Coupled high-resolution marine and terrestrial records of carbon and hydrologic cycles variations during the Paleocene–Eocene Thermal Maximum (PETM)

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Abstract

The Paleocene–Eocene Thermal Maximum (PETM; ~55.8 Ma) is a rapid warming of the ocean/atmosphere system, characterized by a negative carbon isotope excursion (CIE) in both marine and terrestrial carbon (Bowen et al., 2004; Zachos et al., 2001). The onset of the PETM occurred within ~10 kyr and lasted ~200 kyr (Murphy et al., 2010; Rohli et al., 2007). Foraminiferan δ18O and Mg/Ca records and distributions of terrestrial and marine archael lipids indicate warming of up to 3 to 8 °C in deep-sea and mid-latitude surface waters (Kennett and Stott, 1991; Weijers et al., 2007; Zachos et al., 2003, 2006), and ~5 °C warming in Arctic surface waters (Slujs et al., 2006).

Keywords:
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1. Introduction

The Paleocene–Eocene Thermal Maximum (PETM; ~55.8 Ma) is a global warming event that occurred during the Eocene Epoch (56–34 Ma). It is characterized by a negative carbon isotope excursion (CIE) in both marine and terrestrial carbon (Bowen et al., 2004; Zachos et al., 2001). The onset of the PETM is constrained to within ~10 kyr and lasted ~200 kyr (Murphy et al., 2010; Rohli et al., 2007). Foraminiferan δ18O and Mg/Ca records and distributions of terrestrial and marine archael lipids indicate warming of up to 3 to 8 °C in deep-sea and mid-latitude surface waters (Kennett and Stott, 1991; Weijers et al., 2007; Zachos et al., 2003, 2006), and ~5 °C warming in Arctic surface waters (Slujs et al., 2006).

The CIE is indicative of a massive input of 13C-depleted carbon that lowered ocean carbonate saturation, resulting in shoaling of the lysocline depth and dissolution of carbonates (Zachos et al., 2005; Zeebe et al., 2009). Proposed explanations for carbon input(s) include enhanced mantle CO2 outgassing (Bralower et al., 1997; Eldholm and Thomas, 1993), dissociation of methane hydrates (Dickens et al., 1995, 1997; Kennett and Stott, 1991), biomass burning (Kurtz et al., 2003), intrusive-heating of organic-rich marine sediments and subsequent formation and release of methane (Svensen et al., 2004), and drying of restricted seaways leading to oxidation of organic matter (Higgins and Schrag, 2006).

The character of the CIE is a key variable in determining the carbon flux responsible for the PETM. However, a range of environmental and biologic factors can influence the δ13C values of marine and terrestrial PETM records (Bowen et al., 2004; Pagani et al., 2006; Schouten et al., 2007; Smith et al., 2007). For example, PETM records from benthic foraminifera and bulk marine carbonate show a δ13C magnitude of −2 to −2.5‰ (Kennett and Stott, 1991; Thomas et al., 2002), while δ13C records from planktonic foraminifera often show larger CIEs, ranging −2.5 to −4‰ (Handley et al., 2008; Handley et al., 2009).

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Thomas et al., 2002; Zachos et al., 2006). Marine organic carbon and dinocyst δ13C records yield larger, more negative carbon isotope excursions between −2.8‰ and −6‰ (Bolle et al., 2000; Kaiho et al., 1996; Magioncalda et al., 2004; Sijis et al., 2007b), similar to terrestrial bulk organic carbon and carbonates that range from −2.5 to −6‰ (Bowen et al., 2001; Cui et al., 2011; Koch et al., 1995; Magioncalda et al., 2004), while δ13C records of terrestrial leaf-waxes range from −2.8 to −6‰ (Handley et al., 2008; Pagani et al., 2006; Smith et al., 2007). Larger CIEs in terrestrial records have been explained in terms of increased photosynthetic fractionation resulting from increased humidity and soil moisture (Bowen et al., 2004) and shifts in plant types (Smith et al., 2007). However, an evaluation of plant functional-types and their carbon isotope relationships argue for an atmospheric excursion of −4.5‰ (Diefendorf et al., 2010), in line with the CIE observed in the majority of terrestrial δ13C records. Understanding subtle isotopic differences between these records is important in determining carbon cycle dynamics, as well as an accurate mass and source of the carbon responsible for the warming (McInerney and Wing, 2011).

In addition to a massive release of 13C-depleted carbon at the PETM, a rapid rise in temperature occurs in near-concert with aberrations in the hydrologic cycle (Bowen et al., 2004; Pagani et al., 2006) and substantial changes in marine and terrestrial ecosystems (Collinson et al., 2009; Greenwood and Wing, 1995; Thomas et al., 1999; Wilf, 2000; Wing and Harrington, 2001; Wing et al., 2005). In general, the PETM was more humid with higher weathering rates inferred from clay mineralogy of shallow marine and terrestrial sediments (Bolle and Adatte, 2001; Clechenko et al., 2007; Cramer et al., 1999; Crough et al., 2003; Gibbon et al., 2000; Johns et al., 2008; Kopp et al., 2009; Robert and Chamley, 1991; Robert and Kennett, 1994; White and Schiebout, 2008), with evidence for extreme seasonal precipitation in some localities (Schmitz and Pujalte, 2003; Yoshida et al., 2007; Sijis et al., 2006).

For this work, we established carbon and hydrogen isootope compositions of higher-plant derived n-alkanes with bulk organic carbon and marine carbonate isotope ratios from orbitally tuned, marine sediments of the Forada section in northern Italy during the PETM. Although the Forada section was shallower than the majority of studied PETM marine sections, the region did not completely escape some carbonate dissolution during the PETM—a testament to the enormous mass of carbon released. While dissolution appears to have affected marine carbonates, other geochemical and sedimentological properties suggest that the Forada record is complete and continuous, lacking the hiatus associated with carbonate burn-down (Giuberti et al., 2007). Given the limited number of expanded and continuous Paleocene–Eocene boundary sections, the Forada section is an exceptional locality for direct comparison between marine and terrestrial geochemical signatures within a single sedimentary section. Accordingly, we use our new isotope and compound-abundance records to evaluate the relative relationships between hydrologic cycle, temperature, and changes in the terrestrial and marine environments.

