Carbon-isotope stratigraphy from terrestrial organic matter through the Monterey event, Miocene, New Jersey margin (IODP Expedition 313)

Lin Hao Fang, Christian J. Bjerrum, Stephen P. Hesselbo, Ulrich Kotthoff, Francine M.G. McCarthy, Baoqi Huang, and Peter W. Ditchfield

1Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK
2Nordic Centre for Earth Evolution (NordCEE) and Department of Geosciences and Natural Resource Management, University of Copenhagen, Øster Voldgade 10, DK-1350, Copenhagen K, Denmark
3Institut für Geologie, Universität Hamburg, Bundesstrasse 55, 20146 Hamburg, Germany
4Department of Earth Sciences, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario L2S 3A1, Canada
5School of Earth and Space Science, Peking University, 5 Yiheyuan Road, Beijing 100871, People’s Republic of China
6Research Laboratory for Archaeology and History of Art (RLAHA), University of Oxford, South Parks Road, Oxford OX1 3QY, UK

ABSTRACT

The stratigraphic utility of carbon-isotope values from terrestrial organic matter is explored for Miocene siliciclastic sediments of the shallow shelf, New Jersey margin, USA (Integrated Ocean Drilling Program [IODP] Expedition 313). These shallow marine strata, rich in terrestrial organic matter, provide a record of deposition equivalent to the Monterey event, a prolonged interval of time characterized by relatively positive carbon-isotope values recorded from foraminiferal carbonate in numerous oceanic settings. Coherent stratigraphic trends and short-term isotopic excursions are observed consistently in palynological preparation residues, concentrated woody phytoclasts, and individually picked woody phytoclasts obtained from the New Jersey sediments. A bulk organic matter curve shows somewhat different stratigraphic trends but, when corrected for mixing of marine-terrestrial components on the basis of measured C/N ratios, a high degree of conformity with the woody phytoclast record is observed. However, assuming that the correlations based on strontium-isotope values and biostratigraphy are correct, the carbon-isotope record from the New Jersey margin contrasts with that previously documented from oceanic settings (i.e., lack of positive excursion of carbon-isotope values in terrestrial organic matter through the Langhian Stage). Factors that may potentially bias local terrestrial carbon-isotope records include reworking from older deposits, degradation and diagenesis, as well as environmental factors affecting vegetation in the sediment source areas. These possible factors are assessed on the basis of pyrolysis data, scanning electron microscope observations, and comparison to palynological indices of environmental change. Some evidence is found for localized degradation and/or reworking of older woody phytoclasts, but where such processes have occurred they do not readily explain the observed carbon-isotope values. It is concluded that the overall carbon-isotope signature for the exchangeable carbon reservoir is distorted, to the extent that the Monterey event excursion is not easily identifiable. The most likely explanation is that phytoclast reworking has indeed occurred in clinoform toe-of-slope facies, but the reason for the resulting relatively heavy carbon-isotope values in the Burdigalian remains obscure.

INTRODUCTION

Correlation of sedimentary successions by carbon-isotope values of organic and carbonate components has become a routine method in stratigraphy (e.g., Scholle and Arthur, 1980; Jenkyns et al., 2002; Jarvis et al., 2006). This method works on the basis that the measured carbon-isotope signature within a succession is representative of changes in the isotopic signature of the surface Earth carbon reservoirs through time. In particular, distinctive trends or excursions can be matched between sections, providing correlative time lines. In addition to simple analysis of bulk sedimentary organic matter or bulk carbonate, many studies have focused on isolated fractions that are derived from individual materials making up the sedimentary carbon in order to minimize the overprinting or distorting effects of processes such as mixing of different sedimentary components with their own distinct isotopic signatures or diagenetic changes and additions (e.g., Veizer et al., 1999, focusing on brachiopods and belemnites). It is particularly useful that the carbon-isotope composition of terrestrial organic matter tracks that of atmospheric carbon dioxide (Arens et al., 2000; Jahren et al., 2008), and this commonly results in terrestrial carbon-isotope signatures identical to those from coeval marine materials, potentially allowing correlation between marine and non-marine paleoenvironments. Such correlations allow consideration of carbon-cycle-related environmental changes taking place on land at the same time as in the oceans (Koch et al., 1992; Hasegawa, 1997; Gröcke et al., 1999; Gröcke, 2002; Hesselbo et al., 2000, 2007; Hasegawa et al., 2003; Hesselbo and Pienkowski, 2011; Bacon et al., 2011). Although the technique of terrestrial carbon-isotope stratigraphy has shown considerable promise, there are a number of potential pitfalls. One issue is the possibility that a significant proportion of the sedimentary organic matter is reworked from older deposits, a problem one might predict to be acute where sediments are resuspended from continental shelves and redeposited further down the margin during sea-level lowstands (e.g., McCarthy and Mudie, 1998). Additional complications arise because isotope discrimination during formation of terrestrial organic matter seems...
to be a function of temperature and soil moisture independent of $p$CO$_2$, whereas isotope fractionation during formation of marine organic matter is a function of $p$CO$_2$ for some photosynthetic species (e.g., Jahren et al., 2008; Bowen et al., 2004). In the present study we explore these and other problems with respect to sedimentary organic matter from Miocene sequences on the New Jersey margin (USA) drilled for Integrated Ocean Drilling Program (IODP) Expedition 313 (Fig. 1).

Carbon-isotope signatures for the Neogene exchangeable carbon reservoirs are well known based on analysis of multiple oceanic carbonate records (Zachos et al., 2001). For the Miocene in particular, the Monterey event and its carbon-isotope signature is of some prominence (Fig. 2; Vincent and Berger, 1985; Woodruff and Savin, 1985; Flower and Kennet, 1994; Zachos et al., 2001; Abels et al., 2005; Holbourn et al., 2005, 2007; Diester-Haass et al., 2009). This isotopic and paleoenvironmental event was originally defined in the tropical Indian Ocean at Deep Sea Drilling Project Site 216 by Vincent and Berger (1985), and the positive carbon-isotope excursion ($\geq +1.5\%$) was documented for the benthic inorganic carbon reservoir. This event is thought to coincide with a time of extensive burial of organic matter (Woodruff and Savin, 1991; Vincent and Berger, 1985). Combined benthic and planktonic foraminiferal records of the Monterey event have also been published by Cheng et al. (2004), and these data provide substantial evidence of a whole ocean-atmosphere carbon cycle perturbation (Fig. 2).

