

## Chapter 4

### **Extreme warming of mid-latitude coastal ocean during the Paleocene-Eocene thermal maximum: Inferences from TEX<sub>86</sub> and Isotope Data**

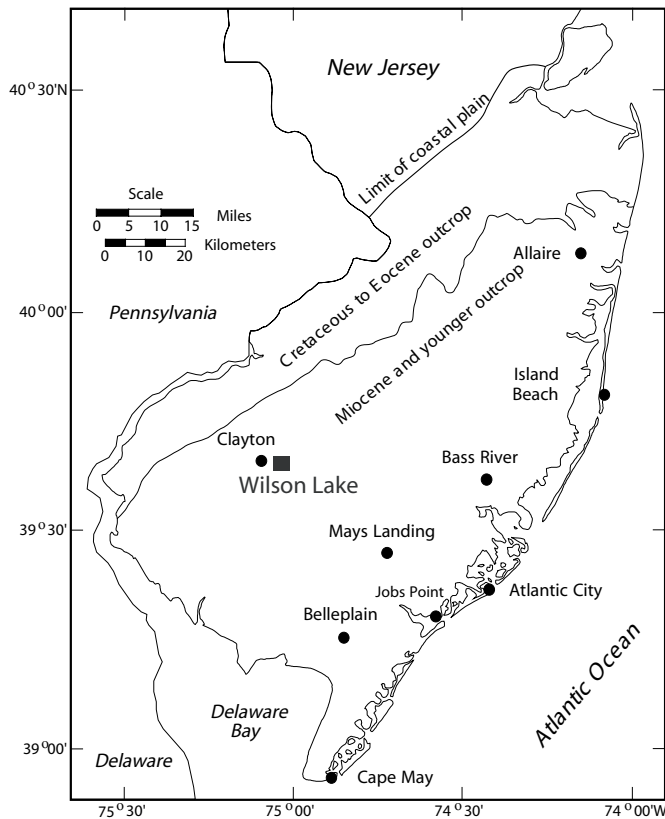
Changes in sea surface temperature (SST) during the Paleocene-Eocene thermal maximum (PETM) have been estimated primarily from oxygen isotope and Mg/Ca records generated from deep-sea cores. Here we present a record of sea surface temperature change across the P-E boundary for a near-shore, shallow marine section located on the eastern margin of North America. The SST record, as inferred from TEX<sub>86</sub> data, indicates a minimum of 8°C of warming, with peak temperatures in excess of 33°C. Similar SST are estimated from planktonic foraminifer oxygen isotope records, although the excursion is slightly larger. The slight offset in the oxygen isotope record, together with higher rates of siliciclastic sediment accumulation (particularly kaolinite) may reflect on seasonally higher runoff and lower salinity.

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### Introduction

The PETM represents one of the more prominent and abrupt climate anomalies in Earth history with sea surface temperatures (SST) increasing by as much as 5°C in the tropics and 8°C in the high latitudes (Thomas et al., 2002; Zachos et al., 2001; Zachos et al., 2003). The peak warmth was sustained for several tens of thousands of years before gradually returning to pre-event levels. Several lines of evidence indicate that a rise in greenhouse carbon levels (CH<sub>4</sub> and/or CO<sub>2</sub>) was responsible for this global warming (e.g., Dickens et al., 1995; Bowen et al., 2004; Svensen et al., 2004). The approximate mass of carbon released is still unknown, but has been estimated to be in excess of 2000 GtC (Dickens et al., 1997), and possibly as high as 4500 GtC (Chapter 1), a range which is roughly comparable to the mass of anthropogenic carbon that could be released over the next several centuries (e.g., Archer, in press).

If the rise in SST documented in open ocean sites was a consequence of greenhouse warming, the impacts on coastal climate should have been substantial as well. For example, SST should have risen by as much, if not more, than observed in the open ocean. Moreover, coastal oceans would have been particularly sensitive to changes in runoff, and hence, precipitation, though the



**Figure 1.** Location map showing the location of Wilson Lake ( $\sim 39^{\circ}39'N$ ;  $75^{\circ}2'W$ ) and other USGS and ODP cores (modified from (Miller, 1997)).

