

## LETTERS

# Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary

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The start of the Palaeocene/Eocene thermal maximum—a period of exceptional global warming about 55 million years ago—is marked by a prominent negative carbon isotope excursion that reflects a massive input of <sup>13</sup>C-depleted ('light') carbon to the ocean–atmosphere system<sup>1</sup>. It is often assumed<sup>2</sup> that this carbon injection initiated the rapid increase in global surface temperatures and environmental change that characterize the climate perturbation<sup>3–7</sup>, but the exact sequence of events remains uncertain. Here we present chemical and biotic records of environmental change across the Palaeocene/Eocene boundary from two sediment sections in New Jersey that have high sediment accumulation rates. We show that the onsets of environmental change (as recorded by the abundant occurrence ('acme') of the dinoflagellate cyst *Apectodinium*) and of surface-ocean warming (as evidenced by the palaeothermometer TEX<sub>86</sub>) preceded the light carbon injection by several thousand years. The onset of the *Apectodinium* acme also precedes the carbon isotope excursion in sections from the southwest Pacific Ocean<sup>8</sup> and the North Sea, indicating that the early onset of environmental change was not confined to the New Jersey shelf. The lag of ~3,000 years between the onset of warming in New Jersey shelf waters and the carbon isotope excursion is consistent with the hypothesis that bottom water warming caused the injection of <sup>13</sup>C-depleted carbon by triggering the dissociation of submarine methane hydrates<sup>1,9,10</sup>, but the cause of the early warming remains uncertain.

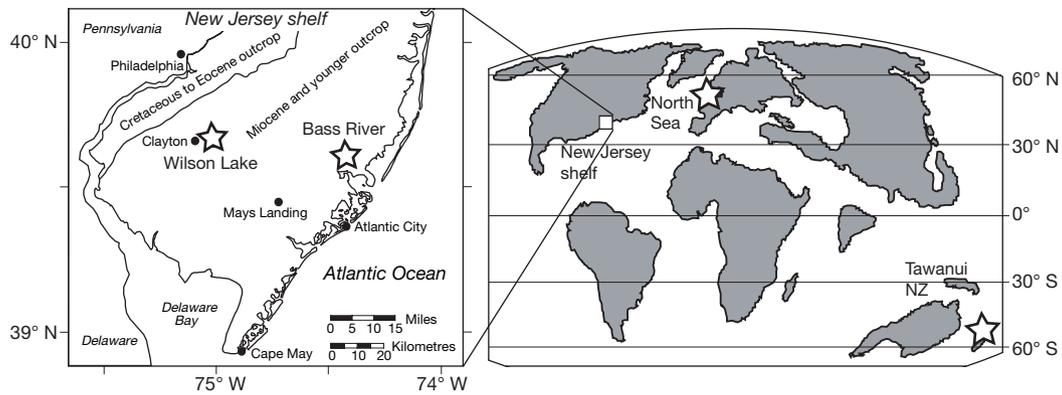
The globally recognized carbon isotope excursion (CIE) at the Palaeocene/Eocene thermal maximum (PETM) marks a >2.5‰ decrease in the stable carbon isotope composition (δ<sup>13</sup>C) of sedimentary components<sup>3,11</sup>. It signifies an enormous (at least 1.5 × 10<sup>18</sup> g) input of <sup>13</sup>C-depleted carbon to the ocean and atmosphere, analogous in both magnitude and composition to current and expected fossil fuel emissions<sup>1,2,12</sup>. One prominent example of biotic change associated with the onset of the CIE is recorded along continental margins, where sediment sequences from all latitudes contain high abundances of dinoflagellate cysts (dinocysts; Supplementary Information) belonging to the subtropical genus *Apectodinium*<sup>6–8,13</sup>; the *Apectodinium* acme. The source and impact of the <sup>13</sup>C-depleted carbon input, however, remain controversial<sup>1,2,12,14</sup>. One possibility is the rapid dissociation of submarine methane hydrates<sup>1</sup>; other theories include the injection of thermogenic methane<sup>15</sup> and oxidation of sedimentary organic carbon<sup>12</sup>. Underlying the current debate is whether the input of <sup>13</sup>C-depleted carbon to the atmosphere caused or resulted from global warming and environmental change.