2. Materials and methods

2.1. Geologic setting and sampling

The Forada section, located in the Venetian pre-Alps region of northern Italy along Forada Creek (46°03′08″N, 12°06′39″E), is a continuous (62 m) outcropping of well-exposed pelagic to hemipelagic limestones, marls, and claystones spanning the Upper Cretaceous to the lower Eocene. PETM sediments were deposited in a near-continental environment in the western Tethys Ocean with a paleo-depth estimated between 600 and 1000 m (Giuberti et al., 2007). Tectonic deformations were less severe than elsewhere in the Alps (Channell and Medizza, 1981), making the pre-Alps suited for studies of the lower Paleogene pelagic record (Giuberti et al., 2007).

Sixty-five samples (500–700 g) were collected spanning roughly 6 m of Paleocene–Eocene boundary section exposed in Forada Creek (Fig. 1). The section was trenched, removing ~50–75 cm of surface sediment, to unweathered rock, and samples were taken at approximately 10 cm resolution in the Eocene clay-marl unit (CMU) and marl-limestone couplets and at 5 cm resolution in the latest Paleocene marls and limestones. Samples were collected with clean instruments, wrapped in baked aluminum foil, and stored in low-bloom Whirl-pak bags prior to extraction.

2.2. Sample extraction and separation

Sediments were freeze-dried, powdered (−500 g), and extracted for 24 h with dichloromethane (DCM):methanol (2:1, v/v) using a Soxhlet extractor. Total lipid extracts were concentrated under a stream of purified nitrogen using a Zymark Turbuvap II evaporator, transferred to 4 ml vials, and further evaporated under a gentle stream of N2 gas. Extracts were then separated by column chromatography using 1 g deactivated silica gel (70–230 mesh) in an ashed Pasteur pipette, and eluted with 2 ml hexane, 4 ml dichloromethane and 4 ml of methanol to obtain the aliphatic, aromatic, and polar hydrocarbons, respectively. Normal-alkanes were further purified from cyclic and branched alkanes using urea addition following (Wakeham and Pease, 1992).

2.3. Compound abundance and characterization

Normal-alkane abundances were determined using a Thermo Trace 2000 gas chromatograph (GC) fitted with a programmable-temperature vaporization injector and flame ionization detector (FID). Samples were processed with a fused silica, DB-1 phase column (60 m × 0.25 mm i.d., 0.25 µm film thickness) with helium as the carrier at a flow of 2 ml/min. GC oven temperature program was 60–
320 °C at 10 °C/min and isothermal for 30 min. Normal-alkanes were identified through comparison of elution times with known n-alkane standards.

Individual n-alkane peak areas were calculated using Xcaliber software version 1.5. Changes in average higher plant chain length (AHPCL) were calculated using the following relationship:

\[
\text{AHPCL} = \frac{(A_{27}(27)) + (A_{29}(29)) + (A_{31}(31))}{(A_{27} + A_{29} + A_{31})}
\]

where \( A \) corresponds to the area of the individual n-alkane peak from the chromatograph trace.

Biomarker identification and abundance were determined using a Thermo Trace 2000 gas chromatograph (GC) fitted with a split/splitless injector (splitless mode, 300 °C). Samples were processed with a fused silica, DB-5 phase column (30 m × 0.25 mm i.D., 0.25 μm film thickness) with helium as the carrier at a flow of 1.5 ml/min. GC oven temperature program was 60–320 °C at 5 °C/min and isothermal for 30 min. A Thermo Trace MS was used for detection with the mass spec scanning from 50 to 800 m/z or exclusively m/z of 57.

A subset of spiked petroleum standards with published biomarker distributions (Peters et al., 2005) were calibrated using NBS-19 and atmospheric N. Standard deviation for \( \delta^{13} \)carbonate determinations using international reference materials (NBS-18 and NBS-19) was ±0.1‰.

2.6. Bulk organic carbon and nitrogen isotope ratios

250 milligrams of powdered sample was placed in a 50 ml Falcon brand centrifuge tube. 30 ml of 1N HCl was added and agitated with a vortex mixer, covered with baked aluminum foil, and placed on a 40 °C hot plate for 12 h to ensure complete dissolution of carbonates. The acidic slurry was diluted with distilled de-ionized (DDI) water, centrifuged, and decanted until a neutral solute pH was achieved. Sample residues were rinsed with approximately 100 ml of DDI water. Residues were dried by placing them in a 65 °C oven for 3 days and loosely covered with aluminum foil. Once dried, residues were weighed into tin capsules and analyzed on a Thermo Finnigan Delta Advantage isotope ratio spectrometer with a Costech Elemental Analyzer and zero-blank autosampler attached. Stable isotope ratios for laboratory reference materials used during CN analysis were calibrated using NBS-19 and atmospheric N. The standard deviations of repeated measurements of reference analyses were 0.3‰ for C and 0.1‰ for N.

2.7. Glycerol dialkyl glycerol tetraether analysis

The polar glycerol dialkyl glycerol tetraether (GDGT) fraction was purified on a 2 g alumina oxide column using DCM:Methanol (1:1, v/v). The GDGT fraction was dried under a stream of purified N₂ gas, dissolved in hexane:isopropanol (99:1, v/v), and then passed through a 0.4 μm PTFE filter. Samples were analyzed and quantified by high performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometer on an Agilent single quadrupole LC/MS 6100 series following instrument methods outlined in Schouten et al. (2007). PETM GDGT estimates of temperature were established using the calibration of Kim et al. (2010):

\[
\text{SST} = 81.5 \times \text{TEX}_{86} - 26.6, \quad (3)
\]

where

\[
\text{TEX}_{86} = \frac{[\text{GDGT}-2] + [\text{GDGT}-3] + [\text{Cren}]}{[\text{GDGT}-1] + [\text{GDGT}-2] + [\text{GDGT}-3] + [\text{Cren}]}.
\]

where Cren’ indicate the crenarchaeol regio-isomer and GDGT-1, GDGT-2 and GDGT-3 indicate GDGTs containing 1, 2, and 3 cyclopentane moieties, respectively (Kim et al., 2010). Other GDGT-SS7 calibrations are provided in the Supplemental materials. A round-robin analysis of GDGT compounds between Yale University, Royal Netherlands Institute for Sea Research, and Harvard University produced temperature estimates within 1 °C of one another for the TEX86 index. Internal reproducibility of calculated temperature is within 1.5 °C for all analysis.