response would have been highly variable both spatially and temporally. Indeed, previous investigations of shallow marine sequences have found evidence of significant environmental perturbation of the coastal oceans during the PETM, including evidence of warming and changes in runoff (Gibson et al., 1993; Bujak and Brinkhuis, 1998; Egger et al., 2003). Much of the paleoclimatic information, however, has been derived from qualitative indexes such as fossil assemblages (Crouch et al., 2001; Crouch et al., 2003b), in part because traditional temperature proxies applied to deep-sea cores, such as oxygen isotopes, are not particularly well suited for application to shallow-marine, land-based sections. The general absence of planktonic foraminifera is one limitation. The effects of meteoric diagenesis, a process that can reset the primary oxygen isotopic composition of carbonates toward lower values, is another. Even where fossils are present and well preserved deviations in local seawater salinity from the global mean increase the uncertainty in estimating temperature from calcareous shell  $\delta^{18}\text{O}_{\text{shell}}$ . In shallow marine settings where runoff is high, the seasonal range in salinity can be several ppt, which can introduce variations in  $\delta^{18}\text{O}_{\text{sw}}$  of more than a per mil. With extreme greenhouse warming, precipitation and runoff should have changed as well, though the direction of change would vary from region to region, further compounding the uncertainty in deriving temperature solely from oxygen isotopes.

In this investigation, we estimate coastal SST during the PETM in a shallow marine sequence using an organic based proxy of SST,  $\text{TEX}_{86}$ , which is derived from the membrane lipids of marine crenarchaeota, a common component of picoplankton (Schouten et al., 2002; Schouten et al., 2003). Studies of core top sediments have demonstrated a strong correlation between the number of cyclopentane rings in crenarchaeotal membrane lipids and mean annual SST ( $r^2 = 0.92$ ). Moreover, culture experiments show that changes in salinity and nutrients do not substantially affect the temperature signal recorded by  $\text{TEX}_{86}$  (Wuchter et al., 2004) and it also seems to be unaffected by redox conditions (Schouten et al., 2004). With the  $\text{TEX}_{86}$  derived SST, we then use the oxygen isotopes to determine if this locality experienced substantial changes in salinity.

The section sampled for this study, Wilson Lake (WL; Fig. 1), is located in New Jersey (39°39N, 75°03W) where the upper Paleocene-lower Eocene is accessible by coring. The P-E boundary interval consists of unconsolidated siliciclastic sands and clays with low carbonate content (<15%) deposited during a sea level transgression (Gibson et al., 1993; Cramer et al., 1999). WL offers several advantages, one of which is high abundances of marine organic matter including dinoflagellates and crenarchaeotal lipids. Moreover, WL samples yield well-preserved planktonic foraminifera with some shells exhibiting porcelain textures (Fig. 2), though poorly preserved specimens are present as well. The well-preserved shells should yield close to primary  $\delta^{18}\text{O}$  values, which in

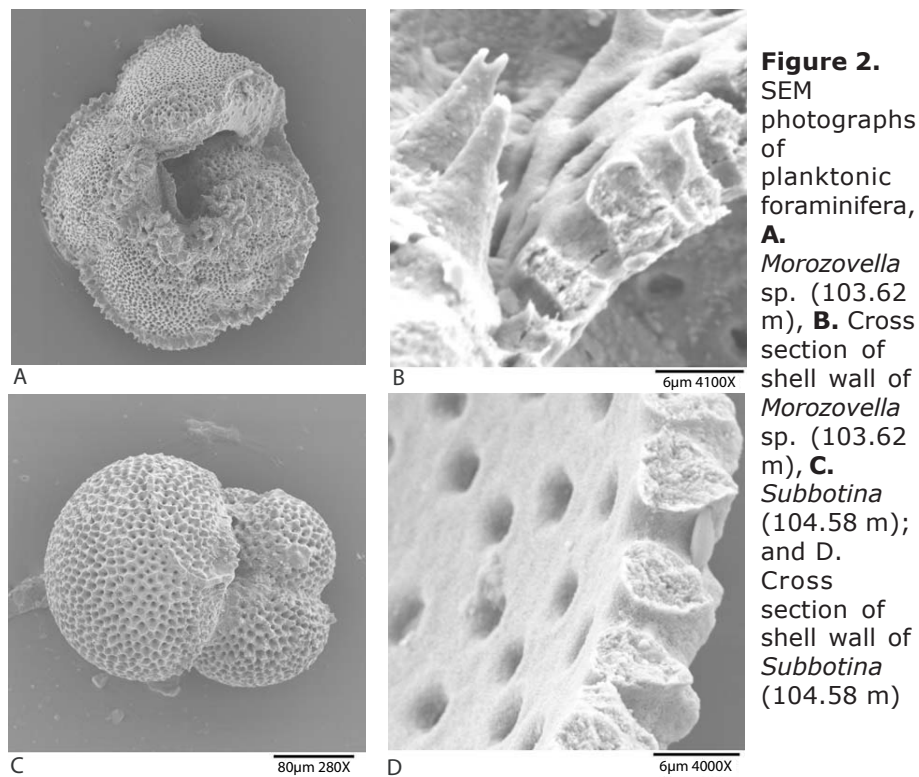
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combination with  $\text{TEX}_{86}$ , can be used to quantify changes in temperature as well as seawater  $\delta^{18}\text{O}$ .

