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A carbon-isotope perturbation at the Pliensbachian–Toarcian boundary: evidence from the Lias Group, NE England

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Abstract – A perturbation in the carbon-isotope record at the time of the Pliensbachian–Toarcian boundary (~ 184 Ma) in the Early Jurassic is reported, based on new data from Yorkshire, England. Two sharp $\delta^{13}C_{org}$ negative excursions, each with a magnitude of ~ −2.5 ‰ and reaching minimum values of −28.5 ‰, are recorded in the bulk organic-matter record in sediments of latest Pliensbachian to earliest Toarcian age. A similar pattern of negative carbon-isotope excursions has been observed at the stage boundary in the SW European section at Peniche, Portugal in $\delta^{13}C_{carbonate}$, $\delta^{13}C_{wood}$ and $\delta^{13}C_{brachiopod}$ records. The isotopic excursion is of interest when considering the genesis and development of the later Toarcian Oceanic Anoxic Event (OAE), as well as the second-order global extinction event that spans the stage boundary. Furthermore, the isotope excursion potentially provides a chemostratigraphic marker for recognition of the stage boundary, which is currently achieved on the basis of different ammonite faunas in the NW European and Tethyan realms.

Keywords: Jurassic, Toarcian, Pliensbachian, carbon-isotope, excursion.

1. Introduction

Much attention has focused on the events surrounding the Early Toarcian Oceanic Anoxic Event (OAE: *c.* 183 Ma) in the Early Jurassic (Jenkyns, 1985, 1988). The relative enrichment with organic matter of certain strata of Early Toarcian age, together with the marine and terrestrial carbon-isotope record, indicates that a large perturbation in the carbon cycle took place at that time. There is less of a consensus on the exact nature and extent of the perturbation, in particular, the significance of the sharp negative carbon-isotope excursion (CIE) which punctuates a broad positive excursion, seen in marine organic-matter ($\delta^{13}C_{org}$) of between ~ −5 ‰ and −7 ‰, reported from the Boreal (NW European) *falciferum* Zone (Jenkyns & Clayton, 1997; Hesselbo *et al.* 2000; Schouten *et al.* 2000; Röhl *et al.* 2001; Jenkyns *et al.* 2002; Cohen *et al.* 2004; Kemp *et al.* 2005). A similar but in most cases more subdued (~ −3.5 ‰ or less) excursion in hemipelagic carbonate is recorded from the corresponding *levisoni* Zone in Portugal (Hesselbo *et al.* 2007; Suan *et al.* 2008*b*), from coeval strata in France (Hermoso *et al.* 2009), and from time-equivalent Tethyan deep-water pelagic and shallow-water platform-carbonate sections in Italy (Jenkyns & Clayton, 1986; Jenkyns, Gröcke & Hesselbo, 2001; Woodfine *et al.* 2008; Sabatino *et al.* 2009).

The positive carbon-isotope excursion associated with the Early Toarcian OAE has been attributed to increased sequestration of isotopically light marine organic matter in ocean sediments under oxygen-depleted conditions, leading to a corresponding ‘heavy’ signal preserved in materials such as marine carbonates, marine organic matter, and fossil wood. This interpretation is supported by the widespread occurrence of organic-rich black shales deposited during this time interval, which essentially define the OAE, and from biomarker evidence for photic-zone sulphate reduction in horizons that show this organic enrichment (Schouten *et al.* 2000; Pancost *et al.* 2004; Bowden *et al.* 2006). In contrast, the negative carbon-isotope excursion has been interpreted by most workers as resulting from input of isotopically light carbon to the shallow ocean, atmosphere and biosphere, from a source such as gas hydrate or thermally metamorphosed shale and coal (Hesselbo *et al.* 2000, McElwain, Wade-Murphy & Hesselbo, 2005; Kemp *et al.* 2005; Svensen *et al.* 2007). Alternative purely palaeoceanographic mechanisms, such as recycling of waters from below a chemocline, are untenable because they are unsupported by modern studies of present-day anoxic basins and fail to explain expression of the isotope excursion in terrestrial materials (Küspert 1982; Van Breugel *et al.* 2006*a*,*b*; cf. McArthur *et al.* 2008).

The Pliensbachian–Toarcian boundary preceding the OAE has received less attention, but remains an important interval in terms of changes in carbon cycling, changes in sea level, faunal turn-over and evolving Early Jurassic palaeoclimate. A sea-level rise across the stage boundary of several tens of metres, marked in many sections by a change from shallower to deeper water facies, has previously been inferred (Hallam, 1981, 1997; Hesselbo & Jenkyns, 1998). The boundary coincides with a relative minimum in seawater strontium-isotope values, with $^{87}Sr/^{86}Sr$ ratios falling to the least radiogenic values seen throughout the Early Jurassic (Jones *et al.* 1994; Jones & Jenkyns,

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2001). The transition from the Pliensbachian into the Toarcian is marked by the initiation of the mass-extinction event, suggesting that changes in climate and palaeoceanography started to occur well before the onset of the OAE (Hallam, 1986; Little & Benton, 1995; Harries & Little, 1999; Aberhan & Fürsich, 2000; Macchioni & Cecca, 2002; Cecca & Macchioni, 2004; Wignall, Newton & Little, 2005; Zakharov *et al*. 2006; Wignall & Bond, 2008).

All of the well-characterized mass extinction events in the geological record were accompanied by perturbations in the global carbon cycle (e.g. Keller & Lindinger, 1989; Arens & Jahren, 2000; Payne *et al*. 2004; Hesselbo *et al*. 2002; Riccardi *et al*. 2007). Such a perturbation has recently been reported for the first time from a Pliensbachian–Toarcian boundary section at Peniche, Portugal, whose ammonite faunas show both Boreal and Tethyan affinities, and where an excursion of ~ -2 ‰ has been seen in the $\delta^{13}C_{carbonate}$ record, in both bulk carbonate and brachiopod calcite (Hesselbo *et al.* 2007; Suan *et al.* 2008*a*). The excursion, with a magnitude of ~ -3 ‰, is also visible in the corresponding $\delta^{13}C$ values of macroscopic fossil wood. In this study, we present new data that show a similar negative CIE in the $\delta^{13}C_{org}$ record from NE Yorkshire, England. We also supply new $\delta^{13}C_{belemnite}$ data from fossils collected near the peak of the $\delta^{13}C_{carbonate}$ excursion at Peniche.

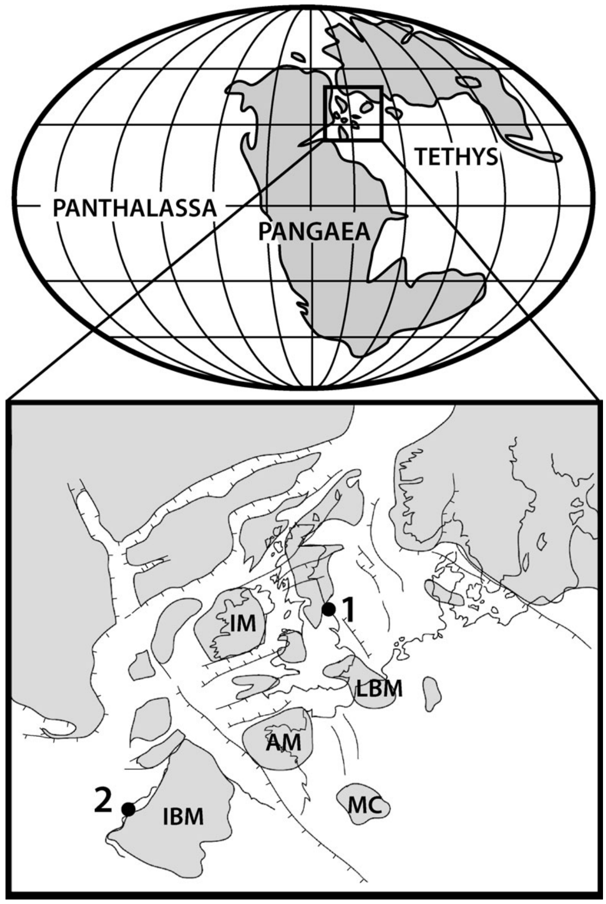

Figure 1. Map to show the palaeogeography of the NW European epicontinental shelf region during the Late Pliensbachian–Early Toarcian interval, and location of study sites. Adapted from Ziegler (1988). 1 – Yorkshire, 2 – Peniche, AM – Armorican Massif, IBM – Iberian Massif, MC – Massif Central, LBM – London–Brabant Massif, IM – Irish Massif.