Studies at high resolution from many pelagic and hemipelagic locations have shown the long-term carbon-isotope excursion of the Monterey event to comprise a number of separate short, $\sim 1\%$ positive excursions, superimposed on the overall positive carbon-isotope values (Woodruff and Savin, 1985, 1991; Fig. 2). Integration with astronomical time scales has resulted in the recognition of nine of these short-term excursions, each identified as having a long-eccentricity 400 k.y. periodicity, and allowing by fit the La2001 astronomical model a refined dating for the whole Monterey event from 16.9 to 13.5 Ma (Holbourn et al., 2007), i.e., the latest Burdigalian, Langhian, and very earliest Serravallian. (We note that the definition of the event changes by author, so Holbourn et al. [2007] do not include strata at the top of the event that were included by Woodruff and Savin [1991].)

The Miocene of the New Jersey margin makes for a particularly useful case study because the sedimentology, stratigraphy, and paleontology of this marginal setting is now well characterized for the Cenozoic, including the interval that spans the Monterey event (Browning et al., 2006, 2008, 2013; Monteverde et al., 2008; Mountain et al., 2010; Miller et al., 2013; J.-N. Proust, 2013, personal commun.). In the present study we present carbon-isotope curves generated by a variety of substrates, comprising bulk organic matter, bulk concentrated phytoclasts, hand-picked phytoclasts, and planktonic foraminifiers, and we compare these data with newly generated pyrolysis data sets of organic matter type, atomic C/N ratios, and relevant palynological analyses. Our overall aim is to improve understanding of the strengths and weaknesses of using terrestrial materials as the basis for carbon-isotope stratigraphic correlation. In addition, our analysis sheds further light on the development of Miocene depositional sequences on the New Jersey margin.

**METHODS**

Phytoclasts are components of a palynological preparation residue made up of recognizable fragments of plant cuticles and woody tissue (Tyson, 1995; Hasegawa et al., 2003), and herein we have studied specifically the woody tissue component of the phytoclast assemblages.

**Palynological Preparation and Analysis**

Standard palynological techniques were used to extract organic matter from sediment samples. Preparation for the majority of samples was carried out at the National Oceanographic Centre, University of Southampton, UK (from 260 to 760 meters below sea floor [mbsf] at Site 29 and from 200 to 450 mbsf at Site 28). A subordinate sample set was prepared at Brock University, Canada (from 600 to 760 mbsf at Site 29, from 400 to 660 mbsf at Site 28, and from 180 to 300 mbsf at Site 27).

At Southampton, a 5 g sample was placed in a plastic beaker and cold hydrochloric acid (30%) added to remove carbonate. After decanting, the sample was washed with deionized water until the pH approached 7. Hydrofluoride acid (60%) was then added with regular stirring until the sample was wholly broken down, and then the sample was decant-washed with deionized water until the pH approached 7 again. Subsequently, the residue was sieved at 15 µm, and the coarse fraction separated into a glass beaker. With most of the water removed from the sample, hydrochloric acid (30%) was added into the beaker and heated until it just boiled (to take neoformed fluorides into solution). The boiled sample in the beaker was rapidly diluted in 500 ml of water and was sieved at 15 µm; the remaining organic matter was put into vial after washing through with deionized water. For each sample one standard slide was made up in Elvacite 2044.

At Brock University, 5 cm$^3$ of sample (measured by liquid displacement) was placed in a Nalgene test tube and a very weak (0.02%) Calgon solution was added. Samples were then placed in a warm (not boiling) water bath until clays were disaggregated, then they were washed in distilled water and centrifuged at 3000 rpm for 3 min. Samples were then sieved using distilled water through a 15 µm Nitex mesh to remove clays and subsequently returned to the test tubes. Weak hydrochloric acid (10%) was then added together with a Lycopodium tablet (Stockmarr, 1971) and samples were again placed in a warm water bath until reaction stopped to remove carbonates. Samples were then washed in distilled water and centrifuged at 3000 rpm for 3 min, and hydrofluoric acid (60%) was added and test tubes returned to the warm water bath. Samples were stirred regularly over a period of approximately one hour, decanted, and rinsed with distilled water until neutral. The residue was again sieved at 15 µm, and the residue was mounted on a glass slide using glycerine jelly.

**Separation and Concentration of Palynological Particulates**

In order to concentrate the terrestrial organic fraction (mostly phytoclasts) from palynological particulates, a further separation procedure was carried out. The organic residues produced by standard palynological preparation techniques were suspended in alcohol, and the microfossils (e.g., dinoflagellates, acritarchs, spores, and pollen) absorbed a sufficient amount of the alcohol to reduce their average density relative to that of phytoclasts (method of Hansen and Gudmundsson, 1979).

Deionized water was placed into the separating funnel and then 5 ml of ethanol onto the water surface. A pipette was used to take and transfer the organic sample into the funnel. After leaving to stand for 10–15 min (depending on the size of the particles), the samples were divided into two parts as “top” and “bottom.” The “bottom” part was collected into 10 ml Teflon tubes, while the “top” part was collected into the 50 ml centrifuge tubes and reclaimed by centrifuge; finally, the top and bottom parts were dried out in a 60 °C oven for 48 h.

The technique of separation takes advantage of the difference in settling rate between the phytoclasts and the microfossils. After this concentration, the marine fraction (dinoflagellates, zooplankton) and the terrestrial pollen and spores, which tend to be hollow and very small, are largely excluded, leaving the phytoclasts. The concentrated phytoclasts were checked by light microscopy and the prevalence...
Figure 1. (A) Location map of the study area, New Jersey margin, USA. ODP—Ocean Drilling Program; DSDP—Deep Sea Drilling Project; AMCOR—Atlantic Margin Coring Program. Contours represent bathymetry in meters. (B) Depth-converted seismic stratigraphic framework and Integrated Ocean Drilling Program Expedition 313 boreholes. (Modified from Mountain et al., 2010.) cdp—common depth point.
of woody phytoclasts confirmed. Some of the larger cuticle fragments were also sedimented with the woody phytoclasts but do not dominate the assemblages.

