Organic geochemistry of the early Toarcian oceanic anoxic event in Hawsker Bottoms, Yorkshire, England

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Abstract

A comprehensive organic geochemical investigation of the Hawsker Bottoms outcrop section in Yorkshire, England has provided new insights about environmental conditions leading into and during the Toarcian oceanic anoxic event (T-OAE; ~183 Ma). Rock-Eval and molecular analyses demonstrate that the section is uniformly within the early oil window. Hydrogen index (HI), organic petrography, polycyclic aromatic hydrocarbon (PAH) distributions, and tricyclic terpane ratios mark a shift to a lower relative abundance of terrigenous organic matter supplied to the sampling locality during the onset of the T-OAE and across a lithological transition. Unlike other ancient intervals of anoxia and extinction, biomarker indices of planktonic community structure do not display major changes or anomalous values. Depositional environment and redox indicators support a shift towards more reducing conditions in the sediment porewaters and the development of a seasonally stratified water column during the T-OAE. In addition to carotenoid biomarkers for green sulfur bacteria (GSB), we report the first occurrence of okenane, a marker of purple sulfur bacteria (PSB), in marine samples younger than ~1.64 Ga. Based on modern observations, a planktonic source of okenane's precursor, okenone, would require extremely shallow photic zone euxinia (PZE) and a highly restricted depositional environment. However, due to coastal vertical mixing, the lack of planktonic okenone production in modern marine sulfidic environments, and building evidence of okenone production in mat-dwelling Chromatiaceae, we propose a sedimentary source of okenone as an alternative. Lastly, we report the first parallel compound-specific $\delta^{13}C$ record in marine- and terrestrial-derived biomarkers across the T-OAE. The $\delta^{13}C$ records of short-chain *n*-alkanes, acyclic isoprenoids, and long-chain *n*-

alkanes all encode negative carbon isotope excursions (CIEs), and together, they support an injection of isotopically light carbon that impacted both the atmospheric and marine carbon reservoirs. To date, molecular $\delta^{13}C$ records of the T-OAE display a negative CIE that is smaller in magnitude compared to the bulk organic $\delta^{13}C$ excursion. Although multiple mechanisms could explain this observation, our molecular, petrographic, and Rock-Eval data suggest that variable mixing of terrigenous and marine organic matter is an important factor affecting the bulk organic $\delta^{13}C$ records of the T-OAE.

Keywords: Toarcian oceanic anoxic event; lipid biomarkers; okenane; photic zone euxinia, stable carbon isotopes; Hawsker Bottoms

1. Introduction

Several transient episodes of enhanced deposition and preservation of organic-rich sediments punctuated the Mesozoic Era. A combination of factors may have caused these intervals, known as oceanic anoxic events (OAEs), including greenhouse conditions and enhanced marine productivity (e.g. Schlanger and Jenkyns, 1976; Jenkyns, 1980; 1988; 2010; Trabucho-Alexandre et al., 2010). The first Mesozoic OAE was the Early Jurassic Toarcian OAE (T-OAE; ~183 Ma), which was associated with elevated extinction rates, enhanced weathering rates, warm temperatures, ocean acidification, and a negative carbon isotope excursion (CIE) (Hesselbo et al., 2000; Cohen et al., 2004; Bambach, 2006; Hesselbo et al., 2007; Jenkyns, 2010; Kiessling and Simpson, 2011). The duration of the T-OAE is not precisely known but may have lasted on the order of several hundred thousand years (Kemp et al., 2005; Suan et al., 2008; Kemp et al., 2011). The Karoo and Ferrar igneous provinces, which erupted at 183 ± 1 Ma, may have coincided with the Pliensbachian-Toarcian extinction (Pálfy and Smith, 2000; Courtillot and Renne, 2003). However, better radiometric dating of the volcanism and OAE are required to confidently link these two events. Although multiple mechanisms have been proposed to account for the Toarcian negative CIE, including methane hydrate dissociation, upwelling of isotopically light waters, thermogenic release of methane, and biomass burning (Hesselbo et al., 2000; Schouten et al., 2000; McElwain et al., 2005; van de Schootbrugge et al., 2005; Finkelstein et al., 2006), the source of the isotopically light carbon remains unclear.

The analysis of sedimentary organic matter provides the opportunity to evaluate environmental and ecological responses to carbon cycle perturbations, as well as potentially constraining the perturbation itself. Previous organic geochemical work across the T-OAE has indicated changes in planktonic community structure and redox chemistry, particularly the development of photic zone euxinia (PZE) (e.g. Farrimond et al., 1989; 1994; Schouten et al., 2000; Pancost et al., 2004; Schwark and Frimmel, 2004; Bowden et al., 2006; van Breugel et al., 2006). However, since biomarker records can reflect local responses, additional comprehensive organic geochemical studies from multiple locations are required to build a global perspective of ecological and environmental change associated with the T-OAE. Here, we investigate the temporal variation of lipid biomarkers, Rock-Eval data, organic petrography, and compound-specific carbon isotopes from the Lower Jurassic section at Hawsker Bottoms, Yorkshire, England.

2. Geologic Setting and Site Description of Hawsker Bottoms, Yorkshire, England

A well-studied section of the Toarcian OAE is located on the Yorkshire coast in northern England. We analyzed sample splits spanning 14 m of an organic-rich, lower Jurassic outcrop section in the Cleveland Basin at Hawsker Bottoms previously studied by Hesselbo et al. (2000). The lithology is dominated by black shales containing discrete levels of calcite concretions and constitutes the Jet Rock *sensu stricto* (Hesselbo and Jenkyns, 1995). The sections around Hawsker Bottoms have been used for defining the ammonite biostratigraphy of the Toarcian (Howarth, 1992).

The Early Jurassic paleogeography of the area, although somewhat uncertain, is depicted in published paleogeographic maps (e.g. Bradshaw et al., 1992). The Cleveland Basin of North Yorkshire was part of a system of shallow epicontinental seas and small extensional tectonic basins linked to the Central Graben via the Sole Pit Basin. The region formed part of the broad epicontinental sea that covered much of northwest Europe. Marine sedimentation was initiated during the Late Triassic, and a succession of marine siliciclastic mudstones accumulated during the Early Jurassic.

The Grey Shale Member of the Whitby Mudstone Formation consists of bioturbated, silty mudstones with beds of calcareous siderite concretions. The mudstones have thin sharp-based beds, wave ripple, and starved ripple laminations (Wignall et al., 2005; Ghadeer and Macquaker, 2011). Grain size and bioturbation intensity decrease toward the top of the unit, and sediment color darkens. The Jet Rock Member consists of dark, organic matter-rich, fissile mudstones with abundant ammonites and horizons of calcareous nodules. The boundary between these two members of the Whitby Mudstone Formation likely represents an increase in water depth in the basin.

The early Toarcian (*D. tenuicostatum* Zone) was a period of major basin subsidence throughout England. Organic matter content fluctuates through the Grey Shales, but increasing levels of organic matter are present from the *D. semicelatum* Subzone to the *C. exaratum* Subzone (*H. falciferum* Zone). Minor shoaling cycles with striped siltstone laminae suggest that water depths were on the order of tens of meters (Powell, 2010). Similarly, sedimentary structures suggest deposition during storms by the effects of waves (Wignall et al., 2005; Ghadeer and Macquaker, 2011). Thus, bottom water conditions were more energetic than is commonly thought, where the water column

was likely shallower than 50 m. Consequently, Hawsker Bottoms likely represents an inner continental shelf environment, which physical oceanographers define as the region where turbulence from the surface and bottom boundary layers effectively homogenizes the whole water column (Lentz and Fewings, 2012). Accordingly, inner shelf environments are typically a few meters to tens of meters deep

The abundance of ammonites in the shales indicates that the water column was at times oxygenated and favorable to nektonic faunas (Powell, 2010). The abundance of thin beds with tops homogenized by bioturbation suggests that long-term, persistent bottom water anoxia did not occur in the basin (Ghadeer and Macquaker, 2011). Besides deposition as bedload by geostrophic flows and density currents, additional sediment was supplied by suspension settling. Textural analyses have shown that much of the sedimentary organic matter was delivered to the seafloor as fecal pellets, flocs, or other organo-mineralic aggregates (Ghadeer and Macquaker, 2011). The contribution of a biogenic component to rock composition varies, and the differences have been attributed to a changing balance of primary production relative to dilution and length of transport path during deposition (Macquaker and Taylor, 1996; Wignall et al., 2005; Ghadeer and Macquaker, 2011).

3. Methods

Powdered rock samples were analyzed by Rock-Eval pyrolysis. The total organic carbon (TOC; %), T_{max} (°C), S_1, and S_2 were determined and used to calculate the hydrogen index (HI) and production index (PI). Kerogen isolates from four samples across the section were mounted onto slides in duplicate and assessed optically under

139 white light and fluorescent light using a Zeiss research microscope and a Zeiss x 40
140 Plank-Neofluar objective. A Zeiss Axioskop, Axio Image D1, and a Zeiss 18 filter set
141 were used to take photomicrographs and fluorescence images.

142 Powdered samples (~ 5 g) were extracted using a Dionex ASE 200 Accelerated
143 Solvent Extractor with a solvent mixture of dichloromethane:methanol 9:1 (v/v).
144 Elemental sulfur was removed from the total lipid extract (TLE). Asphaltenes were
145 separated from the maltene fraction, which was then separated into saturated, aromatic,
146 and polar fractions by silica gel chromatography. The saturated and aromatic fractions
147 were analyzed by gas chromatography-mass spectrometry (GC-MS) and gas
148 chromatography-metastable reaction monitoring-mass spectrometry (GC-MRM-MS).
149 Carbon isotopic measurements of saturated hydrocarbons were made by gas
150 chromatography/combustion/ isotope ratio mass spectrometry (GC-C-IRMS) using a
151 ThermoFinnigan Delta Plus XP coupled to a ThermoFinnigan Trace GC. The mean value
152 of triplicate analyses are reported here in per mil (‰) relative to Vienna Pee Dee
153 belemnite (VPDB), and the standard deviation from the mean value was 0.4‰ or less. A
154 detailed description of methods is included in the supplementary online material (SOM).
155

156 **4. Results and Discussion**

157 *4.1 Rock-Eval analysis*

158 Rock-Eval results provided insight into the thermal maturity and type of organic
159 matter preserved in the Hawsker Bottoms sediments. The TOC percentage (Hesselbo et
160 al., 2000) was plotted for comparison with the HI, PI, and T_{max} (fig. 1). The narrow range
161 of the PI (0.11-0.18) and T_{max} (429-440°C) parameters indicate that thermal maturity is

uniform through the section and at the early stage of oil generation (Peters et al., 2005). Molecular indices of thermal maturity further substantiate this conclusion (see section 4.2).

The HI data reveal that the type of organic matter undergoes a transition that appears to coincide with a lithological transition from medium grey shale to dark grey thin-bedded shale within the limitations of our sampling resolution. The low HI values below -2.5 m are characteristic of type III kerogen, whereas the higher HI values above -3 m are characteristic of type II kerogen (Peters et al., 2005). Type III kerogen is dominated by either terrigenous or highly degraded organic matter, and type II kerogen is typically derived from marine organic matter (Peters et al., 2005).

Published HI values from other T-OAE localities also increase across the initiation of the CIE (Prauss et al., 1991; Schouten et al., 2000; Röhl et al., 2001; Sabatino et al., 2009; Suan et al., 2011). Previous workers have attributed the HI variability to different degrees of organic matter degradation under varying redox conditions (Schouten et al., 2000; Röhl et al., 2001; Sabatino et al., 2009). Alternatively, others have argued that the HI variability represents a shift in the composition of the organic matter (Suan et al., 2011). Petrographic and molecular evidence for the presence of plant-derived material in these sediments (see section 4.3) supports the conclusion that lower HI values at the bottom of the section are due to a larger abundance of terrigenous organic matter relative to marine organic matter.

4.2 Molecular indicators of thermal maturity

The thermal history of the section was further assessed according to molecular thermal maturity parameters (fig. 2). The C_{31} hopane 22S/(22S+22R) ratio was constant through the section and exhibited a narrow range between 0.58 and 0.59. A value of ~0.55 represents the endpoint which is reached around the main phase of oil generation (Peters et al., 2005). The C_{30} hopane βα/(βα+αβ) ratio ranged from 0.08 to 0.11, which is close to values indicative of a mature source rock (Peters et al., 2005). The C_{29} sterane ααα 20S/(20S+20R) ratio varied from 0.52 to 0.57, which is comparable to the endpoint value of 0.52-0.55 (Peters et al., 2005). In summary, molecular thermal maturity indicators corroborate the Rock-Eval results, further supporting a uniform thermal maturity within the early window of oil generation.

Some biomarker-based thermal maturity parameters can be influenced by additional factors such as source and diagenetic effects (Moldowan et al., 1986; Dahl et al., 1993; Peters et al., 2005; Bennett and Olsen, 2007; French et al., 2012). Indeed, two of the thermal maturity parameters presented in figure 2 exhibit some variation tracking changes in lithology and source input, despite the multiple lines of evidence supporting constant thermal maturity through the section. The Ts/(Ts+Tm) ratio, where Tm is C_{27} 17 α-trisnorhopane and Ts is C_{27} 18 α-trisnorhopane, varied from 0.41 to 0.59, whereas the diasterane/sterane ratio of $C_{27\text{-}29}$ compounds ranged from 1.08 to 1.44. Both ratios deviate from a relatively constant pattern in the lower ~2 meters of the section. This pattern is explained by changes in lithology and/or organic matter source input, which is consistent with lower HI values and additional evidence supporting variable terrigenous organic input (see section 4.3).