2. Geological setting

2.a. Hawsker Bottoms, England

Samples were collected from the predominantly argillaceous cliff and foreshore sections at Hawsker Bottoms, NE Yorkshire, England (Fig. 1). This section consists of sideritic ironstones at the base, overlain by mudstones with varying degrees of organic enrichment and containing distinctive levels of concretionary limestone. This site has excellent exposure and has been the subject of many previous studies into Early Jurassic palaeoceanography (e.g. Jenkyns & Clayton, 1997; Hesselbo *et al.* 2000; McArthur *et al.* 2000; Bailey *et al*. 2003; Cohen *et al.* 2004; Kemp *et al.* 2005; Van de Schootbrugge *et al*. 2005; Wignall, Newton & Little, 2005). It is possible to follow individual beds with confidence for some lateral distance along the coast, because of the excellent exposure and easy identification of prominent marker beds (Howarth, 1973). The Hawsker Bottoms exposure features sediments deposited in the Cleveland Basin, which constituted part of the NW European epicontinental shelf during Early Jurassic times (e.g. Hesselbo & Jenkyns, 1995; Bjerrum *et al*. 2001). The fully marine, clay-rich strata are thought to have been deposited in a fairly shallow, periodically anoxic or dysoxic environment (Hallam, 1967). The transition from the inferred very shallow conditions in the latest Pliensbachian to the deeper water conditions associated with the Early Toarcian transgression are represented by a lithological change from dominantly oolitic ironstones and mudstones in the Cleveland Ironstone Formation, to dark, locally laminated mudstones with sideritic nodules in the overlying Grey Shale Formation. A thin bed just above the Pliensbachian–Toarcian boundary (Bed 26 in Fig. 2), known as the Sulphur Band (Howarth, 1973), is an organic-rich level, and probably records a brief but intense period of anoxia in the earliest Toarcian (*Dactylioceras tenuicostatum* Zone, *Protogrammoceras paltum* Subzone) (Wignall 1994).

Samples of Late Pliensbachian age are taken from the Cleveland Ironstone Formation (Bed 38 to Bed 43 of Howarth, 1955). Toarcian samples are taken from the Grey Shale Formation (Bed 1 to Bed 19 of Howarth, 1973), which were collected to a point just above the top of the Red Nodule Beds (Beds 7 to Bed 17, Fig. 2). These correspond to the *Pleuroceras hawskerense* Subzone within the *Pleuroceras spinatum* Zone, through the *P. paltum* and lower *D. clevelandicum* subzones of the *D. tenuicostatum* Zone. Stratigraphic level and ammonite biostratigraphy were determined by reference to Howarth (1955, 1973, 1991) and Howard (1985) and are reported relative to an arbitrary level within the 'Pseudopecten bed' (Bed 28 of Howarth,

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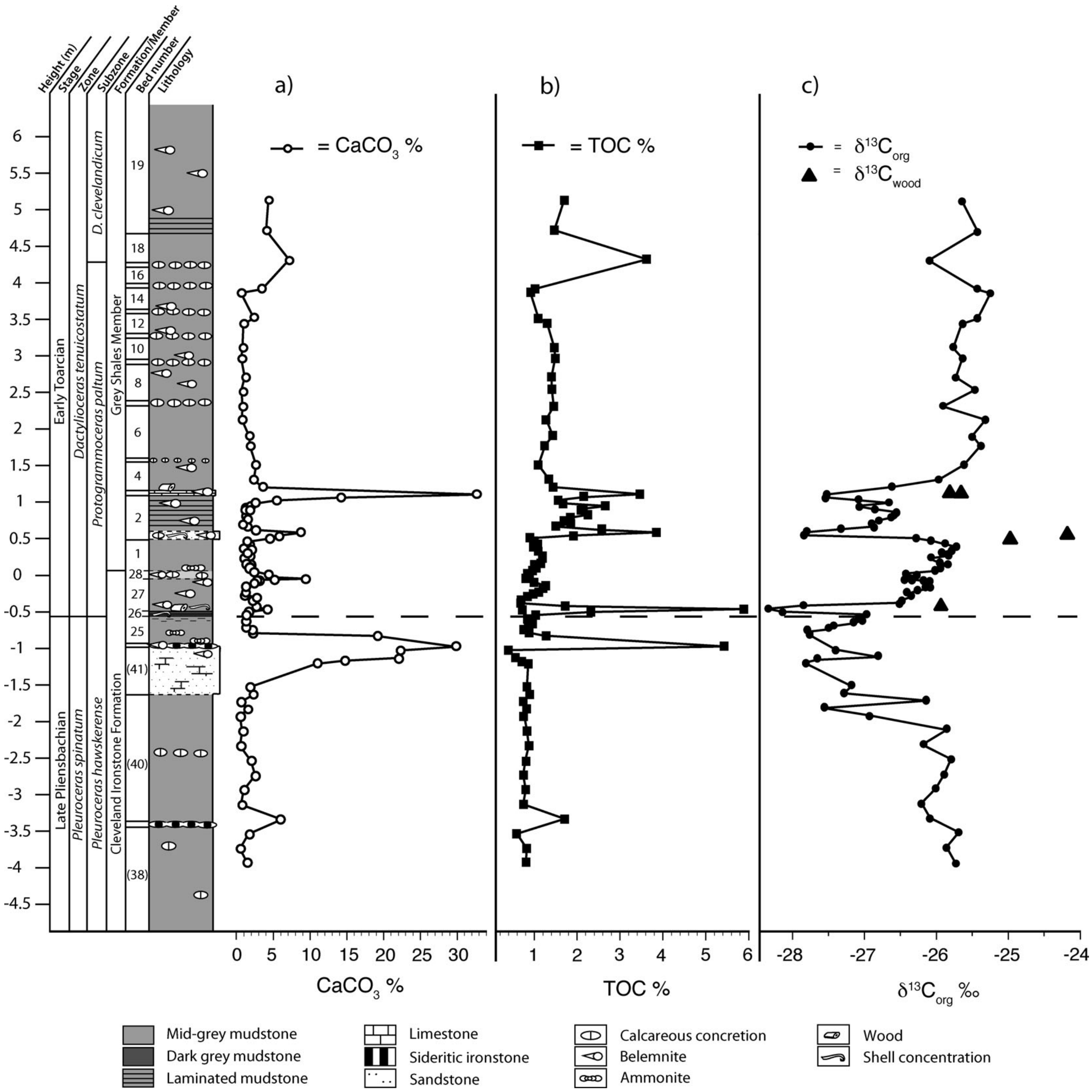

Figure 2. High-resolution data across the Pliensbachian–Toarcian boundary from Hawsker Bottoms. (a) Percentage carbonate (%$CaCO_3$) data. (b) Percentage total organic carbon (%TOC) record. (c) Carbon-isotope record with $\delta^{13}C_{org}$ and $\delta^{13}C_{wood}$ data shown. Graphic log of the Hawsker Bottoms section, ammonite zones and bed numbers as for Figure 3. Long dashed line = Pliensbachian–Toarcian boundary. For data table see online Appendix Table A1, at http://www.cambridge.org/journals/geo.

1973) in the lower *P. paltum* Subzone, approximately 50 cm above the Pliensbachian–Toarcian boundary. The position of the stage boundary in Yorkshire is fixed at a level between the stratigraphically highest *Pleuroceras* and the stratigraphically lowest *Dactylioceras*, and is placed at the base of the Sulphur Band (Bed 26) following Howarth (1973, 1991).

2.b. Peniche, Portugal

The section at Peniche (Fig. 1), where the negative carbon-isotope event at the stage boundary was first identified, is the sole candidate for Global Stratotype Section and Point (GSSP) for the base of the Toarcian (Duarte *et al.* 2004; Elmi, 2006). This section represents an exposed fragment of the Lusitanian Basin, with a sedimentary history ranging from the mid-Triassic to late Callovian (Duarte, 1997). The Lemede and Cabo Carvoeiro formations that span the Pliensbachian–Toarcian boundary were deposited in a marine setting, leading to the deposition of hemipelagic, carbonate-dominated, coccolith-bearing marls and limestones (Hesselbo *et al.* 2007). The excellent coastal exposure of sediments, only weakly affected by diagenesis, has allowed the generation of a continuous high-resolution chemostratigraphic profile.