Carbon-Isotope Analysis and C/N Ratios

**Organic Matter Carbon**

Bulk organic C/N ratios and stable carbon isotope ratios were measured in the Stable Isotope Laboratory at the Department of Geosciences and Natural Resource Management, University of Copenhagen. Freeze-dried samples were crushed with an agate mortar and pestle to <125 μm. Carbonate was removed by treating 1.2 g of sample with 30 ml 1% HCl, and heating on a hot plate for 1 h. The acid-treated sample was then transferred to a centrifuge tube, and washed with Milli-Q water and centrifuged. The sample was further washed until of neutral pH, then freeze-dried and subsequently equilibrated to room temperature in a desiccator. The equivalent of ~0.07 mg of pure carbon from the acid-washed sample was weighed into a tin capsule. Stable carbon-isotope composition and C/N ratio was measured on a EuroVector elemental analyzer coupled to an Isoprime dual-inlet stable isotope mass spectrometer. Every tenth sample was run in duplicate and internal standards were interspersed throughout the batch of samples. Samples were single-point calibrated toward a calibration curve made of 10 different weights of the internal laboratory standard, thus bracketing the pure carbon weights of the samples. The internal standard (AK, of pure active carbon [-25.65‰ V-PDB] homogenized in a mortar with clay-sized pure quartz) has been calibrated to standard USGS24 (-15.99‰ V-PDB), and tested by repeated random sampling of the homogenized mixture. Long-term reproducibility is ±0.1‰.

**Phytoclasts.** Isotope analyses of both bulk concentrated phytoclasts and hand-picked phytoclasts were carried out for this study. Hand-picked phytoclasts were manually separated from concentrated phytoclasts by using a needle under a reflected-light microscope, and in this case only definite woody material was collected and accumulated to around 20–40 μg for each sample (quantities of hand-picked phytoclasts were too small to yield valid C/N ratios). For bulk concentrated woody phytoclasts, dried sample weights ranged from 0.2 mg to 2 mg, depending on recovered quantity.

Phytoclast samples for analysis were dried, weighed, and sealed in tin capsules. These samples were run on a Sercon Europa EA-GSL sample converter connected to a Sercon 20-22 stable isotope ratio mass spectrometer running in continuous flow mode with a helium carrier gas with a flow rate of 70 ml/min. Carbon-isotope ratios were measured against an internal alanine standard (δ¹³C_alanine = -26.9‰ ± 0.2‰ V-PDB [Vienna Peedee belemnite]) using a single-point calibration at the Research Laboratory for Archaeology and History of Art (RLAHA), University of Oxford, UK. The in-house RLAHA alanine standard is checked weekly against USGS40, USGS41, and IAEA-CH-6 international reference materials. Thus the reported results are traceable back to the V-PDB international standard.

**Carbonate Carbon**

Carbon-isotope data were generated from planktonic foraminifers. Two sample sets were combined for the present study. One sample...
set was analyzed at Oxford and comprised a subsample of planktonic foraminifera used for strontium-isotope analyses (Browning et al., 2013) originally picked by Mimi Katz (2011, personal commun.). A second set was picked at Peking University and analyzed at the University of California—Santa Cruz (UCSC).

The foraminiferal data set comprises two parts, single species Globigerina praehalo-oides (surface dwelling, 43 samples, analyzed at UCSC) and, due to lack of sufficient numbers of specimens, species mixtures analyzed at Oxford comprising some or all of the following taxa: Cataprydax paravulus, Dento- globigerinata altispira, Globigerinata glutinata, Globorotaloides suteri, Globigerina woodi, Globoraphidina baroensensis, Globoraphidina langhiana, Globorotalia (Menardella) archemonardii, Globorotalia (Neogloboquadrina) continua, Globorotalia (Jenkinsella) mayeri, Globorotalia (Globigerinella) obesa, Globorotalia (Fohsella) peripheroronda, Globorotalia (Globoconella) praesitula, Globigerinoides obliquus, Globi- gerinoides saccularis, Globigerinoides sicanus, Globigerinoides subquadaratus, Globigerinoides triloba, Sphaeroindellosis disjuncta (16 samples). At Oxford, species mixtures were gently crushed between small plastic plates to open the foraminifer chambers. A drop of methanol was added and each plate cleaned by ultrasonification for 30 min. Methanol was removed with a 2 ml syringe under a reflected-light microscope to ensure minimal inclusion of clay. Finally, the cleaned foraminifers were transferred by brush into vials and dried in an oven at 60 °C. The typical sample weights were ~25–40 µg. Measurement was carried out on a Thermo Scientific MAT 253 stable isotope ratio mass spectrometer (online-coupled to a KIEL IV carbonate device) at the Department of Earth Sciences, University of Oxford. An overall external precision of 0.04‰ for δ13C is reached for samples greater than 20 µg. All carbon-isotope ratios are expressed in per mil (‰), the internationally accepted standard notation, V-PDB.

Pyrolysis Parameters

Total organic carbon (TOC, wt%) of each bulk organic matter sample was analyzed by decarboxylating the sample with HCl, where- after 50 mg was combusted in a LECO CS-200 induction furnace. The hydrogen index of each sample was measured by pyrolyzing 100 mg of decarboxylated sample in a Humble Instruments and Services source rock analyzer (SRA) system in the source rock laboratory at the Geological Survey of Denmark and Greenland. The SRA has been evaluated to give S1, S2, and Tmax data comparable to the commonly used Rock-Eval instrument (Espitalié et al., 1977, 1985), where S1 is measure of free hydrocarbon in the sample (in mg HC/g rock), S2 is a measure of organic compounds generated by thermally cracking kerogen (also in mg HC/g rock), and Tmax is a Rock-Eval pyrolysis thermal maturity parameter based on the temperature at which the maximum amount of pyrolyzate (S2) is generated from the kerogen in a rock sample, and HC = hydrocarbon. Source rock screening data were quality checked and questionable data with TOC contents <0.5 wt% and/or S2 pyrolysis yields <0.2 mg HC/g rock were omitted, as organically lean samples give unreliable HI values (Peters, 1986), where HI is Hydrogen Index, a Rock-Eval pyrolysis parameter defined as S2/TOC x 100, and measured in mg HC/g TOC.