### Facies Description and Methods

The WL P-E boundary section is marked by a distinct transition from glauconitic clayey-sandstones to silty claystones. This together with the absence of mollusks, suggests a middle shelf depositional setting, perhaps tens of kilometers offshore at a paleodepth between 25 and 100 m (Gibson et al., 2000). The upper most Paleocene and lower Eocene were recovered near the bottom of the core between 92 and 112 m. Two unconformities are apparent in the lowermost Eocene (Gibbs et al., 2006), though the P-E transition appears to be relatively complete. Flora representative of nannofossil zones NP9 and NP10 are present, though the exact position of the boundary between these zones is uncertain.

Samples were collected every 20–40 cm over a 20 m interval, disaggregated and wet sieved to isolate the sand fraction from which foraminifera were collected. Stable isotope analyses were carried out on planktonic and benthic foraminifera. The planktonic foraminifera included two taxa that resided in the mixed-layer, *Acarinina soldadoensis* and *Morozovella velascoensis (acuta)*, and a somewhat deeper dweller, *Subbotina triangularis*. Analyses were also carried out on benthic foraminifera



*Cibicidoides*. Measurements were performed on an Autocarb coupled to a PRISM Mass Spectrometer at UCSC. Precision based on replicate analyses of in-house standard CM is better than  $\pm 0.05$  and  $0.10\%$  for C and O isotopes, respectively. All values are reported relative to vPDB.