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2.c. Correlation between Yorkshire and Portugal

A major issue, when comparing datasets from widely spaced sections that belong to different faunal provinces, is achieving an accurate and high-resolution stratigraphic correlation between the two locations. Correlation is hampered for some strata of Early Jurassic age by the fact that different ammonite fauna from distinct geographic locations are used to construct regional biostratigraphic schemes. Correlation between Peniche and Hawsker Bottoms requires temporal control between the mixed Tethyan/Boreal (Peniche section) and the Boreal NW European (Hawsker section) domains. Although some of the crucial ammonite taxa are present in both regions during the Late Pliensbachian–Early Toarcian (*P. spinatum* for example), some ammonite zones are defined on the basis of different taxa. Here, the Boreal *D. tenuicostatum* Zone is taken as broadly age-equivalent to the *D. polymorphum* Zone, and the overlying Boreal *falciferum* Zone equivalent to the *levisoni* Zone in Portugal (Page, 2004; Cecca & Macchioni, 2004). The Pliensbachian–Toarcian boundary at Peniche (Fig. 4) is placed at the base of Bed 15e, 22 cm below the top of the Lemede Formation (Elmi, 2006) and has been proposed as the GSSP for the base of the Toarcian. Bed 15e has the lowest occurrence of the *Dactylioceras (Eodactylites)* at this location and marks the base of the *polymorphum* Zone. The first occurrence of the *Dactylioceras* in NW Europe is deemed to be time-equivalent, although in Yorkshire the species is indeterminate (Howarth, 1991). It should be noted, however, that *Dactylioceras* (*Eodactylioceras*) has been reported co-occurring with the typically Late Pliensbachian *P. hawskerense* in the western Carpathians (Rakus, 1995; Elmi, 2006).

3. Methods and materials

3.a. Location of samples

Sixty-five powdered bulk samples from Hawsker Bottoms were collected using a battery-operated hand-drill at a resolution of between 2 cm and 4 cm over the key interval (between −20 cm and +170 cm, either side of the stage boundary), and at a lower resolution in the uppermost *P. hawskerense* Subzone (every 10 to 20 cm). This collection was supplemented with twenty-two hand specimens taken from higher in the section (Beds 3 to 19: Fig. 2) to extend the record further into the *P. paltum* and *D. clevelandicum* subzones. Five macroscopic wood samples were collected from the exposure at Hawsker Bottoms, all from the lower *P. paltum* Subzone of the Early Toarcian. Some of these wood samples are now preserved as coal, while others have retained their original woody texture. Five additional belemnites from ∼ 1 m above the Pliensbachian–Toarcian boundary (lower *polymorphum* Zone) at Peniche were also collected and analysed to supplement the existing chemostratigraphic database.

3.b. $CaCO_3$, TOC and carbon isotopes

The weight percentage of carbonate (%$CaCO_3$) and total organic carbon (%TOC) present in each sample were determined using a Strohlein Coulomat 702, by comparing the total carbon content of bulk sediment with samples whose organic matter had been removed by roasting at 420 °C (details in Jenkyns, 1988). Drilled bulk samples were analysed directly, whereas hand specimens and wood specimens were first crushed in an agate pestle and mortar. To obtain $\delta^{13}C_{org}$ values, bulk sediment samples were first decarbonated by reacting ∼ 2 g of sediment in a plastic test-tube with 3M HCl in a water bath at ∼ 60 °C. After two hours, the solute was decanted and the process repeated twice more with fresh acid. The sediment was then washed repeatedly with de-ionized water until neutrality was reached. The wood samples were first cleaned using a scalpel to remove any sediment or pyrite and then decarbonated in the same manner as the bulk sediment. The carbon-isotope ratios of the organic matter in the decarbonated samples were determined using a Europa Scientific Geo 20–20 mass spectrometer connected to a Carlo Erba 1108 elemental analyser. The samples were referred to a ‘Nylon 66’ standard ($\delta^{13}C_{nylon} = -26.16 \pm 0.21$ ‰), and the results expressed in δ notation, as a per mil (‰) deviation relative to the Vienna Pee Dee Belemnite (VPDB) standard. The calibration was obtained by analysing two standards between every seven sediment samples. Results are accurate to better than ±0.2 ‰, based on repeat standard results.

3.c. Belemnite samples

Belemnites were washed in distilled water and cleaned using a scalpel to remove any indurated sediment or pyrite from the surface. Samples were fragmented to ∼ 3 mm sized pieces, before being cleaned using first 0.6 M then 0.3 M HCl in a sonic bath. The fragments were inspected by eye to identify the least altered samples and pieces of < ∼ 1 mm size were selected. Calcite from the exterior, apical line, or any dark-coloured growth bands was avoided, as such material is considered to be most prone to diagenetic alteration (Sælen, 1989; McArthur *et al.* 2000; Gomez, Goy & Canales, 2008). The $\delta^{13}C_{belemnite}$ data were generated by crushing selected sub-samples to a fine powder in the pestle and mortar, which were then treated with hydrogen peroxide and acetone and dried at 50 °C for at least one hour. The samples were analysed using a Prism II mass spectrometer with an on-line VG Isocarb common acid-bath preparation system. In the instrument, samples were reacted with purified phosphoric acid at 90 °C. Calibration was made daily using the Oxford in-house (NOCZ) Carrara marble standard. Reproducibility of replicated standards is better than 0.2 ‰. Each belemnite was analysed three times for $\delta^{13}C_{carbonate}$ and the mean value of the three determinations is reported.

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4. Results

4.a. Percentage $CaCO_3$ and TOC, Hawsker Bottoms

The sediments from the studied interval at Hawsker Bottoms are generally low in $CaCO_3$ with an average value of 3.96 % (Fig. 2a). The higher resolution data, from 20 cm below the Pliensbachian–Toarcian boundary to 170 cm above this datum, suggest a possible cyclicity in $CaCO_3$ values with a mean spacing of 52 cm between peaks in carbonate content. The sediments at Hawsker Bottoms have varying %TOC values with an average value of 1.38 %, reaching maximum values of 5.89 % in the Sulphur Band (Bed 26; Fig. 2b). Highest %TOC values coincide with the darkest and most strongly laminated mudstones.

4.b. Bulk organic-matter carbon-isotope record, Hawsker Bottoms

A complex negative $\delta^{13}C_{org}$ excursion, comprising two negative peaks, each with a magnitude of ~ -2.5 ‰ and reaching minimum values of −28.4 ‰, can be seen in the Pliensbachian–Toarcian boundary interval at Hawsker Bottoms (Fig. 2c). The first component of the CIE occurs in the upper *P. hawskerense* Subzone in the latest Pliensbachian, culminating in a value of −28.4 ‰ in the Sulphur Band. The earliest Toarcian samples (base of *P. paltum* Subzone) are characterized by a return to pre-excursion values of ~ -26 ‰, which are then followed by the second negative CIE with a peak in Bed 2 at a minimum value of ~ -27.8 ‰. The return to more positive values of ~ -25.5 ‰ in Bed 4 persists until the onset of the larger negative carbon-isotope excursion in the late *D. tenuicostatum* Zone that is associated with the Early Toarcian OAE (Fig. 3). The entire boundary negative excursion, from pre-excursion values of ~ -26 ‰ in the *P. hawskerense* Subzone to post-excursion values of ~ -25.5 ‰ in the *P. paltum* Subzone, occurs over 3.6 m of section.

Importantly, there is an inverse correlation between %TOC values and $\delta^{13}C_{org}$ values in the Toarcian part of the section. Beds with higher %TOC have the most negative $\delta^{13}C_{org}$ values. In the *P. paltum* Subzone, the beds with the most negative $\delta^{13}C_{org}$ values tend to be the more laminated, dysoxic mudstones such as the Sulphur Band and Bed 2.

4.c. Wood carbon-isotope record, Hawsker Bottoms

The $\delta^{13}C$ values of fossil-wood samples have a range from ~ -24 to ~ -26 ‰, which is in line with previous determinations from the Yorkshire sections (Hesselbo *et al.* 2000). The small number of samples makes comparison with the $\delta^{13}C_{org}$ curve from the bulk sediment difficult, but it is noted that the lowest carbon-isotope values seen in the wood (~ -26 ‰) correspond to the negative excursion (~ -28.5 ‰) observed in the $\delta^{13}C_{org}$ record within the Sulphur Band (Fig. 2c). The persistent ~ 2 ‰ offset in carbon-isotopes between bulk organic-matter and fossil-wood records has been seen in other examples, in which the wood is consistently isotopically heavier than the bulk organic matter (Hesselbo *et al.* 2000).

4.d. Belemnite carbon-isotope record, Peniche

The $\delta^{13}C$ values of five belemnites from above the Pliensbachian–Toarcian boundary at Peniche, Portugal, were analysed and the results combined with existing data from Hesselbo *et al.* 2007 (Fig. 4a). The new samples are situated ~ 1 m above the stage boundary, with the majority clustered ~ 25 cm above the maximum negative carbon-isotope excursion seen in the accompanying $\delta^{13}C_{carbonate}$ record. $\delta^{13}C_{belemnite}$ values from these samples range from ~ -0.6 to $\sim +0.7$ ‰ and are generally more negative than nearly all other Late Pliensbachian–Early Toarcian belemnites from the same section reported in Hesselbo *et al.* (2007). However, as the belemnite record at Peniche does not represent a mono-specific assemblage, it may be that a proportion of the variation in the $\delta^{13}C_{belemnite}$ values could be attributed to inter-species variation. It is difficult to determine whether the clear CIE excursion seen in the carbonate record has also been captured in the belemnite record, because no belemnites that coincide precisely with the lowest part of the negative CIE have been collected at Peniche.