RESULTS

Carbon-Isotope Records

Carbon-isotope values for Site 29 are presented in Figure 3. We focused our analyses at this site because of the three Expedition 313 sites, initial expedition results indicated that the succession at Site 29 provides the most complete and continuous sedimentary record over the interval of the Monterey event (Mountain et al., 2010; Browning et al., 2013).

Column A in Figure 3 shows data from bulk organic matter, column B from planktonic foraminiferal carbonate, column C from phytoclast concentrates, and column D from individually picked phytoclasts. The following points for these data are most noteworthy:

1. The bulk organic matter data overall decrease from relatively heavy carbon-isotope values (~24‰ to ~23‰) between 680 and 610 mbsf (Burdigalian) to lighter values upsection. From 610 to 450 mbsf (Langhian to early Serravallian), carbon-isotope values are intermediate (~24‰ to ~25‰) with small excursions within this range, each defined by several data points. Relatively light values (~26‰ to ~25‰) occur above 450 mbsf (Serravallian). The majority of values are in the range ~23‰ to ~26‰. On average the bulk organic matter is enriched 0.5‰ relative to pyoclast measurements.

2. Data from planktonic foraminifers are quite variable and most range from 0‰ to 2‰. A few values exceed 2‰. Disregarding individual anomalous data points, there is a very weak stratigraphic trend toward heavier carbon-isotope values upsection.

3. Data from the relatively low-resolution set of individually picked phytoclasts show good conformity with data from pyoclast concentrates (as do analyses of raw palynological residues). Data from pyoclast concentrates show coherent stratigraphic trends. From 750 to 730 mbsf (?Aquitanian to early Burdigalian), carbon-isotope values become progressively lighter upsection (from ~23.4‰ to ~26.5‰). Between 730 and 610 mbsf (Burdigalian), carbon-isotope values are relatively heavy (~22‰ to ~25‰).

Above 610 mbsf (Langhian to Serravallian), carbon-isotope values are intermediate (~24‰ to ~26‰) but also show coherent excursions within this approximate range. A notable positive excursion to ~22.5‰ occurs at 475 mbsf, in the earliest Serravallian, which is not present in raw bulk organic matter. There is overall more isotopic variability in the phytoclast record relative to the bulk organic matter, as the standard deviations are 0.94 for pyoclast data and 0.85 for bulk data. However, the overall trends are present in both records.

Correlation of Phytoclast Carbon-Isotope Curves between Expedition 313 Sites

In Figure 4 we show a correlation panel for all three Expedition 313 sites, including the more limited pyoclast data for Sites 28 and 27. Correlation lines between sites are based on best estimates of depths of key seismic stratigraphic surfaces, which take into account all relevant geophysics, biostratigraphy, and strontium-isotope stratigraphy (Miller et al., 2013). Where data density is such that meaningful comparison is possible, the same values and trends are apparent at different sites. This is particularly the case for Sites 28 and 29 for the Langhian to Serravallian interval. Differences occur, as, for example, concerning the narrow positive excursion at 475 mbsf in Site 29, the data can be explained by unconformity in the up-dip, more proximal location, an interpretation fully supported by the seismic stratigraphy (J.-N. Proust, 2012, personal commun.).

Figure 5 shows the enlarged stratigraphic logs and carbon-isotope curves from 615 mbsf to 610 mbsf at Site 28 and from 745 mbsf to 725 mbsf at Site 29 and the correlation line of sequence boundary m5.7. The lithology dramatically changes across the sequence boundary. Below the boundary, lithologies are clay at Site 28 and Site 29; strata immediately above the sequence boundary are glauconite sands at both sites, and upwards turn to less glauconitic sands. Carbon-isotope curves from Site 28 and Site 29 show generally similar trends in this enlarged interval. Both rapidly change from light to heavy carbon-isotope values through the boundary. The values for the lightest points are about –28‰ at Site 27 and about –27‰ at Site 29. We conclude that the carbon-isotope signature of pyoclasts has value for correlation on at least the local scale of Expedition 313 sites.

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Figure 3. All carbon-isotope results for Site 29 set against a lithological log. (A) Bulk organic matter. (B) Planktonic foraminifers. (C) Concentrated phytoclasts and palynological residues. (D) Picked phytoclasts. Lithological log from Mountain et al. (2010), ages from Browning et al. (2013), and dinoflagellate cyst zonation from McCarthy et al. (2013). Refer to Figure 4 for key to lithology. mbsf—meters below sea floor; V-PDB—Vienna PeeDee belemnite.
Figure 4. Correlation panel and concentrated phytoclast carbon-isotope records for Sites 27, 28, and 29. Correlations and ages from Browning et al. (2013) and Miller et al. (2013). Dinoflagellate cyst zonation from McCarthy et al. (2013). Oligocene sequence boundaries marked with an asterisk (*) are not resolvable on seismic reflection profiles (Browning et al., 2013). Grain sizes are standard Udden-Wentworth scale. mbsf—meters below sea floor; V-PDB—Vienna Peedee belemnite.
Pyrolysis Data and C/N Ratios

For pyrolysis, 27 samples were analyzed from Site 27, 34 samples from Site 28, and 65 samples from Site 29. Pyrolysis data and C/N ratios show notable variation through the studied succession (Fig. 7).

Hydrogen Index, Tmax, TOC, and S2

Pyrolysis data are included in the Supplemental File1. Hydrogen index (HI) varies between 50 and 250 mg HC/g TOC (Fig. 6), indicating the sediment is dominated by a type III kerogen, with some levels up to gas/oil prone (Peters, 1986). Tmax of ~420 °C with only a single sample with Tmax of 450 °C (at 597.5 mbsf) indicate that organic matter is still immature (Petersen et al., 2011). A cross-plot of TOC and the S2 peak indicates that the majority of the samples are below good/fair source rock potential, but that some of the more clay-rich samples have good to excellent source rock potential because TOC > 2% and S2 > 6 mg HC/g rock (Peters, 1986; Petersen et al., 2011).