4.3 Biomarker and petrographic evidence of terrigenous organic matter input

A combination of molecular and petrographic analyses was performed to evaluate the relative contribution of terrigenous organic matter through the sampling interval (fig. 3). Previous work has suggested a terrigenous source for C_{19} and C_{20} tricyclic terpanes, which has led to the use of C_{19}/C_{23} and C_{20}/C_{23} tricyclic terpane ratios to identify input of terrigenous organic matter (Noble et al., 1986; Peters et al., 2005). These two ratios display higher values in the lowest part of the section and decrease after the lithological transition at -2.5 meters, indicating relatively greater terrigenous organic matter input in the lowermost part of the sampling interval.

A wide range of PAHs was detected in the Hawsker Bottoms samples, including phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, triphenylene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, indeno[c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, coronene, and retene. PAHs are a diverse set of compounds with multiple documented sources including products of pyrolysis, combustion, hydrothermal activity, and igneous intrusion as well as direct inputs from algae, fungi, vascular plants, and extraterrestrial organics (Kawka and Simoneit, 1990; George, 1992; Jiang et al., 2000; Sephton et al., 2005; Grice et al., 2007; Marynowski and Simoneit, 2009). PAHs have been used to reconstruct the history of wildfires, higher plant input, and anthropogenic activity, where peri-condensed, unsubstituted PAHs are markers for combustion of organic matter (Hites et al., 1977; Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Kruge et al., 1994; Jiang et al., 1998; Arinobu et al., 1999; Finkelstein et al., 2005; Peters et al., 2005; Marynowski and Simoneit, 2009). Some sedimentary PAHs, such as phenanthrene, chrysene, and triphenylene, are more affected

230 by diagenesis or additional sources (Jiang et al., 1998; Grice et al., 2007), so they were
231 not included in the total PAH sum plotted in figure 3b. Although the patterns are not
232 identical, enhanced concentrations of total PAH co-occur with elevated C_{19}/C_{23} and
233 C_{20}/C_{23} tricyclic terpane ratios in the bottom 2 meters of the sampling interval. Some
234 PAHS, such as retene, are thought to derive from higher plants, in particular coniferous
235 resin (Wakeham et al., 1980; Ellis et al., 1996; Jiang et al., 1998; Grice et al., 2005;
236 Peters et al., 2005), although algal and bacterial sources have been reported as well (Wen
237 et al., 2000). Retene was detected in all samples, and its concentration was plotted
238 separately as a marker of higher plant input in figure 3c. Retene was more abundant in
239 the lowest interval of the section, which is consistent with the total PAHs, tricyclic
240 terpane ratios, and HI data.

241 Microscopic analysis of four kerogen samples adds an additional line of evidence
242 supporting stratigraphic variations in kerogen type and organic matter sources. According
243 to the petrographic results, the kerogen is comprised of as much as 80% of terrigenous
244 organic matter in the bottom of the section and about 25-40% in the remainder of the
245 sampling interval (fig. 3d). Since the elemental, molecular, and isotopic composition of
246 organic matter from higher plants is distinct from marine organic matter, HI can reflect
247 the compositional difference of distinct types of organic matter (e.g. Talbot and
248 Livingstone, 1989). Assuming constant HI values for terrigenous and marine organic
249 matter end-members, the percent terrigenous organic matter was estimated through the
250 section using the linear relationship between the percent terrigenous macerals measured
251 by optical microscopy and the corresponding HI (see SOM for more details). Calculated

values of $f_{Terr\ OM}$ ranged from 12 to 85%, where the highest values were found in the lowermost part of the section (fig. 3e).

The stratigraphic change in the relative supply of terrigenous organic matter , which is supported by the HI, molecular, and petrographic results, may have been driven by effects related to rising sea level (Hesselbo, 2008; Suan et al., 2011). Considering that increased rates of continental weathering across the T-OAE would have enhanced delivery of terrigenous material (Cohen et al., 2004), the opposite trend recorded in our data might be best explained by progressive remoteness from the coastline on a gently sloping shelf during sea level transgression (e.g. Macquaker et al., 2010). However, sea level related effects might not be the only factor responsible for the changing signal in relative abundance of terrigenous and marine organic matter. For example, enhanced marine export productivity and/or enhanced marine organic matter preservation could have diluted the input of terrigenous organic matter, thereby changing the relative apparent contribution.

4.4 Biomarker indicators of source and community structure

Since some compounds or compound classes are associated with a particular biological source, metabolism, or physiology, molecular distributions can be informative about changes in microbial community structure. Unlike other intervals of ocean anoxia associated with mass extinction events (e.g. Xie et al., 2005; Cao et al., 2009), algal- and bacterial-derived biomarkers indicative of community structure did not vary significantly through the CIE (fig. 4). Instead, some biomarker indices that typically reflect community structure were more affected by source input at Hawsker Bottoms.

The regular sterane/17α-hopane ratio is used as an indicator of the relative contributions of eukaryote and bacterial biomass. The regular sterane/hopane ratio was calculated using regular C_{27-29} steranes and 17α C_{29-33} hopanes. The regular sterane/17α-hopane ratio exhibited low values below -2.5 m, whereas it was more elevated (>0.5) and relatively constant in the top 10 m of the section. While this offset could be interpreted as a shift from a bacterially dominated environment in the lower part of the section to a eukaryotic environment above -3 m, it is more likely that a change in the organic matter source input is driving the regular sterane/17α-hopane ratio variability. As well as containing low total steroid abundances, terrigenous organic matter can deliver hopanes derived from soil bacteria, thereby lowering the regular sterane/17α-hopane ratio (Peters et al., 2005; Handley et al., 2010; Sãenz et al., 2011; French et al., 2012).

Similarly, small deviations are found at the bottom of the section for the C_{27}/C_{27-30}, C_{28}/C_{27-30}, and C_{29}/C_{27-30} sterane ratios. These ratios included regular steranes as well as diasteranes and are commonly used as indicators of the relative contribution from red algae biomass, chlorophyll-c algae, and green algae, respectively. However, they can also be affected by the delivery of C_{29} steranes derived from land plants (Moldowan et al., 1985; Peters et al., 2005). Indeed, C_{29} sterane was the dominant sterane in samples from the bottom of the section, where it represented nearly half of the total C_{27-30} steranes. The C_{30}/C_{27-30} sterane ratio, on the other hand, which is an indicator of marine pelagophyte algae, was constant throughout the section and represented only a minor proportion of the total steranes abundance.

The 2α-methylhopane index (2-MHI) has been used as an indicator of cyanobacterial input (Summons et al., 1999), although additional sources were later

298 reported (Rashby et al., 2007). The 3β-methylhopane index (3-MHI) is considered a
299 marker for aerobic proteobacteria, including methanotrophs and acetic acid bacteria
300 (Zundel and Rohmer, 1985; Talbot et al., 2003; Farrimond et al., 2004; Talbot and
301 Farrimond, 2007). The 2-MHI and 3-MHI were invariant, and the 3-MHI was in the
302 range of average Phanerozoic marine values (~1-3%) (Farrimond et al., 2004; Cao et al.,
303 2009). Likewise, the 2-MHI also lacked elevated values. Based on elevated 2-MHI, 3-
304 MHI, and nitrogen isotope anomalies, previous workers have reported an increased
305 contribution of diazotrophic cyanobacteria and methanotrophic bacteria during other
306 OAEs (e.g. Kuypers et al., 2004; Cao et al., 2009; Sepúlveda et al., 2009; Luo et al.,
307 2011). The low and invariant contribution of these microbial groups indicates that
308 environmental conditions suitable for their predominance did not prevail at this locality.
309 Thus, enhanced cyanobacterial diazotrophy may not fully explain the previously reported
310 depleted bulk organic $\delta^{15}N$ at this location during the T-OAE (Jenkyns et al., 2001).
311
312 *4.5 Indicators of redox change and depositional environment*
313 A suite of biomarkers was used to assess changes in water column stratification
314 and redox potential, including the gammacerane index, C_{35} homohopane index (C_{35} HHI),
315 pristane/phytane (Pr/Ph) ratio, and the concentration of aromatic carotenoid derivatives
316 (fig. 5). Although some of these parameters can also be influenced by diagenesis, source
317 input, and thermal maturity, they display patterns consistent with a shift towards more
318 intense reducing conditions at least in the sediment porewaters and potentially in the
319 overlying water column.

Although the biological sources of gammacerane are not fully known (Peters et al., 2005), it is a diagenetic product of tetrahymanol, a compound found in bacteriovorous ciliates thriving at the chemocline of stratified water bodies (ten Haven et al., 1989; Sinninghe Damsté et al., 1995). Thus, the occurrence of gammacerane, expressed as the gammacerane index = *[gammacerane/ (gammacerane + 17α,21β* C_{30} *hopane)]*100,* has been used to infer changes in water column stratification in ancient environments. Gammacerane was detected in all of the analyzed samples but became more prominent in those deposited during the OAE, starting at the onset of thin-bedded shales.

Elevated abundances of gammacerane during the T-OAE may reflect the development of seasonal water column stratification, possibly due to stronger seasonality and/or deepening of the water column. In contrast, prior to the T-OAE, seasonality may have been weaker, or the water column may have been too shallow to stratify, even during warm months, due to turbulent mixing. The development of seasonal water column stratification at Hawsker Bottoms during the T-OAE would have aided the development of water column oxygen-depletion, particularly during warm and productive months. However, gammacerane enrichments alone do not necessitate water column anoxia, particularly given the association of its precursor, tetrahymanol, with suboxic waters in the modern (Wakeham et al., 2007; 2012).

The C_{35} HHI and Pr/Ph ratio are recorders of depositional redox conditions in sediments. The C_{35} HHI records the degree of preservation of the extended side chain of C_{35} hopanes derived from intact bacteriohopanepolyols (BHPs) (Köster et al., 1997; Peters et al., 2005). Higher C_{35} HHI values are characteristic of oxygen-depleted marine depositional environments. Pristane and phytane in ancient marine rock extracts and oils

are largely, but not exclusively, derived from the chlorophyll phytyl side chain from photoautotrophs. Redox conditions influence the diagenetic pathway of the phytyl side chain. Reducing conditions promote the conversion of phytol to phytane, and oxic conditions promote the conversion of phytol to pristane (Didyk et al., 1978; Peters et al., 2005). The C_{35} HHI nearly doubled in samples deposited during the OAE compared to those deposited prior to the event. Values of the Pr/Ph ratio >3 recorded at the bottom of the section are suggestive of deposition of terrigenous organic matter under oxic conditions. The Pr/Ph ratio values near or below 1 during the T-OAE, together with the elevated C_{35} HHI, suggest intensification of reducing conditions in the sediment porewaters during deposition.

Biomarkers for anaerobic phototrophic green sulfur bacteria (GSB) have been used to argue for the development of PZE during the T-OAE (Schouten et al., 2000; Pancost et al., 2004; Bowden et al., 2006) and other OAEs (e.g. Cao et al., 2009) based on the physiological requirement of co-occurring reduced sulfur species and light. We detected 2,3,6-aryl isoprenoids, isorenieratane, and chlorobactane in all samples. Unlike previous studies of the T-OAE or any Phanerozoic organic geochemical study of marine samples, trace concentrations of okenane were also identified by GC-MRM-MS in samples above -3 m, whereas it was below detection limit in samples from the lowest 2 meters of the section. Okenone, a photosynthetic pigment belonging to the PSB family Chromatiaceae, is the only known precursor of okenane (Brocks and Schaeffer, 2008). All compounds were compared with an authentic carotenoid standard and an extract from the Barney Creek Formation (BCF; fig. 6; Brocks et al., 2005). Normalizations of the C_{40}

aromatic carotenoid derivatives against the mass of TOC and TLE reveal a similar pattern of elevated concentrations during the anoxic event compared to the pre-event baseline.

In total, all of the organic geochemical redox indicators point towards a shift towards more reducing conditions broadly corresponding with the initiation of the negative CIE. However, sedimentological features, such as starved wave and combined flow ripples, indicate that this area was an energetic, shallow inner shelf environment on the order of tens of meters and probably no deeper than 50 m, where enough oxygen was present in the water column on some timescale to sustain nektonic fauna, including ammonites, and allow for bioturbation at the sediment-water interface through the OAE (Wignall et al., 2005; Powell, 2010; Ghadeer and Macquaker, 2011). We explore different scenarios to reconcile these apparent opposing lines of evidence.

First, the geochemical and sedimentological signals recorded in the rock record are a composite of many processes occurring on different timescales. In the modern ocean, highly productive coastal and continental margin sediments and the overlying water column oscillate between oxic and anoxic conditions over different timescales (e.g. Burdige, 2007). Enhanced productivity and export of organic matter, which are important features of Mesozoic OAEs (e.g. Erba, 2004; Jenkyns, 2010), would have increased the oxygen demand in the water column and sediment porewaters during productive months. During the T-OAE, anoxic conditions may have been restricted to the sediment porewaters during seasons of low productivity, allowing bioturbation to occur when bottom waters were better oxygenated. Conversely, oxygen-deficient waters may have expanded seasonally to the water column during intervals of high productivity and enhanced stratification, as implied by the gammacerane index.