5. Discussion

5.a. Origin of the negative CIE at the stage boundary

The newly recognized complex excursion at the Pliensbachian–Toarcian boundary has several similarities with the negative CIE that is well known from the Early Toarcian OAE, so that the proposed mechanisms to explain its presence will be similar. The various models put forward to explain the perturbation at the OAE have recently been discussed in Cohen, Coe & Kemp (2007) and can be divided into three broad hypotheses: (1) overturning or upwelling of a stratified water mass ('Kuspert model'), (2) massive dissociation of methane clathrates and (3) mechanisms directly relating to magmatism in the Karoo–Ferrar Large Igneous Province (LIP). The relative strengths and weaknesses of these various theories are discussed at length in Cohen, Coe & Kemp (2007), and in the subsequent discussions in McArthur *et al.* (2008), and will not be discussed in great detail here.

For the Pliensbachian–Toarcian boundary excursion, the Küspert model (Küspert 1982), in which isotopically light respired CO_2 is recycled in a restricted basin, is consistent with the apparent absence of the excursion in low-resolution belemnite records from Hawsker Bottoms and the inverse relationship between the %TOC and $\delta^{13}C_{org}$ (Fig. 2b, c) (cf. Sælen *et al.* 1998; Van de Schootbrugge *et al.* 2005; Wignall *et al.* 2006; Hesselbo *et al.* 2000; Jenkyns *et al.* 2002; Hesselbo *et al.* 2007). In contrast, the organic geochemical

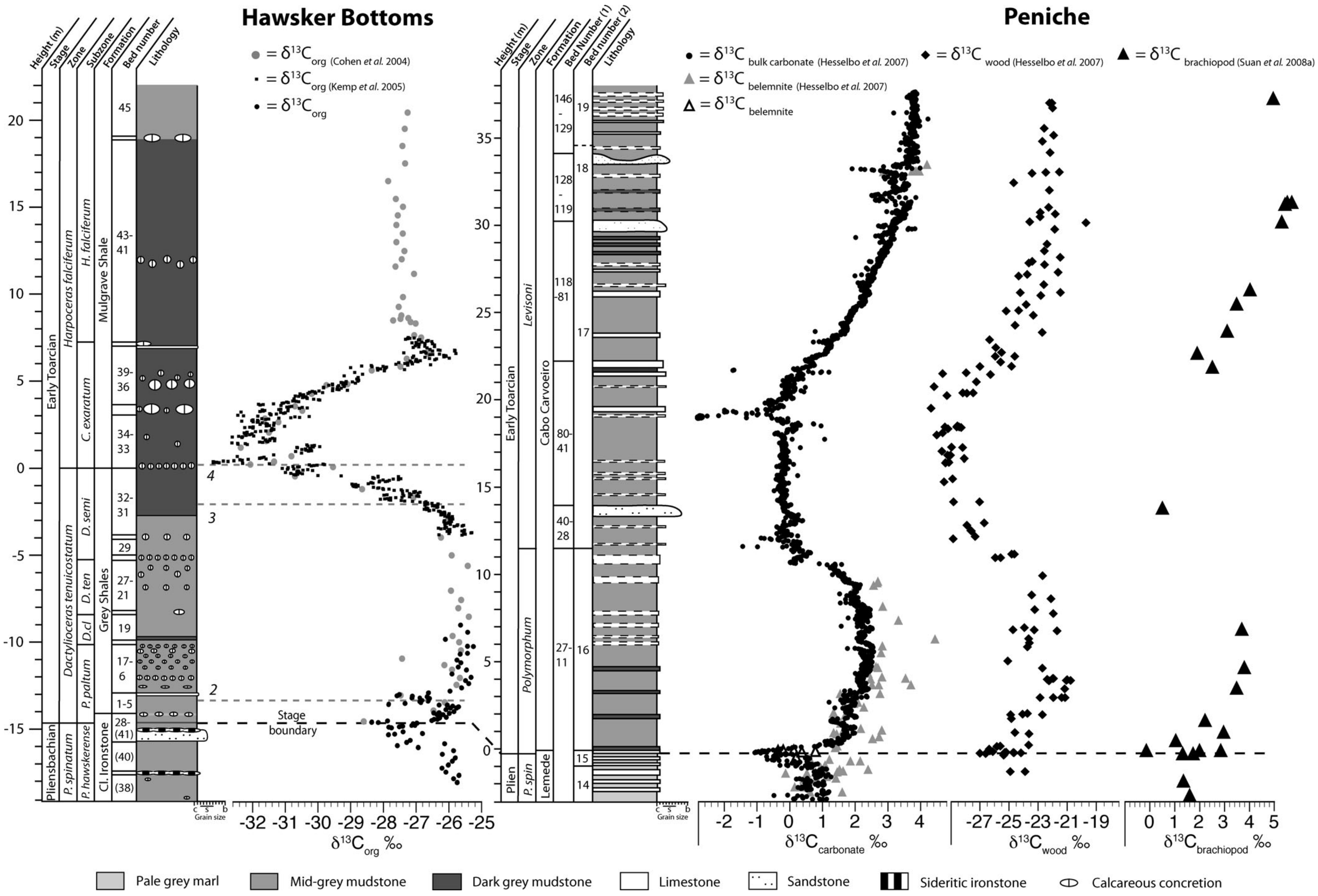

Figure 3. Comparison between carbon-isotope records at Hawsker Bottoms, Yorkshire and Peniche, Portugal. Existing Hawsker Bottoms $\delta^{13}C_{org}$ record (*P. paltum* to *H. falciferum* subzones) from Cohen *et al*. (2004) and Kemp *et al*. (2005), integrated with new high-resolution dataset from upper *P. hawskerense* to base of *D. clevelandicum* subzones (*P. spinatum – Pleuroceras spinatum, P. hawskerense – Pleuroceras hawskerense, P. paltum – Protogrammoceras paltum, D. cl – Dactylioceras clevelandicum, D. ten – Dactylioceras tenuicostatum*, *D. semi – Dactylioceras semicelatum*, *C. exaratum – Cleviceras exaratum, H. falciferum – Harpoceras falciferum,* Cl. Ironstone – Cleveland Ironstone). $\delta^{13}C_{org}$ record compared with carbonate ($\delta^{13}C_{carbonate}$) and wood data ($\delta^{13}C_{wood}$) from Peniche, Portugal (Hesselbo *et al*. 2007) and with brachiopod calcite data from Peniche ($\delta^{13}C_{brachiopod}$) from Suan *et al*. (2008*a*). Graphic log of Hawsker Bottoms section based on field observations and adapted from Cohen *et al*. (2004). Graphic log of the Peniche section adapted from Hesselbo *et al*. (2007) (Plien – Pliensbachian stage, *P. spin – Pleuroceras spinatum* Subzone). Bed numbers and ammonite zonation at Hawsker Bottoms taken from Howarth (1955) (bracketed bed numbers) and Howarth (1973) (unbracketed bed numbers). Portuguese ammonite biostratigraphy and bed numbers taken from Duarte (L. V. Duarte, unpub. Ph.D. thesis, Universidade de Coimbra, 1995) (Bed number 1) and Mouterde (1955) (Bed number 2). Dashed numbered lines in Yorkshire section represent approximate location of extinction steps in Jurassic benthic fauna, as described in Harries & Little (1999). Correlation between sections is based on the assumed age equivalence of the NW European *tenuicostatum* Zone and the Tethyan *polymorphum* Zone, and on GSSP placement of Pliensbachian–Toarcian boundary in Peniche (Elmi, 2006).