Stratigraphically, the HI is highly variable up to 595 mbsf, and progressively increases from 180 to 230 mg HC/g TOC up to 502 mbsf (Fig. 6). HI is variable (50–200 mg HC/g TOC) between 500 and 460 mbsf and then shows steady values (150–170 mg HC/g TOC) up to 364 mbsf. Low values (~50 mg HC/g TOC) occur between 364 and 340 mbsf, but HI recovers to 100 mg HC/g TOC between 340 and 333 mbsf.

Only a weak correlation is present between HI and bulk organic C/N ratios. Only few samples have HI <100 and have C/N ratios of ~20 overlapping with the general bulk organic C/N ratio. There is a tendency for high HI to be associated with enriched bulk δ¹³C values. A few samples plot outside the general sample field in a cross-plot of HI versus δ¹³C, these with HI <80 and heavy δ¹³C values (~24‰ to ~22.5‰) of both phytoclasts and bulk organic matter.

C/N Ratios of Bulk Organic Matter and Separated Phytoclasts

At Site 29, bulk organic matter C/N ratios (C/N₁bulk) vary between 15 and 30, clearly distinguished from the C/N ratios of separated phytoclasts, which vary between 35 and 50 (Fig. 6). (In the present study we have used only C/N ratios of sampling from processed in Southampton to reduce the possibility of introducing artifacts related to processing method.) Stratigraphically, C/N₁bulk ratios between 15 and 20 are related to coarse grain sizes (Fig. 6). However, C/N₁bulk ratios greater than 20 in some cases correspond to

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1Supplemental File. Excel file that contains the following datasets: carbon-isotope values of organic sedimentary components, carbon-isotope values of foraminifers; bulk rock pyrolysis parameters; and palynological assemblages. If you are viewing the PDF of this paper or reading it offline, please visit http://dx.doi.org/10.1130/GES00851.S1 or the full-text article on www.gsapubs.org to view the supplemental file.
Figure 6. Comparison of relevant organic matter parameters for Site 29 (65 samples). (A) Hydrogen index (HI). (B) C/N ratios of bulk organic carbon (black dots) and concentrated phytoclasts (blue squares). (C) Adjusted (vascular plant matter equivalent) bulk organic carbon $\delta^{13}$C (black dots), and concentrated phytoclast $\delta^{13}$C (blue squares). (D) Grain size expressed as percent clay content (from Browning et al., 2013). See Figure 4 for the key to the graphic log. HC—hydrocarbon; mbsf—meters below sea floor; TOC—total organic carbon; V-PDB—Vienna Peedee belemnite.
coarser-grained sediment and in other cases they do not. The C/N_{bulk} ratios are relatively low in the sandy Burdigalian, increasing to high values in the Langhian strata where the sediments are fine grained. The Langhian-Serravallian boundary strata have variable C/N_{bulk} ratios, while the remaining Serravallian is characterized by low to moderate C/N_{bulk} ratios.

**DISCUSSION**

If we accept the dates assigned to strata from 640 to 725 mbsf (Browning et al., 2013), then it appears that the Monterey carbon-isotope excursion, which is well established from diverse oceanic carbonate records, is not clearly developed in the organic-matter fractions analyzed from the New Jersey margin. The analyzed terrestrial organic matter components have relatively heavy values in strata assigned to the Burdigalian, and relatively light values in the Serravallian, somewhat contrary to expected trends of Monterey carbon-isotope excursion, especially with respect to the Burdigalian. In the following sections we explore potential explanations for this observation.

The δ^{13}C of Bulk Organic Matter Adjusted to Vascular Plant Debris Values

The δ^{13}C of bulk organic matter may be adjusted to represent the contemporaneous δ^{13}C of vascular plant debris (i.e., δ^{13}C_{vpc}, where “vpc” refers to “vascular plant, corrected”), a value that should in theory be very similar to the measured δ^{13}C of woody phytoclasts. A modest correlation is observed between phytoclast δ^{13}C_{phy} and δ^{13}C_{vpc} (slope = 0.8, r^2 = 0.5), suggesting that bulk organic matter is composed of a fraction of vascular plant debris (i.e., phytoclasts) (Fig. 7A). In a cross-plot of organic δ^{13}C and C/N there is a clear spatial separation between bulk organic matter and phytoclasts, a pattern mimicking that observed in modern deltalic/coastal-shelf sediments (Hedges et al., 1997; Fig. 7B). Waterborne transport of particles from the land to the ocean combined with local marine production results in a mixing line between the end members of terrestrial plant debris and marine organic matter (Hedges et al., 1997). From this mixing relation it is common to calculate the fraction of vascular plant debris or marine organic carbon in the sediment.

The observed C/N_{bulk} value between 20 and 30 suggests that between 60% and 80% of the organic matter is vascular plant debris. Further, using the mixing line concept, we adjust each sample δ^{13}C_{vpc} to a contemporaneous vascular plant debris δ^{13}C_{vpc} value using the measured δ^{13}C_{bulk} and C/N_{bulk}.

Isotope composition of end members based on modern-day organic matter cannot readily be applied to the Miocene. For example, Miocene marine organic matter has been reported with isotope composition of about −24‰ to −26‰, depending on location, relative to −22‰ today (Diester-Haass et al., 2009). However, we have no reason to suspect that C/N ratios of end members have changed. In calculating an estimated vascular plant debris isotope composition on a point-by-point basis from bulk organic matter, we first identify the slope, \( \alpha \), of the mixing line between end member mean compositions of vascular plant debris (\( \delta^{13}C_{vpc}, C/N_{vpc} \)) and bulk organic matter (\( \delta^{13}C_{bulk}, C/N_{bulk} \)) (Equation 1 in Table 1; Fig. 7B). Given the isotope composition of bulk organic matter at each point (\( \delta^{13}C_{bulk} \)), the isotope composition of the corresponding vascular plant debris (\( \delta^{13}C_{vpc} \))