Unravelling the sequence of events at the onset of the PETM has been difficult, given the rapid nature of the perturbation. Some climate proxy records suggest that onset of warming slightly preceded the CIE<sup>5,16</sup>. However, these records are from slowly accumulating deep marine sediment sections, where bioturbation has blurred various signals and carbonate dissolution reduced temporal resolution, particularly for the onset of the event<sup>17</sup>. Indeed, it has been argued that the evidence for early warming is an artefact of sediment mixing or within the range of normal climatic variability<sup>18,19</sup>. To gain greater temporal resolution, we have generated chemical and biotic records from expanded PETM sediment sections located in shelf areas (Fig. 1). Two of these sections are from the New Jersey shelf at ~40°N palaeolatitude: Ocean Drilling Program (ODP) Site 'Bass River' and United States Geological Survey (USGS) borehole 'Wilson Lake'. We generated carbon isotope and palynological data at these sites, in conjunction with new temperature records based on the organic palaeothermometer TEX<sub>86</sub> ('tetraether index' of tetraether lipids consisting of 86 carbon atoms).

At Bass River, the onset of the CIE was previously identified by a negative step in the δ<sup>13</sup>C of bulk carbonate (δ<sup>13</sup>C<sub>BC</sub>) and foraminifera<sup>20,21</sup>. We have augmented these data by generating δ<sup>13</sup>C records of dinocyst assemblages (δ<sup>13</sup>C<sub>DINO</sub>) (Fig. 2a, Supplementary Fig. 1), and our resolution is over three times higher than the original study at this site<sup>20</sup>. The onset of the CIE is at 357.3 m below surface (m.b.s.) based on the δ<sup>13</sup>C<sub>BC</sub> record (Fig. 2a), the same level as indicated by δ<sup>13</sup>C records from foraminifera<sup>21</sup>. Even though the upper part of the CIE is truncated by a sequence boundary at ~347.0 m.b.s. (Supplementary Fig. 1), the ~10.3-m-thick CIE interval is greatly expanded relative to that found in existing deep marine sections (<3 m). The onset of the *Apectodinium* acme is at 357.7 m.b.s., clearly lying below the base of the CIE by ~40 cm. This is not an artefact of bioturbation because the CIE is identified at the same level in the δ<sup>13</sup>C<sub>DINO</sub> record, which is predominantly derived from *Apectodinium* in this interval (Fig. 2a). Only the first ~120 kyr of the CIE is represented (Supplementary Information), so that sedimentation rates across this interval are 8–10 cm kyr<sup>-1</sup>. Thus, the onset of the *Apectodinium* acme preceded the onset of the CIE at this site by about 4–5 kyr.

To assess the relative timing and magnitude of PETM warming at Bass River, we constructed a temperature record based on TEX<sub>86</sub>. Planktonic foraminifer δ<sup>18</sup>O records are not complete, exhibit much scatter and even within samples the variability in δ<sup>18</sup>O of individual planktonic foraminifera is very large; hence, these records are not suitable for determining the onset of PETM warming (Supplementary Information). The TEX<sub>86</sub> palaeothermometer is based on the