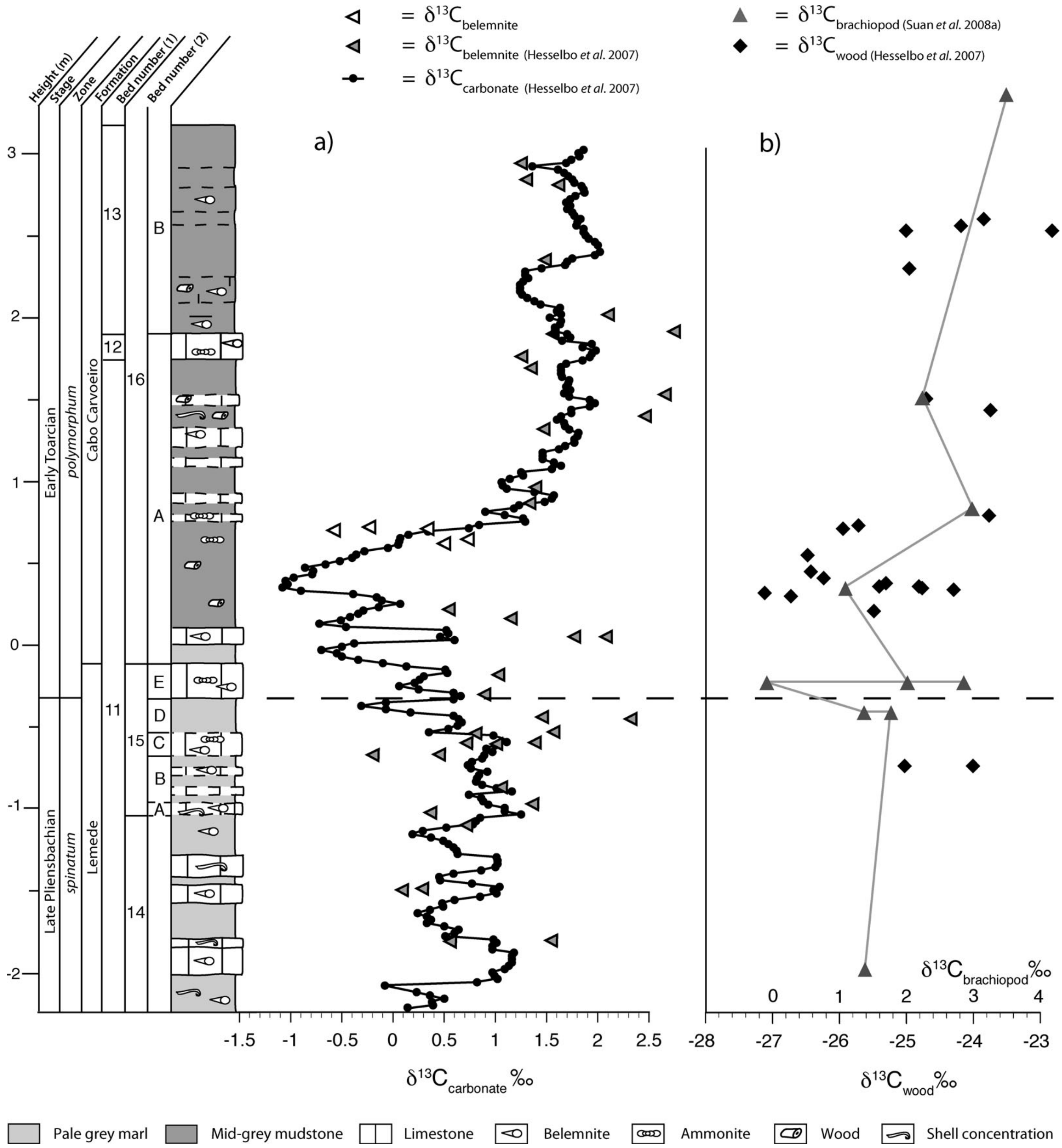

Figure 4. (a) Close-up of boundary sequence at Peniche showing $\delta^{13}C_{carbonate}$ and $\delta^{13}C_{belemnite}$ data taken from Hesselbo *et al.* (2007), with new $\delta^{13}C_{belemnite}$ data points from just above the peak negative excursion interval. Close-up of $\delta^{13}C_{wood}$ data also from Hesselbo *et al.* (2007) and $\delta^{13}C_{brachiopod}$ data from Suan *et al.* (2008*a*) is shown in (b). Bed numbering as for Figure 3. For new $\delta^{13}C_{belemnite}$ data see online Appendix Table A2, at http://www.cambridge.org/journals/geo.

evidence of Van Breugel *et al.* (2006*a*,*b*) suggests that recycled CO_2 from anoxic deep waters plays only a negligible role in influencing the $\delta^{13}C$ of phytoplankton in the overlying waters and the $\delta^{13}C_{org}$ record preserved in the sediment.

Of course, the $\delta^{13}C_{org}$ value represents the isotopic value of bulk organic-matter in the sediment, and therefore any changes in this value may reflect a change in the relative contribution of one type of organic-matter over another. The correlation between the most organically enriched beds and the most isotopically depleted samples at Hawsker Bottoms, suggests the issue may merit further investigation. However, the similarity in the carbon-isotope records of the Late Pliensbachian to Early Toarcian interval between the Peniche and Hawsker Bottoms sections (Fig. 3), in materials ranging from bulk organic-matter and bulk carbonate to fossil-wood and brachiopod calcite, strongly suggests expression of the carbon-cycle perturbation in at least a regional context. The boundary excursion at Peniche is recorded primarily in $\delta^{13}C_{carbonate}$ and occurs entirely within carbonate facies,

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and therefore cannot be explained merely by changes in local organic-matter provenance.

The presence of the stage boundary CIE in the fossil-wood record from Peniche indicates that the perturbation must have affected the atmospheric as well as the marine carbon reservoir. The methane dissociation hypothesis has in the past been the preferred explanation of many authors for the Early Toarcian *falciferum* Zone CIE, because it would have affected the atmospheric $\delta^{13}C$ of CO_2 and can also explain other reported phenomena such as high global temperatures and an increased intensity in weathering inferred from the Os-isotope record (Hesselbo *et al*. 2000; Beerling, Lomas & Gröcke, 2002; Jenkyns, 2003; Cohen *et al.* 2004; Kemp *et al*. 2005; Cohen, Coe & Kemp, 2007). The apparent abrupt onset of the stage boundary CIE at Hawsker Bottoms (Fig. 2c), and the initiation of an extinction step near the same level, supports the notion of a catastrophic event such as release of methane hydrate. The volume of clathrate in the Early Jurassic and its potential susceptibility to destabilization is, however, a major unknown factor. Neither the speed of onset nor the duration of the stage-boundary CIE can be determined, due to the unconstrained sedimentation rate at this section during the Early Jurassic period. Attempts to quantify the sedimentation rate, and therefore the timing of this event, are frustrated by a lack of age constraint. Attempts to quantify relative time using strontium-isotopes are controversial, and the errors associated with utilizing the available radiometric dates are larger than the likely duration of the event itself (McArthur *et al*. 2000). Therefore, at present, it is difficult to use the relative duration of the event to decide which of the suggested mechanisms is most likely to have initiated the CIE.

Recently, comparisons have been made between the Early Toarcian *falciferum* Zone CIE and the Palaeocene–Eocene Thermal Maximum (PETM: ~ 55.8 Ma), in terms of their geochemical signatures and possible causative mechanisms (Cohen, Coe & Kemp, 2007). The Palaeocene–Eocene Thermal Maximum is marked by a pronounced negative CIE of up to -2.5 ‰ in bulk carbonate, and up to -7 ‰ in bulk organic-matter (e.g. Kennett & Stott, 1991; Pagani *et al*. 2006). The event is also associated with benthic faunal extinctions, extensive carbonate dissolution and evidence for a large and rapid global warming event (e.g. Zachos *et al*. 2005; Sluijs *et al*. 2006, 2007; Bowen *et al*. 2006). The negative CIE associated with the Palaeocene–Eocene Thermal Maximum has also been attributed to a sudden methane clathrate dissociation event, due to its apparently short duration (~ 200 ka) and associated temperature spike (e.g. Dickens *et al.* 1995; Dickens, 2000; Thomas *et al*. 2002; Katz *et al.* 2001). However, the potential role of methane clathrate release at the Palaeocene–Eocene Thermal Maximum has recently been called into question (e.g. Higgins & Schrag, 2006). The magnitude of the CIE constrains the maximum amount of biogenic methane ($\delta^{13}C = \sim -60$ ‰) which could have been released into the ocean–atmosphere system during this event, to < 2000 GtC (Gigatons of carbon) (e.g. Dickens, 2000). However, the estimated extent of carbonate dissolution in the oceans during the event requires a far greater carbon input than this (~ 4500 GtC), thus suggesting that biogenic methane cannot be solely responsible for the perturbation (Zachos *et al*. 2005). These considerations may have a bearing on the interpretation of the Early Toarcian, by suggesting that the Jurassic CIEs may also have been triggered by more than one casual mechanism.