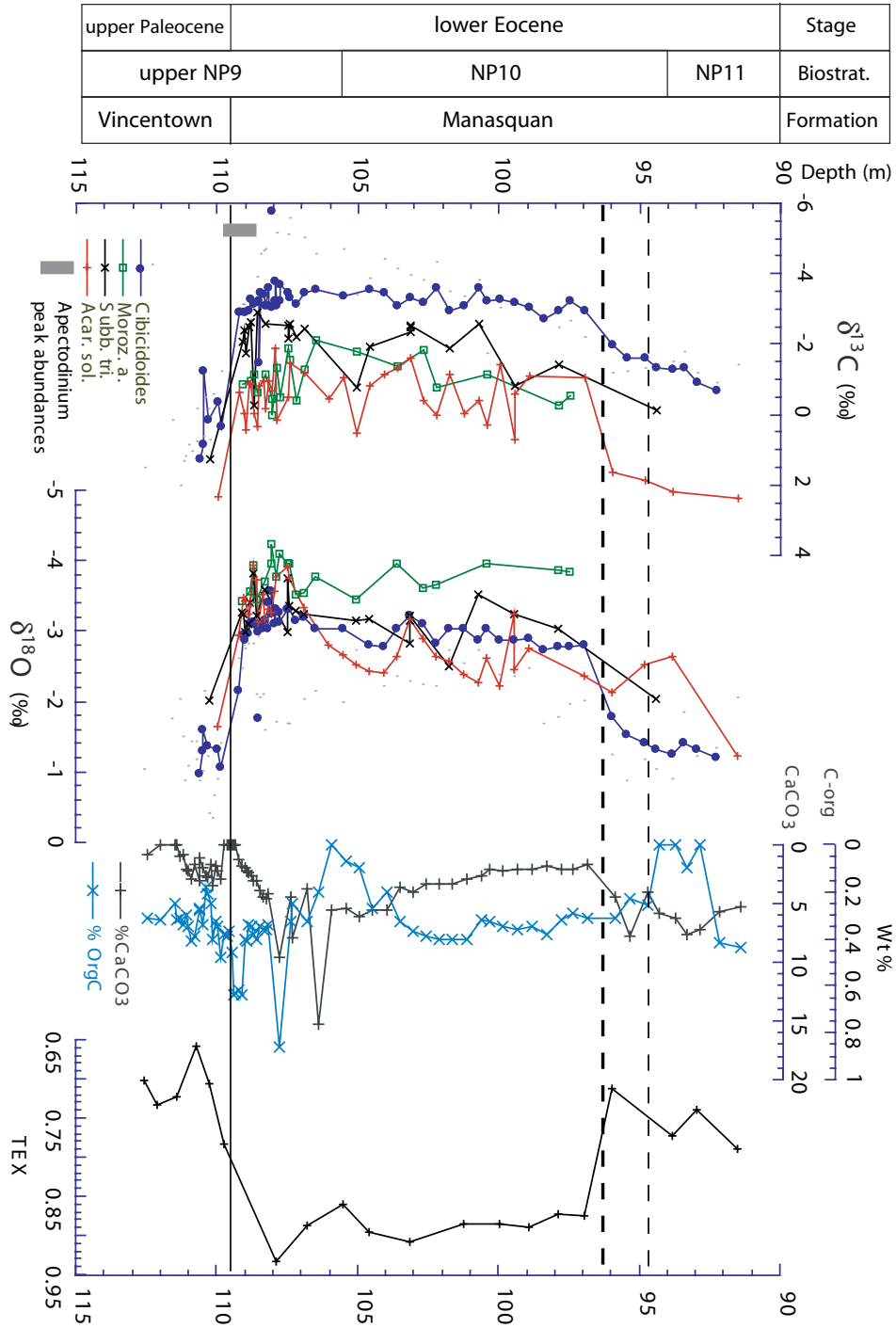
For the TEX<sub>86</sub> analyses, ~20 fine fraction (<63  $\mu\text{m}$ ) samples were selected and analyzed by high performance liquid chromatography/atmospheric pressure positive ion chemical ionization mass spectrometry (Schouten et al., 2002). In brief, the fine fractions were extracted with a Dionex Accelerated Solvent Extractor using a mixture of dichloromethane (DCM) and methanol (MeOH). The extract was fractionated into apolar and polar fractions, containing the crenarchaeotal lipids using a small column with activated alumina and using hexane/DCM (9:1;v/v) and DCM/MeOH (1:1;v/v) as eluents, respectively. Aliquots of polar fractions were dissolved in hexane/propanol (99:1;v/v), and filtered through 0.45  $\mu\text{m}$  PTFE filters. The samples were analyzed with an Thermo Finnigan Quantum Ultra (San Diego, CA, USA) triple quadrupole LC-MS and separation was performed on an Econosphere NH<sub>2</sub> column (4.6  $\times$  250 mm, 5  $\mu\text{m}$ ; Alltech, Derfield, IL, USA), maintained at 30°C. The GDGTs were eluted using a changing mixture of (A) hexane and (B) propanol as follows, 99 A:1 B for 5 min, then a linear gradient to 1.8 B in 45 min. Detection was achieved using atmospheric pressure chemical ionization-mass spectrometry of the eluent. Single Ion Monitoring (SIM) was set to scan the 5 [M+]<sup>+</sup>H ions of the GDGTs with a dwell time of 237 ms for each ion. All TEX<sub>86</sub> analyses were performed at least in duplicate. The concentration of branched and isoprenoid tetraether lipids (BIT index) was measured on 5 samples to constrain the concentration of terrestrial organic matter (Hopmans et al., 2004).

## Results

The WL foraminifera show distinct inter-species carbon isotope patterns not unlike those found in pelagic settings. For example, mixed layer species, *M. velascoensis* and *A. soldadoensis*, yield the highest carbon values, consistent with a near surface habitat, while *S. triangularis* and benthic foraminifera yield the lowest carbon values. The foraminiferal oxygen values on the other hand exhibit weaker gradients, and in some intervals none at all.