3. Results

3.1. Sediment thermal maturity

A subset (n=11) of the thirty-three Forada extracts from throughout the stratigraphic section was analyzed to assess thermal maturity as thermal alteration of organic matter can alter the isotopic composition through exchange of carbon-bound hydrogen. Here we evaluate the thermal maturity of Forada sediments using established hopane and sterane isomerization indices (Peters et al., 2005). Given
the relatively condensed stratigraphic sequence (~6 m), it was not necessary to analyze all samples as all samples were likely exposed to similar thermal stresses, and indeed, we observed little variation in thermal maturity throughout the section. Stereoisomers of \( \text{Tm} \) and \( \text{Ts} \) hopanes were identified. Forada \( \text{Ts}/\text{Ts} + \text{Tm} \) values averaged 0.13 and range between 0.03 and 0.23. In all samples the less stable \( \text{C}_{27} \) hopane (Tm) in much greater concentrations than the more stable Ts, suggesting low thermal maturity. Ts/Ts + Tm values below 0.35 correspond to vitrinite reflectance values of 0.5 and below (Peters et al., 2005) and correspond to immature organic material. In addition, \( \text{C}_{31} \) and \( \text{C}_{32} \) homohopanes were in significant concentrations to measure the homohopane isomerization index \( 22S/22S + 22R \). \( \text{C}_{31} \) homohopanes have a stereocenter in the side chain at C-22 that isomerizes from the biological 20R configuration to an equilibrium mixture of the 20R and 20S diastereomers during thermal maturation. \( 22S/22S + 22R \) values averaged 0.49 and range between 0.40 and 0.55. The majority of samples had greater concentrations of the biological homohopane precursor (22R) than the geological derivative (22S). \( 22S/22S + 22R \) reaches equilibrium at ~0.60 and near the very earliest stages of oil generation temperatures. Similar to the \( \text{Ts}/\text{Tm} \) ratios, \( 22S/22S + 22R \) ratios reach equilibrium at ~0.60 and near the very earliest stages of oil generation temperatures. A subtle +0.8‰ shift from 0.4% to 1.2% in \( \delta^{13} \text{C}_{\text{carbonate}} \) values is observed between ~100 cm and ~60 cm followed by a steady 1.4‰ depletion in \( \delta^{13} \text{C}_{\text{carbonate}} \) from ~60 cm to ~2 cm (Fig. 2). The onset of the CIE is marked by an abrupt negative 2.0‰ change from ~2 cm to 10 cm followed by a +1.3‰ increase between 10 cm and 30 cm. The initial spike in \( \delta^{13} \text{C}_{\text{carbonate}} \) values is followed by a plateau rather than a broad shift to more negative \( \delta^{13} \text{C}_{\text{carbonate}} \) values, and lithologic change from a ~0.2 cm black clay interval followed by a 320 cm thick gray-green (0.2–50 cm) and reddish (50–320 cm) clay marl interval is associated with the base of the Eocene. \( \delta^{13} \text{C}_{\text{carbonate}} \) values remain ~1.0‰ from 30 cm until 260 cm where \( \delta^{13} \text{C}_{\text{carbonate}} \) values become 0.9‰ more negative for 50 cm (270–320 cm). A distinct lithologic change from gray-green marls to limestone-red marl couples occurs at 330 cm with a corresponding shift in \( \delta^{13} \text{C}_{\text{carbonate}} \) values from ~1.3 to ~0.2‰. \( \delta^{13} \text{C}_{\text{carbonate}} \) values steadily become more positive reaching 0.7‰ for the remainder of the section.

\( \delta^{13} \text{C}_{\text{organic}} \) values range between ~24.8 and ~30.2‰ with an average value of ~26.4‰ (Table S1). Latest Paleocene \( \delta^{13} \text{C}_{\text{organic}} \) values averaged ~25.1‰ (Fig. 2). The onset of the CIE represented by the \( \delta^{13} \text{C}_{\text{organic}} \) record is marked by an abrupt ~3.1‰ change from ~15 cm to 5 cm followed by a +1.7‰ shift between 5 cm and 10 cm. As with the \( \delta^{13} \text{C}_{\text{carbonate}} \) record, the onset of the CIE is marked by a spike in \( \delta^{13} \text{C}_{\text{organic}} \) values followed by a plateau rather than a general shift to more negative \( \delta^{13} \text{C}_{\text{organic}} \) values. \( \delta^{13} \text{C}_{\text{organic}} \) values remain ~26.0‰ from 10 to 200 cm where values become 0.9‰ more negative for 60 cm (260–310 cm). \( \delta^{13} \text{C}_{\text{organic}} \) values trend more positive by 1.0‰ for the remainder of the

3.2. Forada bulk carbonate and total organic carbon \( \delta^{13} \text{C} \) records

Bulk carbonate content ranged between 36 and 92 weight percent (wt.%) in the latest Paleocene interval, 17–87 wt.% from 0 to 320 cm within the main body of the carbon isotope excursion and clay-marl unit (CMU), and 52–100 wt.% from 330 to 500 cm during the recovery and equilibration interval (Table S1). The interpretation that the CMU (0–320 cm) is the lithologic expression of the PETM and not a burn-down interval, is supported by micropaleontological data, including calcareous planktonic and benthic foraminiferal biostatigraphy, (Giusberti et al., 2007). Further, sedimentation rates increase five-fold during the clay marl interval compared to the Late Paleocene, indicative of increased continental weathering and increased terrigenous input (Giusberti et al., 2007).