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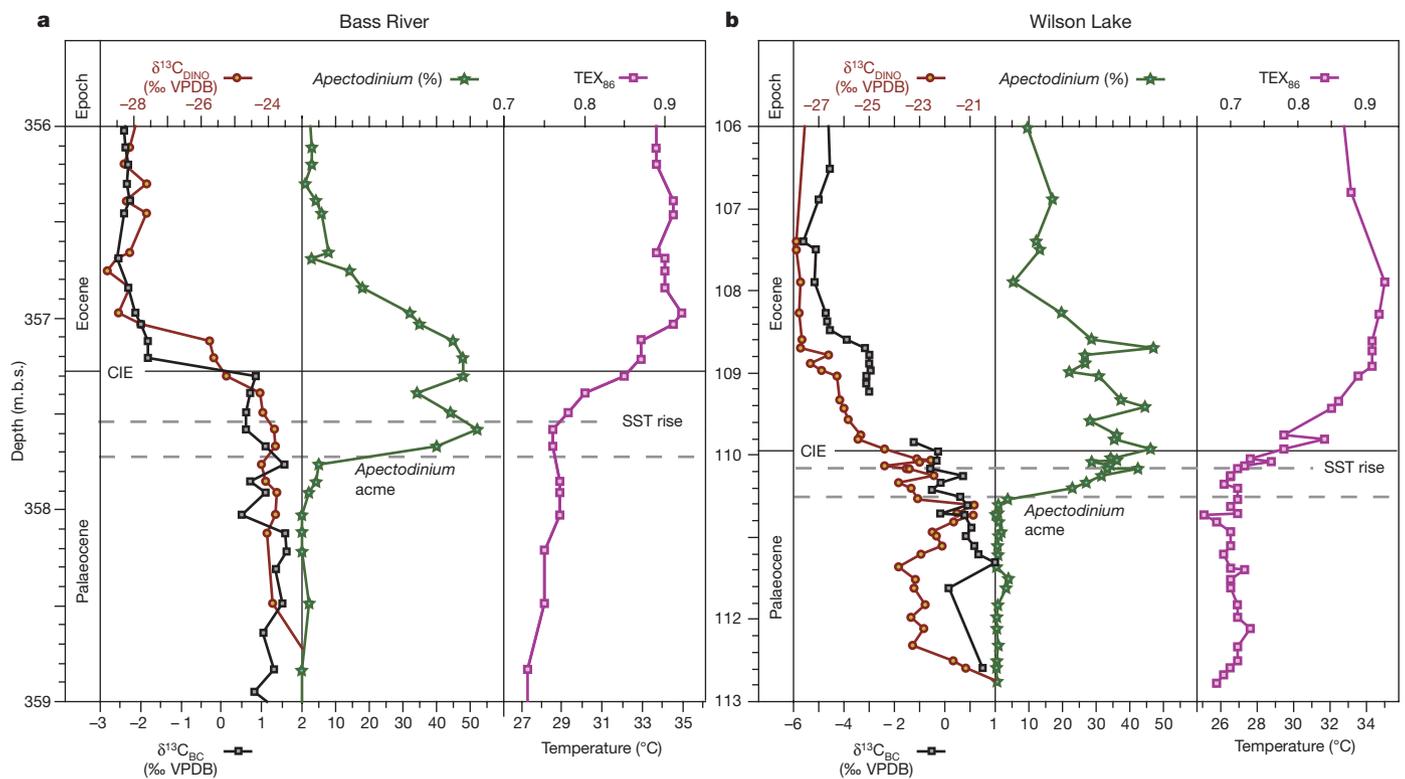
**Figure 1** | Location of the studied sites. Left, drill locations of the Wilson Lake and Bass River cores. Right, locations of all studied sites within a

palaeogeographic reconstruction of the Earth at PETM times (see Supplementary Information for the sources of the maps). NZ, New Zealand.

relative abundance of fossil crenarchaeotal membrane lipids in sediment. In modern marine surface sediments,  $TEX_{86}$  shows a significant linear correlation with mean annual sea surface temperature (SST), independent of nutrient availability or salinity<sup>22,23</sup>. The Bass River  $TEX_{86}$  values are up to 0.92, and thus exceed those measured in modern marine sediment ( $<0.8$ ). Two temperature calibrations can be applied to these high  $TEX_{86}$  values, which suggest surface water warming during the PETM from 28 to 34 °C (ref. 24) or from 31 to 41 °C (ref. 22) (Supplementary Fig. 1). With either calibration, the  $TEX_{86}$  record at Bass River shows gradual warming between  $\sim 357.55$  and 357.0 m.b.s., including intermediate temperatures (Fig. 2a). The record clearly indicates that onset of anomalous warming lies at least  $\sim 25$ –30 cm below the CIE, and that approximately half of the total warming occurred before the onset of the CIE (Fig. 2a). Assuming the above sedimentation rates, the onset of the *Apectodinium* acme

started  $\sim 1$ –1.5 kyr before the onset of warming. In turn, the onset of warming at Bass River preceded the massive input of  $^{13}C$ -depleted carbon by approximately 3–3.5 kyr.