The most prominent feature of the isotope records are large negative excursions in both carbon and oxygen isotope across the Paleocene–Eocene boundary (110–109 m) (Fig. 3). The foraminifer  $\delta^{13}\text{C}$  values decrease by 3–4‰, while the  $\delta^{18}\text{O}$  values decrease by 2.0–2.5‰. Minimum  $\delta^{13}\text{C}$  values of –3.5‰ are recorded by the benthic foraminifera, and  $\delta^{18}\text{O}$  values of –4.3‰ by the mixed layer planktonic foraminifera. These low  $\delta^{13}\text{C}$  values are sustained over a 13 m interval to the base of the lower unconformity at ~96 m. After the initial  $\delta^{18}\text{O}$  decrease in the mixed-layer foraminifer, the records deviate with the *A. soldadoensis* values increasing

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to levels similar to or lower than the benthics, while the *M. velascoensis* values remain low ( $\sim -4.0\text{‰}$ ).

The  $\text{TEX}_{86}$  shows a sharp increase across the boundary that is essentially coincident with the decrease in foraminiferal oxygen isotope values. Application of the modern calibration to these values yields an increase in temperature from 31 to 40°C at the height of the PETM, which are exceedingly high temperatures. However, the modern calibration is based on empirical core top data from 0 to 28°C (Schouten et al., 2002; Schouten et al., 2003). As a result, it was necessary to extrapolate out to higher  $\text{TEX}_{86}$  values to interpret the SSTs. Therefore, we applied the more conservative calibration line based on core top data from 20-28°C as proposed by Schouten et al. (2003) for SST >28°C. This results in temperatures ranging from 25°C prior to and after the PETM to 33°C at the peak of the event. The BIT index for the 5 samples analyzed ranged between 0.05 and 0.14 (Chapter 6).

### ***Dinoflagellates / Palynomorphs***

Palynological assemblages from WL are characterized by the persistent dominance of dinocysts over other palynomorphs, including pollen. The dinocyst succession is marked by the successive dominance of typical late Paleocene – early Eocene taxa such as *Areoligera*, *Spiniferites*, *Cordosphaeridium*, *Senegalinium*, *Membranosphaera* and, notably, *Apectodinium*. The global acme of the latter taxon is also recorded at WL, peaking only at the onset of the PETM (e.g., Bujak and Brinkhuis, 1998; Crouch et al., 2001; Crouch et al., 2003b). The peak abundances of *Apectodinium* fall between 109.42 and 108.69 m, preceding slightly the maximum temperatures derived from  $\delta^{18}\text{O}$  and  $\text{TEX}_{86}$ . An additional peak of *Apectodinium* is recorded in the upper part of the carbon isotope excursion. The sediments are nearly barren of terrestrial palynomorphs, an observation that is consistent with the low BIT index values, suggesting that either river discharge occurred far from the drill site, or vegetation was scarce in the hinterland of WL.

**Figure 3.** (Left) The column to the far left show the lithology and nannofossil biostratigraphic zonations for Wilson Lake plotted versus sub-surface depth (m). The biostratigraphic scheme follows the NP scheme of Martini (Martini, 1971) where the NP9/10 boundary is defined as the first occurrence of *Rhomboaster/Tribrachiatus bramlettei* and the NP10/NP11 boundary is approximated by the first occurrence of *T. orthostylus*. Stable isotope, weight % Corg and %CaCO<sub>3</sub>, and  $\text{TEX}_{86}$  raw data are plotted versus depth. The stable isotope data are from analyses of *Morozovella velascoensis (acuta)*, *Acarinina soldadoensis*, *Subbotina* spp. and *Cibicidoides* spp. The dashed lines at 94.79 and 96.32 m represent unconformities. The lower unconformity truncates the upper portion of the excursion layer. Gray bar in the left panel shows the level of the dinoflagellate *Apectodinium* abundance acme.



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### Discussion

Prior to this work, investigations that have attempted to constrain SST changes across the PETM have mostly focused on the magnitude of the anomalies rather than absolute temperatures (e.g., (Thomas et al., 1999; Zachos et al., 2003; Tripathi and Elderfield, 2004), in part because of potential preservational artifacts (Schrag et al., 1995). The peak SST of 33°C estimated from  $\text{TEX}_{86}$  for this locality is high, especially if it is viewed as an annual mean, rather than summer maximum. In comparison, modern SST along this coast (over the shelf) ranges from 4°C in winter to 28°C in summer (NOAA), with an annual mean of approximately 17°C. Because coastal ocean temperatures often have a strong local/regional overprint, it is probably not valid to assume these paleotemperatures were representative of open Atlantic SST at this latitude. Nevertheless, based on GCM simulations, it appears a zonally averaged summer temperature of 33°C for this paleolatitude (~35-37°N at 55 Ma) would require a  $p\text{CO}_2$  in excess of 2000 ppm (Shellito et al., 2003).