Second, the molecular, paleontological, and sedimentary indicators of redox chemistry apply to different parts of the depositional environment, diagenetic pathways, and have different sensitivities along the redox spectrum. With the exception of the GSB and PSB carotenoid markers, the geochemical parameters reported here do not require strict anoxia or euxinia in the water column. The gammacerane index pattern supports the development of seasonal stratification during the OAE, which would have promoted oxygen depletion of the water column. However, the possibility remains that even during intervals of high productivity and stratification, water column oxygen concentrations at this location were depleted but high enough to sustain organisms with physiological oxygen requirements, thereby explaining the fossil and sedimentary evidence. Additionally, the Pr/Ph ratio and C_{35} HHI pertain primarily to sedimentary redox conditions opposed to water column redox structure. Therefore, the occurrence of intact aromatic carotenoid derivatives merits further discussion to assess water column redox chemistry.

To date, okenane has only been reported in Paleoproterozoic rock extracts and lacustrine Cenozoic extracts (Brocks et al., 2005; Zhang et al., 2011). Given the atmospheric pO_2 during the Mesozoic was near present atmospheric levels (Berner, 2006), its detection in marine samples of this age requires careful interpretation. The PSB family Chromatiaceae blooms in a range of anoxic environments with light and reduced sulfur species, including stratified lakes, fjords, coastal lagoons, estuaries, and coastal microbial mats, but not all Chromatiaceae produce okenone (Brocks and Schaeffer, 2008 and references therein). Okenone-producing planktonic Chromatiaceae dwell in water columns where the chemocline is above 25 m and in 75% of the reported cases less than

411 12 m (Brocks and Schaeffer, 2008). Notably, all of the modern chemocline depth
412 observations for okenone production are based on stratified lake systems. Thus, the lack
413 of okenone in modern marine sulfidic environments presents a "no analogue problem" for
414 ancient marine samples containing okenane that were deposited under atmospheric pO_2
415 close to modern levels.

416 Transient free sulfide has been reported in the water column of intense upwelling
417 zones, including the Arabian Sea, Namibian coast, and the Peruvian coast (e.g Dugdale et
418 al., 1977; Brüchert et al., 2003; Naqvi et al., 2006; Schunck et al., 2013). However, these
419 episodes are typically short lived. In contrast, sulfidic waters persist in some restricted
420 marine basins and fjords, including the Black Sea, Cariaco Basin, Saanich Inlet, and the
421 Framvaren and Effingham Fjords. However, these two types of marine environments
422 (non-restricted, transiently sulfidic and restricted, permanently sulfidic) fail to represent
423 suitable modern analogues for Hawsker Bottoms on several counts. Isorenieratene has
424 been measured in the water column and sediments of some restricted marine basins,
425 particularly fjords and the Black Sea (e.g. Sinninghe Damsté and Schouten, 2006), but
426 GSB carotenoids have not been detected in transiently sulfidic upwelling systems.
427 Furthermore, okenone has not been reported in the water column or sediments of any
428 modern marine transiently or permanently sulfidic environment, with the exception of the
429 upper sediments of Kyllaren fjord, a small, highly restricted basin (Smittenberg et al.,
430 2004; Sinninghe Damsté and Schouten, 2006). Like okenone, modern planktonic marine
431 occurrences of chlorobactene are also limited to semi-enclosed water masses that are not
432 representative of fully marine conditions (e.g. Naeher et al. 2012). Interestingly, multiple
433 emerging lines of evidence suggest the occurrence of a "cryptic sulfur cycle" in some

OMZs, with a potential role for photosynthetic sulfide oxidation (Canfield et al., 2010; Stewart et al., 2012). However, the presence of GSB and/or PSB and their respective carotenoids have yet to be reported in modern OMZs.

Furthermore, the physical oceanographic processes determining the degree of vertical mixing, hence stratification and redox gradient stability, are markedly different between inner shelf environments and sulfidic, silled basins, which are highly restricted and in many classic modern examples, are an order of magnitude or more deeper than estimated paleodepths of Hawsker Bottoms. Although the water column at Hawsker Bottoms became deeper with the sea level transgression across the T-OAE, the depositional environment remained relatively shallow because of its location on a gently sloping shelf (e.g. Macquaker et al., 2010). Consequently, turbulent mixing at the surface and bottom boundary layers would have prevented a stable sulfidic chemocline from developing. On the other hand, considering the limited occurrence of planktonically produced okenone in modern lakes, a planktonic source of okenone at Hawsker Bottoms would imply that, rather than an inner sheld environment, Hawsker Bottoms was a highly restricted coastal basin not reflective of fully marine conditions.

Alternatively, we argue that okenane at Hawsker Bottoms was likely derived from benthic microbial mats based on the lack of modern analogues of okenone-production in marine sulfidic environments, the dynamics of inner shelf physical mixing, and building evidence of okenone-producing, mat-dwelling Chromatiaceae (e.g. Caumette et al., 1991; Airs et al., 2001; Caumette et al., 2004; Meyer et al., 2011). Furthermore, planktonic Chlorobiaceae are not the exclusive source of isorenieratene and chlorobactene. Previous work has documented additional non-planktonic GSB sources of isorenieratene and

chlorobactene, including microbial mats (e.g.Wahlund et al., 1991; Brocks and Summons, 2003; Beatty et al., 2005; Bühring et al., 2011). Although a mixed planktonic and mat origin of the carotenoids cannot be ruled out, it is more likely that the GSB and PSB carotenoids detected in Hawsker Bottoms samples share a source. Previous studies of sedimentary structures in the Toarcian shales of Yorkshire have attributed wavy laminations to microbial mats (O'Brien, 1990), thereby further supporting a sedimentary origin of GSB and PSB carotenoid derivatives detected in Hawsker Bottoms samples. Similar wavy laminated fabrics have been reported in coeval shales in northern European T-OAE sections (Trabucho-Alexandre et al., 2012). Unfortunately, a sedimentary source of the GSB and PSB carotenoid derivatives offers little information about water column redox chemistry. However, this interpretation does not preclude the development of a suboxic, anoxic, or euxinic water column in this region on some timescale during the T-OAE. Instead, additional inorganic geochemical data is required to better assess the water column redox conditions and degree of basin restriction (Algeo and Tribovillard, 2009).

4.6 Compound specific stable carbon isotopic data

A limited number of compound specific $\delta^{13}C$ records of the T-OAE are currently available in the literature. Here, we report the first long-chain *n*-alkane $\delta^{13}C$ records of the T-OAE. Compound specific $\delta^{13}C$ analyses of marine- and terrestrial-derived lipids reveal a shift towards lighter $\delta^{13}C$ values (fig. 7). Short-chain *n*-alkanes, as well as pristane and phytane are typically used as marine indicators, whereas long-chain *n*-alkanes primarily reflect terrigenous sources. The *n*-C_{17}, *n*-C_{18}, and *n*-C_{19} alkanes displayed a negative excursion of ~2–3‰, which is consistent with the ~2–4‰ negative

excursions documented in the partial n-C_{16-20} alkane records from the Toarcian Posidonienschiefer in southwest Germany (Schouten et al., 2000). Pristane and phytane encode a muted excursion (~1.5–2‰) compared to short-chain alkane records, and they also have smaller CIE magnitudes compared to the pristane and phytane isotopic records from the Toarcian Paris Basin and the Posidonienschiefer (~3–4‰) (Schouten et al., 2000; van Breugel et al., 2006). On the other hand, long-chain *n*-alkanes (*n*-C_{27}, *n*-C_{28}, and *n*-C_{29}), which are primarily but not exclusively derived from epicuticular waxes of vascular plants (Eglinton and Hamilton, 1967), display the largest compound specific negative CIE (~4–5‰). The molecular isotopic records appear to register the initiation of the negative CIE earlier than in the bulk organic record, and within the CIE, the compound-specific $\delta^{13}C$ values remain fairly stable while the bulk curve becomes gradually depleted. However, these features could be due to sampling resolution differences. Higher resolution molecular isotopic records are required to better address the timing and structure of the isotopic excursion recorded in different carbon reservoirs.

The absolute magnitude of the bulk organic CIE (~5–7‰) is larger than the CIEs recorded in the molecular records from Yorkshire (this study; ~1.5–5‰), the Paris Basin (~3‰; van Breugel et al., 2006), and the Posidonienschiefer (~2–4‰; Schouten et al., 2000). Identifying the reason behind the CIE magnitude offsets is critical for placing bounds on the magnitude of isotopically light carbon added into the system. Bulk organic matter is comprised of an array of molecularly and isotopically heterogeneous constituents. In addition to environmental perturbations, organic matter source mixing can contribute to bulk organic $\delta^{13}C$ excursions (e.g. Pancost et al., 1999). The comparison of short- and long-chain *n*-alkane isotopic compositions demonstrates that, unlike the

modern, terrigenous organic matter is isotopically heavier than marine organic matter during the Toarcian (fig. 7), which is consistent with previous Toarcian studies (Vetö et al., 1997; Schouten et al., 2000). Multiple lines of evidence presented in section 4.3 highlight a significant transition in the terrigenous organic matter input at Hawsker Bottoms. Indeed, the bottom 2 meters of the study interval are dominated by terrigenous organic matter and are isotopically heavier than the overlying interval that is dominated by marine organic matter. Therefore, an undetermined component of the bulk organic CIE magnitude may be attributed to source mixing effects.

Additional factors could also contribute to the difference in magnitudes between bulk and molecular CIEs. For instance, it is possible that the full CIE was not captured in the molecular isotopic records due to a lower sampling resolution compared to the bulk organic $\delta^{13}C$ records. Alternatively, water availability can modulate the magnitude of the CIE recorded in vascular leaf waxes, as has been discussed for the Paleocene Eocene Thermal Maximum (PETM; e.g. Schouten et al., 2007; Smith et al., 2007), but unlike the PETM, the ratio of angiosperms and conifers would not account for the *n*-alkane and bulk organic CIE magnitude offset because the rise of angiosperms postdates the Early Jurassic (e.g. Heimhofer et al., 2005). Additionally, thermal maturation could influence the $\delta^{13}C$ of individual compounds, which become isotopically heavier with increasing thermal maturity (Clayton, 1991; Clayton and Bjorøy, 1994; Tang et al., 2005).

Nevertheless, while multiple mechanisms may account for the difference between molecular and bulk organic CIE magnitudes, it is significant that a negative CIE is recorded in both marine- and terrestrial-derived lipids, albeit to different degrees. The parallel isotopic change in marine and terrestrial carbon pools recorded at Hawsker

Bottoms further supports previous studies suggesting that the T-OAE was a global carbon cycle perturbation where isotopically light carbon entered the atmospheric, terrigenous, and marine carbon reservoirs (Hesselbo et al., 2000; 2007; Al-Suwaidi et al., 2010; Caruthers et al., 2011; Gröcke et al., 2011). Multiple sources of isotopically light carbon have been proposed, including methane hydrate dissociation, regional upwelling of isotopically light waters in stratified epicontinental seas, thermogenic release of methane from organic-rich strata in contact with dykes, biomass burning, or a combination of these mechanisms (Hesselbo et al., 2000; Schouten et al., 2000; McElwain et al., 2005; van de Schootbrugge et al., 2005; Finkelstein et al., 2006).

Although our study does not provide evidence in support of a specific forcing mechanism, it allows us to narrow down potential mechanisms. A deep-water source of isotopically light carbon is unlikely because of the CIE observed in land plant biomarkers. The lack of evidence for bacterial methanotrophy in our section suggests that methane hydrate dissociation did not supply appreciable methane to the sampling locality. The organic matter source transition complicates the interpretation of PAH abundances as tracers of biomass burning, so a different sampling locality without an organic matter source transition should be studied to test the biomass burning mechanism using PAHs. A cascade of mechanisms rather than a single mechanism likely initiated the T-OAE. However, our results indicate that the influence of source mixing on the bulk organic $\delta^{13}C$ has been previously underestimated and could have potentially affected other bulk isotopic systematics such as nitrogen. Therefore, previous estimates regarding the magnitude of this global perturbation of the carbon cycle should be revisited.

5. Conclusions

We use a multiproxy approach based on bulk geochemistry, lipid biomarkers, and compound-specific stable isotopes to elucidate environmental and ecological changes associated with the T-OAE at Hawsker Bottoms in Yorkshire, England. Molecular indicators and Rock-Eval results suggest that thermal maturity is uniformly in the early oil generation window throughout the sampling interval. The HI data, organic petrography, PAH distribution, and tricyclic terpane ratios indicate a transition in the relative input of terrigenous vs. marine organic matter across a lithological transition. The shift to lower relative abundance of terrigenous organic matter was likely a result of sea level related effects such as coastal proximity, changes in marine organic matter preservation, and/or dilution effects from increased marine productivity.

Organic geochemical redox and depositional environment indicators point towards an overall shift towards more reducing conditions in sediment porewaters and the development of seasonal stratification during the OAE. Previous sedimentological observations require that the water column was not completely anoxic throughout the entire T-OAE, which may seem contradictory at first to the detection of GSB and PSB carotenoids. However, here we present the first occurrence of okenane, a carotenoid marker of PSB, in marine samples younger than the Paleoproterozoic (1.64 Ga). This unexpected finding challenges the interpretation of GSB and PSB carotenoids as markers of PZE in the context of Hawsker Bottoms due to inner shelf vertical mixing, the lack of modern analogues of okenone-production in marine sulfidic environments, and the emerging evidence of okenone-producing mat-dwelling Chromatiaceae. Therefore, in combination with previous reports of microbial wavy lamination in Toarcian shales of

Yorkshire and coeval shales in northern Europe, we argue that okenane, and potentially chlorobactane and isorenieratane, was most likely mat-derived at Hawsker Bottoms.