Latest Paleocene bulk \( \delta^{13} \text{C}_{\text{carbonate}} \) values range between ~0.2 and 1.2‰ with an average of 0.5‰ (Table S1). A subtle +0.8‰ shift from 0.4‰ to 1.2‰ in \( \delta^{13} \text{C}_{\text{carbonate}} \) values is observed between ~100 cm and ~60 cm followed by a steady 1.4‰ depletion in \( \delta^{13} \text{C}_{\text{carbonate}} \) from ~60 cm to ~2 cm (Fig. 2). The onset of the CIE is marked by an abrupt negative 2.0‰ change from ~2 cm to 10 cm followed by a +1.3‰ increase between 10 cm and 30 cm. The initial spike in \( \delta^{13} \text{C}_{\text{carbonate}} \) values is followed by a plateau rather than a broad shift to more negative \( \delta^{13} \text{C}_{\text{carbonate}} \) values, and lithologic change from a ~0.2 cm black clay interval followed by a 320 cm thick gray-green (0.2–50 cm) and reddish (50–320 cm) clay marl interval is associated with the base of the Eocene. \( \delta^{13} \text{C}_{\text{carbonate}} \) values remain ~1.0‰ from 30 cm until 260 cm where \( \delta^{13} \text{C}_{\text{carbonate}} \) values become 0.9‰ more negative for 50 cm (270–320 cm). A distinct lithologic change from gray-green marls to limestone-red marl couples occurs at 330 cm with a corresponding shift in \( \delta^{13} \text{C}_{\text{carbonate}} \) values from ~1.3 to ~0.2‰. \( \delta^{13} \text{C}_{\text{carbonate}} \) values steadily become more positive reaching 0.7‰ for the remainder of the section.

\( \delta^{13} \text{C}_{\text{organic}} \) values range between ~24.8 and ~30.2‰ with an average value of ~26.4‰ (Table S1). Latest Paleocene \( \delta^{13} \text{C}_{\text{organic}} \) values averaged ~25.1‰ (Fig. 2). The onset of the CIE represented by the \( \delta^{13} \text{C}_{\text{organic}} \) record is marked by an abrupt ~3.1‰ change from ~15 cm to 5 cm followed by a +1.7‰ shift between 5 cm and 10 cm. As with the \( \delta^{13} \text{C}_{\text{carbonate}} \) record, the onset of the CIE is marked by a spike in \( \delta^{13} \text{C}_{\text{organic}} \) values followed by a plateau rather than a general shift to more negative \( \delta^{13} \text{C}_{\text{organic}} \) values. \( \delta^{13} \text{C}_{\text{organic}} \) values remain ~26.0‰ from 10 to 200 cm where values become 0.9‰ more negative for 60 cm (260–310 cm). \( \delta^{13} \text{C}_{\text{organic}} \) values trend more positive by 1.0‰ for the remainder of the

Fig. 2. Stable carbon isotope ratios of higher plant \( n \)-alkanes (a), bulk organic carbon (b) and bulk carbonates (c) for the Paleocene–Eocene boundary interval in Forada. Terrestrial higher plant \( n-C_{27}, n-C_{29}, \) and \( n-C_{31} \) \( \delta^{13} \text{C} \) values are shown as crosses, closed circles, and triangles, respectively.

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section coupled with a lithologic change from marls to limestone-red marl couplets at 320 cm.

3.3. Forada terrestrial higher-plants records: δ13C, δD, and compound-distributions

Saturated hydrocarbons are dominated by a homologous series of n-alkanes from n-C25 to n-C35, with n-C27, n-C29, and n-C31 as the most abundant compounds. Normal-alkanes are characterized by an odd-over-even character consistent with terrestrial higher-plant derived materials (Eglinton and Hamilton, 1967) with a CPI value of greater than 2 for all samples. We restrict our analysis and discussion to records expressed by n-C27, n-C29, and n-C31.

Stable carbon isotope values of individual n-alkanes (δ13Cn-alkane) range from −28.1‰ to −34.1‰ with an average value of −30.5‰ (Table 1). In individual samples, δ13Cn-alkane values are generally more 13C-depleted as chain-length increases, similar to relationships that characterize modern plant leaf waxes (Bi et al., 2005; Collister et al., 1994; Zhou et al., 2010). The δ13Cn-alkane of all n-alkanes trend toward more negative away from 0 cm in the Forada section (Fig. 2) corresponding to the CIE expressed by the δ13Carbonate record. Latest Paleocene δ13Cn-alkane values of n-C27, n-C29, and n-C31 range from −28.5 to −30.6‰, −29.2 to −30.6‰, and −29.5 to −32.3‰, respectively. From 0 cm to 20 cm, n-C27, n-C29, and n-C31 δ13Cn-alkane values become more negative (−32.2‰, −32.8‰, and −34.1‰), thus the magnitude of the CIE for the Forada δ13Cn-alkane record is 3.7‰, 3.6‰, and 4.6‰, respectively. Following the onset of the CIE, n-C27, n-C29, and n-C31 δ13Cn-alkane values show a steady progression toward pre-event values within the main body of the CIE and average −30.5‰, −31.3‰, and −31.8‰, respectively. The δ13Cn-alkane values during the recovery phase (as characterized by lithologic changes and δ13Carbonate variations) and post-event intervals are similar to pre-exursion δ13C values.

Stable hydrogen isotope values of n-alkanes (δDn-alkane) range from −126‰ to −153‰ over the studied interval (Table 1). Low molecular concentrations limit the number of possible δDn-alkane measurements compared to δ13Cn-alkane values. However, the entire PETM and pre-event intervals were sampled at higher resolution compared to other n-alkane hydrogen records (Fig. 3). Prior to the onset of the CIE at 0 cm, δDn-alkane values for n-C27 and n-C29 become more D-enriched from −147‰ to −136‰ and −152‰ to −136‰ between −35 cm and −2 cm, respectively, while n-C31 remains relatively constant ranging from −138‰ to −132‰. At the onset of the CIE, δDn-alkane values for n-C27, n-C29, and n-C31 immediately become more D-depleted by 6‰ to 9‰. Between 10 cm and 290 cm, δDn-alkane values for n-C27, n-C29, and n-C31 remain relatively constant. D/H compositions of n-alkanes are more D-enriched above 320 cm and coincident with the recovery phase of the PETM, and stabilize to pre-event values near the end of the CIE.