To confirm the trends at Bass River, we generated a similar data set for the Wilson Lake site. At this site, the CIE is approximately 13.5 m thick, based on both the  $\delta^{13}C_{BC}$  and the  $\delta^{13}C_{DINO}$  record (Supplementary Fig. 2). In the  $\delta^{13}C_{BC}$  record, the base of the CIE is not as clearly marked as at Bass River, primarily due to the absence of carbonate between  $\sim 109.3$  and  $\sim 109.8$  m.b.s. (Fig. 2b). Our  $\delta^{13}C_{DINO}$  record shows background upper Palaeocene values, which are  $\sim 1\%$  heavier than at Bass River, up to  $\sim 110.0$  m.b.s. At this level the transition to true CIE values starts, coinciding with a negative step in the  $\delta^{13}C_{BC}$  record, together implying the base of the CIE to be at this level. Several relatively heavy  $\delta^{13}C_{DINO}$  values occur between  $\sim 110.6$  and  $\sim 110.8$  m.b.s., which are not present in the  $\delta^{13}C_{BC}$



**Figure 2** | High-resolution records across the onset of the PETM at the New Jersey Shelf Sites. **a**, Bass River. Bulk carbonate  $\delta^{13}C$  data are from ref. 21. **b**, Wilson Lake. Part of the  $TEX_{86}$  data are from ref. 25 (see Supplementary Table 1 for details). Solid horizontal lines at  $\sim 357.3$  m.b.s. and  $\sim 110.0$  m.b.s. for Bass River and Wilson Lake, respectively, represent the

onset of the CIE; dashed lines represent the onsets of the *Apectodinium* acme and surface warming. BC, bulk carbonate; DINO, dinocysts; VPDB, Vienna Pee Dee Belemnite; m.b.s., metres below surface. Scale at  $TEX_{86}$  temperatures represents the calibration from ref. 24. See Supplementary Information for the full records.

record. Such values are also not recorded in equivalent strata at Bass River (Fig. 2a), indicating they do not represent a global exogenic  $\delta^{13}\text{C}$  change, and are likely to result from local factors influencing  $\delta^{13}\text{C}_{\text{DINO}}$  at Wilson Lake. The onset of the *Apectodinium* acme at  $\sim 110.4$  m.b.s. clearly lies below the CIE by  $\sim 40$  cm. Given the 13.5 m thickness of the  $\sim 170$  kyr CIE, sedimentation rates average  $\sim 8$  cm kyr $^{-1}$  at this site, so this offset represents about 4–5 kyr. Similar to Bass River, the  $\text{TEX}_{86}$  record at Wilson Lake, updated from ref. 25, indicates intermediate values and several data points suggest that warming occurred before the CIE (from  $\sim 110.15$  m.b.s.). The pre-CIE warming is less clear at Wilson Lake than at Bass River, but the offset of  $\sim 15$  cm implies that warming initiated  $\sim 2$  kyr before the CIE (Fig. 2b).

The somewhat different records at the two sites might represent local processes that affect deposition in neritic settings. For example, Wilson Lake was located closer to shore (Fig. 1) and the record is likely to be less complete than that from Bass River because of breaks in deposition<sup>20</sup>. Although uncertainties in the age models necessarily imply some uncertainties in the duration of the leads and lags, the two New Jersey records show that a pulse in *Apectodinium* and subsequent sea surface water warming preceded the input of the  $^{13}\text{C}$ -depleted carbon that caused the CIE by several thousand years.