The compound-specific $\delta^{13}C$ records of short-chain *n*-alkanes, acyclic isoprenoids, and long-chain *n*-alkanes support a carbon cycle perturbation that affected both the atmospheric and marine systems, which precludes the recycling of isotopically light CO_2 from anoxic waters as the sole mechanism responsible for the T-OAE negative CIE. Notably, compound specific $\delta^{13}C$ records of the T-OAE, including the new data presented here from Yorkshire and previous molecular data from the Paris Basin and the Posidonienschiefer, encode negative CIEs that are smaller in magnitude compared to bulk organic $\delta^{13}C$ records. Many mechanisms could contribute to this observation, particularly variable mixing of terrigenous and marine organic matter, which is supported by the multiple lines of evidence for a transition in organic matter source. Identifying the mechanisms behind the CIE magnitude offsets is important for estimating the magnitude of isotopically light carbon injected into the surface carbon reservoirs.

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Figure Captions:

Fig. 1. Rock-Eval Analysis. A) Total organic carbon (TOC; %) (Hesselbo et al., 2000); B) Hydrogen index (HI; mg HC/g TOC); C) Production index (PI); D) T_{max} (°C).

Fig. 2. Molecular Indicators of Thermal Maturity. A) The C_{31} hopane 22S/(22S+22R) ratio; B) C_{30} hopane βα/(βα+αβ) ratio; C) C_{29} sterane ααα 20S/(20S+20R) ratio; D) Ts/(Ts+Tm) ratio; E) diasteranes/steranes ratio. Note the lack of variation in A, B and C across the section compared to the minor variations exhibited by D and E due to changes in source input and/or lithology.

Fig 3. Terrigenous Organic Matter Indicators. A) Ratios of C_{19}/C_{23} and C_{20}/C_{23} tricyclic terpanes; B) total concentration of PAHs normalized by TOC and TLE; C) concentration of retene normalized by TOC and TLE; D) measured contribution of terrigenous organic matter (OM) by petrographic analysis; E) calculated percentage of terrigenous organic matter ($f_{Terr\ OM}$) based on linear regression ($f_{Terr\ OM}$ (%) = -0.279 * HI + 136; R^2=0.90) of petrographic measurements of terrigenous organic matter (Fig. 3D) and HI (Fig. 1B).

Fig. 4. Source and Community Indicators. A) The ratio of regular steranes/17α-hopanes; B) $C_{27}/C_{27\text{-}30}$ steranes; C) $C_{28}/C_{27\text{-}30}$ steranes; D) $C_{29}/C_{27\text{-}30}$ steranes; E) 2α-methylhopane and 3β-methylhopane indices.

Fig. 5. Redox and Depositional Environmental Indicators. A) Gammacerane index; B) C_{35} homohopane index (C_{35}HHI); C) pristane/phytane (Pr/Ph) ratio; D) concentration of isorenieratane; E) concentration of chlorobactane; F) concentration of okenane. The concentrations of C_{40} carotenoids are semi-quantitative and were normalized against TOC and TLE.

Fig. 6 Gas chromatography - metastable reaction monitoring - mass spectrometry (GC-MRM-MS) chromatogram for the identification of aromatic carotenoid derivatives. MRM chromatograms displaying the 554→134 transition characteristic for chlorobactane and okenane in an authentic standard of combined C_{40} carotenoids (A) and in sample ENR004 at 5.98 m (C). Plots B and D are MRM chromatograms displaying the 546→134 MRM transition characteristic of isorenieratane, renieratane, and renierapurpurane in an authentic standard of combined C_{40} carotenoid (B) and in sample ENR004 (D). Compound abbreviations were used for labels: chlorobactane (Ch); okenane (Ok); isorenieratane (Iso); renieratane (Ren); renierapurpurane (Rpurp).

Fig. 7 Carbon Isotopic records. A) Previously reported $\delta^{13}C_{org}$ from Hawsker Bottoms (Hesselbo et al., 2000; Kemp et al., 2005); B) $\delta^{13}C$ of n-C_{17-19} short-chain n-alkanes; C) $\delta^{13}C$ of pristane and phytane; D) $\delta^{13}C$ of n-C_{27-29} long-chain n-alkanes. Note the different x-axis scales.

References

Airs, R.L., Atkinson, J.E., Keely, B.J., 2001. Development and application of a high resolution liquid chromatographic method for the analysis of complex pigment distributions. J. Chromatogr. A 917, 167–177.

Algeo, T. J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation. Chem. Geol. 268, 211-225.

Al-Suwaidi, A.H., Angelozzi, G.N., Baudin, F., Damborenea, S.E., Hesselbo, S.P., Jenkyns, H.C., Mancenido, M.O., Riccardi, A.C., 2010. First record of the Early Toarcian Oceanic Anoxic Event from the Southern Hemisphere, Neuquén Basin, Argentina. J. Geol. Soc. (London) 167, 633–636.

Arinobu, T., Ishiwatari, R., Kaiho, K., Lamolda, M.A., 1999. Spike of pyrosynthetic polycyclic aromatic hydrocarbons associated with an abrupt decrease in $\delta^{13}C$ of a terrestrial biomarker at the Cretaceous-Tertiary boundary at Caravaca, Spain. Geology 27, 723–726.

Bambach, R.K., 2006. Phanerozoic biodiversity mass extinctions. Annu. Rev. Earth Planet. Sci. 34, 127–155.

Beatty, J., Overmann, J., Lince, M., Manske, A., Lang, A., Blankenship, R., Van Dover, C., Martinson, T., Plumley, F., 2005. An obligately photosynthetic bacterial anaerobe from a deep-sea hydrothermal vent. Proc. Natl. Acad. Sci. U.S.A 102, 9306–9310.

Bennett, B., Olsen, S., 2007. The influence of source depositional conditions on the hydrocarbon and nitrogen compounds in petroleum from central Montana, USA. Org. Geochem. 38, 935–956.

Berner, R., 2006. GEOCARBSULF: A combined model for Phanerozoic atmospheric O_2 and CO_2. Geochim. Cosmochim. Acta 70, 5653–5664.

Bowden, S.A., Farrimond, P., Snape, C.E., Love, G.D., 2006. Compositional differences in biomarker constituents of the hydrocarbon, resin, asphaltene and kerogen fractions: An example from the Jet Rock (Yorkshire, UK). Org. Geochem. 37, 369–383.

Bradshaw, M J, J C W Cope, D W Cripps, D T Donovan, M K Howarth, P F Rawson, I M West, and W A Wimbledon. 1992. “Jurassic.” Geol. Soc., London, Memoirs 13, 107–129.

Brocks, J., Love, G., Summons, R., Knoll, A., Logan, G., Bowden, S., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. Nature 437, 866–870.

Brocks, J., Schaeffer, P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. Geochim. Cosmochim. Acta 72, 1396–1414.

Brocks, J.J., Summons, R.E., 2003. Sedimentary hydrocarbons, biomarkers for early life. In: Treatise on Geochemistry, (Elsevier-Pergamon, Oxford). Chpt. 8.03, pp. 63–115.

Brüchert, V., Jørgensen, B.B., Neumann, K., Riechmann, D., Schlösser, M., Schulz, H., 2003. Regulation of bacterial sulfate reduction and hydrogen sulfide fluxes in the central Namibian coastal upwelling zone. Geochim. Cosmochim. Acta 67, 4505–4518.

Burdige, D., 2007. Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? Chem. Rev.

107, 467–485.
Bühring, S., Sievert, S., Jonkers, H., Ertefai, T., Elshahed, M., Krumholz, L., Hinrichs, K.-U., 2011. Insights into chemotaxonomic composition and carbon cycling of phototrophic communities in an artesian sulfur-rich spring (Zodletone, Oklahoma, USA), a possible analog for ancient microbial mat systems. Geobiol. 9, 166–179.
Canfield, D.E., Stewart, F.J., Thamdrup, B., De Brabandere, L., Dalsgaard, T., Delong, E.F., Revsbech, N.P., Ulloa, O., 2010. A Cryptic Sulfur Cycle in Oxygen-Minimum-Zone Waters off the Chilean Coast. Science 330, 1375–1378.
Cao, C., Love, G.D., Hays, L., Wang, W., Shen, S., Summons, R.E., 2009. Biogeochemical evidence for euxinic oceans and ecological disturbance presaging the end-Permian mass extinction event. Earth Planet. Sci. Lett. 281, 188–201.
Caruthers, A.H., Gröcke, D.R., Smith, P.L., 2011. The significance of an Early Jurassic (Toarcian) carbon-isotope excursion in Haida Gwaii (Queen Charlotte Islands), British Columbia, Canada. Earth Planet. Sci. Lett. 307, 19–26.
Caumette, P., Baulaigue, R., Matheron, R., 1991. *Thiocapsa halophila* sp. nov., a new halophilic phototrophic purple sulfur bacterium. Arch. Microbiol. 155, 170–176.
Caumette, P., Guyoneaud, R., Imhoff, J., Süling, J., Gorlenko, V., 2004. *Thiocapsa marina* sp. nov., a novel, okenone-containing, purple sulfur bacterium isolated from brackish coastal and marine environments. Int. J. Syst. Evol. Microbiol. 54, 1031–1036.
Clayton, C., 1991. Effect of maturity on carbon isotope ratios of oils and condensates. Org. Geochem. 17, 887–899.
Clayton, C., Bjorøy, M., 1994. Effect of maturity on $^{13}C/^{12}C$ ratios of individual compounds in North Sea oils. Org. Geochem. 21, 737–750.
Cohen, A.S., Coe, A.L., Harding, S.M., Schwark, L., 2004. Osmium isotope evidence for the regulation of atmospheric CO_2 by continental weathering. Geology 32, 157–160.
Courtillot, V.E., Renne, P.R., 2003. On the ages of flood basalt events. C. R. Geoscience 335, 113–140.
Dahl, J., Moldowan, J., M., Sundararaman, P., 1993. Relationship of biomarker distribution to depositional environment: Phosphoria Formation, Montana, USA. Org. Geochem. 20, 1001–1017.
Didyk, B., Simoneit, B., Brassell, S., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 272, 216-222.
Dugdale, R., Goering, J., Barber, R., Smith, R., Packard, T., 1977. Denitrification and hydrogen sulfide in the Peru upwelling region during 1976. Deep-Sea Res. 24, 601–608.
Eglinton, G., Hamilton, R., 1967. Leaf epicutular waxes. Science. 156, 1322-1335.
Ellis, L., Singh, R.K., Alexander, R., Kagi, R.I., 1996. Formation of isohexyl alkylaromatic hydrocarbons from aromatization-rearrangement of terpenoids in the sedimentary environment: A new class of biomarker. Geochim. Cosmochim. Acta 60, 4747–4763.
Erba, E., 2004. Calcareous nannofossils and Mesozoic oceanic anoxic events. Mar. Micropaleontol. 52, 85–106.
Farrimond, P., Eglinton, G., Brassell, S., Jenkyns, H., 1989. Toarcian anoxic event in Europe: an organic geochemical study. Mar. Petrol. Geol. 6, 136–147.
Farrimond, P., Stoddart, D., Jenkyns, H., 1994. An Organic Geochemical Profile of the

Toarcian Anoxic Event in Northern Italy. Chem. Geol. 111, 17–33.
Farrimond, P., Talbot, H.M., Watson, D.F., Schulz, L.K., Wilhelms, A., 2004. Methylhopanoids: Molecular indicators of ancient bacteria and a petroleum correlation tool. Geochim. Cosmochim. Acta 68, 3873–3882.
Finkelstein, D.B., Pratt, L.M., Brassell, S.C., 2006. Can biomass burning produce a globally significant carbon-isotope excursion in the sedimentary record? Earth Planet. Sci. Lett. 250, 501–510.
Finkelstein, D.B., Pratt, L.M., Curtin, T.M., Brassell, S.C., 2005. Wildfires and seasonal aridity recorded in Late Cretaceous strata from south-eastern Arizona, USA. Sedimentology 52, 587–599.
French, K.L., Tosca, N.J., Cao, C., Summons, R.E., 2012. Diagenetic and detrital origin of moretane anomalies through the Permian–Triassic boundary. Geochim. Cosmochim. Acta 84, 104–125.
George, S.C., 1992. Effect of igneous intrusion on the organic geochemistry of a siltstone and an oil shale horizon in the Midland Valley of Scotland. Org. Geochem. 18, 705–723.
Ghadeer, S.G., Macquaker, J.H.S., 2011. Sediment transport processes in an ancient mud-dominated succession: a comparison of processes operating in marine offshore settings and anoxic basinal environments. J. Geol. Soc. (London) 168, 1121–1132.
Grice, K., Backhouse, J., Alexander, R., Marshall, N., Logan, G.A., 2005. Correlating terrestrial signatures from biomarker distributions, $\delta^{13}C$, and palynology in fluvio-deltaic deposits from NW Australia (Triassic–Jurassic). Org. Geochem. 36, 1347–1358.
Grice, K., Nabbefeld, B., Maslen, E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. Org. Geochem. 38, 1795–1803.
Gröcke, D., Hori, R., Trabucho-Alexandre, J., Kemp, D., Schwark, L., 2011. An open marine record of the Toarcian oceanic event. Solid Earth 2, 245–257.
Handley, L., Talbot, H.M., Cooke, M.P., Anderson, K.E., Wagner, T., 2010. Bacteriohopanepolyols as tracers for continental and marine organic matter supply and phases of enhanced nitrogen cycling on the late Quaternary Congo deep sea fan. Org. Geochem. 41, 910–914.
Heimhofer, U., P. A. Hochuli, S. Burla, J. M. L. Dinis, and H. Weissert., 2005. Timing of Early Cretaceous angiosperm diversification and possible links to major paleoenvironmental change. Geology 33, 141-144.
Hesselbo, S., 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. P. Geologist Assoc. 119, 19–34.
Hesselbo, S., Jenkyns, H., 1995. A comparison of the Hettangian to Bajocian successions of Dorset and Yorkshire, in: Taylor, P. (Ed.), Field Geology of the British Jurassic. Geological Society of London, pp. 105–150.
Hesselbo, S.P., Gröcke, D.R., Jenkyns, H.C., Bjerrum, C.J., Farrimond, P., Morgans Bell, H.S., Green, O.R., 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. Nature 406, 392–395.
Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V., Oliveira, L.C.V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth Planet. Sci. Lett. 253, 455–470.