Figure 7. (A) Carbon-isotope composition of phytoclasts (\( \delta^{13}C_{phy} \)) versus bulk organic matter (\( \delta^{13}C_{bulk} \), triangles) and calculated vascular plant debris (vpc) (\( \delta^{13}C_{vpc} \), dots) (V-PDB—Vienna Peedee belemnite). Correlation between \( \delta^{13}C_{phy} \) and \( \delta^{13}C_{vpc} \) is stronger (slope = 0.93, r^2 = 0.65) than between \( \delta^{13}C_{phy} \) and \( \delta^{13}C_{bulk} \) (slope = 0.79, r^2 = 0.50), showing that the bulk composition predominantly is a result of mixing between terrestrial and marine end members. (B) Atomic C/N ratios versus \( \delta^{13}C \) of marine and terrestrial organic matter. Measured composition of phytoclasts (green dots) and bulk organic matter (green triangles) are from marine sediments at Site 29. Light blue boxes represent modern end members of vascular plant debris and marine organic matter, while shallow marine sediment samples exhibit a linear mixing between end members (Hedges et al., 1997). The model average mixing line between Miocene end members (dark blue boxes) results in the best fit between observed phytoclast composition and corrected bulk composition calculated from bulk organic matter. The model mixing line uses end-member compositions of phytoclasts (\( C/N = 43, \delta^{13}C = −24.9\% \)) and bulk organic matter (\( C/N = 26, \delta^{13}C = −24.5\% \)) (see Table 1 for equations governing correction). The projected Miocene marine organic matter carbon-isotope value is inferred to have been significantly lighter than for the modern case.
Equation 1: $\alpha = (\delta^{13}C_{\text{vpc}} - \delta^{13}C_{\text{bulk}}) / \left( \frac{C/N_{\text{vpc}} - C/N_{\text{bulk}}}{} \right)$

Equation 2: $\delta^{13}C_{\text{vpc}} = \delta^{13}C_{\text{bulk}} - \alpha \left( \frac{C/N_{\text{vpc}} - C/N_{\text{bulk}}}{} \right)$

Note: C/N—atomic ratio of carbon to nitrogen.

can be calculated from the difference between C/N_{\text{bulk}} and the estimated mean vascular plant debris C/N composition (C/N_{\text{vpc}}), assuming that linear mixing can be applied and that $\alpha$ is constant (Equation 2 in Table 1). The best correlation between observed phytoclast ($\delta^{13}C_{\text{phy}}$) and estimated vascular plant debris composition ($\delta^{13}C_{\text{vpc}}$) is obtained with end-member mean compositions: $\delta^{13}C_{\text{vpc}} = -24.9 \%e$, $\delta^{13}C_{\text{bulk}} = -24.9 \%e$, C/N_{\text{vpc}} = 26; C/N_{\text{bulk}} = 43.

The resulting correlation slope and $r^2$ between the calculated vascular plant debris end member and phytoclast composition is 0.9 and 0.7, respectively (Fig. 7A). This correlation is better than the correlation between bulk organic matter and phytoclasts, suggesting that a mixing line indeed describes the bulk organic matter composition from two end-member compositions. The method is not perfect, because the mixing line is assumed to have a constant slope and fixed C/N ratio of the vascular plant debris end member. C/N ratios can vary depending on the plant assemblage and average terrestrial degradation before the particles enter the marine realm. Bacterial decay of phytoclasts would result in relative N enrichment (Hedges et al., 1997) impacting smaller particles more than the larger phytoclasts extracted and analyzed here. Significant bacterial decay during transport and after deposition most likely would obscure the mixing-line relation and our correction of bulk organic matter. Thus, the correlation between $\delta^{13}C_{\text{phy}}$ and $\delta^{13}C_{\text{vpc}}$ suggests that most of the primary stratigraphic trends in $\delta^{13}C$ of phytoclasts and bulk organic matter remain unobscured by transport and post-depositional bacterial degradation or diagenesis. These observations do not rule out significant alteration of chemical signatures over limited stratigraphic intervals.

**Relationship between Grain Size, Glaucnite Content, and Organic Matter Parameters**

Stratigraphically there does seem to be a relationship between grain size and $\delta^{13}C_{\text{phy}}$ and $\delta^{13}C_{\text{vpc}}$ (Fig. 6). Coarser-grained sediments have organic matter more enriched in $\delta^{13}C$, while finer-grained sediments tend to be relatively $\delta^{13}C$ depleted. However, there are fine-grained intervals with well-defined intermediate $\delta^{13}C_{\text{phy}}$ values, and stratigraphic trends in $\delta^{13}C_{\text{phy}}$ that are not reflected in grain-size trends (e.g., 380–410 mbsf).

Coarser-grained sediments with HI = 50–100 in general have the most positive $\delta^{13}C_{\text{phy}}$ (473, 491–500, 602–617, 625–637, 649, 665–672 mbsf). These low HI values are associated with low C/N_{\text{bulk}} ratios, both potentially a result of bacterial degradation, with accompanying N enrichment at discrete stratigraphic horizons (e.g., Meyers, 1997, and references therein). It is particularly noteworthy that these low HI, low C/N_{\text{bulk}} values occur in strongly glauconitic sediments, the glauconite pointing toward prolonged reworking close to the seafloor prior to final burial. On the other hand, it is also noteworthy that intercalated muddy horizons have heavy carbon-isotope values that are combined with high HI (e.g., 650–665 mbsf). Thus, although terrestrial organic matter in the glauconitic sands may be strongly degraded by bacterial processes, this does not seem to have affected the carbon-isotopic composition and, in any case as discussed below, degradation would not be expected to lead to heavier carbon-isotope values.

**Degradation and Diagenesis**

**General Considerations**

Because the various plant biopolymer components have different carbon-isotope values, change of the overall carbon-isotope values of terrestrial organic matter may take place during transport and deposition as chemical alteration takes place. Specifically, plant lipids and lignin (accounting for 22%–36% of fresh biomass) are depleted in $\delta^{13}C$ by 2‰–5‰ relative to the whole-plant $\delta^{13}C$ value, whereas cellulose and hemicelluloses (accounting for 57%–77% of the fresh biomass) are enriched in $\delta^{13}C$ by 1‰–2‰ relative to whole-plant tissue (Benner et al., 1987), and proteins, accounting for a very small proportion of the biomass, are also isotopically relatively heavy (Deines, 1980). Compositional changes of plant matter continuously occur during transport from the source terrestrial plants through to eventual burial.