Higher-plant average chain-length (AHPCL) decreases from 31.2 to 29.7 between −40 cm and −4 cm towards the onset of the CIE (Table S1, Fig. 3). From −4 cm to the beginning of the CIE, AHPCL increases to 30.8 and abruptly decreases to 29.5 at 5 cm, and then remains relatively stable between 10 and 60 cm with an average value of 29.9 and a range between 29.8 and 30.1. A shift in AHPCL occurs from 29.9 to 31.0 between 60 cm and 90 cm with values near 31 from 90 to 300 cm. After 300 cm to the end of the CIE, AHPCL gradually decreases from 31.0 to 30.0 corresponding to the recovery phase.

The relationship between δ13C values, δD values, and the AHPCL provides insights into the relative contributions of marine and terrestrial higher-plants to the study section. A higher δ13Cn-alkane and δDn-alkane values relative to the AHPCL suggests a greater terrestrial higher-plants input to the study section. In contrast, a lower δ13Cn-alkane and δDn-alkane values relative to the AHPCL suggests a greater marine higher-plants input to the study section.
the Forada sediments and variations in angiosperm- and gymnosperm-specific molecules. Cadalene, derived from higher-plants, were observed in all samples with no significant abundance variation. While only observed in several samples, higher-plant specific dihydro-ar-cucumene was also present. Angiosperm-specific bicadinenes, 1,2,5, and 1,2,7-trimethylnaphtalenes, olenane, and tetra-aromatic der beta amyrin were also targeted. Bicadinenes were observed in 6 of the 11 samples with no significant abundance variation throughout the section while no other angiosperm-specific biomarkers were detected. Gymnosperm-specific Simonellite, Retene, and dehydroabietane were also targeted with none detected in any Forada fraction analyzed.

3.4. Paleocene–Eocene sea-surface temperature estimates

Recovery of the GDGT fraction was low for all samples extracted. Of the 35 samples extracted and analyzed, 15 samples yielded measurable GDGT concentrations (Table S1). The BIT index ranged from 0.660 to 0.997, suggesting significant contribution of terrestrial soil organic material (Hopmans et al., 2004) and consistent with interpretations of increased continental weathering and terrigenous input to the Forada section (Giusberti et al., 2007). The highest BIT index values occur near the onset of the CIE (−4 cm to 10 cm) suggesting the largest influx of terrestrial soil organic matter to the Forada sediment occurred at the start of the PETM. Given the elevated BIT values temperature estimates should be regarded as qualitative, however estimates of Late Paleocene temperatures gradually increase from 29 to 32 °C toward the onset of the CIE. A slight decrease in temperature estimates occur at the onset of the CIE, followed immediately by a 4 °C increase. During the body of the event temperatures remain between 27 and 32 °C. While the absolute temperatures are qualitative, given the elevated BIT values throughout the section the temperature trends are likely valid.

4. Discussion

4.1. A comparison of Forada PETM carbonate, bulk organic, and terrestrial carbon δ¹³C records

The Forada marine δ¹³C_carbonate record is broadly similar to other marine carbonate δ¹³C records (Bains et al., 1999) except for the presence of a sharp positive shift in δ¹³C_carbonate immediately following the onset of the CIE (Bains et al., 1999; Cramer et al., 2003; Zachos et al., 2005). A δ¹³C spike at the initial onset of the CIE is observed in surface-dwelling foraminifera (Kennett and Stott, 1991; Thomas et al., 2002) and terrestrial records (Bains et al., 2003; Bowen et al., 2001), but not in bulk marine carbonates. The absence of a carbon isotope shift in bulk carbonate records is explained by the extent of dissolution, or changes in carbonate fraction, or as a true reflection of regional paleoceanographic characteristics (Stoll, 2005). Bulk carbonate δ¹³C value at Forada become 1.3‰ more positive following the initial 2‰ negative carbon isotope excursion, similar to +1–2‰ changes observed in both Polecat Bench carbonate nodules (Bains et al., 2003) and Site 690 planktonic foraminifera (Bains et al., 2003; Kennett and Stott, 1991; Thomas et al., 2002). The Forada δ¹³C_carbonate and δ¹³C_n-alkane records are similar to the coeval δ¹³C organic record, displaying an abrupt shift following the initiation of the CIE (Fig. 2). These observations are consistent with trends from other high-resolution PETM records and carbon cycle models that predict a sharp negative spike followed by a subtle enrichment in surface- and deep-ocean carbon pools associated with the initial input of ¹³C-depleted CO₂ (Zeebe et al., 2009).

The Forada δ¹³C_carbonate record is similar to other marine bulk CIE records including the presence of a discrete onset, body or plateau, and recovery phase. In contrast, the Forada δ¹³C_n-alkane record shows a clear onset of the CIE, a subtle and gradual ¹³C-enrichment during the main body, and a sharp return to pre-event δ¹³C values immediately

Fig. 3. Stable hydrogen isotope ratios of higher plant n-alkanes (a) with higher plant average chain length values (b) for Forada sediments. Terrestrial higher plant n-C₂₇, n-C₂₉, and n-C₃₁ δD values are shown as crosses, closed circles, and triangles, respectively.