Hites, R.A., Laflamme, R.E., Farrington, J.W., 1977. Sedimentary Polycyclic Aromatic Hydrocarbons: The Historical Record. Science 198, 829–831.
Howarth, M., 1992. The ammonite family Hildoceratidae in the Lower Jurassic of Britain. Palaeontogr. Soc. Monogr. 145, 1–106.
Jenkyns, H., 1988. The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary, and geochemical evidence. Am. J. Sci. 288, 101–151.
Jenkyns, H., Gröcke, D., Hesselbo, S., 2001. Nitrogen isotope evidence for water mass denitrification during the early Toarcian (Jurassic) oceanic anoxic event. Paleoceanography 16, 593–603.
Jenkyns, H.C., 1980. Cretaceous anoxic events: from continents to oceans. J. Geol. Soc. (London) 137, 171–188.
Jenkyns, H.C., 2010. Geochemistry of oceanic anoxic events. Geochem. Geophys. Geosyst. 11, Q03004.
Jiang, C., Alexander, R., Kagi, R.I., Murray, A.P., 1998. Polycyclic aromatic hydrocarbons in ancient sediments and their relationships to palaeoclimate. Org. Geochem. 29, 1721–1735.
Jiang, C., Alexander, R., Kagi, R.I., Murray, A.P., 2000. Origin of perylene in ancient sediments and its geological significance. Org. Geochem. 31, 1545–1559.
Kawka, O.E., Simoneit, B.R.T., 1990. Polycyclic aromatic hydrocarbons in hydrothermal petroleums from the Guaymas Basin spreading center. Appl. Geochem. 5, 17–27.
Kemp, D.B., Coe, A.L., Cohen, A.S., Schwark, L., 2005. Astronomical pacing of methane release in the Early Jurassic period. Nature 437, 396–399.
Kemp, D.B., Coe, A.L., Cohen, A.S., Weedon, G.P., 2011. Astronomical forcing and chronology of the early Toarcian (Early Jurassic) oceanic anoxic event in Yorkshire, UK. Paleoceanography 26, PA4210.
Kiessling, W., Simpson, C., 2011. On the potential for ocean acidification to be a general cause of ancient reef crises. Glob. Change Biol. 17, 56–67.
Killops, S.D., Massoud, M.S., 1992. Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient sediments: evidence for Jurassic vegetation fires. Org. Geochem. 18, 1–7.
Köster, J., van Kaam-Peters, H., Koopmans, M., de Leeuw, J., Sinninghe Damsté, J., 1997. Sulphurisation of homohopanoids: Effects on carbon number distribution, speciation, and 22S/22R epimer ratios. Geochim. Cosmochim. Acta 61, 2431–2452.
Kruge, M.A., Stankiewicz, B.A., Crelling, J.C., Montanari, A., Bensley, D.F., 1994. Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic firestorm and megawave. Geochim. Cosmochim. Acta 58, 1393–1397.
Kuypers, M.M.M., van Breugel, Y., Schouten, S., Erba, E., Sinninghe Damsté, J.S., 2004. N_2-fixing cyanobacteria supplied nutrient N for Cretaceous oceanic anoxic events. Geology 32, 853.
Lentz, S.J., Fewings, M.R., 2012. The Wind- and Wave-Driven Inner-Shelf Circulation. Annu. Rev. Marine. Sci. 4, 317–343.
Luo, G., Wang, Y., Algeo, T.J., Kump, L.R., Bai, X., Yang, H., Yao, L., Xie, S., 2011. Enhanced nitrogen fixation in the immediate aftermath of the latest Permian marine mass extinction. Geology 39, 647–650.
Macquaker, J., Bentley, S.J., Bohacs, K.M., 2010. Wave-enhanced sediment-gravity flows and mud dispersal across continental shelves: Reappraising sediment transport

processes operating in ancient mudstone successions. Geology 38, 947-950.
Macquaker, J., Taylor, K., 1996. A sequence stratigraphic interpretation of a mudstone-dominated succession: the Lower Jurassic Cleveland Ironstone Formation. J. Geol. Soc. (London) 153, 759–770.
Marynowski, L., Simoneit, B.R.T., 2009. Widespread Upper Triassic to Lower Jurassic wildfire records from Poland: Evidence from charcoal and pyrolytic polycyclic aromatic hydrocarbons. Palaios 24, 285–298.
McElwain, J.C., Wade-Murphy, J., Hesselbo, S.P., 2005. Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals. Nature 435, 479–482.
Meyer, K.M., Macalady, J.L., Fulton, J.M., Kump, L.R., Schaperdoth, I., Freeman, K.H., 2011. Carotenoid biomarkers as an imperfect reflection of the anoxygenic phototrophic community in meromictic Fayetteville Green Lake. Geobiol. 9, 321–329.
Moldowan, J.M., Sundararaman, P., Schoell, M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. Org. Geochem. 10, 915–926.
Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship Between Petroleum Composition and Depositional Environment of Petroleum Source Rocks. Am. Assoc. Petr. Geol. B. 69, 1255–1268.
Naeher, S., Geraga, M., Papatheodorou, G., Ferentinos, G., Kaberi, H., Schubert, C. J., 2012. Environmental variations in a semi-enclosed embayment (Amvrakikos Gulf, Greece)- reconstructions based on benthic foraminifera abundance and lipid biomarker pattern. Biogeosciences 9, 5081-5094.
Naqvi, S., Naik, H., Pratihary, A., D'Souza, W., Narvekar, P., Jayakumar, D., Devol, A., Yoshinari, T., Saino, T., 2006. Coastal versus open-ocean denitrification in the Arabian Sea. Biogeosciences 3, 621–633.
Noble, R.A., Alexander, R., Kagi, R.I., Knox, J., 1986. Identification of some diterpenoid hydrocarbons in petroleum. Org. Geochem. 10, 825–829.
O'Brien, N., 1990. Significance of lamination in Toarcian (Lower Jurassic) shales from Yorkshire, Great Britain. Sediment. Geol. 67, 25–34.
Pálfy, J., Smith, P., 2000. Synchrony between Early Jurassic extinction, oceanic anoxic event, and the Karoo-Ferrar flood basalt volcanism. Geology 28, 747–750.
Pancost, R., Crawford, N., Magness, S., Turner, A., Jenkyns, H., Maxwell, J., 2004. Further evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events. J. Geol. Soc. (London) 161, 353–364.
Pancost, R., Freeman, K., Patzkowsky, M., 1999. Organic-matter source variation and the expression of a late Middle Ordovician carbon isotope excursion. Geology 27, 1015–1018.
Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes In Petroleum Systems and Earth History, 2nd ed, The Biomarker Guide: Biomarkers and Isotopes in Petroleum Systems and Earth History. Cambridge University Press.
Powell, J.H., 2010. Jurassic sedimentation in the Cleveland Basin: a review. Proc. Yorks. Geol. Soc. 58, 21–72.
Prauss, M., Ligouis, B., Luterbacher, H., 1991. Organic matter and palynomorphs in the

"Posidonienschiefer" (Toarcian, Lower Jurassic) of southern Germany. Geol. Soc., London Spec. Publ. 58, 335–351.

Rashby, S., Sessions, A.L., Summons, R.E., Newman, D., 2007. Biosynthesis of 2-methylbacteriohopanepolyols by an anoxygenic phototroph. Proc. Natl. Acad. Sci. U.S.A 104, 15099.

Röhl, H., Schmid, A., Oschmann, W., Frimmel, A., Schwark, L., 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: an oxygen-depleted ecosystem controlled by sea level and palaeoclimate. Palaeogeogr. Palaeoclimatol. Palaeoecol. 165, 27–52.

Sabatino, N., Neri, R., Bellanca, A., Jenkyns, H.C., Baudin, F., Parisi, G., Masetti, D., 2009. Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria-Marche Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. Sedimentology 56, 1307–1328.

Sãenz, J.P., Eglinton, T.I., Summons, R.E., 2011. Abundance and structural diversity of bacteriohopanepolyols in suspended particulate matter along a river to ocean transect. Org. Geochem. 42, 774–780.

Schlanger, S.O., Jenkyns, H.C., 1976. Cretaceous oceanic anoxic events: causes and consequences. Geol. Mijnbouw 55, 179–184.

Schouten, S., van Kaam-Peters, H., Rijpstra, W., Schoell, M., Sinninghe Damsté , J., 2000. Effects of an oceanic anoxic event on the stable carbon isotopic composition of Early Toarcian carbon. Am. J. Sci. 300, 1–22.

Schouten, S., Woltering, M., Rijpstra, W.I.C., Sluijs, A., Brinkhuis, H., Sinninghe Damsté, J.S., 2007. The Paleocene–Eocene carbon isotope excursion in higher plant organic matter: Differential fractionation of angiosperms and conifers in the Arctic. Earth Planet. Sci. Lett. 258, 581–592.

Schunck, H., Lavik, G., Desai, D.K., Großkopf, T., Kalvelage, T., Löscher, C.R., Paulmier, A., Contreras, S., Siegel, H., Holtappels, M., Rosenstiel, P., Schilhabel, M.B., Graco, M., Schmitz, R.A., Kuypers, M.M.M., LaRoche, J., 2013. Giant Hydrogen Sulfide Plume in the Oxygen Minimum Zone off Peru Supports Chemolithoautotrophy. PLoS One 8, e68661.

Schwark, L., Frimmel, A., 2004. Chemostratigraphy of the Posidonia Black Shale, SW-Germany. Chem. Geol. 206, 231–248.

Sephton, M.A., Love, G.D., Meredith, W., Snape, C.E., Sun, C.-G., Watson, J.S., 2005. Hydropyrolysis: A new technique for the analysis of macromolecular material in meteorites. Planet. Space Sci. 53, 1280–1286.

Sepúlveda, J., Wendler, J., Leider, A., Kuss, H–J., Summons, R.E., Hinrichs, K–U., 2009. Molecular isotopic evidence of environmental and ecological changes across the Cenomanian–Turonian boundary in the Levant Platform of central Jordan. Org. Geochem. 40, 553–568.

Sinninghe Damsté, J.S., Schouten, S., Biological markers for anoxia in the photic zone of the water column. In: The Handbook of Environmental Chemistry, (Springer-Verlag, Berlin), pp. 127–163.

Sinninghe Damsté, J., Kenig, F., Koopmans, M., Köster, J., Schouten, S., Hayes, J., de Leeuw, J., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochim. Cosmochim. Acta 59, 1895–1900.

Smith, F., Wing, S., Freeman, K., 2007. Magnitude of the carbon isotope excursion at the

Paleocene–Eocene thermal maximum: The role of plant community change. Earth Planet. Sci. Lett. 262, 50–65.

Smittenberg, R.H., Pancost, R.D., Hopmans, E.C., Paetzel, M., and Sinninghe Damsté, J.S., 2004, A 400-year record of environmental change in an euxinic fjord as revealed by the sedimentary biomarker record: Palaeogeogr. Palaeoclimatol. Palaeoecol. 202, 331–351.

Stewart, F.J., Ulloa, O., DeLong, E.F., 2012. Microbial metatranscriptomics in a permanent marine oxygen minimum zone. Environ. Microbiol. 14, 23–40.

Suan, G., Nikitenko, B.L., Rogov, M.A., Baudin, F., Spangenberg, J.E., Knyazev, V.G., Glinskikh, L.A., Goryacheva, A.A., Adatte, T., Riding, J.B., Föllmi, K.B., Pittet, B., Mattioli, E., Lécuyer, C., 2011. Polar record of Early Jurassic massive carbon injection. Earth Planet. Sci. Lett. 312, 102–113.

Suan, G., Pittet, B., Bour, I., Mattioli, E., Duarte, L., Mailliot, S., 2008. Duration of the Early Toarcian carbon isotope excursion deduced from spectral analysis: Consequence for its possible causes. Earth Planet. Sci. Lett. 267, 666–679.

Summons, R.E., Jahnke, L., Hope, J., Logan, G., 1999. 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. Nature 23, 85–88.

Talbot, H., Farrimond, P., 2007. Bacterial populations recorded in diverse sedimentary biohopanoid distributions. Org. Geochem. 38, 1212–1225.

Talbot, H.M., Watson, D.F., Pearson, E.J., Farrimond, P., 2003. Diverse biohopanoid compositions of non-marine sediments. Org. Geochem. 34, 1353–1371.

Talbot, M., Livingstone, D., 1989. Hydrogen Index and Carbon Isotopes of Lacustrine Organic-Matter as Lake Level Indicators. Palaeogeogr. Palaeoclimatol. Palaeoecol. 70, 121–137.