Very few other locations are available where the sequence of events at the onset of PETM can be studied. However, the onset of the *Apectodinium* acme also appears to have started  $\sim 4$  kyr before the CIE in a newly studied sediment section from the central North Sea at  $\sim 55^\circ\text{N}$  palaeolatitude, and, although less clearly, in published data from a section from the southwest Pacific Ocean at  $\sim 55^\circ\text{S}$  palaeolatitude (Supplementary Fig. 3; Supplementary Information). Hence, in mid-latitude regions, a marked increase in *Apectodinium* is the earliest sign of anomalous environmental change associated with the PETM. A baseline requirement for abundant *Apectodinium* appears to have been relatively high temperatures, judging from biogeographical patterns<sup>13</sup>. As *Apectodinium* was abundant in the Arctic Ocean when SSTs reached  $23^\circ\text{C}$  (ref. 6), it should have flourished on the New Jersey shelf during the late Palaeocene if SST was the only environmental control on its abundance. Dinoflagellate assemblages are extremely sensitive to their surroundings, and significant changes in other environmental parameters, perhaps including surface water stratification, salinity and food supply, must have contributed to the *Apectodinium* acme at middle to high latitudes during the PETM<sup>8,13</sup> (Supplementary Information).

One possible constraint on their environmental preferences is derived from recent data from New Jersey (Supplementary Fig. 4) and the Arctic<sup>6</sup>. These indicate that *Apectodinium* locally became outnumbered by typical low-salinity-tolerant taxa, which suggests that very low salinities were not optimal for *Apectodinium*. Occasional pulses of *Apectodinium* in upper Palaeocene strata deposited in the Tethyan Ocean indicate that appropriate conditions occurred episodically and locally at low latitudes before the PETM (Supplementary Information). Such unusual conditions, however, only became globally and uniquely significant at the onset of the PETM. Although surface water parameters causing the *Apectodinium* acme remain unknown, the acme serves as a harbinger to the extensive global environmental change at the PETM.

Warming before the CIE is consistent with the hypothesis that thermal dissociation of submarine gas hydrates caused the CIE<sup>1</sup>. In the present oceans, large amounts of gas hydrate exist within sediments along continental slopes where microbes generate sufficient methane to saturate pore waters at relatively high pressures and low temperatures<sup>26</sup>. Although the distribution of gas hydrates was probably less extensive in the Palaeogene because of warmer deep waters, the mass of gas hydrates may have been similar to or greater than present-day amounts because of enhanced methane production<sup>27</sup>. Given mass estimates for modern gas hydrates<sup>28</sup>, a rapid  $5^\circ\text{C}$  increase in deep ocean temperature, such as inferred for the PETM<sup>3,5,14</sup>, should have released nominally 2,000 Gt of methane, about that

required to cause a  $-3\text{‰}$  excursion in global  $\delta^{13}\text{C}$  records<sup>1</sup>. Crucially, this mechanism necessitates a time lag between initial warming and carbon input because heat must propagate downward from the sea floor to drive an endothermic reaction in underlying sediment. The duration of this time lag should be several thousands of years<sup>9,10</sup>, which agrees with observations in our records.

Our records clearly show that initiation of the *Apectodinium* acme and substantial, rapid warming along the ancient shelf of New Jersey preceded the massive input of  $^{13}\text{C}$ -depleted carbon that caused the CIE. This observation provides a fundamental constraint on mechanisms for global change during the PETM. Potentially, the pre-CIE warming in New Jersey shelf waters was caused by substantial changes in ocean–atmosphere circulation—perhaps associated with an orbitally modulated<sup>29</sup> surpassing of a threshold—which was the initially proposed mechanism for methane hydrate dissociation at the PETM<sup>1</sup>. Alternatively, the warming was driven by an increase in greenhouse gas concentrations that did not significantly affect the  $\delta^{13}\text{C}$  of the exogenic carbon pool and, hence, our  $\delta^{13}\text{C}$  records. An enormous input of mantle-derived carbon is possible because evidence exists for massive volcanism close to the PETM<sup>30</sup>, and because such an injection (with a  $\delta^{13}\text{C}$  of  $-5\text{‰}$  to  $-7\text{‰}$ ) would have minimally affected the  $\delta^{13}\text{C}$  of the ocean–atmosphere reservoir. However, it remains uncertain whether volcanism could have produced  $\text{CO}_2$  at a rate required for rapid global environmental change. Higher net fluxes of  $\text{CO}_2$  from the ocean into the atmosphere could also have caused higher atmospheric concentrations without significantly changing global exogenic  $\delta^{13}\text{C}$ . Pre-CIE warming also could have been caused by an increase in non-carbon greenhouse gases. If the pre-CIE warming was carbon-forced, it directly implies that the warming and ocean acidification during the PETM were caused by at least two sources of carbon with different isotopic compositions, compromising the use of simple mass balance calculations<sup>2,12</sup> to elucidate the origin and volume of the injected carbon and the estimation of climate sensitivity to carbon input. It is important to note that although the *Apectodinium* acme started before the CIE, the dinoflagellate assemblages did not change significantly across the onset of the CIE. This suggests that environmental change was well under way before the injection of  $^{13}\text{C}$ -depleted carbon, at least in New Jersey and the North Sea.