It is well documented that the Karoo–Ferrar LIP on southern Gondwana (centred on modern day South Africa and Antarctica) reached a period of peak volcanic activity at *c.* 183 Ma (Pálfy & Smith, 2000; Pálfy, Smith & Mortensen, 2002), and was therefore broadly coincident with the Late Pliensbachian–Early Toarcian CIEs. A third hypothesis suggests that Karoo-Ferrar sills intruded Permian organic-rich sediments or coals, releasing large amounts of isotopically depleted greenhouse gases to the Toarcian atmosphere (McElwain, Wade-Murphy & Hesselbo, 2005; Svensen *et al*. 2007). A broad range of dates for peak lava emplacement from *c.* 184 to *c.* 178 Ma has been calculated for the Karoo region, indicating that the stage boundary lies within the main extrusive phase of the LIP (Jourdan *et al*. 2005, 2008). It is possible, therefore, that an earlier pulse of thermogenic methane from this region could be partly responsible for the stage boundary CIE seen at Yorkshire and Peniche. Recent work by Gröcke *et al.* (2009) that calls into question the causative role of thermogenic methane from the Karoo basin in the *falciferum* Zone CIE may be of limited relevance because it considers only the case of dyke intrusion into coal, rather than sill intrusion into coal or black shale, the latter being likely to be very much more effective in the generation of large amounts of methane. As suggested in Suan *et al*. (2008*b*), the negative CIE might be attributed directly to volcanic outgassing of isotopically light CO_2. The average carbon-isotopic value of the mantle is generally taken to be only ~ -6 ‰, hence requiring the release of unrealistically large volumes of volcanogenic CO_2 in order to cause such a large perturbation in the carbon cycle. However, mantle xenolith compositions are compatible with an isotopically heterogeneous mantle that may contain reservoirs of very depleted carbon (~ -30 ‰), and flood basalts can exhibit carbon-isotopic values much lighter (~ -24 ‰) than the assumed average mantle value (Deines, 2002; Hansen, 2006). In addition, other authors have identified fractionation processes during degassing as a potential source of isotopically light carbon in basalts (e.g. Mattey, 1991).

The suggestion that Large Igneous Province volcanism played a direct causative role in initiating the stage boundary and Early Toarcian carbon-isotope excursions has, however, been suggested to be incompatible with the Milankovitch cyclicity reported during the *falciferum* Zone Oceanic Anoxic Event excursion (Kemp *et al*. 2005). This assertion is put

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forward on the basis that it is difficult to envisage how a mantle-derived source of depleted carbon could cause fluctuations in the carbon cycle that were apparently paced in time with orbital cycles. This line of reasoning may be countered by supposing that a longer-term global isotopic shift could be modified by Milankovitch-controlled local processes. Notwithstanding this debate, since no such cyclicity has yet been identified within the carbon-isotope record at the stage boundary, and the duration and speed of onset of the event is unclear, a volcanogenic origin for this CIE cannot be discounted.

A reconstructed palaeotemperature record from the Late Pliensbachian–Early Toarcian interval could be used to decipher which mechanism is the most applicable to the stage boundary CIE, since massive methane dissociation should be associated with a temperature maximum (as is seen at the Palaeocene–Eocene Thermal Maximum). Oxygen-isotope ratios from belemnite calcite can be interpreted in terms of changes in palaeotemperature, although care must be taken to consider the many other factors which can affect this ratio, such as taxon-specific effects and unknown initial seawater chemistry. The $\delta^{18}O_{belemnite}$ records from central and northern Spain suggests a gradual decrease in $\delta^{18}O$ values (~ 0 ‰) in the latest Pliensbachian *P. spinatum* Subzone, to between -1.5 and -2.5 ‰ in the *H. serpentinus* Zone (which is considered to be the southern European equivalent of the Boreal *falciferum* Zone) (Gómez, Goy & Canales, 2008). This change is interpreted as a gradual temperature rise from $\sim 13\,^{\circ}$C in the latest Pliensbachian to peak temperatures of ~ 25 to $28\,^{\circ}$C during the late *H. serpentinum* Zone, thus approximately coinciding with the negative CIE of the Toarcian OAE. Such a temperature trend is broadly in agreement with other $\delta^{18}O_{belemnite}$ data from Spain, which show a similar change from ~ 13 to $\sim 25\,^{\circ}$C across the same time interval (Rosales, Quesada & Robles, 2004*a*). Other work using belemnite oxygen isotopes from Yorkshire, however, shows an opposite trend across the stage boundary itself, with $\delta^{18}O$ values changing from ~ -4 ‰ in the latest Pliensbachian to ~ -1 ‰ in the *P. paltum* Subzone of the Early Toarcian (Bailey *et al.* 2003), which could be interpreted as a drop in temperature. This disparity in oxygen-isotope values during the Late Pliensbachian–Early Toarcian has been interpreted in terms of a north–south salinity gradient within the North European (Boreal) seaway at this time (Rosales, Quesada & Robles, 2004*b*, 2006). It would seem, therefore, that inferred palaeotemperature trends from the Early Jurassic do not currently provide unequivocal evidence in support of one mechanism over another to explain the stage boundary CIE.

6. Conclusions

A sharp negative $\delta^{13}C_{org}$ isotope excursion of somewhat complex character and with a magnitude of ~ -2.5 ‰ is present in sedimentary successions across the Pliensbachian–Toarcian boundary in NE Yorkshire, England. This excursion can be correlated with a similar phenomenon of lesser magnitude in the carbonate sedimentary record from coastal Portugal, suggesting a perturbation in the carbon cycle synchronous on at least a regional scale. This excursion will likely provide a useful chemostratigraphic marker for the Pliensbachian–Toarcian boundary. The presence of the excursion in materials ranging from bulk carbonate and bulk organic matter, to brachiopod calcite and fossil wood, suggests the perturbation must have affected the entire ocean–atmosphere system and should be registered in appropriate materials in coeval strata in all parts of the world. Indeed, coincidence with the first phase of extinction in marine benthos at the stage boundary, well before the main phase of anoxia associated with the Early Toarcian OAE, further suggests the event was not simply a localized anomaly. Further high-resolution work across the stage boundary from sites outside of the European epicontinental shelf region is needed to determine the probable cause.

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References

Aberhan, M. & Fürsich, F. T. 2000. Mass origination versus mass extinction: the biological contribution to the Pliensbachian–Toarcian extinction event. *Journal of the Geological Society, London* **157**, 55–60.

Arens, N. C. & Jahren, A. H. 2000. Carbon isotope excursion in atmospheric CO_2 at the Cretaceous-Tertiary Boundary: Evidence from terrestrial sediments. *Palaios* **15**, 314–22.

Bailey, T. R., Rosenthal, Y., McArthur, J. M., van de Schootbrugge, B. & Thirlwall, M. F. 2003. Paleoceanographic changes of the Late Pliensbachian–Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event, *Earth and Planetary Science Letters* **212**, 307–20.

Beerling, D. J., Lomas, M. R. & Gröcke, D. R. 2002. On the nature of methane gas-hydrate dissociation during the Toarcian and Aptian oceanic anoxic events. *American Journal of Science* **302**, 28–49.

Bjerrum, C. J., Surlyk, F., Callomon, J. H. & Slingerland, R. L. 2001. Numerical paleoceanographic study of the Early Jurassic Transcontinental Laurasian Seaway. *Paleoceanography* **16**, 390–404.

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). *Organic Geochemistry* **37**, 369–83.

Bowen, G. J., Bralower, T. J., Delaney, M. L., Dickens, G.R., Kelly, D. C., Koch, P. L., Kump, L. R., Meng, J., Sloan, L. C., Thomas, E., Wing, S. L. & Zachos,

https://doi.org/10.1017/S0016756809990458 Published online by Cambridge University Press

J. C. 2006. Eocene hyperthermal event offers insight into greenhouse warming. *EOS, Transactions of the American Geophysical Union* **87**, 165–9.

Cecca, F. & Macchioni, F. 2004. The two Early Toarcian (Early Jurassic) extinction events in ammonoids. *Lethaia* **37**, 35–56.

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**, 157–60.

Cohen, A. S., Coe, A. L. & Kemp, D. B. 2007. The Late Palaeocene–Early Eocene and Toarcian (Early Jurassic) carbon isotope excursions: a comparison of their time scales, associated environmental changes, causes and consequences. *Journal of the Geological Society* **164**, 1093–1108.

Deines, P. 2002. The carbon isotope geochemistry of mantle xenoliths. *Earth Science Reviews* **58**, 247–78.

Dickens, G. R., O'Neil, J. R., Rea, D. K. & Owen, R. M. 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography* **10**, 965–71.

Dickens, G. R. 2000. Methane oxidation during the Late Palaeocene Thermal Maximum. *Bulletin de la Société géologique de France* **171**, 37–49.

Duarte, L. V. 1997. Facies analysis and sequential evolution of the Toarcian–Lower Aalenian series in the Lusitanian Basin (Portugal). *Communicações do Instituto Geológico e Mineiro* **83**, 65–94.