Tang, Y., Huang, Y., Ellis, G.S., Wang, Y., Kralert, P.G., Gillaizeau, B., Ma, Q., Hwang, R., 2005. A kinetic model for thermally induced hydrogen and carbon isotope fractionation of individual n-alkanes in crude oil. Geochim. Cosmochim. Acta 69, 4505–4520.

ten Haven, H., Rohmer, M., Rullkötter, J., Bisseret, P., 1989. Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. Geochim. Cosmochim. Acta 53, 3073–3079.

Trabucho-Alexandre, J., Dirkx, R., Veld, H., Klaver, G., de Boer, P., 2012. Toarcian Black Shales in the Dutch Central Graben: Record of Energetic, Variable Depositional Conditions during an Oceanic Anoxic Event. J. Sediment. Res. 82, 104-120.

Trabucho-Alexandre, J., Tuenter, E., Henstra, G., van der Zwan, K., van de Wal, R., Dijkstra, H., de Boer, P., 2010. The mid-Cretaceous North Atlantic nutrient trap: Black shales and OAEs. Paleoceanography 25, PA4201.

van Breugel, Y., Baas, M., Schouten, S., Mattioli, E., Sinninghe Damsté, J.S., 2006. Isorenieratane record in black shales from the Paris Basin, France: Constraints on recycling of respired CO_2 as a mechanism for negative carbon isotope shifts during the Toarcian oceanic anoxic event. Paleoceanography 21, PA4220.

van de Schootbrugge, B., McArthur, J.M., Bailey, T.R., Rosenthal, Y., Wright, J.D., Miller, K.G., 2005. Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records. Paleoceanography 20, PA3008.

Venkatesan, M.I., Dahl, J., 1989. Organic geochemical evidence for global fires at the

Cretaceous/Tertiary boundary. Nature 338, 57–60.
Vetö, I., Demeny, A., Hertelendi, E., Hetenyi, M., 1997. Estimation of primary productivity in the Toarcia Tethys- a novel approach based on TOC, reduced sulphur and manganese contents. Palaeogeogr. Palaeoclimatol. Palaeoecol. 132, 355–371.
Wahlund, T., Woese, C., Castenholz, R., Madigan, M., 1991. A thermophilic green sulfur bacterium from New Zealand hot springs, *Chlorobium tepidum* sp. nov. Arch. Microbiol. 156, 81–90.
Wakeham, S., Schaffner, C., Giger, W., 1980. Polycyclic aromatic hydrocarbons in Recent lake sediments--I. Compounds having anthropogenic origins. Geochim. Cosmochim. Acta 44, 403–413.
Wakeham, S.G., Amann, R., Freeman, K.H., Hopmans, E.C., Jørgensen, B.B., Putnam, I.F., Schouten, S., Sinninghe Damsté, J.S., Talbot, H.M., Woebken, D., 2007. Microbial ecology of the stratified water column of the Black Sea as revealed by a comprehensive biomarker study. Org. Geochem. 38, 2070–2097.
Wakeham, S.G., Turich, C., Schubotz, F., Podlaska, A., Li, X., Varela, R., Astor, Y., Sãenz, J.P, Rush, D., Sinninghe Damsté , J.S., Summons, R.E., Scranton, M.I., Taylor, G. T., Hinrichs, K.-U., 2012. Biomarkers, chemistry, and microbiology show chemoautotrophy in a multilayer chemocline in the Cariaco Basin. Deep-Sea Res. I 163, 133-156.
Wen, Z., Ruiyong, W., Radke, M., Qingyu, W., Guoying, S., Zhili, L., 2000. Retene in pyrolysates of algal and bacterial organic matter. Org. Geochem. 31, 757–762.
Wignall, P., Newton, R.J., Little, C.T.S., 2005. The timing of paleoenvironmental change and cause-and-effect relationships during the Early Jurassic mass extinction in Europe. Am. J. Sci. 305, 1014–1032.
Xie, S., Pancost, R., Yin, H., Wang, H., Evershed, R., 2005. Two episodes of microbial change coupled with Permo/Triassic faunal mass extinction. Nature 434, 494–497.
Zhang, C., Zhang, Y., Cai, C., 2011. Aromatic isoprenoids from the 25-65 Ma saline lacustrine formations in the western Qaidam Basin, NW China. Org. Geochem. 42, 851-855.
Zundel, M., Rohmer, M., 1985. Prokaryotic triterpenoids. 1. 3β-Methylhopanoids from *Acetobacter* species and *Methylococcus capsulatus*. Eur. J. Biochem. 150, 23–27.

Figure 1

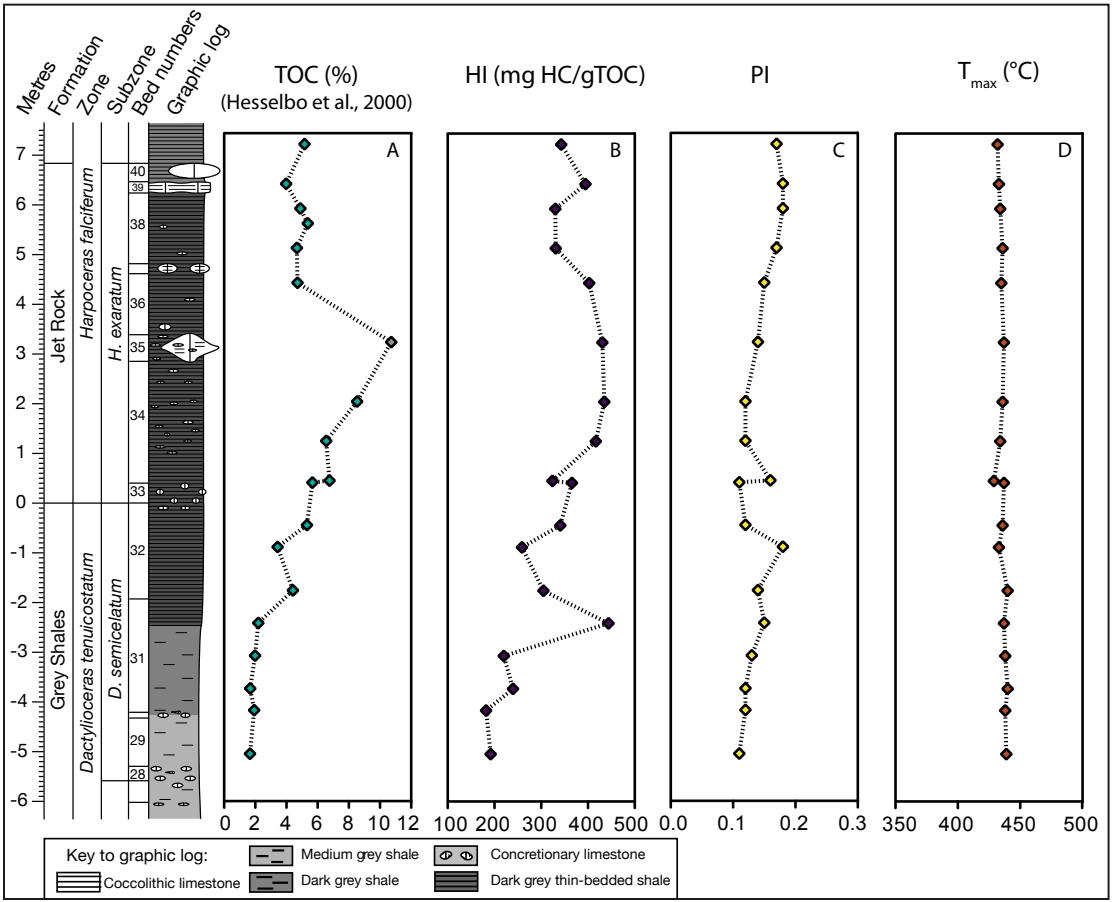

Metres
Formation
Zone
Subzone
Bed numbers
Graphic log
TOC (%)
(Hesselbo et al., 2000)
HI (mg HC/gTOC)
PI
T_{max} (°C)
A
B
C
D
Jet Rock
Grey Shales
Harpoceras falciferum
Dactylioceras tenuicostatum
H. exaratum
D. semicelatum
Key to graphic log:
Coccolithic limestone
Medium grey shale
Dark grey shale
Concretionary limestone
Dark grey thin-bedded shale

Figure 2

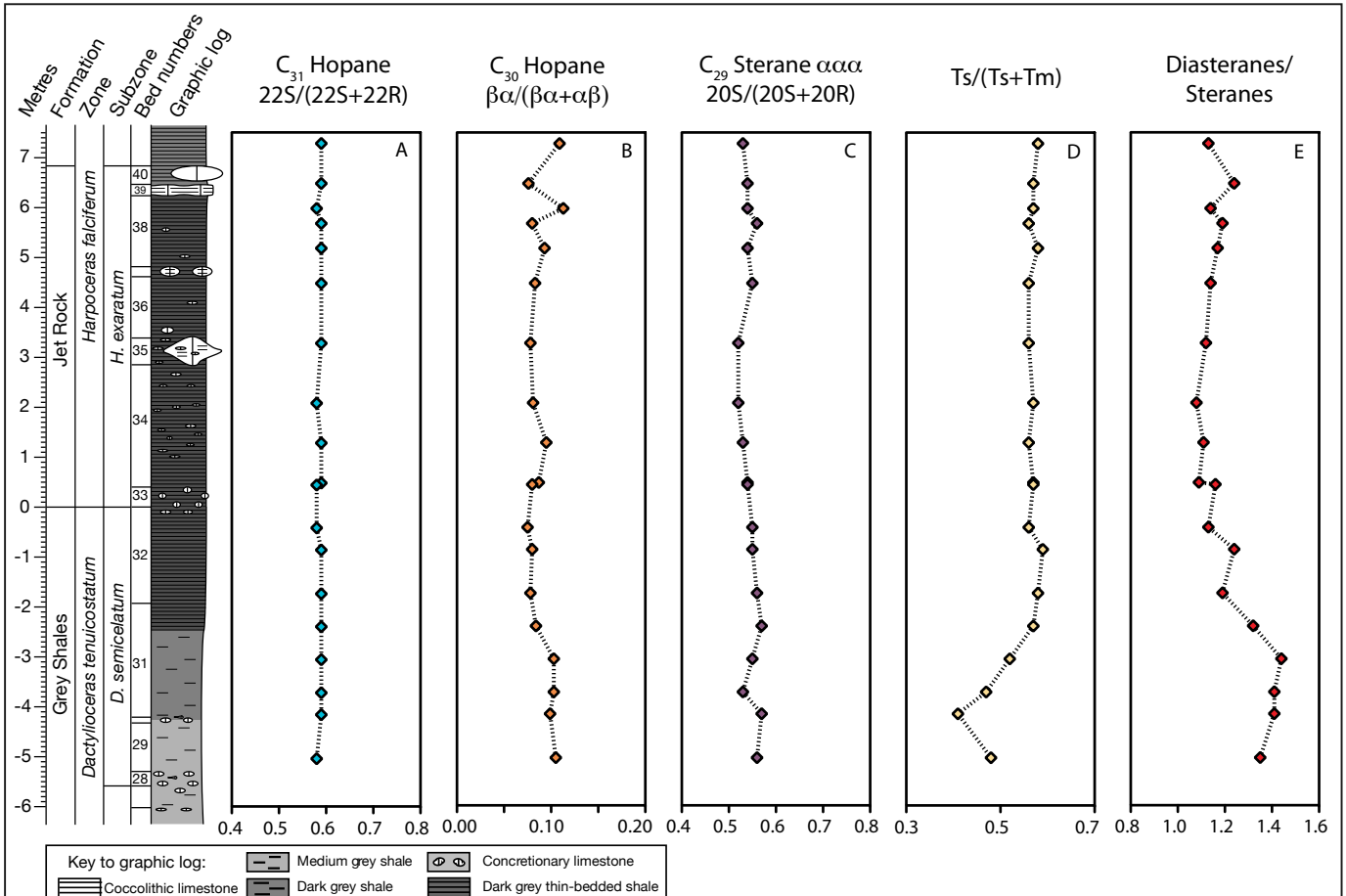

Metres
Formation
Zone
Subzone
Bed numbers
Graphic log
Jet Rock
Grey Shales
Harpoceras falciferum
Dactylioceras tenuicostatum
H. exaratum
D. semicelatum
C31 Hopane 22S/(22S+22R)
C30 Hopane βα/(βα+αβ)
C29 Sterane ααα 20S/(20S+20R)
Ts/(Ts+Tm)
Diasteranes/ Steranes
A
B
C
D
E
Key to graphic log:
Coccolithic limestone
Medium grey shale
Dark grey shale
Concretionary limestone
Dark grey thin-bedded shale