Generally, the biopolymer components of higher plants, in order of increasing degree of preservation potential, are proteins, cellulose, lipids, and lignin, in which the cellulose and lignin take up a large percentage of the total, although depositional environment and history influence this order in some extent (Meyers, 1997; Gröcke, 1998, and references therein). Thus lignin is preferably preserved in sediments after undergoing early degradation and diagenesis (Stout et al., 1988; Hatcher et al., 1989a, 1989b). As a result of loss of cellulose, degradation and diagenesis will lead to a two- to three-fold increase in lignin content (Tyson, 1995, and references therein). Thus, the original $\delta^{13}C$ values of fresh wood undergo alteration toward lighter carbon-isotope values.

Alteration in $\delta^{13}C$ values seems to occur mostly at very shallow burial depths of <1–4 m (Hatcher et al., 1983; Spiker and Hatcher, 1984). Consistent shifts in $\delta^{13}C$ values are not commonly observed in thermally immature organic matter subject to deeper burial (Sackett, 1964, 1989; Dean et al., 1986; Hunt, 1970; Jasper and Gagosian, 1990).

In the present case it is observed that isotopically heavy phytoclast carbon-isotope values occur preferentially in the coarser (i.e., sandy) strata. It is in these coarser sediments that stronger oxidation of organic matter might be predicted (e.g., Meyers, 1997) and, as discussed above, likely reflected in the low HI and low C/N_{\text{bulk}}. Therefore, if degradation and early diagenesis were responsible for the observed stratigraphic patterns in carbon-isotope values, these sandy sediments should contain isotopically lighter rather than heavier phytoclasts. In other words, we observe positive carbon-isotope excursions where we would expect negative excursions if degradation were the principal control on isotopic values (Fig. 7).

**Preservation State of Woody Phytoclads**

Observation with a light microscope (both reflected and transmitted) reveals no significant difference in the appearance of phytoclasts recovered from different lithologies.
such as sand versus mud (associated with the heavy and light carbon-isotope signatures, respectively).

However, scanning electron microscope (SEM) observations do reveal some structural differences. A suite of samples from a range of lithologies at Site 29 were selected from the early Miocene to middle Miocene. The samples were chosen from lithologies representing lowstand and highstand (or transgressive) depositional environments. For each sample, three to four phytoclasts were randomly chosen and consistent ultrastructure was observed for these different pieces within each sample.

Phytoclasts in the mud retain more structure than those in sand (Figs. 8A, 8B), but eroded and coarse surfaces are dominant in the phytoclasts obtained from the sand (Figs. 8C, 8D). This kind of selective preservation goes through the early Miocene and the middle Miocene, although there are obviously different sedimentary environments for the early Miocene and the middle Miocene in Site 29. The contrasting appearances of phytoclasts may be interpreted as reflecting differential degradation prior to burial.

However, the difference of preservation does not necessarily lead to a bias of carbon-isotope values in phytoclasts if all the observed phytoclasts have lost most of their cellulose components. Furthermore, again, selective degradation of cellulose should lead to systematically lighter isotope values rather than the heavier values observed in the sands.

**Carbonate Carbon-Isotope Records in Comparison to Organic Carbon-Isotope Records**

While the carbon-isotope data for single-species analysis and multiple-species analysis are in close agreement, the overall data set shows

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**Figure 8.** Scanning electron (SE) micrographs of selected woody phytoclasts. Some 10–20 phytoclast pieces were randomly selected from each sample. The fragments illustrated here are representative of those assemblages examined. (A) Phytoclast showing good wood ultrastructural preservation, from mud 581.45 mbsf (meters below sea floor), δ¹³C = −26.16‰. (B) Phytoclast showing good ultrastructural preservation, from mud at 666.00 mbsf, δ¹³C = −24.61‰. (C) Phytoclast showing poor ultrastructural preservation, from sand at 500.71 mbsf, δ¹³C = −23.47‰. (D) Phytoclast showing poor ultrastructural preservation, from sand at 663.00 mbsf, δ¹³C = −22.30‰. According to palynological analysis (Fig. 9), the type of wood in the hinterland has not changed significantly through this stratigraphic interval and so the SE micrographs likely (but not definitively) show differences in preservation state for different species of wood.
considerable scatter at closely adjacent stratigraphic levels. The scatter, taken together with the uneven stratigraphic distribution of data points, means that comparison to the detailed structure of the organic carbon-isotope record is difficult (Fig. 3). We note that throughout the Langhian interval the carbon-isotope values are similar to but slightly lighter than those for the Monterey event reported by Cheng et al. (2004) from the South China Sea. One apparently anomalous isotopically light data point occurs at 730 mbsf (Fig. 3). Although this value is <-4‰, and could therefore be entirely the result of diagenetic alteration, it corresponds stratigraphically to isotopically light values in the concentrated phytoclast fraction as well. Thus, this stratigraphic horizon may indeed also be recording an interval of isotopically light carbon in the whole exchangeable atmosphere-ocean reservoir.

**Relation of Carbon-Isotope Values to Palynological Indicators of Environmental Change**

**Changes in Hinterland Vegetation**

Changes in hinterland vegetation might have occurred due to climate change. If different biomes were established through the Miocene interval in the sediment source areas, and these plant communities occupied environments that differed in key attributes such as soil moisture (e.g., Poole et al., 2004), then contrasting carbon-isotope compositions might have resulted. As well as influencing the carbon-isotope compositions of organic matter from the same taxa, such environmental changes may also be characterized by changing dominance of plant groups with intrinsically different isotopic values such as gymnosperms (relatively heavy) versus angiosperms (relatively light) (e.g., Bechtel et al., 2007; Holdgate et al., 2009), or ferns with their even lighter carbon-isotope values (e.g., Brearley, 2010; Watkins and Cardelús, 2012). Contrasts in carbon-isotope compositions can also be caused by changes in the ratio between C3 and C4 plants with their different photosynthetic systems, the latter mainly consisting of members of the Cyperaceae and Poaceae families of sedge and grass.