Duarte, L. V., Perilli, N., Dino, R., Rodrigues, R. & Paredes, R. 2004. Lower to Middle Toarcian from the Coimbra region (Lusitanian Basin, Portugal): sequence stratigraphy, calcareous nannofossils and stable isotope evolution. *Rivista Italiana di Paleontologia e Stratigrafia* **110**, 115–27.

Elmi, P. 2006. Pliensbachian/Toarcian boundary: the proposed GSSP of Peniche (Portugal). *Volumina Jurassica* **4**, 5–16.

Gómez, J. J., Goy, A. & Canales, M. L. 2008. Seawater temperature and carbon isotope variations in belemnites linked to mass extinction during the Toarcian (Early Jurassic) in Central and Northern Spain. Comparison with other European sections. *Palaeogeography, Palaeoclimatology, Palaeoecology* **258**, 28–58.

Gröcke, D. R., Rimmer, S. M., Yoksoulian, L. E., Cairncross, B., Tsikos, H. & van Hunen, J. 2009. No evidence for thermogenic methane release in coal from the Karoo-Ferrar large igneous province. *Earth and Planetary Science Letters* **277**, 204–12.

Hallam, A. 1967. An environmental study of the upper Domerian and lower Toarcian in Great Britain. *Philosophical Transactions of the Royal Society of London, Series B* **252**, 393–445.

Hallam, A. 1981. A revised sea-level curve for the early Jurassic. *Journal of the Geological Society, London* **138**, 735–43.

Hallam, A. 1986. The Pliensbachian and Tithonian extinction events. *Nature* **319**, 765–8.

Hallam, A. 1997. Estimates of the amount and rate of sea-level change across the Rhaetian–Hettangian and Pliensbachian–Toarcian boundaries (latest Triassic to early Jurassic). *Journal of the Geological Society, London* **154**, 773–9.

Hansen, H. J. 2006. Stable isotopes from basaltic rocks and their possible relation to atmospheric isotope excursions. *Lithos* **92**, 105–16.

Harries, P. J. & Little, C. T. S. 1999. The early Toarcian (Early Jurassic) and the Cenomanian–Turonian (Late Cretaceous) mass extinctions: similarities and contrasts. *Palaeogeography, Palaeoclimatology, Palaeoecology* **154**, 39–66.

Hermoso, M., Le Callonnec, L., Minoletti, F., Renard, M & Hesselbo, S. P. 2009. Expression of the Early Toarcian negative carbon-isotope excursion in separated carbonate microfractions (Jurassic, Paris Basin). *Earth and Planetary Sciences Letters* **277**, 193–203.

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**, 392–5.

Hesselbo, S. P. & Jenkyns, H. C. 1995. A comparison of the Hettangian to Bajocian succesions of Dorset and Yorkshire. In *Field Geology of the British Jurassic* (ed. P. D. Taylor), pp. 105–50. Geological Society of London.

Hesselbo, S. P. & Jenkyns, H. C. 1998. British Lower Jurassic sequence stratigraphy. In *Mesozoic–Cenozoic Sequence Stratigraphy of European Basins* (eds P. C. de Graciansky, J. Hardenbol, T. Jacquin, M. Farley & P. R. Vail), pp. 561–81. Society for Sedimentary Geology (SEPM), Special Publication no. 60.

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 and Planetary Science Letters* **253**, 455–70.

Hesselbo, S. P., Robinson, S. A., Surlyk, F. & Piasecki, S. 2002. Terrestrial and marine extinction at the Triassic–Jurassic boundary synchronized with major carbon-cycle perturbation: A link to initiation of massive volcanism? *Geology* **30**, 251–4.

Higgins, J. A. & Schrag, D. P. 2006. Beyond methane: Towards a theory for the Paleocene–Eocene Thermal Maximum. *Earth and Planetary Science Letters* **245**, 523–37.

Howard, A. S. 1985. Lithostratigraphy of the Staithes Sandstone and Cleveland Ironstone Formations (Lower Jurassic) of north-east Yorkshire. *Proceedings of the Yorkshire Geological Society* **45**, 261–75.

Howarth, M. K. 1955. Domerian of the Yorkshire coast. *Proceedings of The Yorkshire Geological Society* **30**, 147–75.

Howarth, M. K. 1973. The stratigraphy and ammonite fauna of the Upper Liassic Grey Shales of the Yorkshire coast. *Bulletin of the British Museum* **24**, 253–77.

Howarth, M. K. 1991. The Ammonite family Hildoceratidae in the Lower Jurassic of Britain. *Monograph of the Palaeontographical Society* **1**, 1–106; **2**, 107–200.

Jenkyns, H. C. 1985. The Early Toarcian and Cenomanian–Turonian anoxic events in Europe: comparisons and contrasts. *Geologische Rundschau* **74**, 505–18.

Jenkyns, H. C. 1988. The Early Toarcian (Jurassic) Anoxic Event: stratigraphic, sedimentary, and geochemical evidence. *American Journal of Science* **288**, 101–51.

Jenkyns, H. C. 2003. Evidence for rapid climate change in the Mesozoic–Palaeogene greenhouse world. *Philosophical Transactions of the Royal Society of London, Series A* **361**, 1885–1916.

Jenkyns, H. C. & Clayton, C. J. 1986. Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. *Sedimentology* **33**, 87–106.

Jenkyns, H. C. & Clayton, C. J. 1997. Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology* **44**, 687–706.

Jenkyns, H. C., Gröcke, D. R. & Hesselbo, S. P. 2001. Nitrogen isotope evidence for water mass denitrification during the early Toarcian (Jurassic) oceanic anoxic event. *Paleoceanography* **16**, 593–603.

JENKYNS, H. C., JONES, C. E., GRÖCKE, D. R., HESSELBO, S. P. & PARKINSON, D. N. 2002. Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *Journal of the Geological Society, London* **159**, 351–78.

JONES, C. E., JENKYNS, H. C., COE, A. L. & HESSELBO, S. P. 1994. Strontium isotopic variations in Jurassic and Cretaceous seawater. *Geochimica et Cosmochimica Acta* **58**, 3061–74.

JONES, C. E. & JENKYNS, H. C. 2001. Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous. *American Journal of Science* **301**, 112–49.

JOURDAN, F., FÉRAUD, G., BERTRAND, H., KAMPUNZU, A. B., TSHOSO, G., WATKEYS, M. K. & LE GALL, B. 2005. Karoo large igneous province: Brevity, origin, and relation to mass extinction questioned by new $^{40}Ar/^{39}Ar$ age data. *Geology* **33**, 745–8.

JOURDAN, F., FÉRAUD, G., BERTRAND, H., WATKEYS, M. K. & RENNE, P. R. 2008. The $^{40}Ar/^{39}Ar$ ages of the sill complex of the Karoo large igneous province: Implications for the Pliensbachian-Toarcian climate change, *Geochemistry, Geophysics, Geosystems* **9**, Q06009, doi:10.1029/2008GC001994.

KATZ, M. E., CRAMER, B. S., MOUNTAIN, G. S., KATZ, S. & MILLER, K. G. 2001. Uncorking the bottle: What triggered the Paleocene/Eocene thermal maximum methane release? *Paleoceanography* **16**, 549–62.

KELLER, G. & LINDINGER, M. 1989. Stable isotope, TOC and $CaCO_3$ record across the Cretaceous/Tertiary boundary at El Kef, Tunisia. *Palaeogeography, Palaeoclimatology, Palaeoecology* **73**, 243–65.

KEMP, D. B., COE, A. L., COHEN, A. S. & SCHWARK, L. 2005. Astronomical pacing of methane release in the Early Jurassic period. *Nature* **437**, 396–9.

KENNETT, J. P. & STOTT, L. D. 1991. Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene. *Nature* **353**, 225–9.

KÜSPERT, W. 1982. Environmental changes during oil shale deposition as deduced from stable isotope ratios. In *Cyclic and Event Stratification* (eds G. Einsele & A. Seilacher), pp. 482–501. Berlin: Springer.

LITTLE, C. T. S. & BENTON, M. J. 1995. Early Jurassic mass extinction: a global long-term event. *Geology* **23**, 495–8.

MACCHIONI, F. & CECCA, F. 2002. Biodiversity and biogeography of middle–late Liassic ammonoids: implications for the Early Toarcian mass extinction. *Geobios* **35**, 165–75.

MATTEY, D. P. 1991. Carbon dioxide solubility and carbon isotope fractionation in basaltic melt. *Geochimica et Cosmochimica Acta* **55**, 3467–73.

MCARTHUR, J. M., COHEN, A. S., COE, A. L., KEMP, D. B., BAILEY, R. J. & SMITH, D. G. 2008. Discussion on the Late Palaeocene–Early Eocene and Toarcian (Early Jurassic) carbon isotope excursions: a comparison of their time scales, associated environmental change, causes and consequences. *Journal of the Geological Society, London* **165**, 875–80.