Figure 3

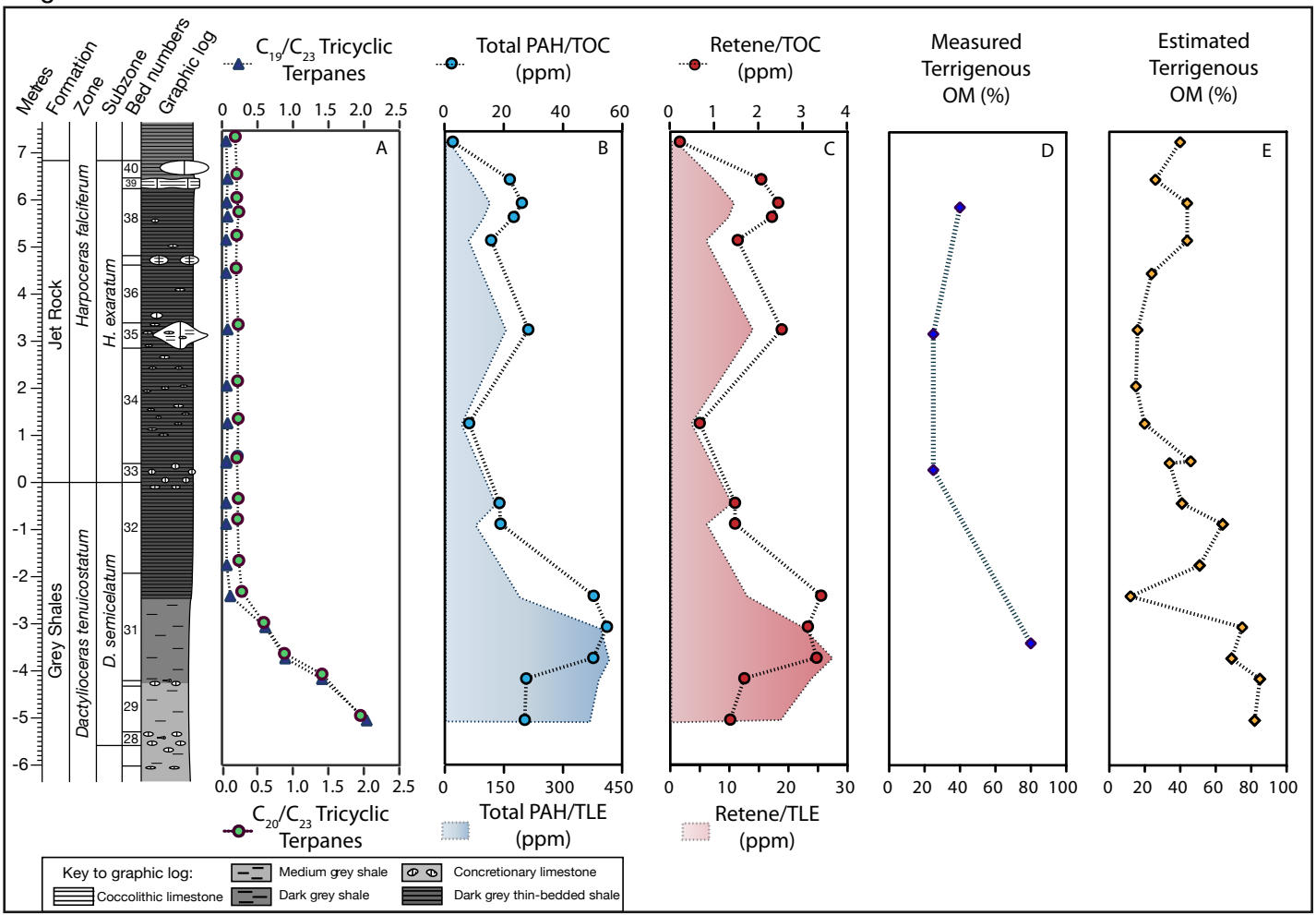

Metres
Formation
Zone
Subzone
Bed numbers
Graphic log
Jet Rock
Grey Shales
Harpoceras falciferum
Dactylioceras tenuicostatum
H. exaratum
D. semicelatum
C19/C23 Tricyclic Terpanes
Total PAH/TOC (ppm)
Retene/TOC (ppm)
Measured Terrigenous OM (%)
Estimated Terrigenous OM (%)
A
B
C
D
E
C20/C23 Tricyclic Terpanes
Total PAH/TLE (ppm)
Retene/TLE (ppm)
Key to graphic log:
Coccolithic limestone
Medium grey shale
Dark grey shale
Concretionary limestone
Dark grey thin-bedded shale

Figure 4

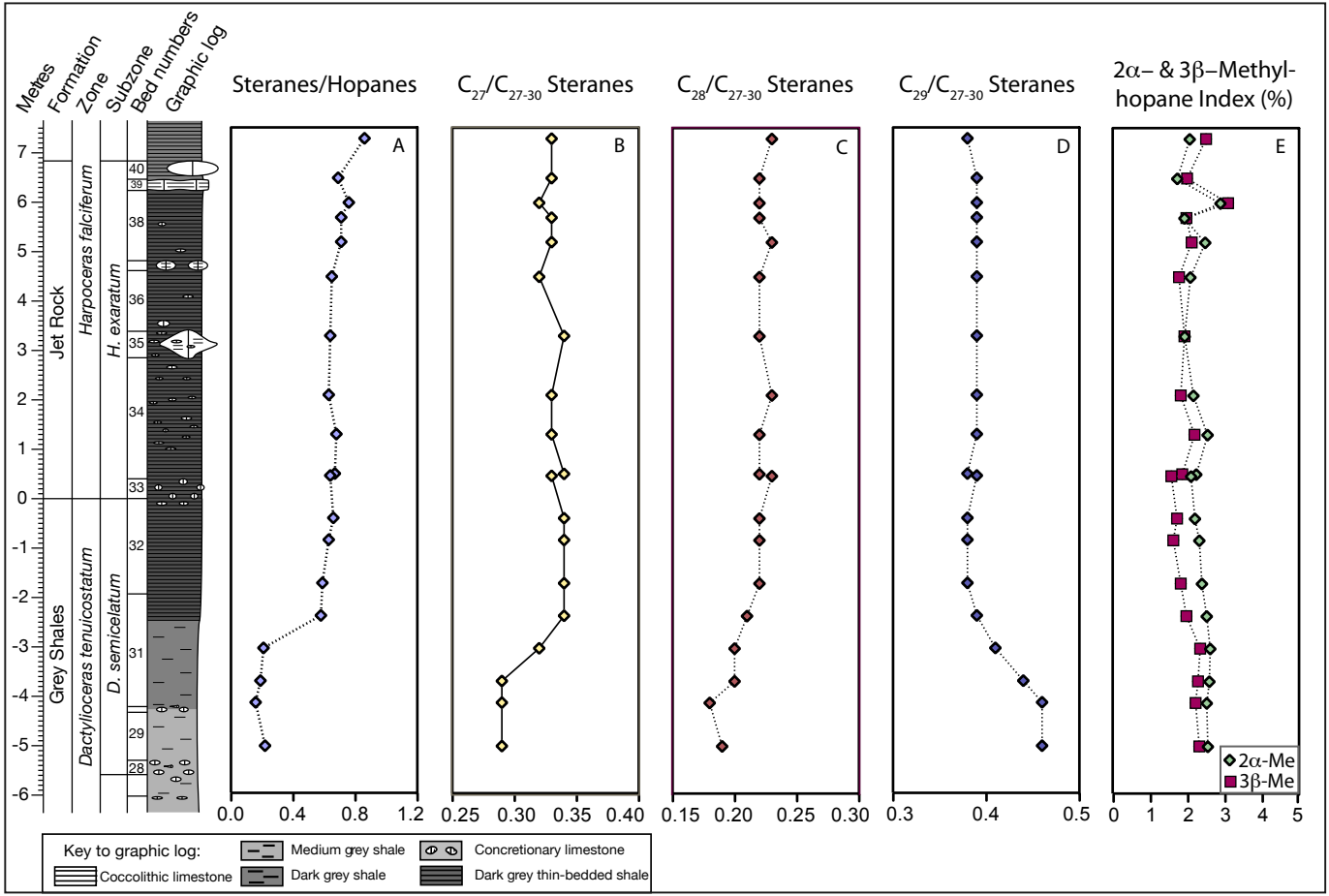

Metres
Formation
Zone
Subzone
Bed numbers
Graphic log
Steranes/Hopanes
$C_{27}/C_{27\text{-}30}$ Steranes
$C_{28}/C_{27\text{-}30}$ Steranes
$C_{29}/C_{27\text{-}30}$ Steranes
2α– & 3β–Methyl-hopane Index (%)
Jet Rock
Grey Shales
Harpoceras falciferum
Dactylioceras tenuicostatum
H. exaratum
D. semicelatum
A
B
C
D
E
2α-Me
3β-Me
Key to graphic log:
Coccolithic limestone
Medium grey shale
Dark grey shale
Concretionary limestone
Dark grey thin-bedded shale

Figure 5

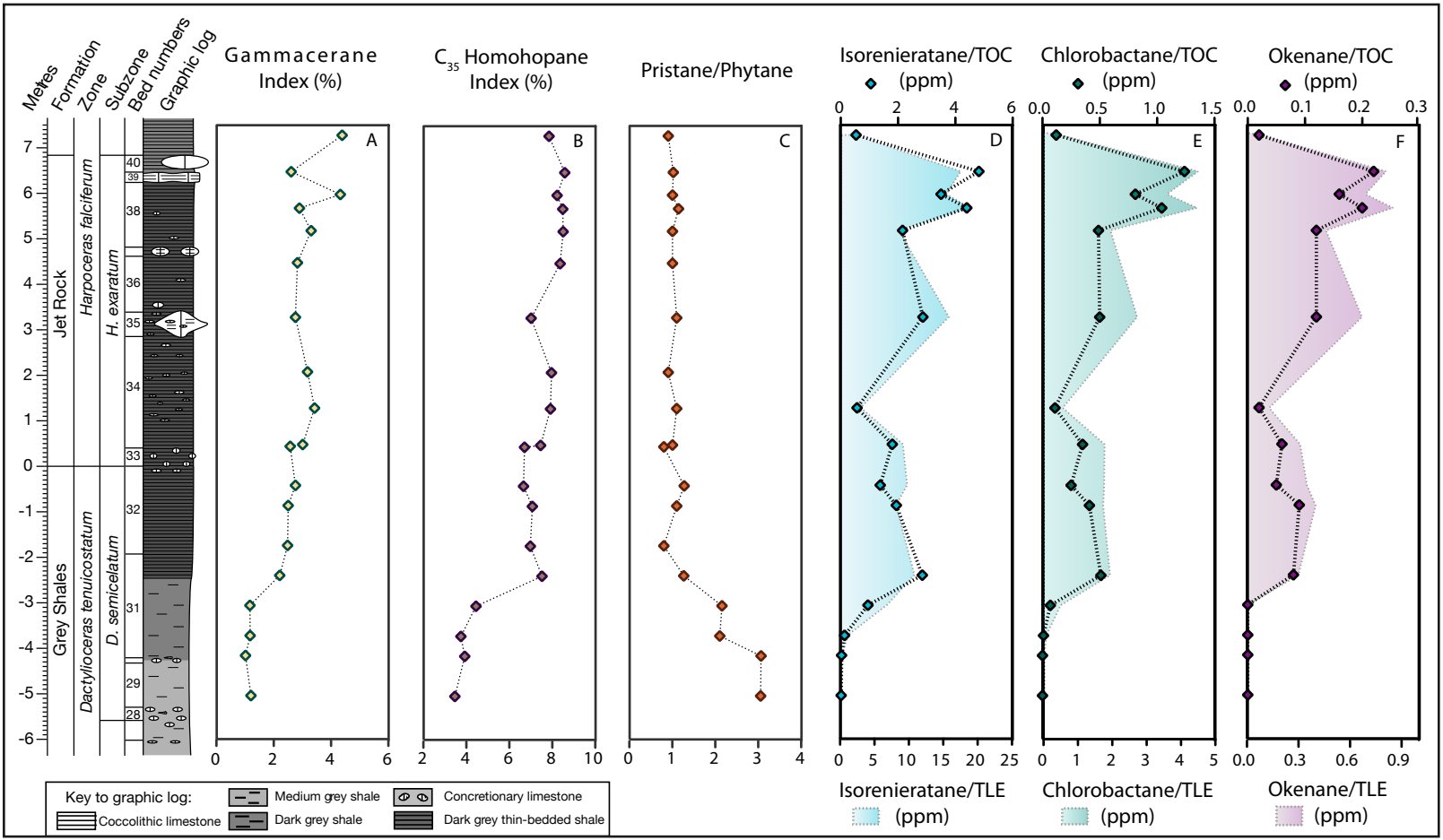

Metres
Formation
Zone
Subzone
Bed numbers
Graphic log
Jet Rock
Grey Shales
Harpoceras falciferum
Dactylioceras tenuicostatum
H. exaratum
D. semicelatum
Gammacerane Index (%)
C35 Homohopane Index (%)
Pristane/Phytane
Isorenieratane/TOC (ppm)
Chlorobactane/TOC (ppm)
Okenane/TOC (ppm)
Isorenieratane/TLE (ppm)
Chlorobactane/TLE (ppm)
Okenane/TLE (ppm)
Key to graphic log:
Coccolithic limestone
Medium grey shale
Dark grey shale
Concretionary limestone
Dark grey thin-bedded shale