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following initiation of the recovery phase. Isotopic differences between these records can be explained in a variety of ways. Leaf waxes are produced throughout the growing season (Pedentchouk et al., 2008; Sachse et al., 2009) and transported to isolated marine settings on the order of days, weeks to years (Conte and Weber, 2002). Carbon-14 dating of fluvial and aeolian transported organic carbon and n-alkanes show these carbon pools are a mix of ancient and modern components (Drenzek et al., 2007; Eglington et al., 1997; Raymond and Bauer, 2001). Comparison of compound-specific and bulk 14C ages from varved marine sediments show that total organic carbon and n-alkanes are 500–4000 yr older than the calendar age of the sediments (Smittenberg et al., 2004). Thus, 14C ages of organic compounds represent a mixture of modern sources and more ancient organic carbon that reflects the mean reservoir storage time in soils prior to erosion and deposition in the basin (Smittenberg et al., 2004). As a result, the δ13C-n-alkane CIE should manifest differently between localities. Accordingly, we interpret the Forada δ13C-n-alkane record as a mixture of 13C-depleted PETM n-alkanes and older 13C-enriched Paleocene soil/sedimentary n-alkanes.

High-resolution chronologies have been developed for ODP Site 690 and Leg 208 (Murphy et al., 2010; Rohl et al., 2000, 2007) along with the onshore marine Forada section (Giusberti et al., 2007). Rohl et al. (2007) and Giusberti et al. (2007) disagree on the duration of the main excursion and recovery interval in Forada (179 ± 17 kyr and 231 ± 22 kyr, respectively). The main difference between these two chronologies is the assignment of different numbers of precessional cycles within the main body and recovery interval. However, a recent 3He-based chronology from Leg 208 suggest a total PETM duration of 234 ± 48/−34 kyr (Murphy et al., 2010) in line with the cycle-based Forada age model of Giusberti et al. (2007), these models are inline with recent age models of Bowen and Zachos (2010). For this study, we use the age model of Giusberti et al. (2007) for Forada and assume a constant sedimentation rate within the individual precessional cycles. Here the first precessional cycle observed in Forada is from 0 to 57 cm and we find a lag between the initial peaks in δ13C-carbonate and δ13C-n-alkane of 10–15 cm. Given this, the δ13C-n-alkane record at Forada appears delayed ~4–5 kyr relative to the δ13C-carbonate record within the considered precessional cycle. These data suggest the average residence time of n-alkanes delivered to Forada sediments to be at least 4000 yr (Fig. 4). In addition, we find the δ13C-carbonate and δ13Corganic responses equivalent, suggesting the bulk marine carbonate and organic carbon pools are coupled (Fig. 4), a supposition supported by bulk organic matter C/N ratios ranging between 2 and 4 (Meyers, 1994). While bioturbation and sediment mixing may have altered the Forada records, the similarity between the δ13C-carbonate and δ13Corganic responses suggest mixing affected each record equally and indicate the terrestrial lag is likely genuine.

Studies of modern soils suggest n-alkanes are highly recalcitrant within developed soils with n-alkane ages and soil depth linearly related (Huang et al., 1999). Radiocarbon ages suggest n-alkanes in soils can be up to 15,000 yr older than the modern (Bo l et al., 1996; Huang et al., 1999; Paul et al., 1997). Thus, under higher weathering rates associated with the PETM, weathering and deposition of older n-alkanes is anticipated. Deeper weathering of old Paleocene-aged n-alkanes likely contributed to the increase in the age of the average n-alkane deposited in Forada sediments.

At any locality, the relative proportion of contemporaneous n-alkanes and older 13C-enriched Paleogene soil/sedimentary n-alkanes could vary as hydrology and weathering evolve during the climate event. For example, the entire Forada CMU interval has been interpreted to reflect a period of increased terrigenous flux that monotonically decreased after the onset of the CIE (Giusberti et al., 2007). If hydrologic changes and its influence on the transport of pre-PETM n-alkanes impacted the δ13C-n-alkane record, then a gradual CIE onset followed by a plateau in Forada δ13C-n-alkane values is expected. However, this is not observed (Fig. 2) and suggests variations in the relative residence time of n-alkanes did not substantially change during the PETM.

Large changes in plant communities have been invoked to explain differences between terrestrial n-alkane and marine δ13C PM records (Schouten et al., 2007; Smith et al., 2007). The majority of terrestrial higher plants produce n-alkanes, and while some species produce unique n-alkane fingerprint (Eglington and Hamilton, 1967), many unrelated species within a single ecosystem can have similar or overlapping n-alkane distributions. Further, n-alkanes and biomarker δ13C values of angiosperms are ~1–2‰ more negative than gymnosperms (Schouten et al., 2007) suggesting that variations in δ13C-n-alkane values could be related to changes in the relative inputs of gymnosperm and angiosperm sources. To resolve these issues, n-alkane isotope records have been combined with pollen abundance (Slujs et al., 2007b), source-specific biomarkers (Schouten et al., 2007) and macrofossil studies (Smith et al., 2007) to interpret ancient terrestrial records. However, n-alkanes (aeolian, fluvial), terpenoid biomarkers (fluvial), macrofossils (fluvial) and pollen (aeolian, fluvial) have different taphonomic transport pathways to marine and terrestrial sediments (Schouten et al., 2007), and these differences can introduce biases through incorporation of reworked pollen and biomolecules. Furthermore, these terrestrial records can have different temporal responses to climate events, similar to the temporal difference observed between the Forada marine and terrestrial δ13C records. However, changes in terrestrial plant communities undoubtedly accompanied climate change in the Forada section’s input area. Subtle changes in plant communities can be interpreted from variations in the higher-plant n-alkane average chain length. Variations in AHPCL can occur due to plant community variations or environmental change. Environmental controls on AHPCL are not well constrained, however, increased average carbon-chain length has been related to increases in temperature and/or aridity (Sachse et al., 2006). At Forada, we observe rapid fluctuations prior to the CIE and a decrease in AHPCL immediately following the onset CIE, suggesting a decrease in aridity and/or temperature, or a large change in plant community. Given concurrent increases in global temperatures, the Forada AHPCL record likely reflects an increase in humidity and/or plant community change. Similar to the Forada δ13C-n-alkane record, the AHPCL record should incorporate a similar lag relative to the marine records.

