPI data, suggesting that vascular plants were an important source of the organic matter in the Site-A and Core-B sediments.

5.2. Preservation of the organic matter

Although CPI values reflect a slightly dominant contribution from terrestrial plants to the bulk organic matter, the predominance of

short-chain over long-chain n-alkanes could also result from a poor preservation of the heavier compounds. Redox conditions govern to a large extent the preservation potential of organic matter, with oxic conditions leading to poor preservation. Because of its sensitivity to redox conditions, the Pr/Ph ratio can be used to evaluate the effect of oxidity during the accumulation of the studied samples (Didyk et al., 1978; Bechtel et al., 2003).

Variations in the Pr/Ph ratios for the studied samples (Figs. 8 and 9) suggest the existence of two different redox regimes governing the depositional settings of the two basins (Catatumbo basin for Site-A and Cesar–Rancheria basin for Core-B). Core-B samples, covering the time

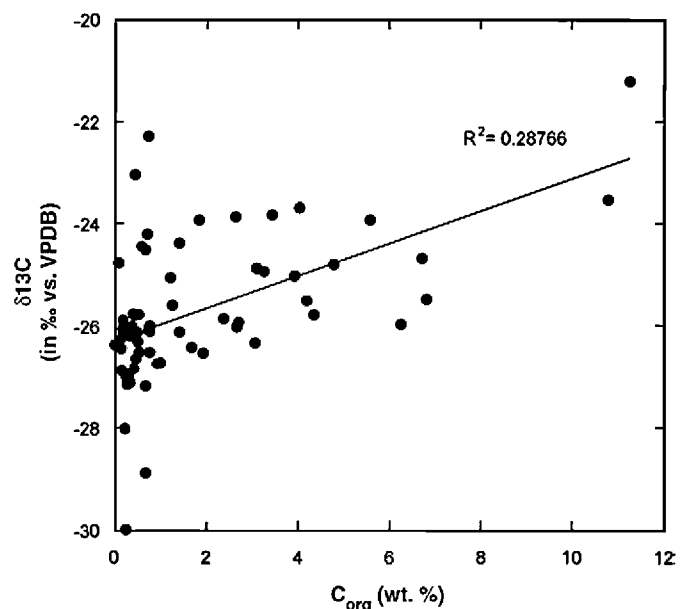


Fig. 11. Cross correlation of non-smoothed $\delta^{13}C_{TOM}$ values vs. composite C_{org} abundances in the Site-A and Core-B samples. The relationship is significant ($p < 0.0001$).

interval from ~66 to 57 Ma, show Pr/Ph values indicative of a change from anoxic (below 450 m) to dysoxic (450–350 m) and possibly oxic conditions (above 350 m). Site-A Pr/Ph values suggest that the organic matter in those sediments was deposited under dysoxic to oxic conditions between 450 and 600 m (Catatumbo Formation), changing to anoxic/dysoxic conditions between 450 and 300 m (Barco Formation), and shifting towards more oxic conditions at depths above 300 m of the section (Cuervos Formation).

This increase in oxic conditions leads to the degradation of less resistant compounds by microorganisms, which can be evaluated through the compounds that they produce (Peters et al., 2005). Hopanes (H1–H8, Figs. 5 and 7) are important constituents of the saturated fraction in the

studied samples, and these compounds are associated with microbial contributions to the bulk organic matter (Peters et al., 2005). For that reason, hopane abundances can be used to estimate the intensity of biomass degradation by using the ratio $\beta\beta/(\beta\beta + \alpha\beta)$ hopanes (Fig. 10) (MacKenzie et al., 1981; Bechtel et al., 2003; Van Dongen et al., 2006).

Commonly, low $\beta\beta/(\beta\beta + \alpha\beta)$ values (below 0.5) are indicators of moderate to high degradation of organic matter, because $\alpha\beta$ hopanes are more kinetically stable as diagenesis degrades sedimentary organic matter. Fig. 10 shows that Site-A and Core-B samples display parallel trends, which suggest that, despite the differences in preservation and contribution from terrestrial sources, the organic matter at both sites experienced similar degradation patterns.