Figure 6

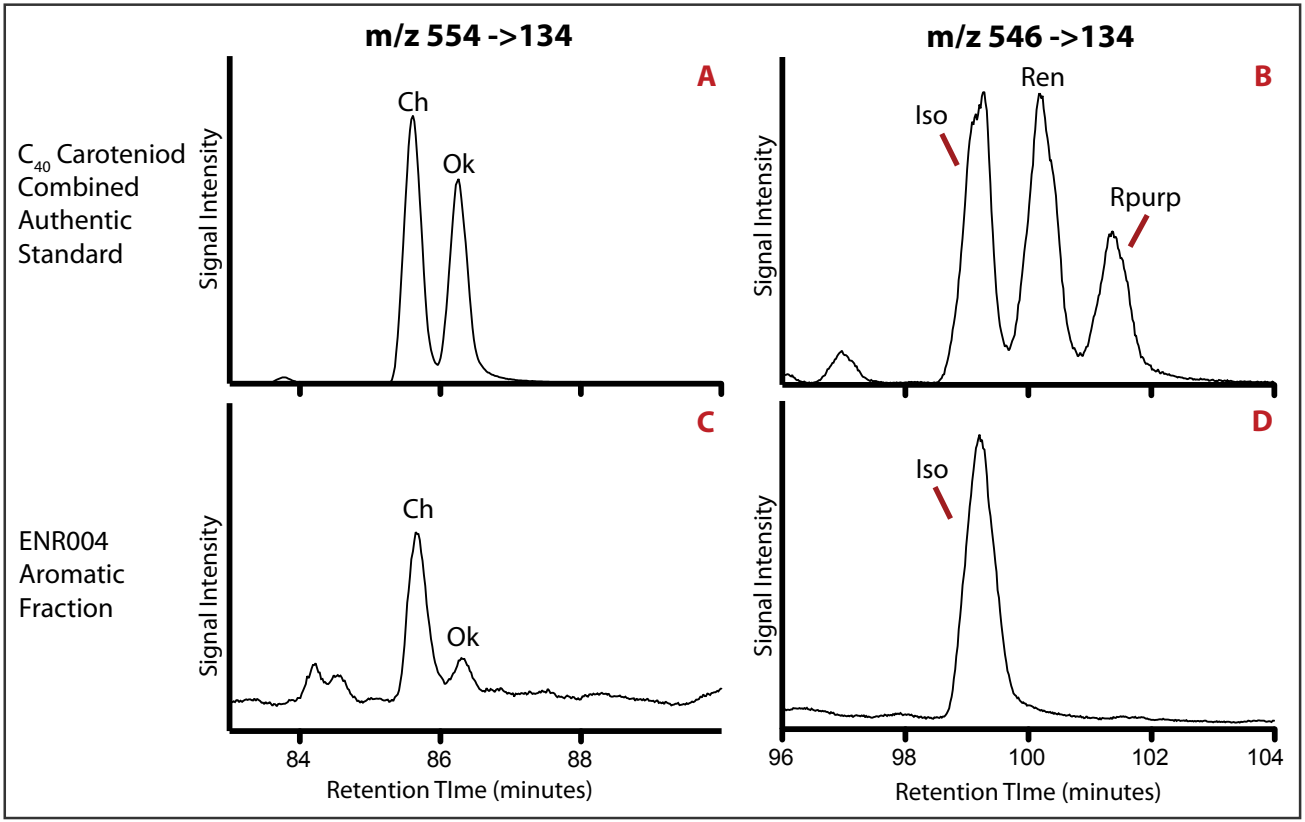
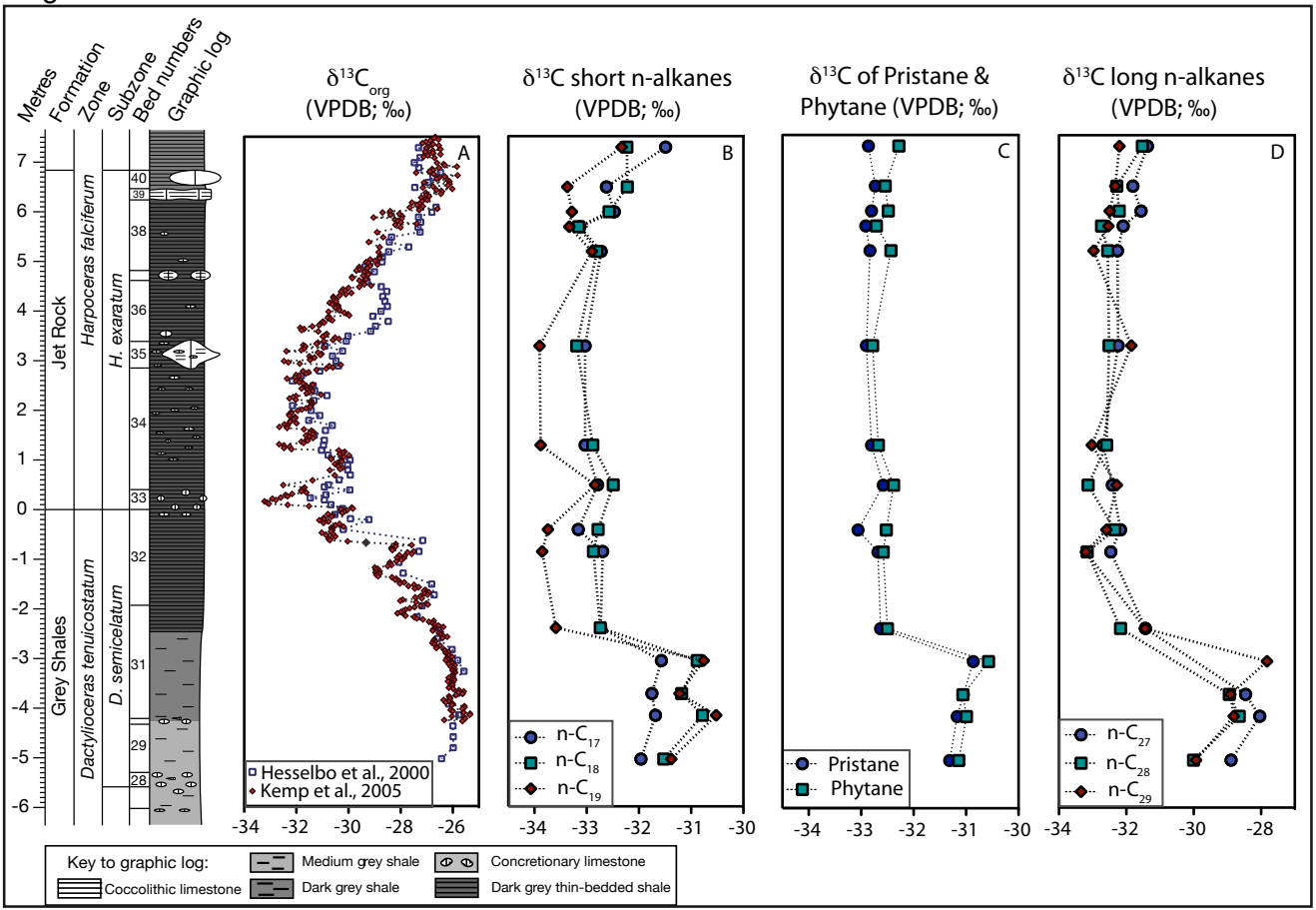

m/z 554 ->134
m/z 546 ->134
A
B
C
D
C_{40} Carotenoid Combined Authentic Standard
ENR004 Aromatic Fraction
Signal Intensity
Ch
Ok
Iso
Ren
Rpurp
84
86
88
96
98
100
102
104
Retention TIme (minutes)

Figure 7


Metres
Formation
Zone
Subzone
Bed numbers
Graphic log
Jet Rock
Grey Shales
Harpoceras falciferum
Dactylioceras tenuicostatum
H. exaratum
D. semicelatum
δ13Corg (VPDB; ‰)
δ13C short n-alkanes (VPDB; ‰)
δ13C of Pristane & Phytane (VPDB; ‰)
δ13C long n-alkanes (VPDB; ‰)
A
B
C
D
Hesselbo et al., 2000
Kemp et al., 2005
n-C17
n-C18
n-C19
Pristane
Phytane
n-C27
n-C28
n-C29
Key to graphic log:
Coccolithic limestone
Medium grey shale
Dark grey shale
Concretionary limestone
Dark grey thin-bedded shale

Supplementary Online Material (SOM)

3.1 Rock-Eval pyrolysis

Powdered sediment samples (~1 g) were analyzed at the University of Newcastle on a Rock-Eval pyrolysis instrument. The total organic carbon (TOC %), T_{max} (°C), S_1, and S_2 were determined. The S_1 and S_2 are expressed in mg hydrocarbons (HC) per gram dry rock. These parameters were used to calculate the hydrogen index (HI) (HI=[100*S_2]/TOC; expressed in mg hydrocarbon (HC)/g TOC) and the production index (PI) (PI= S_1/[S_1+S_2]). The Rock-Eval TOC values and the bulk $\delta^{13}C_{org}$ have been previously reported (Hesselbo et al., 2000).

3.2 Organic petrography

In order to examine the nature of the organic matter, particularly the fraction of terrigenous organic matter, four samples across the section were prepared for optical analysis of the kerogen. Kerogen was isolated from the sample material remaining after lipid extraction as described in section 3.3. The mineral matrix was removed by the sequential addition of HCl and HF. Samples were centrifuged and rinsed between acid treatments, and the residual matter was rinsed with water and methanol. A subsample of each kerogen sample was mounted onto a slide in duplicate and assessed optically under white light and fluorescent light using a Zeiss research microscope and a Zeiss x 40 Plan-Neofluar objective. A Zeiss Axioskop, Axio Image D1, and a Zeiss 18 filter set were used to take photomicrographs and fluorescence images.

The fraction of terrigenous organic matter was estimated for the samples that were not analyzed by organic petrography using the linear relationship between the percent terrigenous organic matter measured by optical microscopy and the corresponding HI:

$$f_{Terr\ OM}\ (\%) = -0.279 * HI + 136 \qquad (1)$$

where the linear regression had an R^2 value of 0.90 and $f_{Terr\ OM}$ represents the terrigenous organic matter as a percentage.

3.3 Biomarker extraction and analysis

Powdered samples (~ 5 g) were extracted using a Dionex ASE 200 Accelerated Solvent Extractor at 1000 psi and 100°C, with a solvent mixture of dichloromethane:methanol 9:1 (v/v). The total lipid extract (TLE) was reacted with acid-activated copper shots to remove elemental sulfur. Asphaltenes were separated (3x) from the maltene fraction by precipitation in n-pentane at 4ºC, and after centrifugation at 3000 rpm for 10 minutes. The maltene fraction was then separated into saturated, aromatic, and polar fractions by silica gel chromatography using hexane, 1:1 (v/v) hexane/dichloromethane, and 7:3 (v/v) dichloromethane/methanol.

The saturated fractions were screened by gas chromatography-mass spectrometry (GC-MS) in full scan using an Agilent 6890 GC equipped with a HP6890 autosampler and interfaced to an Agilent 5973 mass spectrometer. Saturated hydrocarbons were also analyzed by gas chromatography-metastable reaction monitoring-mass spectrometry (GC-MRM-MS) on a Micromass Autospec Ultima mass spectrometer coupled with an Agilent 6890N GC. The analysis was carried out with a 60 m J&W Scientific DB-1 fused silica capillary column (internal diameter: 0.25 mm; 0.25 m film thickness) in pulsed splitless mode. The initial GC oven temperature was programmed to 60°C (held for 2

minutes), ramped to 150°C at 10°C/minute, and then to 315°C at 3°C/minute (held for 24 minutes). The ion source was in EI mode at a temperature of 250°C, an ionization energy of 70 eV, and acceleration voltage of 8000 kV. Tricyclic terpanes and hopanes were identified by MRM using the molecular ion to the m/z 191 transitions. Likewise, steranes were identified by MRM using the molecular ion to m/z 217 transitions.

The aromatic fraction was analyzed by GC-MS in SIM modes. Prior to analysis, 400 ng of an aromatic internal standard, deuterated phenanthrene, was added to each sample. The GC was fitted with a DB-5 stationary phase column, and the GC oven temperature was ramped from 60°C to 150°C at 20°C/minute, and then to 330°C at 4°C/minute (held for 27 minutes). The aryl isoprenoids and isorenieratane was identified in the m/z 134 ion chromatograms and quantified using the internal standard. Absolute quantification is not possible without taking into account relative response factors but our approach does allow an internally consistent estimation across the sample set.

The aromatic fraction was also analyzed by GC-MS in full scan and MRM modes on a Micromass Autospec Ultima mass spectrometer coupled with an Agilent 6890N GC autospec. The GC was fitted with a DB-5 stationary phase column. Polycyclic aromatic hydrocarbons (PAHs) were identified and quantified in full scan mode by their mass spectra and by comparison with a mix of authentic standards, with the exception of retene, coronene, and triphenylene, which were identified by their mass spectra and relative retention time. Aromatic carotenoid derivatives were also analyzed by GC-MRM-MS using parent-daughter reactions. Isorenieratane, okenane, and chlorobactane were identified in characteristic MRM transitions by comparison of retention times to an extract from the Barney Creek Formation (BCF) and a standard mix of hydrogenated

carotenoids containing chlorobactane, okenane, isorenieratane, renieratane, and renierapurpane. Using the MRM data, okenane and chlorobactane were quantified against the GC-MSD quantified isorenieratane. The aromatic carotenoid derivative and PAH concentrations were normalized against mass of TLE and TOC.

Compound specific carbon isotopic measurements of saturated hydrocarbons were made by gas chromatography/combustion/ isotope ratio mass spectrometry (GC-C-IRMS) using a Thermo Finnigan Delta plus XP coupled to a Thermo Finnigan Trace GC. The initial oven temperature was programmed to 60°C (held for 3 minutes), ramped to 180°C at 10°C/min, and then to 320°C at 4°C/min (held for 20 minutes). All samples were bracketed by pulses of in house calibrated reference CO_2 gas and Oztech calibrated reference CO_2 gas. A standard mix of *n*-alkanes (mix A; Arndt Schimmelmann, Indiana University) was analyzed twice a day to monitor the instrument condition. The mean value of triplicate analyses are reported here in permil (‰) relative to Vienna Pee Dee belemnite (VPDB), and the standard deviation from the mean value was better than 0.4‰.