While we do not have concrete evidence for or against a shift in vegetation near the Forada section, it is unlikely that gymnosperms
constituted a major component of this sub-tropical ecosystem prior to, and during the PETM given that Tethyan vegetation was dominated by rainforest and evergreen angiosperms (Utescher and Mosbrugger, 2007) during the latest Paleocene to Eocene. Biomarker abundances support this argument and suggest very limited gymnosperm contributions to Forada sediments. The magnitude of the Forada $\delta^{13}$C$_{\text{(n-alkane)}}$ CIE is only $-3.6$ to $-4.6$$\%$—smaller than other terrestrial $\delta^{13}$C$_{\text{(n-alkane)}}$ records that experience floral shifts, and thus consistent with our interpretations that a gymnosperm-to-angiosperm shift did not occur. Thus, it is possible that the Forada $\delta^{13}$C$_{\text{(n-alkane)}}$ record represents an accurate expression (while lagged) of the global CIE. An intriguing feature of the Forada $\delta^{13}$C$_{\text{(n-alkane)}}$ CIE is its resemblance to the terrestrial carbonate $\delta^{13}$C Polecat Bench section of the Bighorn Basin, Wyoming (Bains et al., 2003; Bowen et al., 2001). For both records, most negative values occur at the base with a sharp peak, followed by a gradual return toward more $\delta^{13}$C-enriched values across the main body. The transition to the CIE recovery phase is sharp in both terrestrial records, and magnitudes of the CIE are very similar between the Forada $\delta^{13}$C$_{\text{(n-alkane)}}$ $-3.5$ to $-4.5\%$ and Polecat Bench $\delta^{13}$C$_{\text{carbonate}}$ Records $-4.0\%$.

4.2. CIE response: Forada compared to other n-alkane $\delta^{13}$C records

As more compound-specific terrestrial plant $\delta^{13}$C records are established, more questions have arisen regarding the terrestrial response to the PETM. To date, seven PETM $\delta^{13}$C$_{\text{(n-alkane)}}$ records (including this study) have been compiled spanning the tropical (Tanzania) to polar latitudes (Lomonosov Ridge) (Handley et al., 2008; Hasegawa et al., 2006; Kaiho et al., 1996; Pagani et al., 2006; Smith et al., 2007) (Crouch and Vischer, 2003; Jaramillo et al., 2010; McCaren et al., 2008). Of these six records, five are terrestrial $\delta^{13}$C$_{\text{(n-alkane)}}$ records extracted from marine sediments either from outcrop (Kaiho et al., 1996, this study) or sediment core samples (Handley et al., 2008; Hasegawa et al., 2006; Pagani et al., 2006), while one was developed from terrestrial paleosols outcroppings (Smith et al., 2007). Global patterns in terrestrial plant’s response to the PETM are becoming apparent. Terrestrial $\delta^{13}$C$_{\text{(n-alkane)}}$ records are depleted in $\delta^{13}$C relative to more conventional marine $\delta^{13}$C excursions of 2 to 3$\%$ (CIEs based on $\delta^{13}$C$_{\text{(n-alkane)}}$ records from New Zealand, Walvis Ridge, Lomonosov Ridge, Bighorn Basin, Wyoming, and Tanzania, and this study are $-2.8\%$ to $-4.3%$ to $-5.1\%$, $4.5-6\%$, $3.7-5.1\%$, $5.3-7\%$, and $-3.6$ to $-4.6\%$, respectively). A larger CIE in terrestrial plant material has been interpreted as a response to enhanced soil moisture and humidity during the PETM (Bowen et al., 2004). Increased moisture availability reduced plant water-stress, allowing for greater $\delta^{13}$C discrimination during terrestrial photosynthesis. However, this explanation requires increases in soil moisture and temperature to overcome the competing driver on photosynthetic fractionation of increased temperature during the PETM (Bowen et al., 2004). Another model argues for changes in forest composition as a way to account for the discrepancy between marine and terrestrial $\delta^{13}$C records (Schouten et al., 2007; Smith et al., 2007). Given that angiosperms have $\delta^{13}$C$_{\text{(n-alkane)}}$ values more negative by 1$\%$—than gymnosperms (Chikaraishi and Naraoka, 2003), an increase in angiosperms relative to gymnosperms during the PETM could account for the CIE inconsistency between $\delta^{13}$C records. While these models may be viable in particular locations and environments, they do not explain the global discrepancy observed between the terrestrial and marine carbon reservoirs as they would require global increases in photosynthetic fractionation or angiosperms. As more terrestrial CIE records become available, increased focus should be placed on explaining this discrepancy.

At Forada, we find a decoupling of the marine and terrestrial response to the CIE during the initial interval (Fig. 4). Specifically, we find the terrestrial $\delta^{13}$C$_{\text{(n-alkane)}}$ response in the initial 15 kyr lacks the $+1.3%$ shift observed in $\delta^{13}$C$_{\text{carbonate}}$ record. Between 15 and 65 kyr after the CIE onset, both $\delta^{13}$C$_{\text{(n-alkane)}}$ and $\delta^{13}$C$_{\text{carbonate}}$ records vary in concert with the $\delta^{13}$C$_{\text{(n-alkane)}}$ record demonstrating higher variance. Finally, between 65 and 75 kyr the marine $\delta^{13}$C$_{\text{carbonate}}$ response lacks the $+2%$ shift observed in the $\delta^{13}$C$_{\text{(n-alkane)}}$ record. Thus, our new Forada record provides evidence for decoupling between marine and terrestrial responses during the initial ~75 kyr of the CIE. However, during the latter (~75 kyr) portion of the event, similar isotopic anomalies emerge (Fig. 4) suggesting that either the marine record was dampened and/or the terrestrial record amplified during the onset of the PETM. Further, the Forada terrestrial CIE is remarkably similar simulations that apply a single pulse of carbon to account for carbon isotope trends (Zeebe et al., 2009).

4.3. Pre-CIE hydrology change and associated plant community and temperature

We found all biomarker thermal maturity parameters to suggest immature organic material. While these biomarkers do not correspond to specific temperatures, these data suggest the sediments have not been exposed to temperatures greater than 60°C. Under these conditions we feel confident that little to no isotopic exchange of the alky1 hydrogen atoms has occurred and suggest the original biologic D/H ratios are preserved in Forada sediments.