MCARTHUR, J. M., DONOVAN, D. T., THIRLWALL, M. F., FOUKE, B. W. & MATTEY, D. 2000. Strontium isotope profile of the early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belemnite palaeotemperatures. *Earth and Planetary Science Letters* **179**, 269–85.

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**, 479–82.

MOUTERDE, R. 1955. Le lias de Peniche. *Comunições dos Servicos Geológicos de Portugal* **36**, 87–115.

PAGANI, M., PEDENTCHOUK, N., HUBER, M., SLUIJS, A., SCHOUTEN, S., BRINKHUIS, H., SINNINGHE DAMSTÉ, J., DICKENS, G. R. & the Expedition 302 scientists. 2006. Arctic hydrology during global warming at the Palaeocene/Eocene thermal maximum. *Nature* **442**, 671–5.

PAGE, K. N. 2004. A sequence of biohorizons for the Subboreal Province lower Toarcian in northern Britain and their correlation with a Submediterranean Standard. *Rivista Italiana di Paleontologia e Stratigrafia* **110**, 109–14.

PÁLFY, J. & SMITH, P. L. 2000. Synchrony between Early Jurassic extinction, oceanic anoxic event, and the Karoo–Ferrar flood basalt volcanism. *Geology* **28**, 747–50.

PÁLFY, J., SMITH, P. L. & MORTENSEN, J. K. 2002. Dating the end-Triassic and Early Jurassic mass extinctions, correlative large igneous provinces, and isotopic events. In *Catastrophic Events and Mass Extinctions: Impacts and Beyond* (eds C. Koeberl & K. G. MacLeod), pp. 523–32. Geological Society of America, Special Paper no. 356.

PANCOST, R. D., CRAWFORD, N., MAGNESS, S., TURNER, A., JENKYNS, H. C. & MAXWELL, J. R. 2004. Further evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events. *Journal of the Geological Society, London* **161**, 353–64.

PAYNE, J. L., LEHRMANN, D. J., WEI, J., ORCHARD, M. J., SCHRAG, D. P. & KNOLL, A. H. 2004. Large perturbations of the carbon cycle during recovery from the End-Permian extinction. *Science* **305**, 506–9.

RAKUS, M. 1995. The first appearance of dactylioceratids in the western Carpathians. *Slovak Geological Magazine* **2**, 165–70.

RICCARDI, A., KUMP, L. R., ARTHUR, M. A. & D'HONDT, S. 2007. Carbon isotopic evidence for chemocline upward excursions during the end-Permian event. *Palaeogeography, Palaeoclimatology, Palaeoecology* **248**, 73–81.

RÖHL, J. H., SCHMID-RÖHL, 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. *Palaeogeography, Palaeoclimatology, Palaeoecology* **165**, 27–52.

ROSALES, I., QUESADA, S. & ROBLES, S. 2004*a*. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque–Cantabrian basin, northern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* **203**, 253–75.

ROSALES, I., QUESADA, S. & ROBLES, S. 2004*b*. Elemental and oxygen isotope composition of Early Jurassic belemnites: salinity vs. temperature signals. *Journal of Sedimentary Research* **74**, 342–54.

ROSALES, I., QUESADA, S. & ROBLES, S. 2006. Geochemical arguments for identifying second-order sea-level changes in hemipelagic carbonate ramp deposits. *Terra Nova* **18**, 233–40.

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**, 1307–28.

SÆLEN, G. 1989. Diagenesis and construction of the belemnite rostrum. *Palaeontology* **32**, 765–98.

SÆLEN, G., TYSON, R. V., TALBOT, M. R. & TELNÆS, N. 1998. Evidence of recycling of isotopically light CO_2 (aq) in stratified black shale basins; Contrasts between the Whitby Mudstone and Kimmeridge Clay formations, United Kingdom. *Geology* **26**, 747–50.

SCHOUTEN, S., VAN KAAM-PETERS, H. M. E., RIJPSTRA, W. I. C., SCHOELL, M. & SINNINGHE DAMSTÉ, J. S. 2000. Effects of an oceanic anoxic event on the stable carbon isotopic composition of early Toarcian carbon. *American Journal of Science* **300**, 1–22.

SLUIJS, A., BOWEN, G. J., BRINKHUIS, H., LOURENS, L. J. & THOMAS, E. 2007. The Palaeocene-Eocene thermal maximum super greenhouse: biotic and geochemical signatures, age models and mechanisms of global change. In *Deep time perspectives on Climate Change: Marrying the Signal from Computer Models and Biological Proxies* (eds M. Williams, A. M. Haywood, J. Gregory & D. N. Schmidt), pp. 323–49. The Micropalaeontological Society, Special Publications, The Geological Society, London.

SLUIJS, A., SCHOUTEN, S., PAGANI, M., WOLTERING, M., BRINKHUIS, H., SINNINGHE DAMSTÉ, J., DICKENS, G. R., HUBER, M., REICHART, G., STEIN, R., MATTHIESSEN, J., LOURENS, L. J., PEDENTCHOUK, N., BACKMAN, J., MORAN, K. & the Expedition 302 Scientists. 2006. 2006. Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum. *Nature* **441**, 610–13.

SUAN, G., MATTIOLI, E., PITTET, B., MAILLIOT, S. & LÉCUYER, C. 2008*a*. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal. *Paleoceanography* **23**, PA1202, doi:10.1029/2007PA001459.

SUAN, G., PITTET, B., BOUR, I., MATTIOLI, E., DUARTE, L. V. & MAILLIOT, S. 2008*b*. Duration of the Early Toarcian carbon isotope excursion deduced from spectral analysis: Consequence for its possible causes. *Earth and Planetary Science Letters* **267**, 666–79.

SVENSEN, H., PLANKE, S., CHEVALLIER, L., MALTHE-SØRENSSEN, A., CORFU, F. & JAMTVEIT, B. 2007. Hydrothermal venting of greenhouse gases triggering Early Jurassic global warming. *Earth and Planetary Science Letters* **256**, 554–66.

THOMAS, D. J., ZACHOS, J. C., BRALOWER, T. J., THOMAS, E. & BOHATY, S. 2002. Warming the fuel for the fire: Evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene thermal maximum. *Geology* **30**, 1067–70.

VAN BREUGEL, Y., BAAS, M., SCHOUTEN, S., MATTIOLI, E. & SINNINGHE DAMSTÉ, J. S. 2006*a*. 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, doi:10.1029/2006PA001305.

VAN BREUGEL, Y., SCHOUTEN, S., PAETZEL, M. & SINNINGHE DAMSTÉ, J. S. 2006*b*. Seasonal variation in the stable carbon isotopic composition of algal lipids in a shallow anoxic fjord: Evaluation of the effect of recycling of respired CO_2 on the $\delta^{13}C$ of organic matter. *American Journal of Science* **306**, 367–87.

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, doi:10.1029/2004PA001102.

WIGNALL, P. B. 1994. *Black Shales*. Geology and Geophysics Monographs, 30. Oxford: Oxford University Press, 130 pp.

WIGNALL, P. B., 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. *American Journal of Science* **305**, 1014–32.

WIGNALL, P. B., MCARTHUR, J. M., LITTLE, C. T. S. & HALLAM, A. 2006. Methane release in the Early Jurassic period. *Nature* **441**, p. E5.

WIGNALL, P. B. & BOND, P. G. 2008. The end Triassic and Early Jurassic extinction records in the British Isles. *Proceedings of the Geologists Association* **119**, 73–84.

WOODFINE, R. G., JENKYNS, H. C., SARTI, M., BARONCINI, F. & VIOLANTE, C. 2008. The response of two Tethyan carbonate platforms to the early Toarcian (Jurassic) oceanic anoxic event: environmental change and differential subsidence. *Sedimentology* **55**, 1011–28.

ZACHOS, J. C., RÖHL, U., SCHELLENBERG, S. A., SLUIJS, A., HODELL, D. A., KELLY, D. C., THOMAS, E., NICOLO, M., RAFFI, I., LOURENS, L. J., MCCARREN, H. & KROON, D. 2005. Rapid acidification of the ocean during the Paleocene–Eocene thermal maximum. *Science* **308**, 1611–15.

ZAKHAROV, V. A., SHURYGIN, B. N., IL'INA, V. I. & NIKITENKO, B. L. 2006. Pliensbachian–Toarcian Biotic Turnover in North Siberia and the Arctic Region. *Stratigraphy and Geological Correlation* **14**, 399–417.

ZIEGLER, P. A. 1988. Evolution of the Arctic–North Atlantic and the western Tethys, *American Association of Petroleum Geologists Memoir* **43**, 198.