Modern calibration of  $\text{TEX}_{86}$  is limited to temperatures below 28°C, making the estimates of absolute temperatures above this value somewhat suspect. Yet, the absolute temperatures computed here are well within the range estimated from oxygen isotopes. In fact, if we use  $\delta^{18}\text{O}_{\text{shell}}$  to estimate temperature assuming an ice-free world (mean ocean  $\delta^{18}\text{O}$  of -1.0‰), but with a local  $\delta^{18}\text{O}_{\text{sw}}$  of -0.5‰ due to evaporation (Zachos et al., 1994), the planktonic foraminiferal temperatures derived for the earliest Eocene are essentially identical to the  $\text{TEX}_{86}$  temperatures, though the upper Paleocene temperatures are offset by 2°C (Fig. 4). Alternatively, if we just consider the temperature anomaly interpreted from  $\text{TEX}_{86}$  values (+8°C), we can estimate relative changes in  $\delta^{18}\text{O}_{\text{sw}}$ /salinity using the planktonic foraminiferal oxygen isotope records. An 8°C rise in temperature should lower  $\delta^{18}\text{O}_{\text{shell}}$  by 1.7‰. The benthic and *A. soldadoensis* excursions were roughly -1.85 and -2.2‰, respectively, implying a possible  $\delta^{18}\text{O}_{\text{sw}}$  change of -0.20 to -0.5‰. This discrepancy could reflect a decrease in local SSS (and  $\delta^{18}\text{O}_{\text{sw}}$ ) due to higher runoff during the PETM. Assuming a  $\Delta\delta^{18}\text{O}/\Delta\text{salinity}$  relationship of 0.15‰/ppt (Fairbanks, 1982), the -0.5‰ residual ( $\Delta\delta^{18}\text{O}_{\text{sw}} = \Delta\delta^{18}\text{O}_{\text{shell}} - \Delta\delta^{18}\text{O}_{\text{TEX}}$ ) would require a modest decrease of roughly 3-4 ppt.