The hypothesis of shifting biomes can be tested by analysis of palynological components throughout the interval in question with taxonomic composition translated into environmental preference (Fig. 9). In this section we examine any possible relationships between carbon-isotope values and palynological indices based on the studies of U. Kotthoff (see the Supplemental File [see footnote 1]) and McCarthy et al. (2013). Note that the data in Figure 9 are particle counts and are not equivalent to mass ratios; most mass is represented by the phytoclasts, and on this basis, mass ratios would be expected to be greater than indicated. However, some fine marine organic matter particulates may have been lost during sieving. Therefore ratios of terrestrial to marine components derived from palynological counts cannot be linearly compared to mixing ratios derived from isotope and C/N values.

Eventual alteration of the pollen record through transport effects (e.g., over-representation of bisaccate pollen) can to a high degree be identified via the content of marine components (dinoflagellate cysts and foraminifer test linings) within the palynological samples: higher values of marine components indicate a longer site-to-shoreline distance and thus stronger over-representation of bisaccate taxa. In light of this, the high values of conifer forest pollen (dominated by bisaccate pollen) in the lowermost part of the examined interval from ~500 to ~740 mbsf at Site 29 are probably partly caused by transport effects, while other increases and the decrease at ~400 mbsf are true signals of vegetation change (Fig. 9; McCarthy et al., 2013).

The non-saccate pollen percentages reveal no significant change in the hinterland vegetation: in some cases, deciduous-evergreen mixed forest pollen (dominated by oak and hickory) show small decreases that are paired with increases in swamp and/or understory vegetation (Fig. 9). These environmental changes, as well as a notable expansion of conifer forests, may be tied to climate changes, but if so, these are probably not of major impact.

Spores are very rare in most of the samples, generally less than 1.5% of combined spores and pollen grains, except for two samples from ~733 and ~605 mbsf that have spores reaching ~5% of the terrestrial palynomorphs. This indicates that ferns and other spore-producing plants played a very minor role in the hinterland vegetation for the interval analyzed, and phytoclasts analyzed in this study must have been only rarely derived from ferns.

Percentages of Cyperaceae remain relatively stable over the whole interval, and Poaceae pollen is virtually absent (combined as “sedges and grasses” in Fig. 9). Therefore, it can be excluded that changes in the carbon-isotope values are mainly altered by changes in the C3/C4 plant ratio. In summary, there are no overwhelming changes in palynomorph content that could explain the observed carbon-isotope ratios through major environmental changes in the sediment source areas.

**Reworking of Terrestrial Organic Matter from Older Deposits**

Seismic stratigraphic evidence shows that there has been considerable erosion and re-deposition of siliciclastic sediments through successive relative sea-level cycles, and this may particularly have been the case during the Burdigalian (Fig. 1). Both seismic stratigraphy and core sedimentology indicate a period of strong erosional degradation of recently deposited clinoform sediment bodies from ~19–18 Ma (J.-N. Proust, 2012, personal commun.). The possibility therefore needs to be considered that older phytoclasts with heavier isotopic values have been reworked into sediments deposited at this time.

If reworking were a significant factor in explaining the observed carbon-isotope profiles, then it follows that Burdigalian deposits contain phytoclasts reworked from a period of overall relatively heavy carbon-isotope values, and/or that Langhian sediments contain phytoclasts reworked from a period of overall relatively light carbon-isotope values.

If we assume reworking of recently deposited sediments, then Langhian sediments may be predicted to contain an abundance of reworked Burdigalian pollen and spores, and Burdigalian sediments may be predicted to contain an abundance of reworked Aquitanian pollen and spores. Unfortunately there is little stratigraphic discrimination possible for early to middle Miocene pollen and spores, but at some horizons there is evidence from corroded palynomorphs that points to some degree of reworking, particularly in the interval between ~696 and ~642 mbsf (Burdigalian), with some samples showing relatively high rates of broken and/or corroded pollen grains. The thick mud-dominated Langhian succession at Site 29 from 600 to 500 mbsf shows no similar direct evidence of incorporation for reworked terrestrial palynomorphs. Indeed, reworking during these times of relative sea-level rise and transgression, leading to a mud-dominated succession, would be very unlikely (cf. McCarthy et al., 2003). We conclude that reworking is unlikely to explain the observed stratigraphic patterns in phytoclast carbon-isotope values in the Langhian strata, although the possibility remains that reworked phytoclasts concentrated in the clinoform toe-of-slope facies may be affecting the Burdigalian carbon-isotope record.

**CONCLUSIONS**

Coherent stratigraphic trends and excursions in carbon-isotope values are observed for a variety of sedimentary organic matter components of the Miocene from the New Jersey margin,
Figure 9. Key palynological indices for Site 29 (35 samples for palynological analysis, and 112 samples for T:M ratio). T:M is the ratio of terrestrial to marine components (McCarthy et al., 2013). Nonsaccate/bisaccate ratio—ratio between pollen without sacci and with sacci (thus more effective airborne and/or floating transport). Pollen percentages for conifer forest taxa (including bisaccate pollen), high-altitude forest taxa, swamp forest taxa, deciduous-evergreen mixed forest taxa, understorey plants, and combined sedges and grasses are based on the total amount of nonsaccate pollen. See the Supplemental File (see footnote 1) for taxa and counts included in the respective vegetation types. See Figure 4 for the key to the graphic log. mbsf—meters below sea floor.
specifically: concentrated phytoclast separates, individually picked woody phytoclasts, and bulk organic matter adjusted on the basis of C/N ratios to be equivalent to vascular plant debris.

Assuming that the ages assigned to the analyzed strata are correct, the terrestrial carbon-isotope stratigraphy for the New Jersey margin does not match well that previously described for the mid-Miocene Monterey event, a positive carbon-isotope excursion, based on mainly benthić foraminifers from oceanic settings. Notably the Burdigalian sediments of the New Jersey margin yield a relatively heavy isotope signature compared to the Langhian sediments.

Explanations for the observed patterns of stratigraphic change may lie with reworking, degradation or diagenetic alteration, or floral change in the hinterland. However, there is little or no observational support for these explanations. Although degradation can be demonstrated on the basis of HI and SEM observation at certain limited horizons (especially characterized by the occurrence of glauconitic sand), these levels are notable for their relatively heavy carbon-isotope values, the opposite of what would normally be expected from selective removal of labile biopolymers. The most likely explanation for our observations is that phytoclast reworking has worked in clinoform toe-of-slope facies, but the reason for the resulting relatively heavy carbon-isotope values produced remains obscure.

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