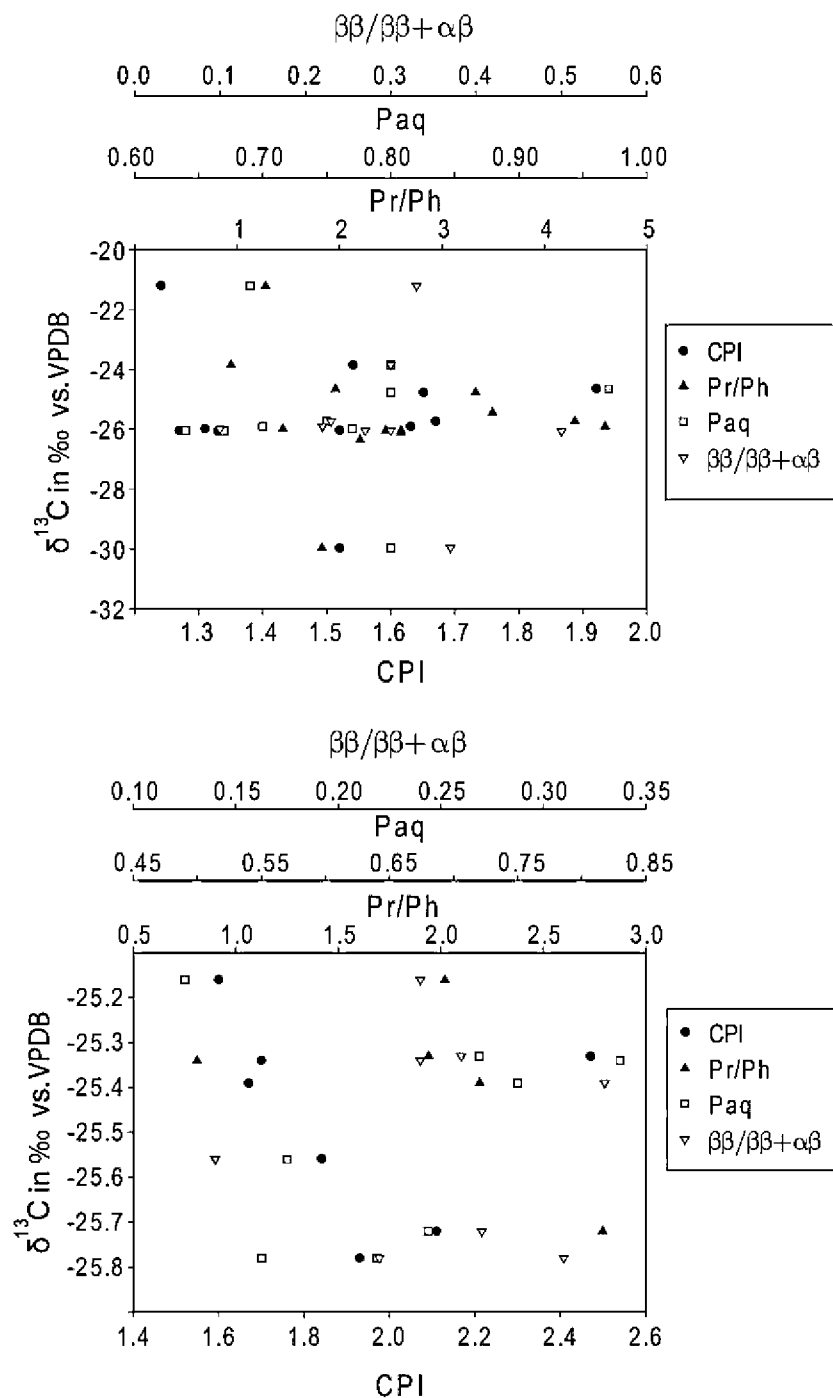


Fig. 12. Cross correlation of non-smoothed $\delta^{13}\text{C}_{\text{TOM}}$ vs. Pr/Ph, $\beta\beta/(\beta\beta + \alpha\beta)$, CPI, and P_{aq} values for the studied sections. Site-A (upper panel) relationships for $\delta^{13}\text{C}_{\text{TOM}}$ vs. Pr/Ph, $\beta\beta/(\beta\beta + \alpha\beta)$, CPI, and P_{aq} are not significant ($p < 0.87, 0.7446, 0.81,$ and $0.77,$ respectively). Core-B (lower panel) relationships for $\delta^{13}\text{C}_{\text{TOM}}$ vs. Pr/Ph, $\beta\beta/(\beta\beta + \alpha\beta)$, CPI, and P_{aq} are not significant ($p < 0.96, 0.9762, 0.54,$ and $0.076,$ respectively).

5.3. Evaluation of $\delta^{13}\text{C}_{\text{TOM}}$ values

The CPI values and the sesquiterpenoid and lupanoid abundances confirm the assumption of a predominant terrestrial origin for the bulk organic matter in the studied sediments, which is also supported by the pollen data. However, the predominant dysoxic–oxic conditions during deposition (as determined from the Pr/Ph values) and the significant levels of biomass degradation during diagenesis (as interpreted from $\beta\beta/(\beta\beta + \alpha\beta)$ values) could imply that the measured $\delta^{13}\text{C}_{\text{TOM}}$ values are different than the original $\delta^{13}\text{C}_{\text{plant}}$ values. To evaluate this potential effect, $\delta^{13}\text{C}_{\text{TOM}}$ values were plotted against our diagenetic proxies (i.e., Pr/Ph, C_{org} , and $\beta\beta/(\beta\beta + \alpha\beta)$). In addition, $\delta^{13}\text{C}_{\text{TOM}}$ values were also plotted against CPI and P_{aq} to evaluate the possible influence of the type of organic matter on the observed trend in $\delta^{13}\text{C}_{\text{TOM}}$ values.