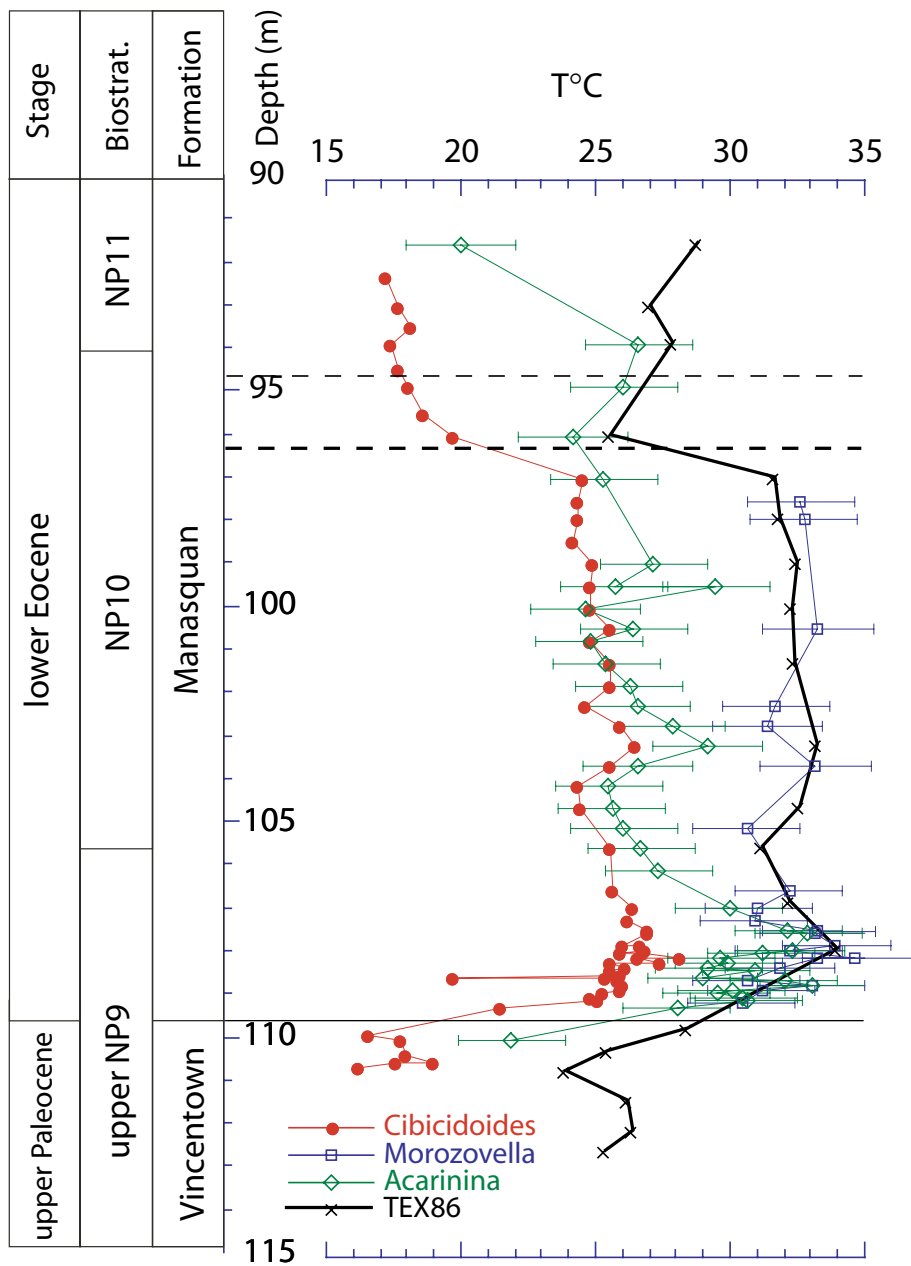
Is a shift toward higher regional runoff and precipitation supported by the other lithologic and paleontologic data? The clay-rich excursion layer is relatively thick and dominated by kaolinite, patterns that have been observed elsewhere and attributed to higher humidity and more intense chemical weathering and runoff (e.g., Gibson et al., 2000; Egger et al., 2003). The *Apectodinium* acme is also associated with higher temperatures and enhanced runoff, stratification, and eutrophic conditions in coastal waters (Bujak and Brinkhuis, 1998; Gibson et al., 2000; Crouch et al., 2003b; Egger et al., 2003). This genus is morphologically very similar to modern cysts almost exclusively produced by heterotrophic



dinoflagellates and thus would have required nutrient rich conditions (Bujak and Brinkhuis, 1998). Nannofossil assemblages also indicate increased fertility during the PETM at WL (Gibbs et al., 2006). Increased discharge by rivers likely supplied the necessary nutrients to fertilize the coastal ocean. On the other hand, there is very little terrestrial organic matter in this core. One possibility is that regional climate in this region became more seasonally extreme during the PETM, with a brief, intense wet season and prolonged dry season. Under this climate regime, the local landscape would have been sparsely vegetated and thus prone to excessive erosion during the wet season, which would explain both the increased flux of terrigenous sediment, and scarcity of terrestrial organic matter.

Although the absolute SST/SSS values estimated for this location should be viewed with some caution until the uncertainties in the  $\text{TEX}_{86}$  temperature calibration are reduced, the estimated peak temperature of  $33^{\circ}\text{C}$  is substantially higher than would be estimated from  $\delta^{18}\text{O}$  of planktonic foraminifera ( $\sim 25^{\circ}\text{C}$ ) from tropical or subtropical deep sea cores, consistent with the notion that the latter are biased toward heavier  $\delta^{18}\text{O}$  values/colder temperatures (e.g., Schrag et al., 1995). As such, this coupled  $\text{TEX}_{86}$ /isotope approach shows promise for quantifying both absolute temperature and salinity change during the PETM, and thus should be applied to other clay rich, shelf sections.

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**Figure 4.** Sea surface temperatures as computed from a) planktonic foraminifera  $\delta^{18}\text{O}$ , and b) the  $\text{TEX}_{86}$ . The oxygen isotope based curves were derived assuming seawater  $\delta^{18}\text{O}_{\text{sw}}$  of  $-0.5\text{‰}$  (SMOW). The errors bars on the planktonic foraminifera curves reflect the range of possible temperatures associated with  $\pm 0.5\text{‰}$  uncertainty in  $\delta^{18}\text{O}_{\text{sw}}$ .