## METHODS SUMMARY

Freeze-dried samples were processed for fully quantitative analyses (including addition of the exote *Lycopodium*) using 30% HCl and 38% HF. Processing of the North Sea samples (Supplementary Information) included oxidation in Schultz's reagent at  $80^\circ\text{C}$ . Residues were placed in an ultrasonic bath for a maximum of 5 min and sieved over a  $15\text{-}\mu\text{m}$  mesh. Slides were analysed at  $500\times$  magnification to a minimum of 200 dinocysts. Absolute quantitative numbers were calculated using the relative number of *Lycopodium*.

Extraction of crenarchaeotal tetraether lipids was performed on freeze-dried samples using accelerated solvent extraction with a dichloromethane/methanol (2:1) mixture, after which polar and apolar fractions were separated. Polar fractions were filtered and analysed using high performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry. Single ion monitoring was used to quantify the abundance of the crenarchaeotal lipids.  $\text{TEX}_{86}$  values were determined at least in duplicate and converted to temperature using the equations from refs 22 and 24 (see text). Abundances of branched tetraether lipids from terrestrial origin appeared very low. The crenarchaeotal lipids are not present in the sediments from the North Sea site due to the relatively high maturity of the organic matter.

For the  $\delta^{13}\text{C}_{\text{DINO}}$  records, dinocysts were isolated using a  $40\text{ }\mu\text{m}$  and a  $125\text{ }\mu\text{m}$  nylon mesh sieve and oven-dried. All  $\delta^{13}\text{C}_{\text{TOC}}$  (North Sea site; Supplementary Information) and  $\delta^{13}\text{C}_{\text{DINO}}$  analyses were done with a Fison NA 1500 CNS analyser, connected to a Finnigan Delta Plus mass spectrometer. Analytical precision determined by replicate analyses was better than  $0.1\text{‰}$ . For the  $\delta^{13}\text{C}_{\text{BC}}$  values, freeze-dried samples were measured using an Autocarb or Optima coupled to a PRISM Mass Spectrometer at UCSC. Precision, based on replicate analyses of in-house standard Carrara Marble, is better than  $\pm 0.05\text{‰}$ . All isotope values are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard.

**Full Methods** and any associated references are available in the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

**Received 11 June; accepted 18 October 2007.**

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**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

**Acknowledgements** This research used samples and/or data provided by the Integrated Ocean Drilling Program. A.S. thanks the Utrecht Biogeology Center, the LPP Foundation and The Netherlands Organisation for Scientific Research (NWO, VENI-grant) and J.C.Z. thanks the National Science Foundation for funding. E. Hopmans and A. Mets (NIOZ) are thanked for analytical assistance with TEX<sub>86</sub> measurements. A. van Dijk, E. van Bentum, C. Blaga, R. Deltrap, D. Menzel, G. Nobbe, J. van Tongeren, N. Welters (all Utrecht University) and D. Andreason and T. Quattlebaum (UC Santa Cruz) are thanked for advice and support regarding analyses. We thank J. Browning, K. Miller, J. Firth and G. Esmay for help regarding the logistics around sampling the Bass River section and E. Thomas for sampling the Wilson Lake section. ConocoPhillips, P. van Veen in particular, is thanked for enabling us to use their North Sea cores. I. Harding, M. Huber, L. Lourens and M. Pagani are thanked for discussions.