Hydrogen isotopes of plant materials reflect a combination of isotopic effects related to photosynthetic pathways, growth forms, water-use efficiency, and the hydrogen isotope composition of source-water used during photosynthesis (Hou et al., 2007; Pedentchouk et al., 2008; Roden et al., 2000). Modern studies have shown $\delta^{13}$D$_{\text{(n-alkane)}}$ values are directly related to meteoric-water $\delta^{13}$D values, as well as rates of transpiration and soil evaporation (Chikaraishi and Naraoka, 2003; Pedentchouk et al., 2008; Sachse et al., 2006, 2009; Smith and Freeman, 2006). In general, PETM $\delta^{13}$D$_{\text{(n-alkane)}}$ records show relatively large isotopic variations (Handley et al., 2008; Pagani et al., 2006; Smith et al., 2007). $\delta^{13}$D$_{\text{(n-alkane)}}$ values from Tanzania shift to 20–40% more positive values at the onset of the PETM and remain relatively stable until an erosional surface limits interpretation during later portions of the PETM (Handley et al., 2008). One mid-latitude $\delta^{13}$D$_{\text{(n-alkane)}}$ record from North American continental interior, shows a 10% D-enrichment prior to the CIE followed by a negative shift (Smith et al., 2007), similar to trends observed in the Arctic where a large enrichment (~55%) was observed near the onset of the CIE followed by a return to pre-event $\delta^{13}$D$_{\text{(n-alkane)}}$ values (Pagani et al., 2006).

While plant community variation across the PETM could affect $\delta^{13}$D values, many of these $\delta^{13}$D shifts have been interpreted in terms of hydrological conditions (Handley et al., 2008; Pagani et al., 2006; Smith et al., 2007). Paleogene general circulation models indicate latitudinal variability in precipitation, with a decrease in total precipitation in low- and mid-latitudes. In higher-latitude continental regions and monsoonal climates, simulated increases in precipitation are observed (Huber and Sloan, 1999; Shellito et al., 2003). Low meridional temperature gradients lead to decreased zonal wind strength and increased tropical evaporation (Huber and Sloan, 1999). These conditions predict a decrease in the meridional isotopic gradient and D-enriched precipitation globally (Pierrehumbert, 2002), as well as smaller D/H changes in the low- to mid latitudes relative to the high latitudes (Pagani et al., 2006).

In general, $\delta^{13}$D$_{\text{(n-alkane)}}$ records are limited by resolution and erosional surfaces. Nevertheless, a broad pattern is emerging with mid- and high latitudes expressing larger negative D/H excursion near the onset of the CIE (Pagani et al., 2006; Smith et al., 2007). The Arctic record follows similar variations when updated age calibrations are used (Slijes et al., 2007). This trend is also expressed in the Forada $\delta^{13}$D$_{\text{(n-alkane)}}$ Record where D-enrichment occurs prior to the event, followed by an abrupt and stable shift to more negative values, ending a gradual change to more positive values during the recovery phase of the PETM (Fig. 3). The shift to more positive $\delta^{13}$D$_{\text{(n-alkane)}}$ values prior to the onset of the CIE suggests early adjustments in hydrological conditions just before the onset of the isotope anomaly. Given the limited resolution of the Forada $\delta^{13}$D$_{\text{(n-alkane)}}$ record compared the $\delta^{13}$C$_{\text{(n-alkane)}}$ record, we cannot assess temporal offsets in the hydrogen
Fig. 5. Carbon isotope, hydrogen isotope, average chain length, and sea-surface temperature records from the Forada section relative to stratigraphic age. Age assignments based on Giusberti et al. (2007). Bulk carbonate δ^{13}C values (a.), δ^{13}C (b.), and δD (c.) values for n-C_{30} Sea-surface temperature estimates from TEX86 (e.), temperature estimates from the Kim et al. (2010) calibration.

isootope values. Nonetheless, high-resolution PETM sea-surface temperature records from the Atlantic coast of North America provide some evidence for warming several thousand year prior to the onset of the CIE (Slujs et al., 2007b). The Forada sea-surface temperature (SST) record also suggests warming of ~2–3 °C prior to the onset of the CIE (Fig. 5). Similarly, pre-event warming ~30 kyr prior to the onset of the CIE has been interpreted from Forada planktonic foraminifera (Luciani et al., 2007), consistent with the SST records. Both planktonic foraminiferal and SST records should not be subject to the temporal offset observed in the terrestrial isotope records at Forada as they are both marine signals. Even so, Forada SST and δDalkane records along with records from the Arctic, and the Bighorn Basin are consistent with fundamental changes in hydrologic cycle prior to the onset of the CIE. The nature and robustness of these changes are purely speculative, but early warming (Secord et al., 2010; Slujs et al., 2007b) or oceanographic and climatic reorganization (Thomas et al., 2002; Tripati and Elderfield, 2004) would appear required.

5. Conclusions

High-resolution carbon and hydrogen isotope PETM records from higher-plant derived biomarkers, bulk organic carbon, and marine carbonate from the continuous and orbitally tuned Forada section in northern Italy were established to assess the marine and terrestrial expressions of the CIE and the character of warming. This work represents the first opportunity to evaluate variations between the two reservoirs at high resolution. We found differences between marine and terrestrial systems in both the temporal expressions of the CIE, as well as the magnitudes of isotope change. All Forada δ^{13}C records show a sharp spike at the onset of the PETM with the CIE determined from δ^{13}Calkane values lagging behind the CIE expressed by both δ^{13}Ccarbonate and δ^{13}Corganic values by 4–5 kyr. These results suggest the incorporation of pre-PETM n-alkanes due to soil erosion and a minimum residence time of soil n-alkanes of ~4000 yr during the initial phase of the CIE. In addition, we found δDalkane values varied prior to, and during, the PETM, consistent with a general global pattern where mid- and high latitude sites demonstrate more negative values near the onset of the CIE. We also observe a shift to more positive δDalkane values prior to the onset of the CIE. These data, coupled with TEX86 temperature estimates, suggest both hydrologic and temperature changed prior to the onset of the CIE.

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