No significant correlation exists between each of the parameters analyzed and $\delta^{13}\text{C}_{\text{TOM}}$ values (Figs. 11 and 12), indicating that neither depositional environment nor the degree of biomass alteration during diagenesis has significantly altered the measured $\delta^{13}\text{C}_{\text{TOM}}$ values. Consequently, considering that similar results were obtained from the organic matter of two different basins, this study indicates that the measured $\delta^{13}\text{C}_{\text{TOM}}$ values could be used for chronostratigraphic purposes, since they are possibly close to those of the ancient plants. The higher CPI could account for differences in the amount of land-plant contribution to the preserved organic matter, which might be the cause for the noise in the Core-B samples.

Although our proxies indicate that the secular shifts in $\delta^{13}\text{C}_{\text{TOM}}$ values recorded in the present study are probably related to changes in original $\delta^{13}\text{C}_{\text{plant}}$ values and not produced by diagenesis or varying contributions from different organic matter sources, some studies (e.g., Hesselbo et al., 2003; Gröcke et al., 2006; Hesselbo et al., 2007) have reported an offset between $\delta^{13}\text{C}_{\text{TOM}}$ and $\delta^{13}\text{C}$ values derived from preserved plant components (e.g., Hesselbo et al., 2003; Gröcke et al., 2006). Consequently, it is important to assess the possible effect of diagenesis (as presented here) to ensure that a $\delta^{13}\text{C}_{\text{TOM}}$ record is a useful chronostratigraphic and paleoclimatic tool. The shifts in isotopic values that occurred in the Colombian tropics (Site-A and Core-B sections) between 65 and 50 Ma reflect the shifts in isotopic values recorded in marine deposits (Zachos et al., 2001), thus confirming a connection between the oceans and terrestrial biomass via the atmosphere. This connectivity implies that long-term changes in marine $\delta^{13}\text{C}_{\text{carbonate}}$ values should cause similar changes in $\delta^{13}\text{C}_{\text{plant}}$ values, which are ultimately reflected in $\delta^{13}\text{C}_{\text{TOM}}$ values.

Fig. 4 shows that, despite minor variations recorded in both marine and terrestrial $\delta^{13}\text{C}$ values, there is a consistent difference between $\delta^{13}\text{C}_{\text{TOM}}$ and $\delta^{13}\text{C}_{\text{carbonate}}$ values. This difference of about -27% is also observed in modern settings (Farquhar et al., 1989; Strauss and Peters-Kottig, 2003). However, Beerling and Royer (2002) and Strauss and Peters-Kottig (2003) suggest that this difference was probably not consistent in the geologic past as a result of different oxygen/carbon dioxide ratios in the atmosphere, which were more significant in the Paleozoic (360–240 Ma). Although this study does not address this issue since oxygen/carbon dioxide ratios between 50 and 65 Ma were not significantly different relative to today's conditions (see fig. 9 in Strauss and Peters-Kottig, 2003), future research should focus on evaluating this potential effect.

6. Conclusions

The secular variations in the carbon cycle that occurred between 65 and 50 Ma, as inferred from marine $\delta^{13}\text{C}_{\text{carbonate}}$ values (Zachos et al., 2001), have now also been recognized in the $\delta^{13}\text{C}_{\text{TOM}}$ values of terrestrial sequences accumulated in the South American tropics for the same time interval. The different biomarker ratios utilized in the present study (CPI, Pr/Ph, P_{aq} , and $\beta\beta/(\beta\beta + \alpha\beta)$ hopanes) show no significant correlation with $\delta^{13}\text{C}_{\text{TOM}}$ values, thus indicating that the secular changes in $\delta^{13}\text{C}_{\text{TOM}}$ values were not caused by

changes in depositional environment, oxygen levels, type of land-plant inputs, or degree of biomass alteration. The similarity in isotopic trends reinforces the assumption of an isotopic connection between the oceans and the terrestrial biomass via the atmosphere, thus making $\delta^{13}\text{C}_{\text{TOM}}$ values a potentially reliable tool for paleoclimatic interpretations and stratigraphic correlations between marine and terrestrial sequences, only if these values reflect those of pristine plant materials, which can be evaluated using biomarkers as demonstrated in this study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.palaeo.2009.03.015.

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