**Author Contributions** A.S., H.B. and J.C.Z. designed the research, A.S. and H.B. carried out the palynology, A.S., G.-J.R. and H.B. the  $\delta^{13}\text{C}_{\text{DINO}}$  and  $\delta^{13}\text{C}_{\text{TOC}}$  analyses, A.S., S.S., G.J.R. and J.S.S.D. the TEX<sub>86</sub> analyses. S.M.B., C.M.J. and J.C.Z. generated the isotope data on carbonate. All authors contributed to interpreting the data and writing the paper.

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## METHODS

**Palynology.** To ~10 g of freeze-dried sediment, a known amount of *Lycopodium* spores was added. Samples were treated with 30% HCl and twice with 38% HF for carbonate and silicate removal, respectively, and sieved over a 15- $\mu\text{m}$  nylon mesh. Samples from the North Sea (Supplementary Information) were sieved in a 15- $\mu\text{m}$  steel mesh sieve and subsequently oxidized for 20 min in Schultz's reagent at 80 °C to reduce the amount of amorphous organic matter. To disaggregate clumps of residue, samples were placed in an ultrasonic bath for a maximum of 5 min, sieved again, and subsequently concentrated to 1 ml, of which 7.5–10  $\mu\text{l}$  was mounted on microscope slides. Slides were analysed at 500 $\times$  magnification to a minimum of 200 dinocysts. Absolute quantitative numbers were calculated using the relative number of *Lycopodium*.

**TEX<sub>86</sub> analyses.** Powdered and freeze-dried sediments (~20 g dry mass) were extracted with a Dionex Accelerated Solvent Extractor using a 9:1 (v:v) 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. Polar fractions were dissolved in hexane/propanol (99:1;v/v), and filtered through 0.45  $\mu\text{m}$  PTFE filters. The samples were analysed with an Agilent 1100 series LC/MSD SL and separation was performed on an Prevail Cyano column (2.1  $\times$  150 mm, 3  $\mu\text{m}$ ; Alltech), maintained at 30 °C. The glycerol dialkyl glycerol tetraethers (GDGTs) were eluted using a changing mixture of hexane and propanol as follows, 99 hexane:1 propanol for 5 min, then a linear gradient to 1.8 propanol in 45 min. Flow rate was 0.2 ml min<sup>-1</sup>. Detection was achieved using atmospheric pressure chemical ionization-mass spectrometry of the eluent. Single ion monitoring was set to scan the 5 [M+H]<sup>+</sup> ions of the GDGTs with a dwell time of 237 ms for each ion. TEX<sub>86</sub> values were determined at least in duplicate and converted to temperature using the equations from refs 22 and 24 (see text). In addition, we measured the abundance of branched and isoprenoid tetraether lipids to estimate the relative abundance of terrestrially derived GDGTs, which appeared very low. GDGTs are not present in the sediments from the North Sea site owing to the relatively high maturity of the organic matter.

**Organic  $\delta^{13}\text{C}$  measurements.** For the  $\delta^{13}\text{C}_{\text{DINO}}$  records, the 40–125  $\mu\text{m}$  size fraction of the palynological residues, which are nearly barren of organic particles other than dinocysts, were isolated using nylon mesh sieves, and oven-dried. For  $\delta^{13}\text{C}_{\text{TOC}}$  analyses (North Sea site; Supplementary Information), samples were freeze-dried and powdered. All  $\delta^{13}\text{C}$  analyses were done with a Fison NA 1500 CNS analyser, connected to a Finnigan Delta Plus mass spectrometer. Analytical precision determined by replicate analyses was better than 0.1‰. All values are reported relative to the VPDB standard.

**Bulk carbonate  $\delta^{13}\text{C}$  measurements.** Freeze-dried samples were measured using an Autocarb or Optima coupled to a PRISM Mass Spectrometer at UCSC. Precision based on replicate analyses of in-house standard Carrara Marble is better than  $\pm 0.05\%$ . All values are reported relative to the VPDB standard.